1

CONFIGURATION AND CONFORMATION OF MACROMOLECULES IN POLYMER CRYSTALS

1.1 CRYSTALS OF POLYMERS

A crystal is a portion of solid matter in which some kind of long-range positional order exists on the level of atomic dimensions in three-dimensional space (1,2). This definition corresponds to a reasonable and generally valid working hypothesis, implying a complete long-range positional order of most of atoms (2). The crystalline state should be, therefore, characterized by the presence of three-dimensional order. “Periodicity” is intended as the quality of a motif recurring at equal intervals in the space. In the ideal limit case, the repetition is endless, whereas in real cases, it extends up to the scale considered as appropriate for the description of material properties (1). In the ideal limit case, the corresponding model crystal is designated as ideal crystal.

In the case of polymers, the concepts of crystal and crystallinity are complex and very far from the ideality because in polymer crystals, the three-dimensional long-range order is never present and the structural disorder inside crystals is a rule rather than an exception (3–10). First of all, at variance with other crystalline materials, such as metals, polymeric materials are never completely crystalline. They are semicrystalline and are generally composed of crystals (lamellae) embedded into an amorphous phase, producing a highly interconnected network (11) (Fig. 1.1). The peculiar semicrystalline character of polymers determines their outstanding physical properties.

In crystals of polymers, the macromolecules are longer than the unit cell parameters and each chain passes through many unit cells. Accordingly, the concept of an ideal crystal of polymers requires infinite molecular mass, completely regular constitution of the macromolecules, completely regular configuration of the units in the macromolecules, and completely regular conformation of the chains (3).

In a slightly enlarged recent definition, a crystal is any solid having an essentially discrete diffraction diagram (12). This definition implies the presence of some kind of long-range three-dimensional periodicity but not necessarily a complete three-dimensional order of atoms. This concept well corresponds to the partial order present in polymer crystals. The requirement of three-dimensional long-range order appears to be violated in polymer crystals, unless it is considered as a limit, mainly for the following reasons: (a) The macromolecules of a polymer are not uniform; that is, they have different molecular masses, a distribution of molecular masses being always present (13); (b) constitutional, configurational, and conformational disorders along the polymer chains are always present (4); and (c) the dimensions of the crystals are very small, mostly in the nanometer range (they are often indicated as crystallites) (11).

Moreover, even in the case of regular constitution, configuration, and conformation, disorder may be present in the crystals due to the presence of defects in
the mode of packing. Disorder in the packing may occur while some structural feature, for instance, some atoms or the axes of helical macromolecules, maintain periodic positions (4). The degree of disorder in the packing or in the single macromolecules is sometimes so high that it is difficult to define this state as crystalline, even though we can still observe crystalline entities with a regular shape by microscopy (optical or electronic). This state can be more properly indicated as intermediate between amorphous phase and ordered crystals (4–7). These crystalline forms that present large amounts of disorder with lack of periodicities in one or two dimensions (e.g., along or normal to the chain axes) are very common in solid semicrystalline polymers and are generally indicated solid mesophases (4–10). In solid mesophases, the presence of a high amount of disorder frequently prevents the definition of a unit cell and only average periodicities along some lattice directions may be defined (4,6).

The issue of long-range versus short-range order in polymer crystals has been extensively treated in the scientific literature (4–10). A modern view of crystallinity and crystalline order in polymers implies that the crystallinity and the capability of polymers to crystallize (crystallizability) are compatible with the presence of a high degree of disorder and the absence, in many cases, of long-range three-dimensional order. This view implies the need to describe the disorder in polymer crystals as a structural feature (4–7) and has required many efforts for the development of experimental techniques and theoretical methods for the study of different types of disorder and the evaluation of the degree of disorder present in the crystals (6,7) (Chapter 5). These methods are part of modern polymer crystallography.

The complex nature of macromolecules in polymeric materials, which always include constitutional and configurational defects along the chain, the polydispersity of the molecular masses, the easy inclusion of defects inside the crystallites, generally prevents obtaining of single crystals of a suitable size for the collection of X-ray diffraction data with the techniques normally used for single crystals of low-molecular-weight compounds (14). The dimensions of polymeric single crystals are instead suitable for electron diffraction. The structural analysis is further complicated by the fact that crystalline polymers are always characterized by a complex morphology, consisting of amorphous, crystalline, and intermediate regions, and the transition from noncrystalline to crystalline regions is considered to be a continuum (11) (Fig. 1.1). In polymeric materials of high crystallinity, the major part of the material is made up of small crystals, called crystallites, forming platelets in which the chains run perpendicular to the most highly developed surfaces. The thickness of the platelets is a few hundred angstroms long. The usual length of the molecular chain is, in general, far greater than the size of crystallites. Hence, each macromolecular chain is considered to pass through several crystalline and noncrystalline regions successively (11) (Fig. 1.1A).

Electron diffraction studies of polymer single crystals have clearly shown that in a single crystal, the molecular chains are generally perpendicular to the crystal plane with a thickness of about 100 Å and a fold on the crystal surface giving rise to folded lamellae, as schematically shown in Figure 1.1B (15,16). Depending on the conditions of preparation, structures containing folded lamellar entities (Fig. 1.1B) or fringed micelle (Fig. 1.1C) may be obtained. Spherulites are an important product of crystallization from the melt (11). They consist of folded-chain lamellae developing radially outward from a central core, giving rise to a “sphere” (11). The fringed micelle and the lamellar models may be regarded as two extreme cases. The lamellar model is usually suitable to explain the structure of polymers with long and flexible chains, as, for instance, polyethylene (PE), polypropylene, and polyesters; the fringed lamellae scheme is
instead a more appropriate model for polymers with stiffer and/or shorter macromolecules, like aromatic polyamides and conjugated polymers. Lamellar structures partially unfold and change to a fringed micelle-like structure upon uniaxial stretching procedures, obtaining fibrous materials (11).

Studies of the crystal structures of polymers are generally performed by X-ray diffraction of uniaxially oriented fibers, or, when fibers cannot be obtained, of powder samples containing randomly oriented crystals (14) (Chapter 3). In all cases, the X-ray diffraction patterns of semicrystalline polymers present a few number of Bragg reflections and a large amount of diffuse scattering. The diffuse scattering originates from the amorphous contribution and the presence of structural disorder (17). The Bragg peaks are broad because of the small average dimensions of crystallites and overlap at high values of the 2θ diffraction angle. Furthermore, the Bragg diffraction rapidly vanishes with increasing diffraction angle (14). Electron diffraction of single crystals generally gives very useful information because of the direct visualization of the reciprocal lattice and, generally, allows an easy determination of the unit cell parameters (18). On the other hand, the electron diffraction intensity of single crystals may be seriously affected by multiple scattering effects and is generally limited by the fact that only a small region of the reciprocal space is usually accessible (18). The paucity and overlapping of diffraction data, even when electron diffraction patterns of single crystals are available, is generally compensated by the use of trial and error methods for solving the crystal structures of polymers, which involves construction of a priori models of the conformation and the packing of the polymer chains in the unit cell (14) (Chapter 3).

The structural analysis is generally also complicated by the fact that polymers very often present a complex polymorphism in the solid state, which, in some cases, may prevent the preparation of a sample containing a single crystalline form (Chapter 2).

1.2 CONSTITUTION AND CONFIGURATION OF CRYSTALLINE POLYMERS

The capability of polymers to crystallize (crystallizability) implies, in general, an “identity period” along the chain axes of the macromolecules. In the corresponding “ideal crystals,” the polymer molecules have an infinite chain length and a perfect regularity in the chemical constitution, in the configuration, and in the conformational sequences of the monomeric units along the chain (3). Therefore, general requirements for the crystallizability of polymers are the regularity in the chemical constitution and in the configuration of long sequences of monomeric units (3, 4, 19). This implies that, for long sequences of polymerized monomers, all the repeating units have the same chemical structure. In addition, whenever a monomeric unit may assume different configurations, the succession of configurations must be regular. The regularity in the succession of configurations of the stereoisomeric centers present along the chains implies, as a direct consequence, that the conformations assumed by macromolecules in the crystals are regular and can be described by a well-defined symmetry (3, 4).

1.2.1 Constitution

The constitution of a molecule specifies which atoms are bound to each other and with what type of bonds, without considering their spatial arrangement. It is the description of the identity and connectivity (and corresponding bond multiplicity) of the atoms in a molecule entity (omitting any distinction arising from their spatial arrangement) (20). In the case of polymers, idealized definitions are required, and the deviations from ideality on the molecular level of real polymers are neglected in such definitions (21a). The definitions of structural features of polymers, related to constitution, configuration, and conformation, are linked to the structure-based nomenclature (21a, b), which is based on the structure of polymer molecules, and the name of a conventional base unit has no relationship to the source from which the unit was prepared (21a, b). The process-based set of definitions is instead linked to the primary definition of polymer through the definition of the term polymerization and monomer (21a, b).

On the basis of the structure-based nomenclature, a constitutional unit is a species of atom or group of atoms present in a chain of a polymer or oligomer molecule (21a). A polymer is regular when its constitution is regular; that is, it can be described by only one species of constitutional unit in a single sequential arrangement (21a). A constitutional repeating unit is the smallest constitutional unit whose repetition describes a regular polymer (21a, b). An irregular polymer is a polymer whose molecule cannot be described by only one species of constitutional unit in a single sequential arrangement (21a).

From any single monomer, different constitutional units may arise during polymerization. For instance, butadiene may polymerize via 1,2 or 1,4 polyaddition and the monomeric units may join the growing chain according to the two constitutional units shown in Scheme 1.1. For isoprene, three different constitutional units may be obtained corresponding to 1,2 or 1,4 or 3,4 polyaddition (Scheme 1.1) (21a).
In vinyl polymers, where the two terminals of the monomeric units unit are not equivalent and a head and a tail of the unit can be distinguished (for instance, the case of propylene), the regularity in the chemical constitution implies a regular enchainment of consecutive monomeric units always head to tail or always tail to head (Scheme 1.2).

In the polymer in Scheme 1.3, the constitutional units a–e can be distinguished. The convention of orienting polymer structures and the corresponding con-
Constitutional units from left to right is generally used. Therefore, the constitutional units a and b are regarded to be different, even though their repetition leads to the same polymer (21a,b). Only the constitutional units a and b are the smallest one completely describing this polymer chain. Either of the constitutional unit a or b of Scheme 1.3 is a constitutional repeating unit and the polymer of Scheme 1.3 is a regular polymer (21a,b).

Defects in the regular constitution may arise from the enchainment of consecutive units via head to head or tail to tail (21a). The polymer of Scheme 1.4 cannot be described by only one species of constitutional unit, such as a or b of Scheme 1.3, in a single sequential arrangement. The polymer of Scheme 1.4 whose molecule consists of a random arrangement of units a and b is an irregular polymer.

On the basis of these definitions, in random copolymers of two different monomers that provide at least two different constitutional units, such as –CH₂CH(R)– and –CH₃CH(Y)–, many other different constitutional units can be distinguished that arise from the random enchainment of the two monomeric units. However, the constitution of the random copolymer cannot be described by any one of these constitutional units alone and, therefore, a random copolymer is necessarily an irregular polymer.

### 1.2.2 Configuration

The configuration of a molecule specifies the spatial disposition of bonds, for an assigned constitution, without considering the multiplicities of the spatial arrangements that may arise by rotation around single bonds. In polymers, the constitutional unit is a constitutional unit having one or more sites of defined stereoisomerism (21a,c,d). A configurational repeating unit is a constitutional repeating unit whose configuration is defined at one or more sites of stereoisomerism in the main chain of a polymer molecule (21c,d). In a regular polymer, a configurational base unit corresponds to the constitutional repeating unit. A configurational repeating unit is the smallest set of one, two, or more successive configurational base units that prescribes configurational repetition at one or more sites of stereoisomerism in the main chain of a polymer molecule. A stereorepeating unit is a configurational repeating unit having defined configuration at all sites of stereoisomerism in the main chain of a polymer molecule (21a,c,d).

The configuration of a polymer is regular and the polymer is defined tactic or stereoregular, when its constitution is regular, the constitutional repeating unit contains centers of stereoisomerism (stereoisomeric centers) that may assume different configurations, and the succession of configurations of successive units is regular and is defined by an assigned law (21,22). A tactic polymer is a regular polymer whose molecules can be described in terms of only one species of configurational repeating unit in a single sequential arrangement. A stereoregular polymer is a regular polymer whose molecules can be described in terms of only one species of stereorepeating unit in a single sequential arrangement, that is, in terms of only one species of configurational repeating unit having defined configuration at all sites of stereoisomerism in the main chain, in a single sequential arrangement (21a,c,d). If the constitutional repeating unit contains more than one site of stereoisomerism, and the configuration of only one stereoisomerism center is defined, the polymer is tactic but not stereoregular. A stereoregular polymer is a tactic polymer where the configurations at all sites of stereoisomerism contained in the constitutional repeating units are defined (21). An atactic polymer is a regular polymer, the molecules of which have equal numbers of the possible configurational base units in a random sequence distribution (21d).

The most important stereoisomeric centers that are found along a polymer chain are

(a) double bonds, which may assume a cis or trans configuration

(b) tetrahedral stereoisomeric centers, that is, carbon atoms along a chain bonded to two different substituents, R₁ and R₂.

An example of case (a) is provided by double bonds present along the chains of polymers of 1,3-dienes with 1,4 additions of the monomeric units, as the 1,4 enchainment of butadiene shown in Scheme 1.1. The cases of poly(butadiene) and poly(isoprene) are shown in Scheme 1.5. The constitutional repeating units are the 1,4 units also shown in Scheme 1.1, whereas the possible configurational base units are shown in Scheme 1.5. The configurational repeating units and the corresponding cis-tactic and trans-tactic polymers are also shown in Scheme 1.5. A cis-tactic polymer and a trans-tactic polymer are tactic polymers in which the main-chain double bonds of the configurational base units are entirely in the cis or trans arrangement, respectively.
(21d). In the case of 1,4-poly(isoprene), the two tactic polymers correspond to naturally occurring polymers such as natural rubbers, and gutta-percha.

The second case of stereoisomerism occurs when tetrahedral stereoisomeric centers are present along the polymer chains. A tetrahedral stereoisomeric center is a carbon atom that is further bonded to two different groups, \( R_1 \) and \( R_2 \) (Fig. 1.2).

It is worth mentioning that stereochemical formulae for polymer chains or pieces of polymer molecules are generally shown as *Fisher projection* rotated through 90° (21d). In a Fisher projection, the atoms or groups attached to a tetrahedral center are projected on the plane of the paper from such an orientation that vertically drawn bonds are considered to lie below the projection plane and horizontal bonds to lie above the plane (21) (in Scheme 1.6), and that the principal chain appears vertical with the lowest-numbered chain member at the top (21) (in Scheme 1.6) (20). This convention is still in use for \( \alpha \)-amino acids and sugars (23). A 90° rotated Fisher projection, used for polymer molecules, is displayed horizontally rather than vertically;

A tetrahedral stereoisomeric center \( C \) present along a polymer chain. \( C \) is a carbon atom tetrahedrally bonded to two different atoms or groups \( R_1 \) and \( R_2 \).

**Figure 1.2.** A tetrahedral stereoisomeric center \( C \) present along a polymer chain. \( C \) is a carbon atom tetrahedrally bonded to two different atoms or groups \( R_1 \) and \( R_2 \).

That is, the principal chain appears horizontal or as hypothetical extended zigzag chains oriented from the left to the right, and the vertically drawn bonds are considered to lie above the projection plane and horizontal bonds to lie below the plane (21). The use of rotated Fisher projections corresponds to the common practice of using horizontal lines to denote polymer backbone bonds. At each individual backbone carbon atom, the horizontal lines represent bonds directed below the plane of the paper, while the vertical lines project above the plane of the paper from the carbon atom (21d). Therefore, the rotated Fisher
projections (a) and (a') of Scheme 1.7 correspond to the three-dimensional arrangements (b) and (b') and to the zigzag chains (c) and (c'), respectively (21d). Moreover, the Fisher projections (d) and (d') correspond to the zigzag chains (e) and (e'), respectively.

Unless otherwise stated, the drawing of configurational base unit, configurational repeating units, stereo-repeating units, and so on, always provides information regarding relative configurations (21d). The absence from a formula of any one of the horizontal or vertical lines at a tetrahedral stereoisomeric center, or of cis or trans designations at double bonds, indicates that the configuration of that stereoisomeric center is not known.

In a polymer molecule, the two portions of the main chain attached to any constitutional unit may be, in general, nonidentical; consequently, a backbone carbon atom that also bears two different side groups may be considered to be a chiral center (21d).

Two configurational units that correspond to the same constitutional unit are considered to be enantiomeric if they are nonsuperposable mirror images. Two nonsuperposable configurational units that correspond to the same constitutional unit are considered to be diastereoisomeric if they are not mirror image.

In a regular polymer molecule, as poly(propylene) -[CH(CH₂)₂-CH₂]ₙ-, the constitutional repeating unit is -CH(CH₃)₂-CH₂- and the corresponding configurational base units are shown in Scheme 1.8. The configurational base units (1) and (2) are enantiomeric, while the configurational units (1) and (3) of Scheme 1.9 are

Scheme 1.6. Fisher projection of a tetrahedral structure ((1),(2)) and rotated Fisher projection (through 90°) used for polymers (3).

Scheme 1.7. Rotated Fischer projections of pieces of polymer molecules (a), (a'), (d), (d'), and corresponding three-dimensional arrangements (b) and (b') and zigzag chains (c), (c'), (e), (e').
not enantiomeric because the constitutional units are different species. Both the configurational base units (1) and (2) of Scheme 1.8 are the configurational repeating unit and stereorepeating unit of isotactic polypropylene (iPP) and no matter which of the two base units is taken because the two infinite chains, one built up of identical configurational units (1) and the other built of identical configurational units (2), are not enantiomeric and differ only in the chain orientation (Scheme 1.8).

According to these definitions, an isotactic polymer is a regular polymer whose molecules can be described in terms of only one species of configurational base unit (having chiral or prochiral atoms in the main chain) in a single sequential arrangement (21a,c,d). In an isotactic polymer, the configurational repeating unit is identical to the configurational base unit (Scheme 1.8) (21d). A syndiotactic polymer is a regular polymer whose molecules can be described in terms of alternation of configurational base units that are enantiomeric (21a,c,d). In a syndiotactic polymer, the configurational repeating unit consists of two configurational base units that are enantiomeric (21a,c,d). The simplest possible stereorepeating units and the corresponding stereoregular polymers of poly(propylene) (isotactic, syn-dirotactic and hypothetical heterotactic) are shown in Scheme 1.10. It is apparent that in syndiotactic polypropylene (sPP), two enantiomeric configurational base units ((1) and (2) of Scheme 1.8) are connected to form the configurational repeating unit (2) of Scheme 1.10. In both iPP and sPP, the configurational repeating unit coincides with the stereorepeating unit, and the tactic polymer is also stereoregular because all sites of stereoisomerism are defined.

In the regular poly(ethylidene) –[CH(CH3)]n–, the constitutional repeating unit is –CH(CH3)–, whereas the configurational base units, the configurational repeating units, and the corresponding isotactic and syndiotactic polymers (in rotated Fisher projections and zigzag chains) are shown in Scheme 1.11.

For the polymer –[CH(COOR)CH(CH3)2]n–, there are two possible tetrahedral stereoisomeric centers. The four possible configurational base units are shown in Scheme 1.12. If only the ester-bearing main-chain stereoisomeric site in each constitutional repeating unit has defined stereochemistry, the configurational repeating unit is (5) in Scheme 1.12 and the corresponding polymer is a tactic (isotactic) polymer ((6) in Scheme 1.12). If two enantiomeric configurational base units are connected into the configurational repeating units (7) of Scheme 1.12, the corresponding polymer is syndiotactic ((8) of Scheme 1.12). Both polymers (6) and (8) of Scheme 1.12 are tactic polymers but are not stereoregular because the configuration at the stereoisomeric center –CH(CH3)– is not defined. A stereoregular polymer is always a tactic polymer, but a tactic polymer is not always a stereoregular polymer because a tactic polymer need not have all sites of stereoisomerism defined (21a,c,d).
A ditactic polymer is a tactic polymer that contains two sites of defined stereoisomerism in the main chain of the configurational base unit. The same polymer \([\text{CH(COO)}\text{RCH(CH}_3)_2\text{]}\_n\) of Scheme 1.12 is stereoregular when it is ditactic, that is, when the configurations at both sites of stereoisomerism are defined. The corresponding disisotactic and dis syndiotactic polymers are shown in Scheme 1.13 (polymers (1)–(3)). It is worth noting that polymer (4) of Scheme 1.13 does not represent a different dis syndiotactic polymer. Disisotactic or dis syndiotactic polymers are isotactic or syndiotactic polymers, respectively, that contain two chiral or prochiral atoms of defined stereochemistry in the main chain of the configurational base unit (21d).

A polymer such as \([\text{CH=CH–CH(CH}_3)_2\text{]}\_n\) has two main-chain sites of stereoisomerism: the double bond and the chiral tetrahedral carbon atom. The four possible configurational base units are shown in Scheme 1.14 (units (1)–(4)). The polymer may be tactic with respect to the double bond only (cis-tactic or trans-tactic) and atactic with respect to the chiral carbon atom if there is a random distribution along the chain of equal numbers of units containing the chiral atoms in the two possible configurations (units (3) and (4)). In this case, the configurational repeating units coincide with the configurational base units (1) and (2) of Scheme 1.14. The polymer may be atactic with respect to the double bond and tactic with respect to the tetrahedral chiral carbon.
Scheme 1.12. Constitutional repeating unit for the regular polymer −[CH(COOR)CH(CH\textsubscript{3})\textsubscript{n}]\textsubscript{r}, containing two possible tetrahedral stereoisomeric centers, four possible configurational base units ([1], [2], [3], and [4]), configurational repeating units ([5] and [7]) when only the ester-bearing main-chain stereoisomeric site in each constitutional repeating unit has defined stereochemistry, and corresponding isotactic (6) and syndiotactic (8) polymers.

Scheme 1.13. The two diisotactic ([1] and [2]) and the only disyndiotactic ([3] = [4]) polymers of the stereoregular polymer −[CH(COOR)CH(CH\textsubscript{3})\textsubscript{n}]\textsubscript{r}. 
carbon atom (isotactic or syndiotactic) if there is a random distribution of equal number of units in which the double bond is cis and trans (units (1) and (2)). In this case, the configurational repeating units are the configurational base units (3) or (4) for the isotactic repetition and unit (5) of Scheme 1.14 for the syndiotactic one.

The polymer is completely atactic when it contains, in a random distribution, equal numbers of the four possible configurational base units (1)–(4) of Scheme 1.14, which have defined stereochemistry at both sites of stereoisomerism. The polymer is di tactic when it is tactic with respect to both stereoisomeric centers, the double bond
and the chiral tetrahedral carbon atom. In this case, it is also **stereoregular**. For the stereoregular polymers, the *stereorepeating units* are shown in Scheme 1.4 and correspond to the polymers cis-isotactic, trans-isotactic, cis-syndiotactic, and trans-syndiotactic, respectively.

In regular poly(α-olefins) identical constitutional units are enchaired, as in Scheme 1.3, and the tetrahedral stereoisomeric carbon atom (atom C₇ in Fig. 1.2) is generally bonded along the chain backbone to two similar atoms (atoms C₆₋₁ and C₆₊₁ in Fig. 1.2). This implies that the tetrahedral stereoisomeric center C₇ is not an **asymmetric carbon atom** and the **tetrahedral structure is not chiral**. The asymmetric carbon atom is a traditional definition chosen by van’t Hoff for a carbon atom that is tetrahedrally bonded to four different atoms or groups, for example, Cabcd (Fig. 1.3A), none of the groups being the mirror image of the others (20). The asymmetric carbon atom is said to be a **chirality center** since it lies at the center of a chiral tetrahedral structure; that is, it holds a set of ligands in a spatial arrangement, which is not superposable to its mirror image (20). The chirality center is a generalized extension of the concept of the asymmetric carbon atom to central atoms of any element in not necessarily tetrahedral structures (20).

In the case of a polymer molecule as in Figure 1.2, the tetrahedral stereoisomeric center C₇ is not a chirality center since the two groups C₆₋₁ and C₆₊₁ are indistinguishable. The two carbon atoms C₆₋₁ and C₆₊₁ might be distinguishable as long as the chain ends of the polymer are different. However, in long polymer chains, the chain ends are indistinguishable; hence, the manifestation of the chirality, such as the optical activity, is precluded by the high molecular weight of polymers, which makes the chain ends an unimportant part of the chain structure (24). Therefore, the stereoisomeric centers C₇ in Figure 1.2, as the methine carbon atoms of polypropylene (Scheme 1.2), are not chirality centers but, according to the IUPAC nomenclature, they are **prochiral** (20). An achiral molecular entity, or part of it considered on its own, is called prochiral if it can be made chiral by the replacement of an existing atom (or achiral group) by a different one (20b). Similarly, an atom of a molecule that becomes a chirality center by replacing one of the two stereochemotopic groups attached to it by a different group is said to be a **prochirality center**. In other words, an achiral object having at least one pair of features that can be distinguished only by reference to a chiral reference frame is said to be **prochiral** (20a). An achiral object, which is capable of becoming chiral in two desymmetrization steps, is, sometimes, described as **proprochiral**. The geometric property of an achiral object (or spatial arrangement of atoms), which is capable of becoming chiral in a single desymmetrization step, is defined **prochirality**. For a tetrahedrally bonded atom, prochirality requires a structure Caacd (Fig. 1.3B), where none of the groups a, c, and d is the enantiomer of another. Therefore, the stereoisomeric center C₇ in Figure 1.2 is **prochiral** because it has the capability of becoming chiral in a single desymmetrization step, as the replacement of one of the two stereochemotopic atoms or groups (groups a in Fig. 1.3B) with a different one.

Names of chiral compounds whose absolute configuration is known are differentiated by prefixes R and S, assigned by the **sequence-rule procedure** (20) (Cahn, Ingold, and Prelog [CIP priority] (25)). Of the identical pair of stereochemotopic atoms or groups in a prochiral compound, that one which leads to an (R)-compound when considered to be preferred to the other by a sequence rule procedure (CIP priority) (25) is termed **pro-R**, and the other group is defined **pro-S**.

**Figure 1.3.** (A) An asymmetric carbon atom (chirality center) that lies at the center of a chiral tetrahedral structure. (B) A prochiral structure with a carbon atom at the center of a tetrahedral Caacd with two equal groups a. The prochiral structure may become chiral in a single desymmetrization step, as the substitution of one of the two stereochemotopic atoms or groups a with a different group. (C) Of the identical pair of stereochemotopic atoms or groups a in the prochiral compound Caacd, that one which leads to an (R)-compound when considered to be preferred to the other by a sequence rule procedure (CIP priority) (25) is termed **pro-R**, and the other group is defined **pro-S**.
chemical bonds rather than that of the atoms (3). Let \( l_1 \) and \( l_2 \) be two bonds adjacent to the carbon atom \( C_n \) which carries two different substituents \( R_1 \) and \( R_2 \) (Fig. 1.4). The two bonds \( l_1 \) and \( l_2 \) are **configurationally different** even though the carbon atom \( C_n \) is not asymmetric and is a **prochirality center** (3,26). The two bonds can be distinguished from a configurational point of view as (+) or (−) bonds (3). The inherent asymmetry of a bond adjacent to a stereoisomeric center \( C_i \) along a chain \( C_i C_{i+1} \ldots C_{i+n} \) is defined using a (+) sign when, looking along the \( C_{i+1} C_i \) bond, the substituents \( R_{i+1} \) and \( R_i \) are next to each other clockwise (3), with the convention that \( R_1 \) is bulkier than \( R_2 \), according to the **sequence-rule procedure** (CIP priority) (25) (Fig. 1.4). If these substituents succeed each other counterclockwise, the bond is defined with the (−) sign (3). It is apparent from Figure 1.4 that if the bond \( l_1 \) has a (+) character with respect to the stereoisomeric center \( C_l \), \( l_2 \) must have a (−) character and vice versa. Bonds astride a tetrahedral stereoisomeric center are always opposite in sign. Two monomeric units are identical from the configurational point of view if the bonds adjacent to the tetrahedral stereoisomeric center are characterized by the same (+) and (−) characters; they are enantiomeric if the signs (+) and (−) are reversed (3). In the **enantiomeric configurational base units** of a regular vinyl polymer (as poly(propylene) of Scheme 1.8), the two bonds adjacent to the tertiary carbon atom (the **prochirality center**) are, indeed, characterized by opposite signs (Fig. 1.5).

According to the definition of stereoregular polymer given earlier, as a regular polymer whose molecules can be described in terms of only one species of configurational repeating unit having defined configuration at all sites of stereoisomerism in the main chain (stereo-

**Figure 1.4.** Definition of (−) and (+) bonds adjacent to a tetrahedral stereoisomeric, prochiral center (3). The substituent \( R_1 \) is bulkier than \( R_2 \) according with the sequence-rule procedure (CIP priority) (25). (Reproduced with permission from Reference 4. Copyright 2003 by Wiley Interscience.)

**Figure 1.5.** Enantiomeric configurational base units of regular vinyl polymers with indication of the (+) and (−) characters of the bonds adjacent to the stereoisomeric center.

**Figure 1.6.** Rotated Fisher projections and zigzag chains of isotactic and syndiotactic vinyl polymers with indication of the ordered sequences of (+) and (−) bonds. (A) Isotactic polymer. (B) Syndiotactic polymer.

**repeating unit), in a single sequential arrangement** (21c,d), the stereoregularity of a polymer chain necessarily implies a regular succession of couples of (+) and (−) bonds. Isotactic polymers, which are defined as **regular polymers whose molecules can be described in terms of only one species of configurational base unit (having chiral or prochiral atoms in the main chain)** in a single sequential arrangement (21a,c,d), are characterized by a regular enchainment of monomeric units having the same configuration, hence by a **regular succession of (+) and (−) bonds** (3) (Fig. 1.6A). The isotactic chain in Figure 1.6A with the bond sequence . . . (−) (+)(−)(+)(−) . . . , built up by enchainment of identical
configurational units (1) in Figure 1.5, and the isotactic chain having bond sequence \ldots (+)(-)(+)(-)(+)(-) \ldots , built up by the enchainment of the enantiomeric configurational units (2) in Figure 1.5, are configurationally identical and differ only in the chain orientation.

**Syndiotactic polymers, defined as regular polymers whose molecules can be described in terms of alternation of the configurational base unit that are enantiomeric** (21a,c,d), are characterized by a regular enchainment of monomeric units having alternatively enantiomeric configurations, which produces **couples of adjacent bonds having the same sign** (3) (Fig. 1.6B). Also for the syndiotactic polymer, the chain in Figure 1.6B with bond sequence \ldots ( )(+)(+)( )\ldots and the syndiotactic chains having bond sequence \ldots (+)( )(+)( )\ldots are configurationally identical and differ only in the chain orientation.

For the regular poly(oxypropylene) \([-\text{CH}_2-\text{-CH(CH}_3\text{)}-\text{O}]_{\text{n}}\), the stereoisomeric center is a really asymmetric carbon atom; the constitutional repeating unit is \(-\text{CH}_2-\text{CH(CH}_3\text{)}-\text{O}\) and two enantiomeric configurational base units are possible. The two isotactic chains made by a regular enchainment of the two possible enantiomeric configurational units, corresponding to the bond sequence \ldots (-)(+)(-)(+)(-)(+)\ldots and \ldots (+)(+)(-)(-)\ldots , are shown in Figure 1.7. In this case, the two chains correspond to two nonidentical configurations, as expected because of the asymmetry of the tertiary carbon atoms.

This definition of (+) and (-) bonds for the description of the configuration of tetrahedral sites of stereoisomerism that are prochirality centers is useful because it allows the easy treatments of possible configurations in cases of any complexity (3). Moreover, the (+) and (-) characters of the bonds are strictly related to the accessibility of gauche or gauche conformations of the bonds and, therefore, to the formation of right- or lefthanded helical conformations (3) (see Section 1.5.3 and Fig. 1.30).

### 1.2.3 Relative Configurations

The description of the structure of a polymer molecule generally implies the description of the local arrangements present in the molecules, in particular, the relative configurations of stereoisomeric centers present in relatively short portions of the molecule. A **constitutional sequence** is a defined portion of a polymer molecule comprising constitutional units of one or more species (21c,d). A **configurational sequence** is a constitutional sequence in which the relative or absolute configuration is defined at one or more sites of stereoisomerism in each constitutional unit in the main chain of a polymer molecule. A **stereosequence** is a configurational sequence in which the relative or absolute configuration is defined at all sites of stereoisomerism in the main chain of a polymer molecule (21c,d).

A couple of consecutive, but not necessarily contiguous, tetrahedral stereoisomeric centers, made by constitutionally equivalent carbon atoms that have a symmetrically constituted connecting group (if any), defines a **diad** (Fig. 1.8) (21c,d). **Stereosequences terminating in tetrahedral stereoisomeric centers at both ends, and which comprise two, three, four, five, and so on, consecutive centers of that type, may be called diads, triads, tetrads, pentads, and so on, respectively** (21d).

Relative configurations of consecutive, but not necessarily contiguous, constitutionally equivalent carbon atoms that have a symmetrically constituted connecting group (if any) are defined as **meso** or **racemo** (Fig. 1.8) (21d). In the **meso** relative configuration, the two stereoisomeric centers have the same configuration, whereas in the **racemo** relative configuration, the two connected units are enantiomeric (21d).

It is worth noting that in the chain of isotactic poly(oxypropylene) in Figure 1.7, a couple of consecutive tertiary carbon atoms does not define a diad and cannot be considered as in a **meso** arrangement because the connecting group \(-\text{O}-\text{CH}_2-\) lacks the necessary symmetry.

**Figure 1.7.** Rotated Fisher projections and zigzag chains of isotactic poly(oxypropylene) with indication of the ordered sequences of (+) and (-) bonds.
Stereoregular vinyl polymers can be defined in terms of the regular sequences of diads; thus, an isotactic vinyl polymer consists of entirely meso diads and corresponds to an ordered succession of meso relative configuration, \(-\text{mmm}m\). A syndiotactic vinyl polymer consists of entirely racemo diads corresponding to an ordered succession of racemo relative configuration, \(-\text{r}rr\text{r}rr\) (21d). Similarly, a vinyl polymer consisting entirely of \(\text{mm} \Rightarrow \text{m}\) triads is called a heterotactic polymer. In Figure 1.9, the definition of isotactic and syndiotactic polymers, in terms of the regular succession of meso and racemo diads (21d), is compared in the case of polypropylene with the definition based on the regular succession of bonds having (+) and (−) characters (3).

When two tetrahedral stereoisomeric centers are contiguous, as in the constitutional repeating unit \(-\text{CHA}–\text{CHB}–\) with \(A \neq B\), the relative configurations are designed with a different nomenclature. The relative configuration at two contiguous carbon atoms in the main chains bearing substituents A and B, respectively, with \(A \neq B\), is designed as erythro or threo (Fig. 1.10) (21d). This is in analogy with the terminology for carbohydrate systems in which the substituents are \(-\text{OH}\) (20a).

Also in this case, the use of configurational signs (+) and (−) for the designation of the intrinsic chirality of bonds is very useful for the description of the relative configuration. Two configurational signs, for example, (+, +), can be assigned to the bond connecting the two stereoisomeric centers, assuming that substituents A and B have CIP priority compared to the hydrogen atom (Fig. 1.10). The first sign indicates the intrinsic chirality of the bond with respect to the first carbon atom bearing substituent A, whereas the second sign indicates the intrinsic chirality of the same bond with respect to the second carbon atom bearing substituent B (Fig. 1.10). The pairs (−, +) or (+, −) define a relative erythro configuration, whereas the pairs (+, +) or (−, −) define a relative threo configuration (3) (Fig. 1.10).
When the two substituents, A and B, bonded to the stereoisomeric centers are equal, as in –CHA–CHA–, the two carbon atoms are constitutionally equivalent as in the cases of Scheme 1.11, so that the relative configurations must be designed as meso and racemo, instead of erythro and threo, respectively.

The erythro/threo terminology can be extended to similar systems in which a higher level of substitution exists, as in –CAX–CBY–, to denote the relative placements of those two substituents, one for each backbone carbon atom, which rank highest according to the sequence-rule procedure (A and B in –CAX–CBY– if
A and B have CIP priority compared to X and Y, respectively) (21d).

Regular polymers of the kind \((\text{CHA–CHB})_n\) may be ditactic (21d). A full configurational description requires a combination of terms as *erythro*, *threo*, *meso*, or *racemo* with a term such as diisotactic or disyndiotactic (21d). An *erythro* and *threo* diisotactic polymers and only one disyndiotactic polymer can be obtained. The use of configurational signs of backbone bonds allows for an easy description of all cases (3,27). A regular alternating succession of \((+,+\) and \((-,-\) bonds corresponds to a *threo*-diisotactic polymer; the regular succession of \((+,-\) bonds corresponds to the *erythro*-diisotactic polymer; and the succession \(\ldots (+,+)(+,-\ldots \) corresponds to the disyndiotactic polymer (Fig. 1.11) (3,21d,27).

It is worth noting that the disyndiotactic polymer in Figure 1.11 cannot be expressed as *erythro*-disyndiotactic nor as *threo*-disyndiotactic. The polymers in Figure 1.12 can be instead designed as *erythro*- and *threo*-disyndiotactic (21d), corresponding to the successions of bonds chirality \(\ldots (-,-) (+,-) (+,+)(-,-) (-,-) \ldots \) and \(\ldots (-,+)(-,-) (+,+)(-,-) \ldots \), respectively, where b is the bond \(-\text{CH}_2-\text{CH}_2-\) with no configurational sign.

When substituents A and B are joined in a ring, it is possible to distinguish *erythro* and *threo* cases for both the diisotactic and disyndiotactic polymers (Fig. 1.13) (21d). If the rings are symmetrical with \(A = B\), the polymers are designed *meso*-diisotactic and *racemo*-diisotactic (21d).

As discussed earlier, the general requirement for the crystallizability of polymers is the regularity in the
chemical constitution and in the configuration of long sequences of monomeric units (3,4,19). Copolymers of different monomers that are able to cocrystallize in the same lattice may be considered as possible exceptions to the need of the regularity in the chemical constitution. For instance, in the case of vinyl polymers, it is possible to accommodate into the crystalline lattice different comonomeric units having lateral groups with different shapes and dimensions. Isotactic copolymers of butene and 3-methylbutene (28) or isotactic copolymers of styrene and o-fluorostyrene (29) are crystalline in the whole range of composition, whereas propene and 1-butene comonomeric units are able to cocrystallize at any composition in both isotactic (30–33) and syndiotactic copolymers (34,35). Isomorphism of comonomeric units also occurs in copolymers of acetaldheyde and n-butyrdehyde, which are crystalline over the whole range of composition (36). Analogous isomorphism of comonomeric units has been observed in trans-1,4-copolymers of butadiene and 1,3-pentadiene (37), or in copolymers of vinylidenefluoride and vinylfluoride (38). These examples indicate that the requirement concerning the regularity in the configuration (stereoregularity) is more stringent than that concerning the regularity in the chemical constitution in order for a polymer be crystalline (3). However, it has been recently clarified that, in some cases, the presence of defects of stereoregularity, even at high concentrations, does not prevent the crystallization. The role played by the disorder in the crystallization of polymers will be discussed in the next chapters (Chapter 4). In the case of iPP and sPP, the controlled introduction of defects of stereoregularity, through synthesis with single-center metalorganic catalysts, has been used to tailor the physical properties of the materials by controlling the crystallization behavior (see Chapter 7).

1.3 CONFORMATION

The conformations of a molecule are the different spatial arrangements of the atoms in a molecule of a given constitution and configuration that may arise by rotation around single bonds (20,21). The geometry of a molecule is fully described by the internal coordinates, that is, bond lengths, bond angles, and torsion angles. If a specific A–B bond is denoted as A–B, the bond length is written as $b(A, B)$ (21d). The bond angle formed by three consecutive atoms A–B–C is written as $\tau(A, B, C)$, which may be abbreviated, if there is no ambiguity, to $\tau(B)$, $\tau(B')$, $\tau(B'')$, or $\sigma$ (21d). In a system of four consecutive atoms, A–B–C–D, or three consecutive bonds, $l_1$, $l_2$, and $l_3$, the angle between the plane defined by the triplets of neighboring atoms ABC (or defined by the two bonds $l_1$ and $l_3$) and the plane defined by the atoms BCD (or defined by the bonds $l_1$) is the torsion angle or dihedral angle or internal rotation angle of A and D around the bond B–C (Fig. 1.14) (20,21d). The torsion angle of A and D around the bond B–C is also defined as the angle between the projections of the bonds A–B ($l_1$) and C–D ($l_3$) onto a plane normal to the bond B–C ($l_2$) (21d). The torsion angle is written in full as $\theta(A_1, B, C_2, D_3)$, which may be abbreviated, if there is no ambiguity, to $\theta(B_1, C_2)$, $\theta(B_1)$, or $\theta^B$, and so on. (21d) In the eclipsed conformation in which the projection of the bonds A–B ($l_1$) and C–D ($l_3$) coincide, the torsion angle $\theta$ is given the value 0° (synperiplanar or cis conformation) (20,21d). The torsion angle is considered positive (+$\theta$) or negative ($-$ $\theta$) depending on whether, when the system is viewed along the central bond $l_2$ in the direction B–C (or C–B) (Fig. 1.14), the bond to the front atom A ($l_1$) (or D ($l_1$)) requires the smaller angle of clockwise or anticlockwise rotation, respectively, in order that it may eclipse the bond to the rear atom D ($l_3$) (or A ($l_1$)) (20,21d). The torsion angles are measured in the range $-180^\circ < \theta < +180^\circ$ rather than in the range 0–360° (20,21d). Conformations referring to torsion angles $\theta(A, B, C, D)$, where A, B, C, and D are main-chain atoms, are described as cis or synperiplanar (C), gauche or synclinal (G), anticalinal (A), and trans or antiperiplanar (T), corresponding to torsion angles within $\pm 30^\circ$, respectively, $0^\circ$, $60^\circ$, $120^\circ$, and $180^\circ$ (20,21d). The terms cis, gauche, and trans are used especially for polymers (21d). The symbols $G^+$, $G^-$ (or $A^+$, $A^-$) refer to torsion angles of similar type but opposite known sign, that is, = $+60^\circ$ and $= 60^\circ$ (or $+120^\circ$ and $= 120^\circ$). The notation $G$, $G$, A, and $\AA$ (and T, $\bar{T}$, C, $\bar{C}$ whenever the torsion angles are not exactly equal to 180° and 0°, respectively) is reserved for the designation of enatiomorphous conformations, that is, conformations of opposite but unspecified sign (21d). When necessary, a
deviation from the proper value of the torsion angle can be indicated by the sign (−), as, for example, G(−), G′(−), G(−), G(−) (21d).

1.4 RELATIONSHIPS AMONG INTERNAL PARAMETERS OF MACROMOLECULES

For small deformations from the tetrahedral value (109.47°), the sum of the six bond angles on a given atom may be kept as approximately constant and equal to 6 × 109.47°. More precise relationships, valid even for non-negligible deformation of the bond angles from the tetrahedral value, can be described for the two systems in Figure 1.15, corresponding to methylene and methine groups, under the assumption of a local C₈ symmetry for the system C—CH₂—C (Fig. 1.15A), and a local C₃v symmetry for the system C—CHC—C (Fig. 1.15B). For the system C—CH₂—C, the plane H—C—H is perpendicular to the plane C—C—C. The angle C—C—C (τ₁) is different from the angle H—C—H (τ₂). The four angles C—C—H (τ₃) are equal so that the local symmetry is Cᵥ. The three bond angles τ₁, τ₂, and τ₃ are related as in Equation 1.1:

\[
\sin(\tau_3/2) = [1 + \cos(\tau_1/2)\cos(\tau_2/2)]^{1/2}/2^{1/2}.
\]  

(1.1)

For C—CH₃C—C (Fig. 1.15B), the three bond angles τ₁, τ₂, and τ₃ are equal among themselves but different from the three equal angles H—C—C (τ₄), thus giving a C₃v symmetry. The two bond angles τ₁ and τ₂ are related by Equation 1.2:

\[
\sin(\tau_1/2) = (3^{1/2}/2)\sin(\tau_2).
\]  

(1.2)

For a system of the kind in Figure 1.16A and for a strictly tetrahedral carbon atom, the three torsion angles C₁—C₂—C₃—R₁ (θ₁), C₁—C₂—C₃—R₂ (θ₂), and C₁—C₂—C₃—R₃ (θ₃) are related by Equation 1.3, Equation 1.4, and Equation 1.5, where θ is the angle between the pair of planes C₂C₃R₂, C₂C₃R₃, which are all equal to 120° (Fig. 1.16B):

\[
\theta_1 = \theta_2 - \psi = \theta_3 + \psi = \theta_2 - 120^\circ = \theta_3 + 120^\circ
\]  

(1.3)

\[
\theta_2 = \theta_1 + \psi = \theta_2 - 120^\circ = \theta_1 + 120^\circ
\]  

(1.4)

\[
\theta_3 = \theta_1 - \psi = \theta_2 + \psi = \theta_1 - 120^\circ = \theta_2 + 120^\circ
\]  

(1.5)

In the case that the bond angles at the carbon C₁ are not strictly tetrahedral, as in the systems in Figure 1.17A and Figure 1.15A, the relationships between torsion angles are slightly different because the values of the angles between the pair of planes C₂C₃C₁, C₂C₃H”, C₂C₃H’” are different. The three bond angles τ₁, τ₂, and τ₃ at the carbon C₁ are related by Equation 1.1, and the three torsion angles C₁—C₂—C₃—C₄ (θ₁), C₁—C₂—C₃—H” (θ₂), and C₁—C₂—C₃—H’” (θ₃) are related by Equation 1.6, Equation 1.7, and Equation 1.8 (Fig. 1.17B), where θ is the angle between the planes C₂C₃C₄ and C₂C₃H” and between the planes C₂C₃C₄ and C₂C₃H’”, whereas θ’ is the angle between the planes C₂C₃H’” and C₂C₃H’” (Fig. 1.17B):

\[
\theta_1 = \theta_2 - \psi = \theta_3 + \psi
\]  

(1.6)

\[
\theta_2 = \theta_1 + \psi' = \theta_1 + \psi
\]  

(1.7)

\[
\theta_3 = \theta_1 - \psi = \theta_2 + \psi'.
\]  

(1.8)
\[ \sin(\psi/2) = \sqrt{\frac{1}{2} \left( 1 + \frac{\sin(\tau_1/2)\cos(\tau_2/2)}{\sqrt{\sin^2(\tau_1/2)\cos^2(\tau_2/2) + \sin^2(\tau_2/2)}} \right) } \]

(1.9)

\[ \psi' = 360° - 2\psi. \]

(1.10)

For the system in Figure 1.15A and Figure 1.17, if \( \tau_1 = 113° \) and \( \tau_2 = 108° \), the angles \( \psi \) and \( \psi' \) are \( \psi = 121.2° \) and \( \psi' = 360° - 2\psi = 117.6° \).

In the case of the system in Figure 1.18A, corresponding to the case in Figure 1.15B, the bond angles \( \tau_1 \) and \( \tau_2 \) at \( C_3 \) are defined by Equation 1.2, and the three torsion angles \( C_1-C_2-C_3-C'_4(\theta_1) \), \( C_1-C_2-C_3-C''_4(\theta_2) \), and \( C_1-C_2-C_3-H(\theta_3) \) are related by the same Equation 1.6, Equation 1.7, and Equation 1.8, where the angle \( \psi \) between the planes \( C_2C_3C'_4 \) and \( C_2C_3C''_4 \) is defined by Equation 1.11, whereas the angle \( \psi' \) between the planes \( C_2C_3C'_4 \) and \( C_2C_3H \), and between the planes \( C_2C_3C''_4 \) and \( C_2C_3H \), is defined by Equation 1.12:

\[ \cos\psi = \frac{(3/4)\sin^22\tau_2 - \sin^2\tau_2}{(3/4)\sin^22\tau_2 + \sin^2\tau_2} \]

(1.11)

\[ \psi' = (360° - \psi)/2. \]

(1.12)

For the system in Figure 1.15B and Figure 1.18, if \( \tau_1 = 111° \), then \( \tau_2 = 107.9° \) and \( \psi = 124.0° \) and \( \psi' = 118.0° \).

These examples show that Equation 1.3, Equation 1.4, and Equation 1.5 are only approximate even for small deviations from strict tetrahedral geometry.

Restrictions of availability of torsion angles are imposed by the configuration (aside from those arising from nonbonded interactions). In the system in Figure 1.19A, and assuming for the sake of simplicity a perfectly tetrahedral geometry of the carbon \( C_3 \), as in Figure 1.16A, the three torsion angles \( C_1-C_2-C_3-R_1(\theta_1) \), \( C_1-C_2-C_3-R_2(\theta_2) \), and \( C_1-C_2-C_3-R_3(\theta_3) \) are related by different relationships depending on the configuration of the tetrahedral chiral center \( C_3 \). For the configuration in Figure 1.19B, Equation 1.13 and Equation 1.14 are valid, whereas for the configuration in Figure 1.19D, Equation 1.15 and Equation 1.16 hold:

\[ \theta_2 = \theta_1 + 120° \]

(1.13)

\[ \theta_3 = \theta_1 - 120° \]

(1.14)

\[ \theta_4 = \theta_1 - 120° \]

(1.15)

\[ \theta_5 = \theta_1 + 120° \]

(1.16)
TABLE 1.1. Values of Bond Angles $\tau_1$, $\tau_2$, and $\tau_3$ and Values of Dihedral Angles $\psi$ and $\psi'$ (Defined in Fig. 1.15, Fig. 1.17, and Fig. 1.18) for Not Strictly Tetrahedral Systems in Figure 1.15, under the Assumption of a $C_2$ Symmetry (as for a Methylene Carbon Atom C–CH₂–C in Fig. 1.15A and Fig. 1.17) or a $C_n$ Symmetry (as for a Methine Carbon Atom C–CHR–C in Fig. 1.15B and Fig. 1.18).

<table>
<thead>
<tr>
<th>Methylene Carbon Atom (Cₙ Symmetry)</th>
<th>Methine Carbon Atom (Cₙ Symmetry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$ (deg) $\tau_2$ (deg) $\tau_3$ (deg) $\psi$ (deg) $\psi'$ (deg)</td>
<td>$\tau_1$ (deg) $\tau_2$ (deg) $\psi$ (deg) $\psi'$ (deg)</td>
</tr>
<tr>
<td>110 108 109.7 120.76 118.48</td>
<td>110 108.94 121.32 119.34</td>
</tr>
<tr>
<td>111 108 109.45 120.91 118.18</td>
<td>111 107.90 123.95 118.025</td>
</tr>
<tr>
<td>112 108 109.19 121.06 117.88</td>
<td>112 106.81 126.80 116.60</td>
</tr>
<tr>
<td>113 108 108.93 121.21 117.58</td>
<td>113 105.66 129.89 115.06</td>
</tr>
<tr>
<td>114 108 108.67 121.36 117.28</td>
<td>114 104.44 133.28 113.36</td>
</tr>
<tr>
<td>115 108 108.41 121.50 117.0</td>
<td></td>
</tr>
<tr>
<td>116 107 108.37 122.11 115.78</td>
<td></td>
</tr>
<tr>
<td>117 107 108.11 122.25 115.50</td>
<td></td>
</tr>
</tbody>
</table>

The bond angles $\tau_1$ and $\tau_3$ are calculated from $\tau_2$ from Equation 1.1 and Equation 1.2, whereas the dihedral angles $\psi$ and $\psi'$ are calculated from Equation 1.9, Equation 1.10, Equation 1.11, and Equation 1.12 for the $C_2$, and $C_n$ systems, respectively.

A list of some typical values of bond angles and dihedral angles $\psi$ and $\psi'$ for the systems in Figure 1.15, Figure 1.17, and Figure 1.18, under the assumption of $C_2$, and $C_n$ symmetries, is reported in Table 1.1.

1.5 CONFORMATION OF POLYMER CHAINS IN THE CRYSTALLINE STATE

1.5.1 Basic Principles

The conformations of a molecule are the different spatial arrangements of the atoms in a molecule of a given constitution and configuration that may arise by rotation around single bonds (20,21). The conformation assumed by polymer molecules in the crystalline state depends on the configuration of the stereoisomeric centers present along the chains. The general requirement that in polymer crystals the chemical constitution of polymer molecules and the succession of configurations of the stereoisomeric centers present along the chains must be regular, implies, as a direct consequence, that the conformations assumed by macromolecules in the crystals are regular (3). The repetition of identical units along the chain axis in the crystalline state implies that the molecular chains must be built up of structural units that are related by a well-defined symmetry (3,4). The conformation assumed by polymer chains in the crystalline state is defined by two basic principles, the equivalence principle and the principle of minimum internal conformational energy (3,19,39–41).

(1) The Equivalence Principle. The conformation of a polymer chain in the crystalline state is defined by a succession of equivalent structural units, which occupy geometrically (not necessarily crystallographically) equivalent positions with respect to the chain axis. The chain axis is parallel to a crystallographic axis of the crystal.

(2) Principle of Minimum Internal Conformational Energy. The conformation of a polymer chain in a crystal approaches one of the minima of the internal conformational energy, which would be taken by an isolated chain subjected to the restrictions imposed by the equivalence principle.

1.5.2 The Equivalence Principle

The equivalence principle is a working hypothesis that chain monomeric units (the structural units) are geometrically equivalent (3,19,21,e.g.39–41). The (chain) conformational repeating unit is the smallest structural unit of a polymer chain with a given conformation that is repeated along the chain through symmetry operations, which comprises a translation (21d,e.g). The conformational repeating unit is the structural unit of the equivalence principle, which occupies geometrically (not necessarily crystallographically) equivalent positions with respect to the chain axis (3).

In polymer crystals, one of the translations of the lattice must relate atoms belonging to the same macromolecules. The identity period, or chain repetition distance, is the shortest distance along the chain axis for translational repetition of the chain structure (21e,g). The crystallographic identity period parallel to the chain axis should preferably be designated $c$ in descriptions of macromolecular crystallography (21d). A repeating
**TABLE 1.2. Possible Symmetry Operators for the Conformations of Polymers**

<table>
<thead>
<tr>
<th>Operator</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$l$</td>
<td>Identity operator</td>
</tr>
<tr>
<td>$t$</td>
<td>Translation</td>
</tr>
<tr>
<td>$c$</td>
<td>Glide plane</td>
</tr>
<tr>
<td>$m$</td>
<td>Mirror plane</td>
</tr>
<tr>
<td>$d$</td>
<td>Mirror plane</td>
</tr>
<tr>
<td>$i$</td>
<td>Inversion center</td>
</tr>
<tr>
<td>$2$</td>
<td>Twofold rotation axis</td>
</tr>
<tr>
<td>$c_1$</td>
<td>Rotation axis</td>
</tr>
<tr>
<td>$s(A^*M/N)$</td>
<td>Screw or helical symmetry</td>
</tr>
</tbody>
</table>

The conformational repeating unit is, in general, a fraction of the repeating unit and often corresponds, but not necessarily, to a single monomeric unit. The necessary geometric equivalence of structural units along an axis allows definition of the possible types of geometric symmetry that a linear macromolecule may achieve in the crystalline state. The conformation of a macromolecule is generally defined in terms of its symmetry. The possible symmetry elements for a chain conformation must be compatible with the chemical constitution and configuration of the macromolecules. They must be such as to leave the chain axis unchanged. For instance, a threefold rotation axis perpendicular to $c$ is not a possible symmetry operator of the conformation of a macromolecule. The only symmetry operators compatible with a chain repetition are shown in Table 1.2.

The helix is the molecular conformation of a spiral nature, generated by the screw symmetry, that is, by regularly repeating rotations around the backbone bonds of a macromolecule (21d,e,g). In the description of helices and of the helical symmetry $s(A^*M/N)$, the following parameters and symbols are employed (21d,e,g). The helix residue is the smallest set of one or more successive configurational base units that generates the whole chain through helical symmetry (21e,g). The symbol $s$ stands for the screw axis, coincident with the chain axis, and the class of the helix $A$ is the number of skeletal chain atoms contained within the helix residue (21d,e,g). $M$ is the integral number of residues contained in $N$ turns, corresponding to the identity period $c$ ($M$ and $N$ must be prime to each other). The class of helix $A$ may be dropped if deemed unnecessary so that the helix may be simply denoted as $s(M/N)$ (3,21d,e,g). Important parameters of the symmetry operator are

$n = M/N$ is the number of conformational repeating units or residue per turn.

The unit height $h = c/M$ is the translation along the helix axis per conformational repeating unit or residue.

The unit twist $t = 2\pi N/M$ is the angle of rotation about the helix axis per conformational repeating unit or residue, that is, the angle of rotation about the axis on passing from one atom of the $i$th residue to the equivalent atom of the successive residue. The unit twist is taken as positive angle for a counterclockwise rotation;

The helical pitch $p = c/N$ is the translation along the helix axis per turn of the helix.

These parameters, in particular, the unit twist, define the helix sense. The right-handed sense of a helix traces out a clockwise rotation moving away from the observer; the left-handed sense traces out an anticlockwise rotation moving away from the observer (21d). Chains of identical helical conformation and helix sense (chirality) are isomorphous. Chains of opposite chirality but equivalent conformation are enantiomorphous. Helices with symmetries $s(M/N)$ and $s(M/(M-N))$ are equivalent and enantiomorphous, and, if the unit twist is defined as the angle between $0^\circ$ and $180^\circ$, they are characterized by the same modulus $|t|$ of the unit twist, but opposite sign, $-t$ and $t$, respectively. A right-handed $s(M/N)$ helix has a positive value of the unit twist comprised between $0^\circ$ and $180^\circ$, corresponding to a counterclockwise rotation for passing from one atom to the corresponding atom of the successive conformational repeating unit (or
Conformation of polymer chains in the crystalline state

### TABLE 1.3. Possible Chain Symmetry of Some Crystalline Polymers

<table>
<thead>
<tr>
<th>Line Repetition Group</th>
<th>Polymers</th>
<th>Specific Symmetry</th>
</tr>
</thead>
<tbody>
<tr>
<td>s(A*M/N)1 particular case t1</td>
<td>Isotactic poly(propylene), $M/N = \frac{s}{1}, A = 2$</td>
<td>s(3/1)1</td>
</tr>
<tr>
<td></td>
<td>trans-1,4-Poly(isoprene), (α-form)</td>
<td></td>
</tr>
<tr>
<td>s(A*M/N)2 particular case t2</td>
<td>Syndiastic poly(propylene), (forms I and II), $M/N = \frac{2}{1}, A = 4$</td>
<td>s(2/1)2</td>
</tr>
<tr>
<td></td>
<td>Syndiastic poly(propylene) (form IV) ($T_G \alpha T_G \beta$ conformation)</td>
<td></td>
</tr>
<tr>
<td>tm</td>
<td>Nylon 7,7</td>
<td></td>
</tr>
<tr>
<td>tc</td>
<td>cis-1,4-Poly(isoprene)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>trans-1,4-Poly(isoprene), (α-form)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Poly(1,1-difluoroethylene), (modification 2)</td>
<td></td>
</tr>
<tr>
<td>ti</td>
<td>meso-Diisotactic alternating ethylene-cis-2-butene copolymer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>trans-1,4-Poly(1,3-butadiene), (form I)</td>
<td></td>
</tr>
<tr>
<td>s(A*2/1)m</td>
<td>trans-Polypentenamer (trans-poly(1-pentenylene)), $A = 5$</td>
<td>s(5*2/1)m</td>
</tr>
<tr>
<td>s(A*2/1)d</td>
<td>Nylon 6 (planar chain conformation), $A = 7$</td>
<td>s(7*2/1)d</td>
</tr>
<tr>
<td>tdm</td>
<td>Nyle 6,6 (planar chain conformation)</td>
<td></td>
</tr>
<tr>
<td>tcm</td>
<td>Syndiastic 1,2-poly(1,3-butadiene)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Syndiastic poly(propylene), (form III)</td>
<td></td>
</tr>
<tr>
<td>tci</td>
<td>cis-1,4-Poly(1,3-butadiene)</td>
<td></td>
</tr>
<tr>
<td>s(A*2/1)dm</td>
<td>Polyethylene, $A = 1$</td>
<td>s(1*2/1)dm</td>
</tr>
</tbody>
</table>

Residue). In the corresponding enantiomorphous left-handed $s(M/(M-N))$ helix, the unit twist is negative with modulus comprised between 0° and 180°, corresponding to a clockwise rotation for passing from one atom to the corresponding atom of the successive residue, or is positive with a value higher than 180°, corresponding to a counterclockwise rotation for passing from one atom to the corresponding atom of the successive unit.

Some of the symmetry elements are not compatible with the constitution and configuration of the single chain. For instance, whenever the constitutional unit has a directional character, as, for instance, in nylon 6 or polyisoprene, symmetry elements such as 2, m, and i are ruled out automatically. For polyamides of the general type –CO–(CH$_n$)$_m$–CO–NH–(CH$_m$)$_m$–NH–, an inversion center is only possible if $n$ and $m$ are both even. Moreover, rotation axes $r_i$ with rotation around the chain axis for a single chain may be consistent only for very particular constitutional repeating units and very particular values of the rotation angle $2\pi/n$.

All the possible symmetry operators compatible with a chain repetition can be appropriately combined into the line repetition groups (3,21d,e,g). The line repetition groups are the possible symmetries of arrays extending in one direction with a fixed repeating distance (3,21d,e,g). The possible combinations of the symmetry operators are limited by the constitution and the configuration of the chain polymer. The screw operator cannot combine with the inversion center $i$, mirror planes $m$ and $d$, and the glide plane $c$, which would change the helix sense, while the twofold axis perpendicular to the chain axis is the only symmetry operator compatible with the screw repetition, except the special cases $M = 1$, $N = 1$ ($s = t$), and $M = 2$, $N = 1$. Thirteen line repetition groups, indicated in Table 1.3, have been defined. In the symbol of the groups, the first letter $s$ or $t$ indicates whether the repetition along the axis is helicoidal (rotation plus translation) or translatory (simple translation), then there are the symbols of the symmetry elements of Table 1.2 sufficient to specify the full symmetry of the chain. The conformation of polymers is completely defined in terms of the chain symmetry (3,4,19,21d,e,g,42).

It is worth noting that the ideal periodic conformation of isolated polymer chains may be also described by the so-called rod group symmetry (Table 1.4) (21h,i). For rod groups, space is filled according to a periodic repetition of a motif along one direction defined as singular and is nonperiodic in the two remaining directions. Whereas the line repetition group description has been developed in the polymer science community, rod groups originate in the crystallographic community and are more systematic. However, for reasons related to space filling, in the case of crystallographic rod groups, only two-, three-, four-, and sixfold screw axes are considered. Since such limitations do not exist in the case of isolated chains for which any helical symmetry may
in principle be acceptable, rod groups are a subset of those applicable to ideal crystalline chain conformations.\(^1\) As shown in the examples of Table 1.4, although symbols are generally different, there is complete correspondence of symmetry elements in the rod group and the line repetition group conventions. In the former case, symmetry elements and their symbols are the standard crystallographic symmetry elements (21h). For line repetition groups, symbols are defined in references (21d,e,g).

The compatibility relationships between configuration and possible line repetition groups have been established for a number of polymers. When the constitutional unit has a directional character in which the two directions of the chains are intrinsically nonequivalent, such as polyamido acids and polysisoprene, the possible line repetition groups are only those that allow the repetition of structural units having the same orientation (isoclinic units), that is, \(s(M/N)\) and \(t1\). For example, in polyamido acids, the line repetition group \(s(M/N)\) is not compatible with the constitution because it would change the NH–CO group into CO–NH (3). Moreover, if a polyamido acid contains asymmetric \(\alpha\)-carbon atoms of identical chirality, only helical structures are possible (41). An extended chain \(\beta\)-conformation (2/1 helix) and an intramolecularly hydrogen bonded \(\alpha\)-conformation (18/5 = 3.6 helix) are possible, as shown for the first time by Pauling et al. (41). The glide plane \(c\) must be ruled out because it would repeat a carbon atom with a given chirality into the enantiomorphous form.

The chains of a vinyl polymer cannot have symmetry operators such as \(d\) or \(i\) because of the chemical constitution. The screw symmetry and the glide plane, corresponding to the line repetition groups \(s(M/N)\), \(s(M/N)\) and \(tc\), and \(tcm\), are only possible for a vinyl polymer (43). The chain symmetry \(s(M/N)\) is compatible with an isotactic configuration, whereas the line repetition symmetries \(s(M/N)\) and \(tc\) and \(tcm\) are compatible with a syndiotactic configuration (3,4). In fact, for syndiotactic polyolefins in helical conformation \(s(M/N)\), the twofold axis 2 must pass through the methylene carbon atom, leaving the (+) and (−) nature of the symmetry-related bonds unchanged (Fig. 1.6). For the \(tc\) or \(tcm\) symmetries, the glide plane \(c\) repeats a \((+, +)\) pair of bonds into the \(a\) succeeding \((−, −)\) pairs according to the configuration of syndiotactic polymers (Fig. 1.6). The mirror plane \(m\) is also compatible with a vinyl polymer in the case of planar or nearly zigzag chains. Examples of

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**Table 1.4. Symmetry Group Symbols of Some Linear Polymers according to Both the Rod-Group (21h) and the Line Repetition Group (21d,e,g) Description**

<table>
<thead>
<tr>
<th>Rod Group (21h)</th>
<th>Line Repetition Group (21d,e,g)</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>(p1)</td>
<td>(t1)</td>
<td>((E)-1,4-Polysisoprene, i.e., poly[(E)-1-methylbut-1-ene-1,4-diyl] )</td>
</tr>
<tr>
<td>(p3)</td>
<td>(s(3/1))</td>
<td>Isotactic polypropylene ((M_1 = 3))</td>
</tr>
<tr>
<td>(p222)</td>
<td>(s(2/1))</td>
<td>Syndiotactic polypropylene ((M_1 = 2), forms I and II)</td>
</tr>
<tr>
<td>(pm11)</td>
<td>(tm)</td>
<td>Nylon 7,7, i.e., poly([N,N'-(heptane-1,7-diyl)heptanediamide] )</td>
</tr>
<tr>
<td>(pc11)</td>
<td>(tc)</td>
<td>Poly(vinylidene fluoride), i.e., poly([1,1-difluorotene] ) (form 2)</td>
</tr>
<tr>
<td>(p1)</td>
<td>(ti)</td>
<td>((E)-1,4-Poly(2,3-dimethylbutadiene) )</td>
</tr>
<tr>
<td>(p211)</td>
<td>(t2)</td>
<td>Syndiotactic polypropylene (form IV)</td>
</tr>
<tr>
<td>(p4cm)</td>
<td>(s(2/1)dm)</td>
<td>Polyethylene</td>
</tr>
</tbody>
</table>
regular conformations of polymers with indication of the symmetry elements are reported in Figure 1.20 and Figure 1.21.

Chains of iPP assume in the crystalline state a threefold helical conformation (44,45) with a chain axis (identity period) of 6.5 Å (Fig. 1.20A). The line repetition group is s(3/1), which indicates the presence of only the threefold screw axis (the symbol 1 indicates that there is no further symmetry elements but the identity). The constitutional repeating unit, the configurational base units, and the configurational repeating unit for iPP are shown in Scheme 1.8 and Scheme 1.10. The conformational repeating unit coincides with the helix residue and corresponds to the constitutional repeating unit and the configurational repeating unit (Scheme 1.10), which, in turn, correspond to one monomeric unit of the appropriate configuration (Scheme 1.8). The single monomeric unit is the conformational repeating unit because it is the smallest structural unit of the polymer chain that is repeated along the chain generating the whole chain through the symmetry elements (the screw axis) (Fig. 1.20A). The class of the helix is, therefore, $A = 2$. In the identity period ($c = 6.5 \text{ Å}$), there are three conformational repeating units or residues ($M = 3$) and one turn of the helix ($N = 1$). The repeating unit, therefore, corresponds to three monomeric units. The symmetry operation $s(3/1)$ corresponds to a rotation of $2\pi/3$ around the chain axis and a translation of $c/3 = 2.17 \text{ Å}$ along the chain axis. The parameters of the helix are the number of residues (conformational repeating units) along the identity period per turn of the helix, $n = M/N = 3$; the unit height, $h = c/M = 2.17 \text{ Å}$; the unit twist, $t = 2\pi N/M = 2\pi/3$; and the helical pitch, $P = c/N = 6.5 \text{ Å}$.

In the case of sPP, the chains may assume at least two different conformations in the crystalline state (Fig. 1.20B,C), found in different polymorphic forms (46–49), the twofold helical conformation with identity period...
generating a pair of monomeric units, the helix residue, which, in turn, is repeated along the chain through the twofold helical symmetry generating the whole chain (Fig. 1.20B). The class of the helix is \( A = 4 \). The single monomeric unit is, therefore, the conformational repeating unit because it is the smallest structural unit that is repeated along the chain generating the whole chain through application of the twofold axis and the screw axis. In the identity period \( c = 7.4 \) Å, there are two residues \( (M = 2) \) (four conformational repeating units = four monomeric units) and one turn of the helix \( (N = 1) \). The repeating unit corresponds, therefore, to four monomeric units. The symmetry operation \( s(2/1) \) corresponds to a rotation of \( \pi \) around the chain axis and a translation of \( c/2 = 3.7 \) Å along the chain axis. The parameters of the helix are the number of residues along the identity period per turn of the helix, \( n = M/N = 2 \); the unit height, \( h = c/M = 3.7 \) Å; the unit twist, \( \tau = 2\pi N/M = \pi \); and the helical pitch, \( P' = c/N = 7.4 \) Å.

For the fully extended trans-planar conformation of sPP, the line repetition group is \( t \) or \( tcm \) \((46,48,49)\). The glide plane \( c \) containing the chain axis repeats one monomeric unit into the successive one, with change of chirality of the stereoisomeric center, by reflection and translation of \( c/2 \) along the chain axis (Fig. 1.20C). The mirror plane perpendicular to the chain axis also connects two monomeric units. The conformational repeating unit corresponds to one monomeric unit, and in the identity period \( c = 5.1 \) Å are contained two conformational repeating units. The repeating unit corresponds, therefore, to two monomeric units.

Models of chain conformations of 1,4-trans and 1,4-cis-poly(butadiene) are reported in Figure 1.21 \((19,50-53)\) as examples of line repetition groups \( t \) and \( tc \), where the repetition along the chain axis is only translatory (simple translation). For the 1,4-trans-polybutadiene (Fig. 1.21A), the inversion centers are placed in the middle of the double bonds and of the CH\(_2\)-CH\(_2\) single bonds. For the cis-tactic polymer (Fig. 1.21B), besides the inversion centers placed at the middle of the CH\(_2\)-CH\(_2\) single bonds, a glide plane \( c \) containing the chain axis is also present. The combination of the inversion center and the glide plane produces a twofold rotation axis perpendicular to the chain axis. For both 1,4-trans- and 1,4-cis-poly(butadiene), the constitutional repeating unit corresponds to the monomeric unit \(-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-\), whereas the conformational base units and the configurational repeating units are shown in Scheme 1.5. In both cases, the conformational repeating unit corresponds to a half monomeric unit (Fig. 1.21). In fact, the inversion centers repeat the first half monomeric unit \(-\text{CH}_2-\text{CH}=\) into the second half (Fig. 1.21). Then, in the trans-tactic polymer, the monomeric

**Figure 1.21.** Models of chain conformations of trans-1,4- (A) and cis-1,4- (B) poly(butadiene) in projections parallel and perpendicular to the chain axis. The line repetition groups are \( t \) (A) and \( tc \) (B) for the trans- and cis-tactic polymers, respectively, corresponding to the identity periods \( c = 4.7 \) and 8.6 Å. The black filled bonds correspond to the double bonds. For the 1,4-trans-polybutadiene (A), the inversion centers \( i \) \((\sim)\) placed at the middle of the double bonds and of the CH\(_2\)-CH\(_2\) single bonds are indicated. For the cis-tactic polymer (B), the glide plane \( c \) containing the chain axis (dashed line) and the inversion centers \( i \) \((\sim)\) placed at the middle of the CH\(_2\)-CH\(_2\) single bonds, are also indicated. (Reproduced with permission from Reference 53. Copyright 1960 by Nicola Zanichelli.)

\( c = 7.4 \) Å (Fig. 1.20B), and the trans-planar conformation with identity period \( c = 5.1 \) Å (Fig. 1.20C). For the helical conformation, the line repetition group is \( s(2/1)2 \), which indicates the presence of the twofold screw operator \( s(2/1) \) and of twofold rotation axes \( (2) \) perpendicular to the chain axis, crossing each methylene carbon atoms (Fig. 1.20B) \((46,47,49)\). The conformational repeating unit corresponds to the constitutional repeating unit and, hence, to a single monomeric unit, that is, one half of the configurational repeating unit (Scheme 1.10). The helix residue corresponds to two conformational repeating units and coincides with the configurational repeating unit; that is, it corresponds to two successive monomeric units. In fact, neighboring monomeric units repeat each other through the twofold rotation axes perpendicular to the chain axis (Fig. 1.20B),
Figure 1.22. (A) Model of the trans-planar conformation of the chains of polyethylene. The twofold screw axis s(2/1), the mirror plane d parallel to the projection plane, the mirror planes m perpendicular to the chain axis, the twofold rotation axes perpendicular to the chain axis and the inversion centers i are indicated. (B) Model of the nearly trans-planar conformation of the chains of nylon 6 in the α-form (55). The twofold screw axis s(2/1) is indicated. In the maximum symmetry s(2/1)d, for a perfect trans-planar conformation, the mirror plane d corresponds to the plane of projection of the zigzag chain. The oxygen and nitrogen atoms are indicated with black and gray filled balls, respectively. (C) Model of the chain conformation of trans-polypentenamer (56). The twofold screw axis s(2/1) and the mirror plane m perpendicular to the chain axis are indicated. The periodicities in the three models are not in scale. (C: Reproduced with permission from Reference 3, Copyright 1968 by Marcel Dekker.)

unit is repeated by the simple translation, generating the whole chain (Fig. 1.21A). In the cis-tactic polymer, the monomeric unit is repeated in the successive one by the glide plane (Fig. 1.21B). Therefore, a half monomeric unit is the smallest structural unit, the conformational repeating unit, which is repeated along the chain generating the whole chain through application of the inversion centers and the simple translation, for the trans-tactic polymer (Fig. 1.21A), and of inversion centers and the glide plane for the cis-tactic polymer (Fig. 1.21B). For the 1,4-trans-polybutadiene, in the identity period c = 4.7 Å, there are two conformational repeating units, that is one monomeric unit (Fig. 1.21A). The repeating unit corresponds, therefore, to one monomeric unit. In the identity period of 1,4-cis-polybutadiene, c = 8.6 Å, there are four conformational repeating units, that is, two monomeric units (Fig. 1.21B). The repeating unit corresponds, therefore, to two monomeric units.

Combinations of more than two local symmetry elements are observed in syndiotactic polyvinylchloride (the mirror plane m, the twofold axes 2 perpendicular to the chain axis and the glide plane c) and PE (twofold screw axis, mirror planes m and d, glide plane c, twofold axis 2, inversion center i). Examples of polymers with chains in nearly trans-planar conformation characterized by a twofold helical symmetry combined with other different symmetry elements are shown in Figure 1.22. In the case of PE, the fully extended trans-planar conformation (Fig. 1.22A) presents all the possible symmetry elements compatible with the chain repetition (mirror planes m and d, glide plane c, twofold axis 2, and inversion center i), leading to the most symmetrical chain conformation observed in a polymer (line repetition group s(2/1)dm) (54). The twofold screw axis coincident with the chain axis, the mirror plane d, corresponding to the plane of the zigzag chain, and the mirror planes m perpendicular to the chain axis and
containing the hydrogen atoms (Fig. 1.22A) are the symmetry elements sufficient to specify the full symmetry of the chain. The combinations of these elements generate the twofold rotation axes 2 perpendicular to the chain axis, passing through each carbon atom and in the middle of the backbone bonds, the inversion centers \(i\), and the glide plane \(c\) containing the chain axis (Fig. 1.22A). The conformational repeating unit is \(-\text{CH}–\), which is the smallest structural unit that is repeated along the chain generating the whole chain through application of the twofold screw axis. The conformational repeating unit coincides with the helix residue and corresponds to the constitutional repeating unit (the structure-based name of PE is, indeed, poly(methylene) (21a,b,f)). The class of the helix is, therefore, \(A = 1\). In the identity period \(c = 2.5\ \text{Å}\), there are two conformational repeating units, that is, one monomeric unit (the repeating unit) (Fig. 1.22A).

Similar twofold helical symmetry characterizes the nearly trans-planar conformation of nylon 6 (Fig. 1.22B) (55). The line repetition group is \(s(2/1)d\) for a perfect trans-planar conformation or \(s(2/1)\) for the conformation slightly distorted from the perfect fully extended trans-planar conformation (Fig. 1.22B) (55). The constitutional repeating unit for nylon 6 is \(-\text{CO}–\text{CH}–\text{NH}–\), which corresponds to the conformational repeating unit, being the smallest structural unit that is repeated along the chain generating the whole chain through application of the twofold screw axis (Fig. 1.22B). The helix residue corresponds to the conformational repeating unit. The class of the helix is, therefore, \(A = 7\). In the identity period \(c = 17.2\ \text{Å}\) for the \(\alpha\)-form), there are two residues (\(M = 2\)) (two conformational repeating units, i.e., two monomeric units) and one turn of the helix (\(N = 1\)). The repeating unit corresponds, therefore, to two monomeric units (Fig. 1.22B).

An example of combination of the twofold screw axis with a mirror plane perpendicular to the chain axis is provided by some trans-polyalkenamers (poly(1-alkenylene)), as trans-polyheptenamer or trans-polyoctenamer (trans-poly(1-pentenylene)) \([\text{CH}=\text{CH}–(\text{CH}_2)_\nu]–\), shown in Figure 1.22C (56).

The constitutional repeating unit of trans-polyoctenamer is \(-\text{CH}–\text{CH}–(\text{CH}_2)_\nu–\) (the structure-based name is, indeed, poly(1-pentenylene), whereas the process-based name is poly(cyclopentene), being prepared from the ring-opening polymerization of cyclopentene (21b)). The conformational repeating unit corresponds to a half constitutional repeating unit. In fact, the mirror plane \(m\) perpendicular to the chain axis, passing through the central \(\text{CH}_2\) group of the constitutional unit \(\text{=CH}–(\text{CH}_2)_\nu–\text{CH}=\), repeats the first half constitutional unit into the second half (Fig. 1.22C). The helix residue corresponds to two conformational repeating units, connected by the mirror plane \(m\), and coincides with the constitutional repeating unit. The helix residue is repeated along the chain through the twofold helical symmetry generating the whole chain (Fig. 1.22C). The class of the helix is, therefore, \(A = 5\). The half constitutional repeating unit is, therefore, the conformational repeating unit because it is the smallest structural unit that is repeated along the chain generating the whole chain through application of the mirror plane \(m\) and the twofold screw axis. In the identity period \((c = 11.9\ \text{Å})\), there are two residues \((M = 2)\) (four conformational repeating units = two constitutional repeating units) and one turn of the helix \((N = 1)\). The repeating unit corresponds, therefore, to two constitutional repeating units.

The chain conformations of nylon 6,6 (57) and nylon 7,7 (58) are shown in Figure 1.23 as examples of line repetition groups characterized by inversion centers and mirror planes \(m\) along with a simple translation. For nylon 6,6, inversion centers are located in the middle of the central \(\text{CH}=\text{CH}–\text{CH}–\text{CO}–\) and

![Figure 1.23](image-url)
\(-\text{NH}(\text{CH}_2)_2\text{NH}^–\), whereas in nylon 7,7 the mirror planes m perpendicular to the chain axis cross the central methylene carbon atoms belonging to the constitutional units \(-\text{CO}(\text{CH}_2)_2\text{CH}–(\text{CH}_2)_2\text{CO}–\) and \(-\text{NH}(\text{CH}_2)_2\text{CH}–(\text{CH}_2)_2\text{NH}–\). The constitutional repeating unit is for both polymer \(-\text{CO}(\text{CH}_2)_2\text{CO}–\text{NH}(\text{CH}_2)_2\text{NH}–\), whereas the conformational repeating unit is one half the constitutional repeating unit, which is repeated along the chain generating the whole chain through application of the inversion centers (for nylon 6,6) or the mirror planes m (for nylon 7,7) and the simple translation. In the case of nylon 7,7, and in other nylons with odd numbers of CH₂ groups, a twisted conformation in the region of the amide group has been found (58). The amide plane is, indeed, tilted approximately 30° with respect to the chain axis so as to form in the crystal all hydrogen bonds perfectly, and the plane of the trans-planar CH₂ groups is oriented nearly parallel to the chain axis (Fig. 1.23C) (58).

1.5.2.1 Symmetry Relations for Cylindrical Coordinates

The conformation of a given conformational repeating unit with respect to an axis may be defined in terms of a set of cylindrical coordinates \((\rho, \phi, z)_i\), the axis \(z\) being coincident with the chain axis. The successive structural units are geometrically equivalent to the given unit because they are related by the symmetry operators of Table 1.2 and have cylindrical coordinates \((\rho, \phi, z)_i\) that are symmetry related to those of the given unit \((\rho, \phi, z)_j\). Successive geometrically equivalent structural units and the corresponding cylindrical coordinates are shown in Figure 1.24 (43). The cylindrical coordinates of symmetry-related adjacent structural units for some of the line repetition groups are reported in Table 1.5 (3). The application of the symmetry elements of Table 1.2 to the given unit may produce isomorphous or enantiomorphous structural units and isoclined or anticlined units (Fig. 1.24). Structural units with cylindrical coordinates related by one change of the sign of \(\phi\) or \(z\) are enantiomorphous; structural units related by no change of the sign or by two changes of sign of \(\phi\) and \(z\) are isomorphous (43, 59). Structural units related by no change of the sign of \(z\) are isoclined, whereas structural units related by a change of the sign of \(z\) are anticlined (43, 59). Therefore, a regular succession of equivalent structural units may be obtained in four different ways, producing adjacent isomorphous-isoclined, isomorphous-anticlined, or enantiomorphous-isoclined and enantiomorphous-anticlined units (3, 43).

The repetition of adjacent isomorphous and isoclined units may be effected only through the operation of a screw axis \(s(M/N)\), that is, rotation around the chain axis plus translation. Starting from the given structural unit of cylindrical coordinates \((\rho, \phi, z)_i\), the successive \(x\) equivalent isomorphous and isoclined structural units along the helical chain, obtained by application of a screw axis \(s(M/N)\), have cylindrical coordinates \((\rho, \phi_i + \pi, z_i + \lambda h)\), where \(t\) is the unit twist of the helix \(t = 2\pi N/M\) and \(h\) is the unit height \(h = c/M\) (Table 1.5). The repetition of isomorphous and anticlined structural units occurs through the application of a binary axis perpendicular to the chain axis (Fig. 1.24). The cylindrical coordinates of the structural units related by the twofold axis are \((\rho, \phi, z)\) and \((\rho, -\phi, -z)\), if the binary axis 2 is at \(z = 0\) and \(\phi = 0\) (Table 1.5). Paired of adjacent anticlined structural units may repeat along the chain through the operation of a screw axis, as in the case of sPP in Figure 1.20B for the line repetition group s(2/1)2. The repetition of enantiomorphous and isoclined structural units occurs through application of a glide plane with translation parallel to the chain axis (Fig. 1.24) and the cylindrical coordinates of the related units are \((\rho, \phi, z)\) and \((\rho, \phi, z + c/2)\) (Table 1.5). Finally, the repetition of enantiomorphous and anticlined structural units occurs through the application of inversion centers or mirror planes \(m\) perpendicular to the chain axis. The cylindrical coordinates of the related units are \((\rho, \phi, z)\) and \((\rho, \phi + \pi, -z)\), in the case of the inversion centers,
TABLE 1.5. Cylindrical Coordinates of Equivalent Structural Units Obtained from the Given Unit with Cylindrical Coordinates (ρ, φ, z) by the Application of the Indicated Symmetry Elements of the Different Line Repetition Groups

<table>
<thead>
<tr>
<th>Line Repetition Group</th>
<th>Cylindrical Coordinates of Equivalent Structural Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>s(A*/M:N)1 ρ, ψ, z</td>
<td>ρ, ψ + 2πN/M, z + c/M (M/N screw axis)</td>
</tr>
<tr>
<td>s(A*/M:N)2 ρ, φ, z</td>
<td>ρ, −φ, −z (2 axis)</td>
</tr>
<tr>
<td>2 in z = 0, φ = 0</td>
<td>ρ, φ, z + c (t)</td>
</tr>
<tr>
<td>tm</td>
<td>ρ, φ, z (mirror m)</td>
</tr>
<tr>
<td>td</td>
<td>ρ, φ, z (mirror d)</td>
</tr>
<tr>
<td>tc</td>
<td>ρ, φ, z + c/2 (glide plane c)</td>
</tr>
<tr>
<td>ti</td>
<td>ρ, φ, z (mirror m)</td>
</tr>
<tr>
<td>s(A*/2/1)m ρ, φ, z</td>
<td>ρ, φ + π, z + c/2 (2/1 screw axis)</td>
</tr>
<tr>
<td>s(A*/2/1)d ρ, φ, z</td>
<td>ρ, φ + π, z + c/2 (2/1 screw axis)</td>
</tr>
<tr>
<td>tdm</td>
<td>ρ, φ + π, z + c/2 (mirror m)</td>
</tr>
<tr>
<td>tdm</td>
<td>ρ, φ + π, z + c/2 (mirror d)</td>
</tr>
<tr>
<td>tcn</td>
<td>ρ, φ + π, z + c/2 (glide plane c)</td>
</tr>
<tr>
<td>tci</td>
<td>ρ, φ + π, z + c/2 (mirror m)</td>
</tr>
<tr>
<td>s(A*/2/1)d m ρ, φ, z</td>
<td>ρ, φ + π, z + c/2 (2/1 screw axis)</td>
</tr>
<tr>
<td>s(A*/2/1)d m ρ, −z</td>
<td>ρ, φ + π, z + c/2 (2/1 screw axis)</td>
</tr>
</tbody>
</table>

Note: The z-axis is coincident with the chain axis.

and (ρ, φ, z) and (ρ, φ, −z) in the case of the mirror plane m (Table 1.5).

The threefold helical conformation of iPP (Fig. 1.20A) is an example of a succession of isomorphous-iso-inclined units along the chain. sPP in the twofold helical conformation s(2/1)2 is an example of a regular succession of alternately isomorphous-anti-inclined structural units symmetry related in pairs by twofold axes perpendicular to the chain axis (Fig. 1.20B). The successive pairs of adjacent units repeat themselves along a binary helix. The models with ti symmetry of the regular conformation of cis-1,4-poly(isoprene) (cisPI) (Fig. 1.25A), proposed by Bunn (60), of trans-1,4-poly(isoprene) (transPI) in the α-form (51,61) (Fig. 1.25B) and of syndiotactic cis-1,4-poly(1,3-pentadiene) (62) (Fig. 1.25C), are examples of a succession of alternately enantiomorphous-iso-inclined structural units. The structural units repeat themselves through a glide plane c containing the chain axis with translation of c/2 parallel to the chain axis. Finally, the models of the conformations of trans-1,4-poly(1,3-butadiene) (transPBD) with ti symmetry (Fig. 1.21A) and nylon 7,7 with tm symmetry (Fig. 1.23C) are examples of a succession of alternately enantiomorphous-anti-inclined structural units, related by the inversion center, in the case of trans-1,4-poly(1,3-butadiene) (Fig. 1.21A), or the mirror plane m perpendicular to the chain axis in the case of nylon 7,7 (Fig. 1.23C).
1.5.2.2 Application of the Equivalence Principle: Stereoregular Vinyl Polymers

The equivalence principle strongly limits the possible conformations assumed by polymers in the crystalline state. The implications of the equivalence principle in the case of isotactic and syndiotactic vinyl polymers can be discussed considering segments of chains of vinyl polymers in Figure 1.26. Let the bonds $l_{-1}$ and $l_1$ be two bonds adjacent to the same CH$_2$ group, and the bonds $l_i$ and $l_{i+1}$ two bonds adjacent to the same CHR group. The bonds $l_{R1}$ and $l_{R2}$ are the bonds connecting the methine carbon atoms to the side group R. With every $l_i$ bond, two torsion angles $\theta_i$ and $\theta'_i$ may be associated. The torsion angle $\theta_i$ is the backbone torsion angle around the bond $l_i$ (Fig. 1.26), that is, the angle between the $l_{i-1}l_i$ and $l_{i+1}l_i$ planes, whereas the torsion angle $\theta'_i$ is related to the conformation of three consecutive bonds comprising the bond $l_i$ and the bond $l_{R2}$, that is, the angle between the $l_i l_{i+1}$ and $l_{R2}$ planes (Fig. 1.26). The values of torsion angles of two bonds adjacent to the same CH$_2$ group (CHR group), that is, the bonds $l_i$ and $l_{i+1}$, are always connected by Equation 1.17, regardless of the relative configuration of successive tetrahedral centers of stereoisomerism (isotactic or syndiotactic). The torsion angles relative to bonds adjacent to the same methylene groups are, instead, different in isotactic and syndiotactic polymers. The torsion angles $\theta'_{i-1}$ and $\theta_i$ are connected by Equation 1.18 for isotactic polymers and by Equation 1.19 for syndiotactic polymers.

\[ \theta_{i-1} + \theta'_{i-1} = \theta_i + \theta'_{i+1} \]  (1.17)
\[ \theta_{i-1} + \theta_i = \theta'_{i+1} + \theta'_i \]  (1.18)
\[ \theta_{i-1} - \theta_i = \theta'_{i+1} - \theta'_i. \]  (1.19)

Equation 1.18 and Equation 1.19 are necessary and sufficient conditions in order for a vinyl polymer to be isotactic or syndiotactic (43).

Equation 1.17, Equation 1.18, and Equation 1.19 can be easily explained on the basis of the relationships among bond angles and torsion angles for approximately tetrahedral carbon atoms (Section 1.4). In fact, for the system of two bonds $l_i$ and $l_{i+1}$ adjacent to the same methine carbon atom (CHR group) (Fig. 1.26), corresponding to the systems in Figure 1.15B and Figure 1.18A with local C$_{3v}$ symmetry, the torsion angles $\theta_i$ and $\theta'_i$ (corresponding to the torsion angles $\theta_i$ and $\theta'_i$ in Figure 1.18A,B) and the torsion angles $\theta'_{i-1}$ and $\theta'_{i+1}$ are related by Equation 1.20 and Equation 1.21 (Fig. 1.27), similar to Equation 1.6, Equation 1.7, and Equation 1.8:

\[ \theta'_{i} = \theta_{i-1} + \psi_i \]  (1.20)
\[ \theta'_{i+1} = \theta_{i-1} - \psi_i. \]  (1.21)

where $\psi_i$ is the angle between the planes C$_i$C$_{i+1}$C$_{i-1}$ and C$_i$C$_{i+1}$C$_i$ and between the planes C$_i$C$_{i+1}$C$_i$ and C$_i$C$_{i+1}$C$_{i-1}$ (Fig. 1.26 and Fig. 1.27) and is defined by Equation 1.11. Equation 1.20 and Equation 1.21 give Equation 1.17: $\theta_i + \theta'_{i+1} = \theta'_i + \theta'_{i-1}$.

For the system of two bonds $l_{i-1}$ and $l_i$ adjacent to the same methylene carbon atom (CH$_2$ group) (Fig. 1.26), corresponding to the systems in Figure 1.15A and Figure 1.17A with local C$_{3v}$ symmetry, the torsion angles $\theta'_{i}$ and $\theta'_{i+1}$ and the torsion angles $\theta_i$ and $\theta'_i$ (Fig. 1.26) are

\[ \theta'_{i-1} - \theta'_{i} = 1 \psi_i \]  (1.23)
\[ \theta'_{i+1} - \theta'_{i-1} = -1 \psi_i.\]

**Figure 1.27.** Newman projections along the bonds C$_i$C$_{i+1}$ ($l_i$) and C$_{i-1}$C$_i$ ($l_{i-1}$) showing the relationships between the torsion angles $\theta_i$ and $\theta'_i$ and the torsion angles $\theta'_{i-1}$ and $\theta'_{i+1}$. The angle $\psi_i$ is the angle between the planes C$_i$C$_{i+1}$C$_{i-1}$ and C$_i$C$_{i+1}$C$_i$ and between the planes C$_i$C$_{i+1}$C$_i$ and C$_i$C$_{i+1}$C$_{i-1}$. The Newman projections are relative to the $l_i$ bond with (+) chirality and $l_{i-1}$ bond with (−) chirality, as in the scheme of the isotactic chain in Figure 1.26.
related by Equation 1.22 and Equation 1.23 for an isotactic polymer (Fig. 1.28A) and by Equation 1.24 and Equation 1.25 for a syndiotactic polymer (Fig. 1.28B).

**Isotactic**

θ₁ = θ₁ = −ψ₁ (1.22)

θ₁ = θ₁ + ψ₁ (1.23)

**Syndiotactic**

θ₂ = θ₂ = −ψ₂ (1.24)

θ₂ = θ₂ + ψ₂ (1.25)

where ψ₁ is the angle between the planes C₁C₂C₃ and C₁C₂R₃, and ψ₂ is the angle between the planes C₄C₅C₆ and C₅C₆R₅ (Fig. 1.28). Since ψ₁ = ψ₂, Equation 1.22 and Equation 1.23 give Equation 1.18 for an isotactic polymer: θ₁ = θ₁ = θ₁ = θ₁, whereas Equation 1.24 and Equation 1.25 give Equation 1.19 for a syndiotactic polymer: θ₂ = θ₂ = θ₂ = θ₂.

It is possible to establish from relationships 1.17–1.19 the possible symmetry operators in the repetition of equivalent structural units along the chain of a regular vinyl polymer and the corresponding succession of torsion angles of main-chain bonds:

1. If two successive structural units are isomorphous-isoclined, related by a screw axis, the torsion angles are related by the following:

   \[ θ_{i-1} = θ_{i+1} \text{ and } θ'_{i-1} = θ'_{i+1} \]  
   \[ θ_i = θ_{i+2} \text{ and } θ'_{i} = θ'_{i+2} \]  

2. If two successive structural units are isomorphous-antiparallel, related by a twofold axis perpendicular to the chain axis, passing through the carbon atom of the CH₂ groups, the torsion angles are related by the following:

   \[ θ_{i-1} = θ_i \text{ and } θ'_{i-1} = θ'_{i} \]  
   \[ θ_{i+1} = θ_{i+2} \text{ and } θ'_{i+1} = θ'_{i+2} \]  

3. If two successive structural units are enantiomorphous-isoclined, related through a glide plane containing the chain axis, the torsion angles are related by the following:

   \[ θ_{i-1} = −θ_{i+1} \text{ and } θ'_{i-1} = −θ'_{i+1} \]  
   \[ θ_i = −θ_{i+2} \text{ and } θ'_{i} = −θ'_{i+2} \]  

Substituting Equation 1.28 in Equation 1.17 gives Equation 1.19, indicating that a glide plane structure is compatible only with a syndiotactic configuration of the chain. If tetrahedral angles along the chain are assumed, then one of the two torsion angles θ₁ or θ₁ must be equal to 180°.

4. If two successive structural units are enantiomorphous-antiparallel, related through a mirror plane normal to the chain axis, the main-chain conformation is fully trans-planar. Such a conformation is a degenerate case of cases 1–3.
A summary of the relationships among torsion angles for isotactic and syndiotactic vinyl polymers with different symmetries is reported in Table 1.6. In conclusion, from the equivalence principle and the relationships of Table 1.6, an isotactic polymer must have a helical conformation, characterized by a succession of torsion angles along the chain . . . θ, θ, θ, θ, θ, θ, . . . ; a syndiotactic polymer may assume either a helical conformation associated with twofold axis normal to the chain axis characterized by a succession of torsion angles . . . θ, θ, θ, θ, θ, . . . , or a glide plane chain conformation characterized by a succession of torsion angles along the chain . . . θ, θ, −θ, −θ, . . .

### 1.5.3 Principle of Minimum Conformational Internal Energy

Once the symmetry of the chain of a crystalline polymer having a given regular configuration has been assigned using the equivalence principle, the actual conformation assumed by the chain is determined by energetic factors, as defined by the principle of the minimum internal conformational energy. The energetic factors that determine the conformation of polymer chains (63) are (a) the bond orientation effect, (b) the intramolecular interactions between neighboring side groups or between side groups and backbone atoms, and (c) packing effects.

In saturated molecules, the bond orientation effect favors staggered conformations of the bonds, that is, the *trans* (T) conformation, corresponding to a torsion angle θ = 180°, and *gauche*’ (G’) and *gauche*’ (G) conformations, corresponding to torsion angles +60° and 60°, respectively. For single bonds adjacent to double bonds, *anti*clinal (A’), *anti*clinal (A’), and cis (C) conformations, corresponding to internal rotation angles θ = +120°, −120°, and 0°, respectively, are instead favored (Fig. 1.29).

Intramolecular interactions between neighboring side groups or between side groups and backbone atoms may induce deviations from the staggered conformations in overcrowded molecules, as occurs, for example, in isotactic vinyl polymers with bulky side groups. Packing effects generally do not influence the conformation of the chains in the crystal as long as the conformational internal energy of the isolated chain corresponds to a deep energy minimum. If the energy differences between different conformations are greater than a few hundred calories per mole of chain atom, the choice of conformation is not influenced by the possible energy differences associated with packing efficiency. Therefore, the conformation actually assumed by the chains in the crystal state is such that the internal energy of the chain, considered as not subjected to crystal-field forces, is the lowest, or very near to the lowest.

The threefold helical conformations (TG’), and (G–T), found in the crystals of iPP (44,45) may be easily justified by the application of these principles. The configuration of iPP corresponds to an alternating succession of (+) and (−) bonds (Fig. 1.9A and Fig. 1.30A). If θ₁ and θ₂ are the torsion angles of two successive bonds of the chain belonging to a given structural unit (the conformational repeating unit), the equivalence principle imposes that successive structural units are geometrically equivalent and, for an isotactic relative configuration, can be obtained only through the application of a screw axis. Isotactic polymers must have a

### Table 1.6. Relationships between the Torsion Angles for Isotactic and Syndiotactic Vinyl Polymers with Chain Characterized by Different Symmetries; the Torsion Angles Are Defined with Reference to the Chains in Figure 1.26

<table>
<thead>
<tr>
<th>Configuration and Symmetry</th>
<th>Relationships among Torsion Angles</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Always</td>
<td>θ₁ + θ₁⁺ = θ₁⁻ + θ₁⁻⁺</td>
<td>(1.17)</td>
</tr>
<tr>
<td>Isotactic</td>
<td>θ₁⁻ + θ₁⁺ = θ₁⁻⁺ + θ₁⁻⁺⁺</td>
<td>(1.18)</td>
</tr>
<tr>
<td>Syndiotactic</td>
<td>θ₁⁻ + θ₁⁺ = θ₁⁻⁺⁺ + θ₁⁻⁺⁺⁺</td>
<td>(1.19)</td>
</tr>
</tbody>
</table>
| Helix                      | θ₁⁺⁻ = θ₁⁺⁻⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺⁺++){digest}{

**Figure 1.29.** Anticlinal (A’ and A’) and cis (C) conformations of minimum torsional energy for single bonds adjacent to double bonds in systems of the type –CH=CH–CH₂ – (as in polybutadiene). Atoms 1 and 2 are in anticylindrical, and atom 3 is in cis conformation with respect to the carbon atom 4 joined by a double bond. The Newman projection along the single bond =C–C– adjacent to the a double bond in a polymer chain of the type –CH=CH–CH₂–CH₂– shows a conformations of minimum torsional energy with the two hydrogen atoms in cis and anticylindrical (A’) conformations and the methylene carbon atom in anticylindrical (A’) conformation with respect to the CH group joined by the double bond.
Possible line repetition groups for isotactic (A) and syndiotactic (B) polypropylene, according to the equivalence principle and corresponding sequences of torsion angles $\theta_1$ and $\theta_2$, and bond angles $\tau_1$ and $\tau_2$, and relationships between torsion angles according to the symmetry elements. For each line repetition group, the corresponding possible conformations and values of the torsion angles $\theta_1$ and $\theta_2$, according to the principle of minimum conformational internal energy, are indicated. $T = \text{trans}$, $G = \text{gauche}$. (Reproduced with permission from Reference 4. Copyright 2003 by Wiley Interscience.)

**Figure 1.30.** Possible line repetition groups for isotactic (A) and syndiotactic (B) polypropylene, according to the equivalence principle and corresponding sequences of torsion angles $\theta_1$ and $\theta_2$, and bond angles $\tau_1$ and $\tau_2$, and relationships between torsion angles according to the symmetry elements. For each line repetition group, the corresponding possible conformations and values of the torsion angles $\theta_1$ and $\theta_2$, according to the principle of minimum conformational internal energy, are indicated. $T = \text{trans}$, $G = \text{gauche}$. (Reproduced with permission from Reference 4. Copyright 2003 by Wiley Interscience.)

According to the principle of the staggered bonds, the torsion angles $\theta_1$ and $\theta_2$ tend to be trans (T) or gauche (G). Intramolecular interactions impose some important constraints (3). Figure 1.31 clearly shows that bonds with chirality corresponding to a (+) sign tend to assume only $G^--$ or T conformations. In fact, according to Equation 1.6, Equation 1.7, and Equation 1.8 and Equation 1.20 for a system in Figure 1.18A, the side group CH₃ is in trans conformation when the backbone torsion angle $\theta_2$ is in $G^+$ conformation ($\theta'_2 = \theta_2 + \psi = T$) (Fig. 1.31B), whereas it is in a less favored gauche conformation ($\theta'_2 = G^+$) with unfavored intramolecular interactions, when the backbone torsion angle $\theta_2$ is in $G^-$ conformation (Fig. 1.31C). Analogously, Figure 1.32 shows that bonds with chirality corresponding to a (−) sign tend, instead, to assume only $G^-$ or T conformations (3). In this case, ($\theta'_2 = \theta_2 - \psi$) less intramolecular interactions there exists for $\theta_2 = T$, $\theta'_2 = G^-$ (Fig. 1.32A) and for $\theta_2 = G$, $\theta'_2 = T$ (Fig. 1.32C).

Moreover, further conditions restricting the possible conformations arise from the fact that a $G^-$ bond cannot be followed by a $G^-$ bond (Fig. 1.33A), and from the fact that the pair of torsion angles $\theta_1$ and $\theta_2$ adjacent to a methylene carbon atom cannot be TT for an isotactic diad and cannot be TG or GT for a syndiotactic diad (Fig. 1.33). These three conditions impose that for the pair of chain bonds (+) and (−) ($\theta_1$ and $\theta_2$) adjacent to a methylene carbon atom in iPP (Fig. 1.30A), staggered conformations like ($G^T$), ($G^G$), ($G^-G^-$), ($TG^-$), and (T,T) are prohibited. The only possible con-
Figure 1.31. Portion of polypropylene chain showing the configurational signs (+) and (−) of the backbone bonds C₂–C₃ and C₃–C₄ and Newman projections along the bond C₂–C₃ for conformations with θ₂ = T (A), G⁺ (B), and G⁻ (C), which indicate that the bond C₂–C₃ with intrinsic chirality corresponding to a (+) sign tends to assume only G⁺ (B) or T (A) conformations because when θ₂ = G⁻ (C), the side group CH₃ is in a less favored gauche conformation (θ₂ = G⁺) with unfavored intramolecular interactions.

Figure 1.32. Portion of polypropylene chain showing the configurational signs (−) and (+) of the backbone bonds C₂–C₃ and C₃–C₄ and Newman projections along the bond C₂–C₃ for conformations with θ₂ = T (A), G⁺ (B), and G⁻ (C), which indicate that the bond C₂–C₃ with intrinsic chirality corresponding to a (−) sign tends to assume only G⁻ (C) or T (A) conformations because when θ₂ = G⁺ (B), the side group CH₃ is in a less favored gauche conformation (θ₂ = G⁻) with unfavored intramolecular interactions.

Formations are (G⁺T) and (TG⁻), which can be followed only by (G⁻T) and (TG⁺), respectively, giving the regular successions of torsion angles (G⁺T)₀ and (TG⁻)₀ corresponding to a left- and right-handed threefold helical conformation, respectively (44,45) (Fig. 1.30A).

In the case of sPP, the configuration corresponds to an alternating succession of couples of (+),(+) and (−),(−) bonds (Fig. 1.9B and Fig. 1.30B). As discussed earlier and as shown in Table 1.6, bonds of successive geometrically equivalent structural units are related by
to the trans-planar conformation (48,49,65). In the tc and tcm symmetries, two successive monomeric units are related by a glide plane parallel to the chain axis so that the torsion angles θ1 and θ2 adjacent to a methylene carbon atom of two successive monomeric units have opposite values. When a mirror plane perpendicular to the chain axis, crossing the methine carbon atom, is also present ( tcm symmetry), θ1 = θ2. Since G′G′ and TG sequences are forbidden, the minimum conformational energy principle imposes that, for the tc and tcm symmetries, the only possible conformation is (TTTT), corresponding to the fully extended trans-planar conformation (Fig. 1.30B).

1.5.4 Relationships between Internal Coordinates and Conformational Parameters

The parameters of a chain conformation that can be determined from the X-ray diffraction data are the identity period (chain axis c) and the repeating unit, that is, the number of monomeric units in the identity period and, for helical conformation, the unit height h = c/M and the helical pitch P = c/N (see Chapter 3). These conformational parameters depend on the internal coordinates (bond lengths, bond angles, and torsion angles) of the macromolecules. The relationships between the conformational parameters and the internal coordinates have been derived for chain conformations with glide, helical, and translational symmetries (66–74). For instance, for helical conformations s(M/N) mathematical equations that give explicitly the helical parameters, that is, the unit height h = c/M and the unit twist t = 2πN/M, as a function of bond lengths, bond angles, and torsion angles, have been derived by Shimanouchi and Mizushima (66), Hughes and Lauer (67), and Miyazawa (68). The conformational parameter equations for polymers with glide plane symmetry conformations have been successively reported by Ganis and Temussi (70) and Tai and Tadokoro (73). These analytical procedures allow determination of the possible conformations of the chain and setting up molecular models from the experimental values of the identity period and of the repeating unit.

The analytical equations have been derived for infinite extended skeletal polymer chain of the type \( M_1 \rightarrow M_2 \rightarrow \ldots \rightarrow M_n \rightarrow M_{n+1} \rightarrow \ldots \), where \( M_i \) is the ith skeletal atom, \( b_i \) is the bond length \( M_i \rightarrow M_{i+1} \), \( τ \) is the bond angle at \( M_i \) (\( \angle M_i \rightarrow M_{i+1} \rightarrow M_{i+2} \)), and \( θ_i \) is the torsion angle around the bond \( M_i \rightarrow M_{i+1} \). In the case of helical conformations of infinite polymer chains, the helical parameters related to the internal coordinates are \( ρ \), \( d_ρ \), and \( t_ρ \), where \( ρ \) is the radius of the helix, that is, the distance of the \( i \)th atom from the helix axis, and \( d_ρ \) and \( t_ρ \) are the translation along the axis and the angle of rotation.

Equation 1.27 and Equation 1.27′ or Equation 1.28 and Equation 1.28′. If \( θ_1 \) and \( θ_2 \) are the torsion angles of two successive bonds of the chain, the equivalence principle imposes that the only possible successions of torsion angles are those shown in Figure 1.30B:

1. \( \ldots θ_1 \cdot θ_2 | \ldots θ_2 | \ldots θ_1 | \ldots θ_2 | \ldots \) corresponding to the s(M/N)2 symmetry
2. \( \ldots θ_1 | \ldots θ_2 | \ldots θ_1 | \ldots θ_2 | \ldots \) corresponding to the tcm symmetry
3. \( \ldots | \ldots θ_1 | \ldots θ_2 | \ldots θ_1 | \ldots θ_2 | \ldots \) corresponding to the tcm symmetry

where dots and vertical bars indicate placement of CH₂ and CH₂ groups, respectively.

In the s(M/N)2 symmetry, two successive monomeric units are related by a twofold rotation axis perpendicular to the chain axis centered on the methylene carbon atoms. According to the principle of the minimum conformational energy and the constraints discussed earlier, the possible conformations are (TTG′G′), and (GG TT), corresponding to right- and left-handed twofold helical conformations, respectively (Fig. 1.30B), found in the crystals of the most stable polymorphic forms of sPP (46,47,49,64), and (TTTT), corresponding
about the axis, respectively, on passing from the \( i \)th atom to the \( j \)th. According to Hughes and Lauer (67), the molecular models can be classified as one-atom chains \(-(M)_{\infty}−, or two-atom chains \(-(M_i−M_j)_{\infty}, where \( M_i \) and \( M_j \) are two nonequivalent atoms of the backbone chain in the polymer. These two cases have been easily extended to \(-(M_i−M_j−...−M_k)_{\infty}− for \( n = 3, 4, 5, \) and 6 (68), and for these models, concise mathematical equations for the helical parameters are given in terms of the internal coordinates (68). According to the given definition (68), for a polymer \(-(M_i−M_j−...−M_k)_{\infty}, the internal coordinates are the bond lengths \( b_{12}, b_{23}, b_{34}, \) and \( b_{4i}; the bond angles \( \tau_1, \tau_2, \tau_3, \) and \( \tau_4; \) and the torsion angles \( \theta_{12}, \theta_{23}, \theta_{34}, \theta_{4i}, \) whereas the helical parameters are \( \rho_1, \rho_2, \rho_3, \rho_4, d_{12}, d_{23}, d_{34}, d_{4i}, t_{12}, t_{23}, t_{34}, \) and \( t_{4i}. \) For a generic chain \(-(M_i−M_j−...−M_k)_{\infty}, the unit height \( h \) and the unit twist are given by Equation 1.29 and Equation 1.30 (68):

\[
\begin{align*}
    h & = c/M = d_{12} + d_{23} + \ldots + d_{n-1,n} + d_{n1} \\
    t & = 2\pi N/M = t_{12} + t_{23} + \ldots + t_{n-1,n} + t_{n1},
\end{align*}
\]

1.29 1.30

The general mathematical equations for the helical parameters \( h, t, \) and \( \rho \) in terms of molecular parameters derived by Shimanouchi and Mizushima (66) have been rewritten into more simplified forms by Miyazawa (68) in terms of bond lengths and trigonometric functions of bond and torsion angles:

\[
\cos(t/2) = \frac{(1 + a_{12} + a_{23} + a_{34})^{1/2}}{2} \quad (1.31)
\]

\[
\begin{align*}
    r_i (a_{13} + a_{4i}) & + r_i (a_{23} + a_{34}) \\
    h \sin(t/2) & = \frac{+ r_i(1- a_{13} - a_{23} + a_{34})}{2(1-a_{13} - a_{23} + a_{34})^{1/2}} \quad (1.32)
\end{align*}
\]

\[
2\rho_i(1-\cos t) + h^2 = r_i^2 + r_i^2 + r_i^2, \quad (1.33)
\]

where \( a_{ij} \) and \( r_i \) are elements of the matrices \( A \) and \( R \) and \( r_i^2 + r_i^2 + r_i^2 \) is the square of the distance between the atom \( M_i \) of a repeating unit and the corresponding atom \( M_i \) of the succeeding unit:

\[
A = \begin{bmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{bmatrix} \quad (1.34)
\]

\[
\begin{align*}
    A_{ij} & = A_{ij}^0 + A_{ij}^0 A_{i-1,j}^0 A_{i-1,j}^0 A_{i,j}^0; \\
    B_{n-1,n} & = A_{n-1,n}^0 B_{n1} + A_{n-1,n}^0 A_{n1}^0 B_{n1}; \\
    B_{n1} & = A_{n1}^0 B_{n1} + A_{n1}^0 A_{n1}^0 B_{n1}. \\
\end{align*}
\]

1.35

\[
A_i^0 = \begin{bmatrix} -\cos \tau_i & -\sin \tau_i & 0 \\ \sin \tau_i & -\cos \tau_i & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad (1.36)
\]

\[
A_i^0 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \cos \theta_i & -\sin \theta_i \\ 0 & \sin \theta_i & \cos \theta_i \end{bmatrix} \quad (1.37)
\]

\[
B_i = \begin{bmatrix} b_i \\ 0 \end{bmatrix}. \quad (1.38)
\]

The \( A \) and \( R \) matrix elements are calculated by the use of Equation 1.34 and Equation 1.35, and then the values of \( h, t, \) and \( \rho \) are calculated successively by the use of Equation 1.31, Equation 1.32, and Equation 1.33 (68). Although Equation 1.31, Equation 1.32, Equation 1.33, Equation 1.34, and Equation 1.35 apply to any helical polymers, more concise and useful equations may be obtained for simple cases of one-atom and two-atom chains (68).

(a) Helical Symmetry and One-Atom Chain \(-\(M)_{\infty}\). For a one-atom chain \(-\(M)_{\infty}, the skeleton contains only one kind of atom and the chain is characterized by a bond length \( b, \) a bond angle \( \tau, \) and a torsion angle \( \theta. \) The helical parameters \( \rho, \ h = d, \) and \( t \) are given by Equation 1.39, Equation 1.40, and Equation 1.41 derived by Shimanouchi and Mizushima (66) in terms of the internal coordinates:

\[
2\cos t = -\cos \tau - \cos \tau \cos \theta + \cos \theta - 1 \quad (1.39)
\]

\[
h = [b^2(1-\cos \theta)(1-\cos \tau)/(3+\cos \tau-\cos \theta+\cos \tau \cos \theta)]^{1/2} \quad (1.40)
\]

\[
\rho = [2b^2(1+\cos \tau)/(3+\cos \tau-\cos \theta+\cos \tau \cos \theta)]^{1/2}. \quad (1.41)
\]

These equations have been reformulated by Miyazawa (68) on the basis of the general equations: Equation 1.31, Equation 1.32, Equation 1.33, Equation 1.34, Equation 1.35, Equation 1.36, Equation 1.37, and Equation 1.38, where

\[
\begin{align*}
    r_{1} & = b, r_{2} = r_{3} = 0, (1 + a_{11} + a_{22} + a_{33}) = (1 + \cos \theta) (1 + \cos \tau) \) and \( (1 \cos \tau) \) and \( (1 + \cos \theta) \) and \( (1 + \cos \tau) \) and \( a_{33} = \sin \theta \) sin \( \tau. \)
\end{align*}
\]

\[
\cos(t/2) = \cos(\theta/2) \sin(\tau/2) \quad (1.42)
\]

\[
h \sin(t/2) = b \sin(\theta/2) \sin(\tau/2) \quad (1.43)
\]

\[
2\rho^2(1-\cos t) + h^2 = b^2. \quad (1.44)
\]
deviated from the exact trans value are calculated (Table 1.7).

(b) Helical Symmetry and Two-Atom Chain –(M₁–M₂)–. A two-atom chain –M₁–M₂–M₃–M₄– consisting of two kinds of skeleton atoms M₁ and M₂, is characterized by two bond lengths b₁₂ and b₂₁, two bond angles τ₁ = M₁-M₂-M₃ and τ₂ = M₂-M₃-M₄, and two torsion angles θ₁ and θ₂, around the two nonequivalent skeleton bonds M₁-M₂ and M₃-M₄, respectively (Fig. 1.34). The equations for the helical parameters are derived from the elements of A and R matrices (Eq. 1.34 and Eq. 1.35):

$$A = A_{12}^0 A_{21}^2 A_{31}^0 A_{32}^i$$

$$R = B_{12} + A_{12}^0 A_{21}^2 B_{21},$$

and Equation 1.31 and Equation 1.32 can ultimately be written in the form

$$h \sin \left( \frac{t}{2} \right) = (b_{12} + b_{21}) \sin \left( \frac{\theta_{12} + \theta_{21}}{2} \right) \sin \left( \frac{\tau_1}{2} \right) \sin \left( \frac{\tau_2}{2} \right)$$

$$- (b_{12} - b_{21}) \sin \left( \frac{\theta_{12} - \theta_{21}}{2} \right) \cos \left( \frac{\tau_1}{2} \right) \cos \left( \frac{\tau_2}{2} \right).$$

Similar equations for a two-atom chain have been derived in different forms by Hughes and Lauer (67):

$$1 + 2 \cos t = \cos \tau_1 \cos \tau_2 (1 + \cos \theta_{12} \cos \theta_{21})$$

$$- \sin \tau_1 \sin \tau_2 (\cos \theta_{12} + \cos \theta_{21})$$

$$+ (\cos \tau_1 + \cos \tau_2) \sin \theta_{12} \sin \theta_{21}$$

$$+ \cos \theta_{12} \cos \theta_{21}.$$
The torsion angles \( \theta_{12} \) and \( \theta_{21} \) are calculated assuming reasonable values of bond lengths \( b \) and bond angles \( \tau \).

\[ h = \left[ b_{12} (\cos \tau_1 \cos \tau_2 - \cos \tau_1 \sin \tau_1 \sin \tau_2 \cos \theta_{12}) \right]^{1/2} + b_{21} (\cos \tau_1 \cos \tau_2 - \cos \tau_1 \sin \tau_1 \sin \tau_2 \cos \theta_{21}) \right]^{1/2} / 2^{1/2} \sin(t/2). \]  

(1.49)

Isotactic vinyl polymers with helical \( s(M/N) \) symmetry are examples of two-atom chain.

The geometry of the chain is determined by the values of the internal coordinates (Fig. 1.34) and by the relationships imposed by the helical symmetry (Table 1.6). The experimental helical parameters \( h \) and \( t \) of some isotactic polymers and the calculated internal coordinates according to Equation 1.46 and Equation 1.47 or Equation 1.48 and Equation 1.49 are reported in Table 1.8. In calculating the bond angles and torsion angles, it is assumed that \( b_{12} = b_{21} = b \) and \( \tau_1 = \tau_2 = \tau \). Assuming reasonable values of \( b \) and \( \tau \), the two torsion angles \( \theta_{12} \) and \( \theta_{21} \) can readily be calculated by Equation 1.46 and Equation 1.47 or Equation 1.48 and Equation 1.49.

For iPP with chains in \( s(3/1) \) helical conformation and chain axis \( c = 6.5 \) \( \text{Å} \) (44,45), the torsion angles were calculated to be \( \theta_{12} = 197^\circ \) and \( \theta_{21} = 67^\circ \) by assuming the bond length \( b = 1.54 \) \( \text{Å} \) and bond angle \( \tau = 110^\circ \), or \( \theta_{12} = 180^\circ \) and \( \theta_{21} = 60^\circ \) by assuming the bond angle \( \tau = 114^\circ \) (Table 1.8). The bond angle of 114° is greater than the tetrahedral angle and is the more reasonable value due to the steric repulsion among nonbonded carbon atoms that favor values of the torsion angles \( \theta_{12} = 180^\circ \) and \( \theta_{21} = 60^\circ \) (44,45).

Other examples of two-atom chain polymers are polyoxymethylene \(-(\text{CH}_2\text{O})_n\) (39,78) and polyisobutylene \( -\text{(CH}_3\text{C(CH}_3\text{)}_2)_n\) (63,79,80).

Chains of polyoxymethylene assume a \( s(9/5) \) helical conformation with an identity period of 17.3 \( \text{Å} \) (39,78). Assuming \( b_{12} = b_{21} = b \) and \( \tau_1 = \tau_2 = \tau \), and, according to the model proposed by Huggins (39), \( \theta_{12} = \theta_{21} = 0 \) Equation 1.46 and Equation 1.47 become (68)

\[ \cos(t/4) = \cos(\theta/2) \sin(t/2) \]  

(1.50)

\[ (h/2) \sin(t/4) = b \sin(\theta/2) \sin(t/2). \]  

(1.51)

From the helical parameters \( h = 2d_{12} = 2d_{21} = 1.922 \) \( \text{Å} \) and \( t = 2t_{12} = 2t_{21} = 200^\circ \), and assuming \( b = 1.43 \) \( \text{Å} \), the calculated values of the bond angle and torsion angle for the Huggins model (39) are \( \tau = 110.9^\circ \) and \( \theta = 77.4^\circ \). However, the bond angles \( \tau_1 \) and \( \tau_2 \) may be different, and if \( \tau_1 \) is assumed to be 113°, then the values of \( \tau_2 \) and of the torsion angle \( \theta \) were calculated to be \( \tau_2 = 109^\circ \) and \( \theta = 77.4^\circ \). This indicates that the torsion angle is independent from the difference \( \tau_1 - \tau_2 \) and that the average value of \( \tau_1 + \tau_2 / 2 = 111° \) is practically coincident with the value of 110.9° calculated assuming \( \tau_1 = \tau_2 \) (68).

For the polyisobutylene, the helical parameters \( h = 2.328 \) \( \text{Å} \) and \( t = 225^\circ \), according to the model proposed by Liquori (79b) of \( s(8/5) \) helical conformation of the chain. Assuming \( b = 1.54 \) \( \text{Å} \), and \( \tau_{12} = \tau_{21} \) and \( \theta_{12} = \theta_{21} \), the calculated bond angle and torsion angle are \( \tau = 114^\circ \) and \( \theta = 97^\circ \). The value of the torsion angle is appreciably distorted from the gauche value (60°) due to large steric repulsion among the methyl groups of adjacent monomeric units. However, the determination of the crystal structure of polyisobutylene by X-ray diffraction has
revealed that the conformation of the chains is considerably deformed from the uniform 8/5 helix due to intermolecular interactions (80). The chain presents only a 2/1 helical symmetry and the **helix residue**, which is repeated along the chain through the twofold helical symmetry generating the whole chain, corresponds to four monomeric units (the crystallographic asymmetric unit). In the identity period (c = 18.6 Å) there are two asymmetric units (two helix residues), that is, eight monomeric units (80).

In practice, the calculations of the internal coordinates for a two-atom chain from the experimental values of the helical parameters using Equation 1.46 and Equation 1.47 or Equation 1.48 and Equation 1.49 are performed by varying the torsion angles \( \theta_{12} \) and \( \theta_{21} \), assuming fixed values of bond lengths and bond angles (Fig. 1.34), up to find a reasonable combination of the values of the unit height and unit twist. Maps of the values of the unit twist \( t = 2\pi N/M \) and unit height \( h = c/M \) for a two-atom chain, calculated from Equation 1.46 and Equation 1.47 assuming a bond length \( b = 1.53 \) Å and bond angles \( \tau_1 = 113^\circ \) and \( \tau_2 = 111^\circ \), as a function of the torsion angles \( \theta_{12} \) and \( \theta_{21} \), are shown in Figure 1.35 (4).

The contours lines join identical values of the unit twist \( t \) (Fig. 1.35A) and of the unit height \( h \) (Fig. 1.35B). In Figure 1.35A, for each curve, the values of \( t \) and of the number of conformational repeating units or residue per turn of the helix \( n = M/N = 2\pi t \) are also indicated.

In the plot in Figure 1.35A, the diagonal \( \theta_{12} = 2\pi - \theta_{21} \) separates enantiomorphous helices

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**Figure 1.35.** Maps of the values of the unit twist \( t = 2\pi N/M \) (A) and unit height \( h = c/M \) (B) for a two-atom chain, calculated from Equation 1.46 and Equation 1.47 assuming a bond length \( b = 1.53 \) Å and bond angles \( \tau_1 = 113^\circ \) and \( \tau_2 = 111^\circ \), as a function of the torsion angles \( \theta_{12} \) and \( \theta_{21} \). The bond and torsion angles are defined in Figure 1.34. The contours lines join identical values of the unit twist \( t \) (A) and of the unit height \( h \) (B). Curves corresponding to the same values of the unit twist are reported at intervals of 20° from 60° to 300° (A), whereas the curves corresponding to the same values of the unit height are reported at intervals of 0.2 Å from 0.8 to 2.4 Å (B). In part A, for each curve, the values of \( t \) (from 60° to 300°) and of the number of conformational repeating units or residue per turn of the helix \( n = M/N = 2\pi t \) are indicated, whereas in part B, the values of \( h \) (in Å) are indicated. The curves relative to values of unit twist \( t \) and \( (360°-t) = -t \), separated by the diagonal \( \theta_{12} = 360° - \theta_{21} \), correspond to enantiomorphous \( s(M/N) \) and \( s(M/(M-N)) \) helices (A). For instance, the curve relative to \( t = 120° \) and \( n = 3 \) corresponds to the \( s(3/1) \) helix and the curve \( t = 240° - 120° \) and \( n = 3/2 = 1.5 \) corresponds to the enantiomorph \( s(3/2) \) helix (Fig. 1.36), the curve relative to \( t = 100° \) and \( n = 3.6 - 18/5 \) corresponds to the \( s(18/5) \) helix and the curve \( t = 260° - 100° \) and \( n = 1.38 = 18/13 \) corresponds to the enantiomorph \( s(18/13) \) helix. (Reproduced with permission from Reference 93. Copyright 1992 by the Società Chimica Italiana.)
with identical number of units per turn \( n = M/N \) and identical modulus but opposite sign of the unit twist. In fact, as described in Section 1.5, if the unit twist is taken as an angle of rotation between \( 0^\circ \) and \( 180^\circ \), helices with symmetries \( s(M/N) \) and \( s(M/(M - N)) \) are equivalent and enantiomorphous, and are characterized by the same modulus \( \pm t \) of the unit twist but opposite sign, \( +t \) and \( -t \), respectively. A right-handed \( s(M/N) \) helix has a positive value of the unit twist \( 0^\circ < t < 180^\circ \), corresponding to a **counterclockwise** rotation for passing from one atom to the corresponding atom of the successive conformational repeating unit (or residue), that is, to go from an atom with coordinate \( z = z_0 \) to the helically equivalent atom having coordinate \( z = z_0 + h \), where \( h \) is the unit height \( h = c/M \). In the corresponding enantiomorphous left-handed helix, the unit twist is negative \(( -t \) \) with modulus comprised between \( 0^\circ \) and \( 180^\circ \), corresponding to a **clockwise** rotation for passing from one atom to the corresponding atom of the successive unit, as for the right-handed helix. In this case, the helix has \( M - N \) turns in the identity period with \( s(M/(M - N)) \) symmetry, a complete repetition occurring after \( M - N \) counterclockwise turns of the helix, and the number of units per turn is \( n = M/(M - N) \) (Fig. 1.35A). This definition of the unit twist and the corresponding chirality of helices are illustrated in Figure 1.36 in the case of the right-handed \( s(3/1) \) and left-handed \( s(3/2) \) helices of IPP.

In the plot in Figure 1.35A the diagonal \( \theta_{12} = \theta_{23} \) joins the representative points of uniform helices and separate helices related by a twofold rotation axis perpendicular to the chain axis. If the map in Figure 1.35A is calculated assuming equal values of the bond angles \( \tau = \tau_1 = \tau_2 \), as in a one-atom chain, doubling the \( n \) values and halving the \( t \) values along the diagonal \( \theta_{12} = \theta_{23} \) will give the numbers of units per turn and the unit twist for a one-atom chain.

The map of the values of the unit height in Figure 1.35B presents the same symmetry as in the map of the unit twist (Fig. 1.35A). If the map

---

**Figure 1.36.** Side views and projections along the chain axis of the right-handed (A) and left-handed (B) 3/1 helix of isotactic polypropylene. If the unit twist is taken as an angle of rotation between \( 0^\circ \) and \( 180^\circ \), the right-handed \( s(3/1) \) helix (A) is characterized by a positive value of the unit twist \( t = 2\pi/3 = 120^\circ \), corresponding to a **counterclockwise** rotation for passing from one atom to the corresponding atom of the successive conformational repeating unit (arrows in A). The enantiomorphous left-handed helix (B) is characterized by a negative value of the unit twist \( t = -120^\circ \) with modulus comprised between \( 0^\circ \) and \( 180^\circ \), corresponding to a **clockwise** rotation for passing from one atom to the corresponding atom of the successive residue (B, continuous arrows). In this definition of the left-handed helix with unit twist \( t = -120^\circ \), the number of units per turn is the same as that of the right-handed helix \( n = 3/1 \). The unit twist of the left-handed helix may be also taken as a positive angle with a value higher than \( 180^\circ \) \( (t = 240^\circ - 2\pi/3) \), corresponding to a **counterclockwise** rotation for passing from one atom to the corresponding atom of the successive unit (B, dashed arrows). In this case, the helix has two turns in the identity period with \( s(3/2) \) symmetry, and the number of units per turn is \( n = 3/2 \). Helices with \( s(3/1) \) and \( s(3/2) \) symmetries are equivalent and enantiomorphous and are characterized by the same modulus of the unit twist \( \pm t \), but opposite sign, \( +120^\circ \) and \( -120^\circ \), respectively, or by positive values of the unit twist \( t \) and \( 360^\circ - t \), respectively.
in Figure 1.35B is calculated assuming equal values of the bond angles $\tau = \tau_1 = \tau_2$, as in a one-atom chain, halving the $h$ values lying on the diagonal $\theta_{12} = \theta_1$ obviously will give the unit height for a one-atom chain having the same values of bond length and bond angle.

The pair of torsion angles $\theta_1$ and $\theta_2$ corresponding to the experimental values of the unit twist $t$ and unit height $h$ can be easily found from the maps in Figure 1.35 by the intersection of the curves relative to the values of $t$ and $h$. An example is presented in Figure 1.37, which shows that for the s(7/2) helix of the chains of isotactic poly(4-methyl-1-pentene) (iP4MP) (81a) with experimental values of $t = 2\pi(2/7) = 102.8^\circ$ and $h = 1.98 \text{ Å} (c = 13.86 \text{ Å})$, the torsion angles are $\theta_{12} = 168^\circ$ and $\theta_{23} = -73^\circ$ (or $\theta_{12} = -73^\circ$ and $\theta_{23} = 168^\circ$), corresponding to a right-handed helix, whereas for the left-handed 7/2 helix (with s(7/5) symmetry) with $t = 257.2^\circ = 102.8^\circ$ and $h = 1.98 \text{ Å}$, the torsion angles are $\theta_{12} = 73^\circ$ and $\theta_{23} = 192^\circ = 168^\circ$ (or $\theta_{12} = 192^\circ = 168^\circ$ and $\theta_{23} = 73^\circ$).

(c) Helical Symmetry and Three-Atom Chain –(M$_1$–M$_2$–M$_3$)$_n$–. A polymer chain consisting of three kinds of skeleton atoms, M$_1$, M$_2$, and M$_3$, is characterized by the bond lengths $b_{12}$, $b_{23}$, and $b_{11}$, the bond angles $\tau_1$, $\tau_2$, and $\tau_3$, and the torsion angles $\theta_{12}$, $\theta_{23}$, and $\theta_{31}$ around the three nonequivalent skeleton bonds M$_1$–M$_3$, M$_2$–M$_3$, and M$_3$–M$_1$, respectively. The equations for the helical parameters are derived from the elements of $A$ and $R$ matrices (Eq. 1.34 and Eq. 1.35) (68):

$$A = A_{12}^m A_{23}^m A_{31}^m A_{12}^m A_{23}^m A_{31}^m \quad R = B_{12} + A_{12}^m A_{23} B_{23} + A_{12} B_{12} A_{23}^m A_{31} B_{31},$$

and Equation 1.31 and Equation 1.32 can be written in the form

$$\begin{align*}
\cos(t/2) &= \cos(\theta_{12}/2 + \theta_{23}/2 + \theta_{31}/2) \\
\sin(t/2) &= \sin(\theta_2/2) \sin(\theta_3/2) \sin(\theta_1/2) \\
-\cos(\theta_{12}/2 + \theta_{23}/2 + \theta_{31}/2) &= \cos(\theta_1/2) \cos(\theta_2/2) \cos(\theta_3/2) \\
-\cos(\theta_{12}/2 - \theta_{23}/2 + \theta_{31}/2) &= \cos(\theta_1/2) \cos(\theta_2/2) \cos(\theta_3/2) \\
-\cos(\theta_{12}/2 + \theta_{23}/2 - \theta_{31}/2) &= \cos(\theta_1/2) \cos(\theta_2/2) \cos(\theta_3/2) \\
h \sin(t/2) &= (h_{12} + h_{23} + h_{31}) \sin(\theta_{12}/2 + \theta_{23}/2 + \theta_{31}/2) \\
\sin(\theta_{23}/2) = \sin(\theta_{23}/2 + \theta_{31}/2) &= \sin(\theta_1/2) \sin(\theta_2/2) \sin(\theta_3/2) \\
-(-h_{12} + h_{23} + h_{31}) &= \cos(\theta_1/2) \cos(\theta_2/2) \sin(\theta_3/2) \\
-(-h_{12} - h_{23} + h_{31}) &= \cos(\theta_1/2) \cos(\theta_2/2) \sin(\theta_3/2) \\
-(-h_{12} + h_{23} + h_{31}) &= \sin(\theta_{12}/2 + \theta_{23}/2 - \theta_{31}/2) \\
\sin(\theta_{12}/2 - \theta_{23}/2 + \theta_{31}/2) &= \sin(\theta_1/2) \cos(\theta_2/2) \cos(\theta_3/2) \\
-(-h_{12} + h_{23} + h_{31}) &= \sin(\theta_{12}/2 + \theta_{23}/2 - \theta_{31}/2) \\
\cos(\theta_1/2) \cos(\theta_2/2) \cos(\theta_3/2) &= \cos(\theta_1/2) \sin(\theta_2/2) \sin(\theta_3/2). 
\end{align*}$$

Figure 1.37. Map as a function of the torsion angles $\theta_{12}$ and $\theta_{23}$ of the loci of points for which the value of the unit twist is equal to $t = 102.8^\circ$ ($n = M/N = 7/2 = 3.5$) and $t = -102.8^\circ = 257.2^\circ$ ($n = M(N - M) = 7/5 = 1.4$) (continuous lines), corresponding to a 7/2 helix, and the value of the unit height is $h = 1.98$ Å (dashed lines), corresponding to the chain conformation of form I of isotactic poly(4-methyl-1-pentene) (c = 13.86 Å) (81a). The curves are calculated from Equation 1.46 and Equation 1.47 assuming bond lengths $b = 1.53$ Å and bond angles $\tau_1 = 113^\circ$ and $\tau_2 = 111^\circ$. The intersection points of the curves of the unit twist and unit height are indicated by white and black circles and provide the pairs of torsion angles $\theta_{12}$, $\theta_{23}$) that correspond to the right-handed 7/2 helix (white circles) and the left-handed 7/5 helix (black circles) for the unit height observed in form I of isotactic poly(4-methyl-1-pentene) (81a). The pairs of torsion angles $\theta_{12} = 168^\circ$, $\theta_{23} = -73^\circ$ and $\theta_{12} = -73^\circ$, $\theta_{23} = 168^\circ$ (white circles) correspond to the right-handed 7/2 helix, whereas the pairs $\theta_{12} = 73^\circ$, $\theta_{23} = 192^\circ = -168^\circ$ and $\theta_{12} = 192^\circ = -168^\circ$, $\theta_{23} = 73^\circ$ (black circles) correspond to the left-handed 7/2 helix with symmetry s(7/5).
An example of chains with \( n = 3 \), \(-(\alpha_{1} \cdots \alpha_{n})\), is provided by polyamides or poly(\( \alpha \)-amino acids) \(-(CH_{2}HR-CO-NH)_{n}\) \((88)\). According to Pauling and Corey \((82)\), accepted values of the bond lengths and bond angles for polyamides are \( b_{12}(C_{\alpha} C) = 1.53 \) Å, \( b_{23}(C-N) = 1.32 \) Å, \( b_{34}(N-C_{\alpha}) = 1.47 \) Å, \( \tau_{1}(N C_{\alpha} C) = 110^{\circ} \), \( \tau_{2}(C_{\alpha} C N) = 114^{\circ} \), and \( \tau_{3}(C N-C_{\alpha}) = 123^{\circ} \), and the torsion angles about the CO-NH bond has been established to be \( \theta_{23} = 180^{\circ} \). With this fixed geometry, Equation 1.52 and Equation 1.53 can be written:

\[
\cos(t/2) = -0.817 \sin(\theta_{12}/2 + \theta_{31}/2) - 0.045 \sin(\theta_{12}/2 + \theta_{31}/2) \tag{1.54}
\]

\[
h \sin(t/2) = 2.967 \cos(\theta_{12}/2 + \theta_{31}/2) - 0.664 \cos(\theta_{12}/2 + \theta_{31}/2). \tag{1.55}
\]

From the experimental values of the identity period \( c \) and of unit twist \( t \) and unit height \( h \), the values of the torsion angles \( \theta_{12}(C_{\alpha}-C) \) and \( \theta_{31}(N-C_{\alpha}) \), calculated according to Equation 1.54 and Equation 1.55 for various conformations of polyamides, are reported in Table 1.9.

It is apparent that for polyamides that assume the \( \alpha \)-helical conformations \((88)\), the bonds \( C_{\alpha}-C \) and \( N-C_{\alpha} \) are in the stable gauche conformation \((41)\). The parallel and anti-parallel-chain extended conformations are both characterized by a twofold screw axis. The bonds \( C_{\alpha}-C \) and \( N-C_{\alpha} \) of the anti-parallel-chain extended conformation are slightly deviated by \( 30^{\circ} \) from the \( \text{trans} \) conformation, whereas they are in the less stable anti-cisinal (=120\( ^{\circ} \)) conformation in the parallel-chain extended conformation. The parallel-chain extended conformation is, therefore, considered less stable than the anti-parallel-chain extended conformation. Many polyamides crystallize in both \( \alpha \) helix \((41)\) and extended conformations, as, for instance, poly-L-alanine \((83)\). Polyglycine crystallizes into two crystalline forms \((84)\); form I is in the anti-parallel-chain extended conformation \((85)\), whereas form II is in the 3/1 helical conformation \((86)\). \( \beta \)-Keratin is in the parallel-chain extended conformation \((85)\). Most of polyamides or proteins in the extended form have been found to be in accord to the anti-parallel-chain extended conformation \((87)\).

Other examples of three-atom polymer chain \(-(\alpha_{1} \cdots \alpha_{n})\) are poly(ethylene oxide) (PEO) \(-(CH_{2}-CH_{2}-O)_{n}\) \((88,89)\) and isotactic poly(tert-butylethylene oxide) (PBEO) \((90)\). A uniform 7/2 helical conformation with GTT sequence of the torsion angles \( \theta_{12} \theta_{23} \theta_{31} \) and an identity period of 19.30 Å was firstly proposed for the chains of PEO \((88)\). The values of the torsion angles \( \theta_{12}(C-C) = 65.0^{\circ} \) and \( \theta_{23}(C-O) = \theta_{31}(O-C) = 188.3^{\circ} \) were determined from the values of the helical parameters and the identity period \((88)\). From the determination of the crystal structure \((89)\) the torsion angles were found considerably distorted from the uniform helix, with values slightly different in different monomeric units. The conformation is essentially the 7/2 helix and consists nearly of GTT sequences with average values of torsion angles \( \theta_{12}(C-C) = 68.4^{\circ} \) and \( \theta_{23}(C-O) = \theta_{31}(O-C) = 186.0^{\circ} \) \((89)\). Such a distortion from the uniform helix was found to be due to intermolecular interactions \((89)\). The models of uniform 7/2 helical and distorted helical conformation of PEO are shown in Figure 1.38.

Isotactic PBEO \(-(CH_{2}-CH(t-Bu)-O)_{n}\) has a true asymmetric carbon atom in each monomeric unit \((90)\). Therefore, there are two optical isomers, rectus \((R)\) and sinister \((S)\). The crystalline form I of the racemate isotactic poly((RS)tert-butylethylene oxide) is characterized by chains in 9/4 helical conformation and identity period \( c = 24.65 \) Å \((90)\). Assuming bond lengths \( b(C-C) = 1.54 \) Å, \( b(C-O) = 1.43 \) Å, and all the bond angles \( \tau = 109^{\circ}28\)\(^{\circ}\), the three torsion angles \( \theta_{12}(CH-O), \theta_{23}(O-CH_{2}), \) and \( \theta_{31}(CH_{2}-CH) \) can be found from Equation 1.52 and Equation 1.53 by changing the three torsion angles each covering from \( 0^{\circ} \) and \( 360^{\circ} \), to find the combination that gives the helical parameters \( t = 160^{\circ} \) and

<table>
<thead>
<tr>
<th>Conformation</th>
<th>( c (\text{Å}) )</th>
<th>( M/N )</th>
<th>( h (\text{Å}) )</th>
<th>( t (\text{deg}) )</th>
<th>( \theta_{12}(C_{\alpha}-C) (\text{deg}) )</th>
<th>( \theta_{31}(N-C_{\alpha}) (\text{deg}) )</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha ) Helix</td>
<td>27</td>
<td>18/5</td>
<td>1.5</td>
<td>100</td>
<td>-47</td>
<td>-58</td>
<td>((41))</td>
</tr>
<tr>
<td>Polyamide form II</td>
<td>9.3</td>
<td>3/1</td>
<td>3.1</td>
<td>120</td>
<td>-144</td>
<td>+76</td>
<td>((84,86))</td>
</tr>
<tr>
<td>Parallel-chain extended</td>
<td>6.5</td>
<td>2/1</td>
<td>3.25</td>
<td>180</td>
<td>+112</td>
<td>-118</td>
<td>((85))</td>
</tr>
<tr>
<td>Anti-parallel-chain extended</td>
<td>7.0</td>
<td>2/1</td>
<td>3.5</td>
<td>180</td>
<td>+145</td>
<td>-142</td>
<td>((85))</td>
</tr>
</tbody>
</table>
right-handed 9/4 helix, the model I in Figure 1.39 (with $\theta_{12}(\text{CH–O})=263^\circ=97^\circ$, $\theta_{23}(\text{O–CH}_2)=180^\circ$, and $\theta_{31}(\text{CH}_3–\text{CH})=73^\circ$) for the $S$ polymer, and the model II ($\theta_{12}(\text{CH–O})=73^\circ$, $\theta_{23}(\text{O–CH}_2)=183^\circ$, and $\theta_{31}(\text{CH}_3–\text{CH})=-97^\circ$) for the $R$ polymer. The model I of conformation with $\theta_{12}(\text{CH–O})=263^\circ=97^\circ$, $\theta_{23}(\text{O–CH}_2)=180^\circ$, and $\theta_{31}(\text{CH}_3–\text{CH})=73^\circ$ has been confirmed in the determination of the crystal structure of isotactic poly(tert-butylethylene oxide) (90).

On the basis of the general method (Eq. 1.31, Eq. 1.32, Eq. 1.33, Eq. 1.34, Eq. 1.35, Eq. 1.36, Eq. 1.37, and Eq. 1.38), Miyazawa has also reported more complex analytical equations for polymer chains $-(\text{M}_1\text{M}_2\ldots\text{M}_n)-$ with $n = 3, 4, 5, and 6$ (68). Sugeta and Miyazawa (71) have reformed the equations to matrix formulas that are suitable for computer calculations. An example of chains $-(\text{M}_1\text{M}_2\ldots\text{M}_n)-$ with $n = 4$ is provided by syndiotactic vinyl polymers $-(\text{CH}_2–\text{CHR–CH}_2–\text{CHR})_n-$ (see point d).

(d) Chains with $s(M/N)2$ Helical Symmetry. Chains with $s(M/N)2$ helical symmetry are typical of syndiotactic vinyl polymers $-(\text{CH}_2–\text{CHR–CH}_2–\text{CHR})_n-$ and can be included in the case of the four-atom chain $-(\text{M}_1\text{M}_2\text{M}_3\text{M}_4)-$ in the
model of Miyazawa (68). According to this model, the internal coordinates of the chain –(M₁–M₂–M₃–M₄)ₜ are the bond lengths \(b_{12}, b_{23}, b_{34}\), and \(b_{41}\); the bond angles \(\tau_{1}, \tau_{2}, \tau_{3}\), and \(\tau_{4}\); and the torsion angles \(\theta_{12}, \theta_{23}, \theta_{34}\), and \(\theta_{41}\) (68). The equations for the helical parameters are more complex but similar to Equation 1.52 and Equation 1.53 reported for the chain –(M₁–M₂–M₃)ₜ. For a vinyl polymer –(CH₃–CHR–CH₃–CHR)ₜ in s(M/N)₂ helical conformation, the twofold axes perpendicular to the chain axis cross the methylene carbon atoms; therefore, \(b_{12} = b_{41}, b_{23} = b_{34}, \tau_{2} = \tau_{4}, \theta_{12} = \theta_{23}, \) and \(\theta_{23} = \theta_{34}\) (conformation and sequence of torsion angles (1) in Fig. 1.30). The internal coordinate are, therefore reduced to \(b_{12}, b_{23}, \tau_{1}\), and \(\theta_{12}\) with a sequence of torsion angles \(\ldots \theta_{5}\theta_{3}\theta_{2}\theta_{1}\theta_{12}\ldots\) (Fig. 1.30). Assuming \(b_{12} = b_{23} = b\) and \(\tau_{1} = \tau_{2} = \tau\), the following general equations: Equation 1.31, Equation 1.32, Equation 1.33, Equation 1.34, Equation 1.35, Equation 1.36, Equation 1.37, and Equation 1.38 for the helical parameters become:

\[
\cos(t/2) = \cos(\theta_{12} + \theta_{23}) \sin^{4}(\tau/2) + \cos^{4}(\tau/2) - \\
[2 \cos\theta_{12} + 2 \cos\theta_{23} + \cos(\theta_{12} - \theta_{23})] \sin^{2}(\tau/2) + \cos^{2}(\tau/2)
\]

\[h \sin(t/2) = 4b \sin(\theta_{12} + \theta_{23}) \sin^{4}(\tau/2) - 4b \sin(\theta_{12} + \sin(\theta_{23}) \sin^{2}(\tau/2) \cos^{2}(\tau/2).\]

sPP in the stable helical forms I and II is characterized by chains in s(2/1)₂ helical conformation with identity period \(c = 7.4\) Å (Fig. 1.20B) (46,47,49). The unit height is \(h = c/2 = 3.7\) Å and the unit twist is \(t = 180^\circ\). Assuming a bond length \(b = 1.54\) Å and a bond angle \(\tau = 114^\circ\), the torsion angles were calculated from Equation 1.52 and Equation 1.53 to be \(\theta_{12} = 171^\circ\) and \(\theta_{23} = -57^\circ\) (68).

Similar equations for vinyl polymer chains fulfilling the s(M/N)₂ symmetry have been derived by Ganis and Temussi (70) in a different form. Assuming \(b_{12} = b_{23} = b\) and \(\tau_{1} = \tau_{2} = \tau\),

\[
\cos t = \cos^{2}(\tau/2) - (1/2) \sin^{2} \tau(1 + \cos\theta_{12}) (1 + \cos\theta_{23}) + \sin^{2}(\tau/2) \cos(\theta_{12} + \theta_{23})
\]

\[h = \frac{b \sin^{2} \tau [\tan^{2}(\tau/2) \sin(\theta_{12} + \theta_{23}) - \sin\theta_{12} - \sin\theta_{23}]}{2 \sin t}.\]

(e) Chains with Glide Plane Symmetry. The main conformational parameter of chains with glide plane symmetry is the identity period per monomeric unit \(p = c/l\), where \(M\) is the number of monomeric units within the chain axis \(c\). The conformational parameter equations for polymers with glide plane symmetry conformations have been reported by Ganis and Temussi (70) and successively by Tai and Tadokoro (73). For a generic polymer chains –(M₁–M₂– \ldots \ldots Mₙ–Mᵣ–Mₙ–Mᵣ– \ldots \ldots Mₖ–Mᵣ– \ldots \ldots Mₙ)ₜ whose constitutional repeating unit is composed of \(n\) atoms, the geometry is defined by \(n\) bond lengths \(b_i\), \(n\) bond angles \(\tau_i\), and \(n\) torsion angles \(\theta_i\) that \(b_i\) is the bond length \(M_i-1-M_i\), \(\tau_i\) is the bond angle \(M_i-1-M_i-M_i-1\), and the torsion angle \(\theta_i\) is the torsion angle around the bond \(M_i-1-M_i\) (70,73,74). The glide plane symmetry imposes the conditions that \(b_i = b_{rin}, \tau_i = \tau_{rin}, \) and \(\theta_i = -\theta_{rin}\) (Table 1.6). The cases of chains with \(n = 2\) and \(n = 4\) are common examples of chains with glide plane symmetry. Examples of the case \(n = 2\), –(M₁–M₄)ₜ, are provided by the chains of syndiotactic vinyl polymers in Figure 1.20C and Figure 1.30, whereas common examples for the case \(n = 4\), –(M₁–M₄–M₄–M₁)ₜ, are the chains of 1,4-polydienes in Figure 1.21B and Figure 1.25.

For the chains with two skeleton atoms in the constitutional repeating unit \(n = 2\), –(M₁–M₄)ₜ, the internal coordinates under the assumption of the glide plane symmetry are reduced to \(b_i, b_{23}, \tau_i, \theta_i, \theta_i\), and \(\theta_i\) with a sequence of torsion angles \(\ldots \theta_i \theta_i \ldots (1)\) (Fig. 1.30 for a syndiotactic vinyl polymer). Assuming \(b_1 = b_2 = b, \tau_1 = \tau_2 = \tau, \) the identity period per monomeric unit \(p = c/l\), is given by Equation 1.60:

\[p = 2b \sin(\tau/2) [\sin^{2}(\tau/2) + \cos^{2}(\tau/2) \sin^{2}(\tau_i/2)]^{1/2}\]

(1.60)

with \(\theta_i = 180^\circ\) for any value of \(\theta_i\).

sPP in the metastable form III is characterized by chains having a glide plane symmetry (Fig. 1.20C), with identity period \(c = 5.1\) Å and two monomeric units within the identity period \(n = 2\) (46,48,49,65). Assuming bond lengths \(b_1 = b_2 = b = 1.54\) Å and bond angles \(\tau_1 = \tau_2 = \tau = 111^\circ\), the torsion angle calculated from Equation 1.60 is \(\theta_2 = 180^\circ\) and \(\theta_1 = 180^\circ\) corresponding to the extended trans-planar conformation (46,48,49,65).

Yokouchi et al. (74) have derived more general equations relating the conformational parameters and internal coordinates that can be applied...
not only to polymer chains with helical or glide plane symmetries but also to chains with only translational symmetry. In a polymer chain with \( n \) main-chain bonds in the conformational repeating unit with fixed values of bond lengths and bond angles, the number of independent torsion angles is \( n \) for helical chains \((n - 1)\), if the number of monomer units per turn is given, \( n - 1 \) for chains with glide plane symmetry, and \( n - 3 \) for polymers with translational symmetry only. If the identity period \( c \) is fixed, the independent variables are further reduced by one \((74)\). Practical application of this method needs the variation of the only independent variables, reducing the amount of calculations \((74)\). The method is, therefore, useful for polymers with complex conformations with a large number of variable \( n \).

### 1.6 HELICAL CONFORMATIONS IN ISOTACTIC AND SYNDIOTACTIC POLYMERS

The geometries of helical conformations in isotactic and syndiotactic polymers with \( s(M/N) \) and \( s(M/N)^2 \) symmetries, respectively, show interesting differences that can be evidenced by the values and sign assumed by the unit twist \( t \) \((4,91–93)\). Portions of chains of isotactic and syndiotactic vinyl polymers with indication of the succession of torsion angles according to the helical \( s(M/N) \) and \( s(M/N)^2 \) symmetries, respectively, are reported in Figure 1.40. Maps of the values of the unit twist \( t \) and unit height \( h \) as a function of the torsion angles \( \theta_{12} \) and \( \theta_{21} \), as defined in Figure 1.34 and Figure 1.40, for a generic isotactic vinyl polymer of helical \( s(M/N) \) symmetry have already been shown in Figure 1.35. Similar maps for a generic syndiotactic vinyl polymer, according to a \( s(M/N)^2 \) symmetry of the chain, may be calculated with the methods described in the previous section \((\text{Eq. 1.56 and Eq. 1.57, Section 1.5.4d)}\) \((68)\), or the general method of Yokouchi et al. \((74)\).

The maps in Figure 1.41 present the same symmetry as in the maps of the isotactic chains in Figure 1.35. In the plot in Figure 1.41A, the diagonal \( \theta_{12} = 360° - \theta_{23} \) separates enantiomorphous helices with identical numbers of units per turn \( n = M/N \) and identical moduli but opposite signs of the unit twist. The enantiomorphous helices are characterized by values of the unit twist \( t \) and \( (360° - t) = -t \), corresponding to the symmetries \( s(M/N) \) and \( s(M/(M\,N)) \), respectively. For instance, as in the map of the isotactic chains in Figure 1.35A, the curve relative to \( t = 120° \) corresponds to the hypothetical \( s(3/1) \) helix, and the symmetry-related curve relative to \( t = 240° = -120° \) corresponds to the enantiomorphic \( s(3/2) \) helix. The curve relative to \( t = 150° \) corresponds to the \( s(12/5) \) helix and the curve \( t = 210° = -150° \) corresponds to the enantiomorphic \( s(12/7) \) helix.

However, the comparison between the maps of the unit twist for isotactic \((\text{Fig. 1.35A})\) and syndiotactic

![Figure 1.40. Portions of chains of isotactic (A,B) and syndiotactic (A',B') vinyl polymers. Two equivalent successions of configurations, corresponding to the two configurational signs (+) and (−) of the bonds, are shown for both isotactic and syndiotactic polymers. The sequences of torsion angles \( \theta_{12} \theta_{21} \theta_{12} \cdots \) for the isotactic chain and \( \theta_{12} \theta_{21} \theta_{12} \cdots \) for the syndiotactic chains, is imposed assuming helical conformations with \( s(M/N) \) and \( s(M/N)^2 \) symmetries, respectively.](image-url)
(Fig. 1.41A) polymers indicates that only one set of symmetry-related curves corresponds to any given value of the unit twist $t$ (different from $180^\circ$) for the isotactic polymer, while there are two such sets for the syndiotactic polymers (91–93). For instance, in the map of the syndiotactic polymers in Figure 1.41A, there are two different (nonequivalent) curves relative to the unit twist $t = 120^\circ$, corresponding to the 3/1 helix, along with the two corresponding different (nonequivalent) curves relative to the unit twist of opposite sign $t = 240^\circ = -120^\circ$, corresponding to the enantiomorphous 3/2 helix. The map in Figure 1.35A for the isotactic chains presents, instead, only one curve relative to the unit twist $t = 120^\circ$ and the corresponding enantiomorphous curve relative to the unit twist $t = 240^\circ = -120^\circ$.

For sake of simplicity and for using the same symbols for the torsion angles in isotactic and syndiotactic chains, as in the formalism already shown in Figure 1.30, let us indicate the two torsion angles adjacent to the methine carbon atoms as $\theta_1$ and $\theta_2$, so that the torsion angles in Figure 1.40 and Figure 1.41 (and in Fig. 1.35 and Fig. 1.37) become $\theta_{12} = \theta_1$, $\theta_{23} = \theta_2$ and $\theta_{31} = \theta_3$.

As shown in Figure 1.37, for isotactic polymers, the curves corresponding to a given value of the unit twist $t$ (Fig. 1.35A) generally intersect the curves corresponding to a given value of the unit height $h$ (Fig. 1.35B) into four different points. For syndiotactic polymers, the intersection between a given value of $t$ (Fig. 1.41A) and a given value of $h$ (Fig. 1.41B) occurs, instead, in eight points (91–93). It is apparent from Figure 1.37 that these intersection points correspond for isotactic polymers to only one set of four pairs of torsion angles of the kind

\[
\begin{align*}
(a) \ (\theta_1, \theta_2) & \quad (b) \ (\theta_2, \theta_1) \\
(\overline{a}) \ (-\theta_2, -\theta_1) & \quad (\overline{b}) \ (-\theta_1, -\theta_2).
\end{align*}
\]  

(1.61)

For syndiotactic polymers, the intersection points correspond to two different sets of the four pairs of torsion angles of Equation 1.61.
The pair of torsion angles (\(\pi\)) corresponds to a chain conformation that is enantiomorphous to the chain corresponding to the pair of torsion angles (a). Analogously, the pairs of torsion angles (b) and (b) correspond to enantiomorphous helical chains.

As an example, for a generic isotactic polymer, the curves relative to the unit twist \(|\ell| = 144^\circ\) (i.e., \(\tau = 144^\circ\) and the corresponding enantiomorph \(\tau = 216^\circ = -144^\circ\)) and the unit height \(h = 2.0\) Å are reported in Figure 1.42A. Analogously, for a generic syndiotactic polymer, the curves relative to \(|\ell| = 144^\circ\) (i.e., \(\tau = 144^\circ\) and the corresponding enantiomorph \(\tau = 216^\circ = -144^\circ\)) and \(h = 4.0\) Å are reported in Figure 1.42B. The latter values of unit height \(h\) and unit twist \(|\ell|\) are those found for the helical conformation of the chains in the crystal structure of form II of syndiotactic poly(1-butene) (sPB) (91,94).

For the isotactic polymer (Fig. 1.42A), there are four intersection points corresponding to the four conformations indicated by Equation 1.61 with \(\theta_1 = 28^\circ, \theta_2 = -156^\circ\). The two conformations (a) (with \(\theta_1 = 28^\circ, \theta_2 = 156^\circ\)) and (b) (with \(\theta_1 = -156^\circ, \theta_2 = 28^\circ\)) are geometrically equivalent as far as the main-chain atoms are concerned since both give rise to chains of the kind \(\ldots \theta_1 \theta_2 \theta_3 \theta_4 \ldots\). When the chirality of the bonds is taken into account (Fig. 1.40A or B), only one of the two conformations (a) and (b) is energetically feasible. They correspond to energy minima for two possible equivalent configurations of the isotactic chain, shown in Figure 1.40A and B, respectively. In fact, as discussed in Section 1.5.3, bonds with chirality corresponding to a (+) sign tend to assume only G' or T conformations, whereas bonds with chirality corresponding to a (-) sign tend to assume only G or T conformations (3). Therefore, the torsion angle \(\theta_1\) (=\(\theta_{12}\) in Fig. 1.40) is \(\theta_1 = +28^\circ\) when the bond has a (+) chirality, and the torsion angle \(\theta_1\) (=\(\theta_{31}\) in Fig. 1.40) is \(\theta_1 = 156^\circ\) (conformation (a)) when the bond has a (-) chirality, as for the chain in Figure 1.40A. In the case of the chain in Figure 1.40B, the configurational signs of the bonds adjacent to the methine carbon atoms are reversed, and the torsion angle \(\theta_1\) (=\(\theta_{12}\)) tends to be \(-156^\circ\) and \(\theta_2\) (=\(\theta_{31}\)) tends to be \(+28^\circ\) (conformation (b)).

It is, however, worth noting that the configurations of the two chains in Figure 1.40A and B are equivalent...
being interconverted with each other by a simple rotation of 180° around an axis perpendicular to the chain axis. Hence, without loss of generality, we can consider only the isotactic chain in Figure 1.40A with the determined chirality of the bonds. This allows disregard of conformation (b) and (⃗b), and considering only the helical conformation relative to the intersection (a), and the corresponding enantiomorphic helix, corresponding to the intersection (⃗a). Projections of a chain of an isotactic polymer in the helical conformation (a) \( \theta_1 = 28°, \theta_2 = -156° \) and the corresponding enantiomorphic conformation (⃗a) \( \theta_1 = 156°, \theta_2 = 28° \) are shown in Figure 1.43.

According to the definition of a unit twist in Section 1.5.4, for a helix \( s(M/N) \), the unit twist \( t = 2\pi N/M \) should be taken as the angle of the **counterclockwise** rotation to go from an atom with coordinate \( z = z_0 \) to the helically equivalent atom of the successive residue having coordinate \( z = z_0 + h \), where \( h \) is the unit height \( h = c/M \). By associating two vectors perpendicular to the chain axis, having origin on the chain axis and crossing two consecutive methylene carbon atoms of the isotactic chains in Figure 1.43, it is immediately apparent that the helix with conformation (a) \( (\theta_1 = 28°, \theta_2 = 156°) \) is characterized by a unit twist \( t = 216° = -144° \), while the helix with conformation (⃗a) \( (\theta_1 = 156°, \theta_2 = -28°) \) is characterized by unit twist \( t = 144° \). The helix (a) is, therefore, left-handed with 5/3 symmetry \( (t = 2\pi 3/5 = 216°) \), whereas the helix (⃗a) is right-handed with 5/2 symmetry \( (t = 2\pi 2/5 = 144°) \). A right-handed helix grows along the chain axis counterclockwise, whereas a left-handed helix grows clockwise. In Figure 1.43A, the right-handed screw sense of the main-chain carbon atom bonds is associated with a value of \( t \) lower than 180°, \( t = 2\pi 2/5 = 144° \), and, hence, with a 5/2 symmetry. In the case of the left-handed helix, in order to go from an atom at \( z = z_0 \) to the corresponding atom related by the helix operator, it is necessary to rotate in the same direction by an angle higher than 180°, \( t = 216° \). This implies that a complete repetition occurs after three counterclockwise turns of the helix (Fig. 1.43A). Therefore, the left-handed screw sense is associated with \( t = 2\pi 3/5 = 216° \) and the 5/3 symmetry.

For the syndiotactic polymer with helical symmetry \( s(M/N)2 \), in Figure 1.42B, there are eight intersection points (a), (⃗a), (a’), (⃗a’), (b), (⃗b), (b’), and (⃗b’), corresponding to two nonequivalent sets of conformations of the kind given by Equation 1.61 with:

\[
(a) \theta_1 = 72°, \theta_2 = 147° \text{ and } (a’) \theta_1 = 74°, \theta_2 = -164°.
\]

Also, in this case, the conformations (a) \( (\theta_1 = 72°, \theta_2 = 147°) \) and (b) \( (\theta_1 = 147°, \theta_2 = 72°) \) are geometrically equivalent because they correspond to energy minima for two possible equivalent configurations of the syndiotactic chain, shown in Figure 1.40A’ and B’, respectively. Analogously, conformations (a’) \( (\theta_1 = 74°, \theta_2 = -164°) \) and (b’) \( (\theta_1 = 36°, \theta_2 = -164°) \) are equivalent because they are energetically feasible for the chirality of the bonds present in the chains in Figure 1.40A’ and B’, respectively. Hence, without loss of generality, we can consider only the syndiotactic chain in Figure 1.40A’ with the determined chirality of the bonds. This allows disregard of conformations (b) and (⃗b), and considering only the helical conformation relative to the intersections (a) and (a’), and the corresponding enantiomorphic helices relative to the intersections (⃗a) and (⃗a’), respectively. Projections of a chain of a syndiotactic polymer in the helical conformations (a) \( \theta_1 = 72°, \theta_2 = 157° \) and (a’) \( \theta_1 = 74°, \theta_2 = 164° \), and the corresponding enantiomorphic conformations (⃗a) \( \theta_1 = -147°, \theta_2 = -72° \) and (⃗a’) \( \theta_1 = 164°, \theta_2 = -74° \), respectively, are shown in Figure 1.44.

It is apparent from Figure 1.44 that the two pairs of enantiomorphous helices (a), (⃗a) and (a’), (⃗a’) are not geometrically equivalent. While for isotactic polymers only one pair of \( M/N \) and \( M/(M - N) \) enantiomorphous helices, corresponding to defined values of the unit twist and the unit height, exists, for syndiotactic polymers,
two different pairs of helices exist in correspondence of the same values of the unit twist and unit height. If the unit twist is defined as the angle of counterclockwise rotation to go from an atom with coordinate \( z = z_0 \) to the helically equivalent atom having coordinate \( z = z_0 + h \), as for isotactic polymers, the difference between these pairs of helices can be evidenced in the following way (93). For vinyl polymers with chains with \( s(M/N)2 \) symmetry, the helix residues related by the helical symmetry correspond to two monomeric units, which, in turn, are related by twofold rotation axes perpendicular to the chain axis and crossing the methylene carbon atoms (Fig. 1.30B). Let us associate vectors along these twofold axes having directions that bisect alternatively the \( \mathrm{H–C–H} \) bond angle \( \mathbf{v}_1 \) and \( \mathbf{v}_3 \) in Fig. 1.44) and the \( \mathrm{C–C–C} \) bond angle at the methylene carbon atoms \( \mathbf{v}_2 \) in Fig. 1.44) (95). Let \( \alpha \) be the angle between two successive twofold axes \( \mathbf{v}_1 \) and \( \mathbf{v}_2 \) in Fig. 1.44). The unit twist \( t \) is the angle between two corresponding atoms of neighboring residues, that is, the angle between two consecutive twofold axes connected by the helix symmetry \( \mathbf{v}_1 \) and \( \mathbf{v}_2 \) in Fig. 1.44). The relationship between the unit twist \( t \) and the angle \( \alpha \) may be \( t = 2 \alpha \) or \( t = 360 - 2 \alpha \), depending on the relative orientation of the twofold axes and on the values of the unit twist (Fig. 1.44).

According to the definition of the unit twist, it is apparent that the conformations (a) and \( (\overline{\alpha}) \) are enantiomorphous helices. The conformation (a) is characterized by \( t = 144^\circ \) and \( \alpha_1 = t/2 = 72^\circ \); therefore, it is a right-handed \( 5/2 \) helix, whereas the conformation \( (\overline{\alpha}) \) is characterized by \( t = 216^\circ \), \( \alpha_1 = (360 - t)/2 = 72^\circ \) and is a left-handed \( 5/3 \) helix (Fig. 1.44). The conformations \( (\overline{\alpha})' \) and \( (\overline{\alpha})'' \) are another pair of enantiomorphous \( 5/3 \) and \( 5/2 \) helices, respectively, characterized by a different value of \( \alpha \). The conformation \( (\overline{\alpha})' \) is characterized by \( t = 216^\circ \) and \( \alpha_2 = t/2 = 108^\circ \) and is, therefore, a left-handed \( 5/3 \) helix, whereas the conformation \( (\overline{\alpha})'' \) is characterized by \( t = 144^\circ \), \( \alpha_2 = (360 - t)/2 = 108^\circ \) and is a right-handed \( 5/2 \) helix. Therefore, for syndiotactic polymers, there exist two different \( M/N \) helical conformations, characterized by different values of the backbone torsion angles but the same values of unit twist and unit height and hence, the same number of structural units \( M \) and turns \( N \) of the helix per chain repeat. The only difference is related to the different orientation of two successive twofold axes perpendicular to the chain axis, that is, the different values of \( \alpha \) (Fig. 1.44) (4, 93).

The four kinds of helices in Figure 1.44 defined in terms of \( M \) residues (\( M \) repeating pairs of monomeric units) in \( N \) turns can be differentiated with reference to the screwing of the single monomeric units. In fact, a

---

Figure 1.44. Side views and projections along the chain axis of helices of a syndiotactic polymer having unit height \( h = 4.0 \) Å and unit twist \( \| t = 144^\circ \), observed for the form II of syndiotactic poly(1-butene) (91,94), corresponding to the intersection points (a), (\( \overline{\alpha} \)), (a'), and (\( \overline{\alpha}' \)) in Figure 1.42B. The conformation (a) corresponds to the right-handed helix with \( s(5/2)2 \) symmetry \( (t = 144^\circ \) and \( \alpha_1 = 72^\circ \)); the conformation \( (\overline{\alpha}) \) corresponds the left-handed helix with \( s(5/3)2 \) symmetry \( (t = 216^\circ \) and \( \alpha_1 = 108^\circ \), and the conformation \( (\overline{\alpha})' \) corresponds to a right-handed helix with \( s(5/2)2 \) symmetry \( (t = 144^\circ \) and \( \alpha_2 = 108^\circ \)) (93). (Reproduced with permission from Reference 93. Copyright 1992 by the Società Chimica Italiana.)
(5/2) helix ((a) or (a')) may have 10 monomeric units in 2 (10/2 helix) or 7 (10/7 helix) turns, and a (5/3) helix ((a) or (a')) may have 10 monomeric units in 3 (10/3 helix) or 8 (10/8 helix) turns. With reference to Figure 1.44, we note that, looking at the CH atoms, the right-handed 5/2 helix (a) may be considered as having a mean twist angle \( \tau = \alpha_t = 360(2/10) = 72^\circ \) and then 10 monomeric units in two turns (10/2 helix), whereas the right-handed 5/2 helix (a') may be considered as having a mean twist angle \( \tau = \alpha_t = 360(7/10) = 252^\circ = 108^\circ \) and then 10 monomeric units in seven turns (10/7 helix). The left-handed 5/3 helix (a) may be considered as having a mean twist angle \( \tau = \alpha_t = 360(6/10) = 288^\circ = -72^\circ \) and then 10 monomeric units in eight turns (10/8 helix), whereas the left-handed 5/3 helix (a') may be considered as having a mean twist angle \( \tau = \alpha_t = 360(3/10) = 108^\circ \) and then 10 monomeric units in three turns (10/3 helix) (4,93).

1.7 CONFORMATIONAL ENERGY CALCULATIONS

The intramolecular potential energy is very important in determining the conformations of macromolecules, both in the crystalline state and in the amorphous or solution state. Calculations of the potential energy of single molecules are useful for the prediction of the most stable molecular conformation starting from the chemical structure (96–102). This information is useful in setting up suitable models of the conformation and packing for the structure analysis. Moreover, these calculations may also be useful to clarify the factors that govern the conformation and the crystal structure already determined experimentally, generally by diffraction techniques. In the calculations of energy for finding the most stable conformation and the most stable crystal packing, only the internal potential energy is generally considered, and the contribution of entropy is assumed to be negligibly small in the crystals. However, the stability of states should be discussed in terms of vibrational free energy by taking entropy into account (14,103).

The potential energy may be taken, in general, as a sum of different terms as stretching energy \( E_s \), bending energy \( E_b \), torsional energy \( E_{\theta} \), nonbonded energy \( E_{ab} \), and electrostatic energy \( E_{el} \). For a chain molecule of \( N \) atoms, the various energy terms are calculated for all bonds, all bond angles, all torsion angles, and all the nonbonded and electrostatic interactions:

\[
E = \sum_s E_s + \sum_b E_b + \sum_t E_t + \sum_{nb} E_{nb} + \sum_{el} E_{el},
\]

(1.62)

where the summations are taken over all bonds, all bond and torsion angles, and all interactions between couple of atoms.

The stretching \( E_s \) and bending \( E_b \) energies are the energy contributions associated with the deformation of bond lengths and bond angles, respectively, with respect to the equilibrium values of bond length and bond angle. For small displacements from the minimum energy value, the stretching and bending energies \( E_s \) and \( E_b \) take the form of a harmonic potential:

\[
E_s = \frac{1}{2} K_s (b - b_0)^2,
\]

(1.63)

\[
E_b = \frac{1}{2} K_b (\tau - \tau_0)^2,
\]

(1.64)

where \( b_0 \) and \( \tau_0 \) are the value of the bond length and bond angle chosen as energetic minima, and \( K_s \) and \( K_b \) are the force constants that depend on the particular kind of bond. The experimental values of the force constants \( K_b \) for organic molecules allow only very small displacements of the bond lengths \( b \) from the equilibrium value of \( b_0 \) in order to relax unsuitable nonbonded interactions. In fact, bond lengths, as determined by X-ray diffraction, are generally almost constant in different molecules if the atoms are in similar electronic environments. The bending force constants \( K_b \) are such that allow more significant displacements of the bond angle \( \tau \) from the value of \( \tau_0 \) and, generally, displacements of even \( 5^\circ \) from the minimum energy values do not imply very large energy differences, which are always lower than \( RT \) at room temperature (102).

The torsional energy \( E_{\theta} \) is the energy contribution associated with rotation around single bonds and is usually taken as a sinusoidal function of the torsion angle \( \theta \). For the rotation around single bonds connecting two tetrahedral (sp\(^3\)) carbon atoms, that is adjacent to two other single bonds, the torsional energy is

\[
E_{\theta} = \frac{1}{2} E_{\theta 0} (1 + \cos 3\theta),
\]

(1.65)

where \( E_{\theta 0} \) is the internal rotation potential barrier. Staggered conformations (trans, \( \theta = 180^\circ \) and gauche, \( \theta = \pm 60^\circ \)) are favored over eclipsed (cis, \( \theta = 0 \) and anti-clinal, \( \theta = 120^\circ \)). For rotations around single bonds connecting tetrahedral (sp\(^3\)) and trigonal (sp\(^2\)) carbon atom, that is, a single bond adjacent to a double bond C–C, C=C, the torsional energy is

\[
E_{\theta} = \frac{1}{2} E_{\theta 0} (1 - \cos 3\theta),
\]

(1.66)
in this case, the axis of the double bond tend to be eclipsed (cis, θ = 0 or antitcinal, θ = ±120°) in respect to a single bond (Fig. 1.29). For instance, while in ethane the relative positions of two hydrogen atoms are trans and gauche in the minimum energy, in the case of propylene, the minimum energy relative positions of the hydrogen atoms of the methyl group with respect to the carbon atom joined by the double bond are antitcinal or cis (Fig. 1.29).

The internal rotational potential $E_i$ originates from the exchange repulsion between the electrons belonging to the atoms neighboring the bond. For C–C bonds adjacent to single bonds, a value of $E_{ij} = 11.7$ kJ/mol has been taken by Flory (102), whereas a lower value of 4.2 kJ/mol has been assumed for single bonds adjacent to a double bond (102). The barriers around single bonds between C–N and C–O atoms adjacent to the planar amide and ester groups are even lower. Finally, for the C(O)–O bonds of esters and C(O)–N bonds of amides, the torsional energy $E_i$ is usually taken as a different sinusoidal function:

$$E_i = \frac{1}{2}E_0(1 + \cos \theta_0).$$

In general, the function for the torsional energy $E_i$ may be written as

$$E_i = \frac{1}{2}E_0(1 + \cos n\theta),$$

where $n$ is an integer number that depends on the type of bond.

The nonbonded energy $E_{ab}$ arises from the interactions between atoms, which are not directly bonded and are separated by more than two bonds and depend on the distance $r_{ij}$ between each pair of atoms $i$ and $j$. Various functions have been proposed for the nonbonded energy. The most widely used analytical expressions are the Lennard–Jones–Jones function:

$$E_{ab} = \frac{d_{ij}}{r_{ij}^{12}} - \frac{e_{ij}}{r_{ij}^6}$$

and the Buckingham function:

$$E_{ab} = a_{ij} \exp(-b_ir_{ij}) - \frac{c_{ij}}{r_{ij}^n},$$

where $d_{ij}$ and $e_{ij}$ in the Lennard–Jones function and $a_{ij}$, $b_{ij}$, and $c_{ij}$ in the Buckingham function are constants depending on the nature of the atoms $i$ and $j$. In the above-mentioned two functions, the first term represents repulsion of the atoms and the second term represents the van der Waals attraction between the atoms $i$ and $j$. The parameters $d_{ij}$ and $e_{ij}$ are either obtained experimentally from the second virial coefficient of gases or calculated from the Slater–Kirkwood equations (101):

$$e_{ij} = \frac{3\eta a_{ij}q_{ij}}{4\pi \sqrt{m(\sqrt{\alpha_i/N_i} + \sqrt{\alpha_j/N_j})}}$$

$$d_{ij} = \frac{1}{2}e_{ij}r_{ij}^{6},$$

where $e$ is the electronic charge, $h$ is the Planck constant, $m$ is the electronic mass, $\alpha_i$ and $N_i$ are the atomic polarizability and effective number of outer shell electrons of the $i$th atom, respectively, and $r_{ij}$ is the sum of the van der Waals radii ($r_i$) of the atoms $i$ and $j$, and is the distance of the atoms that corresponds to the minimum of the energy in the Lennard–Jones function.

The electrostatic energy $E_{el}$ is generally calculated using a point charge model that assumes formal charges in the atoms or groups so as to fit the observed dipole moments of polar bonds, and a Coulomb potential is assumed:

$$E_{el} = \frac{q_iq_j}{\varepsilon r_{ij}},$$

where $q_i$ and $q_j$ are the formal charges on the atoms $i$ and $j$, and $\varepsilon$ is the dielectric constant.

The force constants $K_i$ and $K_n$, the internal rotation potential barrier $E_{in}$ and the parameters $d_{ij}$ and $e_{ij}$ in the Lennard–Jones function for the nonbonded energy and the formal charges $q_i$ and $q_j$ define the force field used for the calculation of the potential energy. Various authors have reported consistent force fields for calculations of the conformational energy (98,101,102,104). The parameters given by Flory (102) are reported in Table 1.10.

### 1.7.1 Setting Up Molecular Models: Coordinate Transformations

The potential functions described earlier for the nonbonded and electrostatic energies are function of the interatomic distance. Therefore, for the calculation of the potential energy, it is convenient to express the atomic positions in terms of Cartesian coordinates. The conformation of polymers is usually given using the internal coordinates, that is, bond length, bond angles, and torsion angles. The Cartesian coordinates of the atoms can be calculated from the internal coordinates by Eyring’s transformation (105).
% TABLE 1.10. Parameters of the Potential Functions of the Force Field Given by Flory (102) for Calculations of the Conformational Energy

<table>
<thead>
<tr>
<th>Torsion Angle</th>
<th>$E_i$ (kJ/mol)</th>
<th>$n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C–C$<em>{sp^3}$–C$</em>{sp^3}$–C</td>
<td>11.7</td>
<td>3 (Eq. 1.65)</td>
</tr>
<tr>
<td>C–C–C–C</td>
<td>4.2</td>
<td>3 (Eq. 1.66)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bond Angle</th>
<th>$\kappa_i$ (kJ × mol$^{-1}$ × deg$^{-2}$)</th>
<th>$\tau_i$ (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{sp^3}$–C$</em>{sp^3}$–C</td>
<td>0.184</td>
<td>109.47</td>
</tr>
<tr>
<td>C–C$_{sp^3}$–H</td>
<td>0.121</td>
<td>109.47</td>
</tr>
<tr>
<td>H–C$_{sp^3}$–H</td>
<td>0.100</td>
<td>109.47</td>
</tr>
<tr>
<td>C$<em>{sp^3}$–C$</em>{sp^2}$–C$_{sp^2}$</td>
<td>0.174</td>
<td>125</td>
</tr>
<tr>
<td>C$<em>{sp^3}$–C$</em>{sp^2}$–H</td>
<td>0.101</td>
<td>117.5</td>
</tr>
<tr>
<td>C$<em>{sp^3}$–C$</em>{sp^2}$–H</td>
<td>0.098</td>
<td>117.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nonbonded Interacting Pair*</th>
<th>$d_i^{-1}10^{-3}$ (kJ × mol$^{-1}$ × Å$^{-1}$)</th>
<th>$e_i$ (kJ × mol$^{-1}$ × Å$^3$)</th>
<th>$\Sigma r_i$ (Å)$^4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$<em>{sp^3}$–C$</em>{sp^3}$</td>
<td>1666.4</td>
<td>1532</td>
<td>3.6</td>
</tr>
<tr>
<td>C$<em>{sp^3}$–C$</em>{sp^2}$</td>
<td>2595.9</td>
<td>1867</td>
<td>3.75</td>
</tr>
<tr>
<td>C$_{sp^3}$–H</td>
<td>238.7</td>
<td>536</td>
<td>3.10</td>
</tr>
<tr>
<td>C$_{sp^3}$–O</td>
<td>1023</td>
<td>1324</td>
<td>3.40</td>
</tr>
<tr>
<td>C$_{sp^3}$–CH$_3$</td>
<td>4016.8</td>
<td>2691</td>
<td>3.80</td>
</tr>
<tr>
<td>C$<em>{sp^2}$–C$</em>{sp^2}$</td>
<td>4065.6</td>
<td>2311</td>
<td>3.90</td>
</tr>
<tr>
<td>C$_{sp^2}$–H</td>
<td>393.6</td>
<td>666</td>
<td>3.25</td>
</tr>
<tr>
<td>C$_{sp^2}$–CH$_3$</td>
<td>6274.1</td>
<td>3305</td>
<td>3.95</td>
</tr>
<tr>
<td>H–H</td>
<td>30.6</td>
<td>197</td>
<td>2.60</td>
</tr>
<tr>
<td>H–CH$_3$</td>
<td>544.3</td>
<td>965</td>
<td>3.30</td>
</tr>
<tr>
<td>H–O</td>
<td>133</td>
<td>447</td>
<td>2.90</td>
</tr>
<tr>
<td>O–O</td>
<td>632</td>
<td>1178</td>
<td>3.20</td>
</tr>
<tr>
<td>O–CH$_3$</td>
<td>2502</td>
<td>2299</td>
<td>3.60</td>
</tr>
<tr>
<td>CH$_3$–CH$_3$</td>
<td>9682.2</td>
<td>4727</td>
<td>4.00</td>
</tr>
</tbody>
</table>

*The methyl groups are considered as spherical domains and are treated as different atomic species.

*Sum of the van der Waals radii for each pair of atomic species at which corresponds the minimum of the nonbonded energy $E_{nb}$.

For a generic polymer, chains of $n$ atoms $M_1$–$M_2$–…–$M_n$, where $M_i$ is the $i$th skeletal atom, $b_i$ is the bond length $M_{i+1}$–$M_i$, $\tau_i$ is the bond angle $M_{i+1}$–$M_i$–$M_{i+2}$, and the torsion angle $\theta_i$ is the torsion angle around the bond $M_{i+1}$–$M_i$ (74). The space frame of a molecule of $n$ atoms depends on $3n$–6 internal coordinates. A right-handed Cartesian coordinate system $X$ is defined as a basic coordinate system so that the first atom is at the origin, the second atom lies on the $x$-axis, and the third atom is on the $xy$-plane, as shown in Figure 1.45. The bond vector that connects the atom $M_1$ to the atom $M_2$ is defined by the vector $b_1$, and the coordinates of the $j$th atom in the $X$ system is defined by the column vector $X(j)$.

The vectors $X(1)$ and $X(2)$ define the coordinates of the first and second atoms $M_1$ and $M_2$:

$$X(1) = \begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}$$

$$X(2) = \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} b_2 \\ 0 \\ 0 \end{bmatrix}.$$  (1.74)

The vector $X(3)$ that defines the coordinates of the third atom $M_3$ may be obtained by the sum of two vectors $b_2$ and $b_3$:

$$X(3) = \begin{bmatrix} x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} -b_3 \cos \tau_2 \\ b_3 \sin \tau_2 \\ 0 \end{bmatrix} + \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} = \begin{bmatrix} x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} x_2 \\ y_2 \\ z_2 \end{bmatrix} + \begin{bmatrix} -b_3 \cos \tau_2 \\ b_3 \sin \tau_2 \\ 0 \end{bmatrix}.$$  (1.75)

The coordinates $X(4)$ of the fourth atom $M_4$ depend not only on the bond lengths $b_3$, $b_2$, and $b_4$ and bond angles $\tau_2$ and $\tau_3$, but also on the torsion angle $\theta_3$. The coordinates $X(4)$ can be obtained as the sum of the vector $X(3)$ and the vector $b_4$. 
the final recursion formula becomes

\[
X(j) = A_j^3 \mathbf{T}_{j-1} \mathbf{B}_j + X(j-1). \tag{1.85}
\]

The formula (Eq. 1.85) allows for the calculation of the Cartesian coordinates of all atoms from the internal coordinates and is particularly suitable for computer calculations.

### 1.7.2 Calculation of the Conformational Energy for Isotactic and Syndiotactic Polymers

The conformation of the chains of isotactic polymers in the crystalline state is generally helical and corresponds to a succession of nearly trans and gauche torsion angles, the exact values depending on the bulkiness of the side groups. Molecular mechanics calculations have been extensively used for the prediction of the chain conformation of polymers in the crystal (105). Calculations of the conformational energy of chains in the crystals are based on the principle of minimum internal conformational energy, which states that the conformation of a polymer chain in a crystal approaches one of the minima of the internal conformational energy, which would be taken by an isolated chain subjected to the restrictions imposed by the equivalence principle (Section 1.5). This means that packing effects generally do not influence the conformation of the chains in the crystal as long as the conformational internal energy of the isolated chain corresponds to a deep energy minimum. Therefore, calculations of the conformational energy of chains in the crystals are performed on an isolated macromolecule under the constraints imposed by the equivalence principle. As a consequence, a succession of backbone torsion angles \( \ldots, \theta_1, \theta_0, \theta_1, \theta_2, \ldots \) (Fig. 1.30) is generally assumed for isotactic polymers, corresponding to the assumption that the chains assume in the crystals regular helical conformation with line repetition symmetry \( s(M/N) \) (Section 1.5.2). The conformational energy is, therefore, a function of only the two backbone torsion angles \( \theta_1 \) and \( \theta_2 \).

The conformational energy maps as a function of the torsion angles \( \theta_1 \) and \( \theta_2 \) for chains of various isotactic polymers, calculated for chain models having the chirality of bonds as in Figure 1.30A and for fixed values of the bond angles \( \tau_1 = 113^\circ \) and \( \tau_2 = 111^\circ \), are reported in Figure 1.46. The energy maps of isotactic polypropylene (43), polystyrene (iPS) (106), polybutene (iPB) (106,107), and poly(4-methyl-1-pentene) (iP4MP) (108) are shown. The maps in Figure 1.46 are symmetric with respect to the diagonal \( \theta_1 = 360^\circ - \theta_2 \), which separates equivalent energy minima corresponding to enantiomorph helical conformations (right-handed and left-handed helices \( s(M/N) \)). The presence in the map of iP
in Figure 1.46B of two equivalent energy minima is apparent, indeed, corresponding to the right-handed (G'T)ₙ (θ₁ = -60°, θ₂ = 180°) and left-handed (TG')ₙ (θ₁ = 180°, θ₂ = 60°) threefold helical conformation with symmetry s(3/1) (and s(3/2)). According to the discussion of Section 1.5.3, since the calculations have been performed for a chain model in which the bonds corresponding to the torsion angles θ₁ and θ₂ have (−) and (+) configurational signs, respectively (Fig. 1.30A), the results in Figure 1.46 confirm that in the energy minima, the torsion angle θ₁ may assume values of −60° or 180°, whereas the torsion angle θ₂ may assume the values 180° or +60°.

In the case of iPS, besides the two absolute minima corresponding to the threefold helical conformation found in the most stable crystalline form of iPS (109), a minimum of higher energy in the region of the trans-planar conformation (θ₁ = θ₂ = 180°) is also present (Fig. 1.46A). In fact, the planarity of the benzene rings makes the trans-planar conformation energetically feasible. This is in agreement with the observation of the disordered conformation found in crystalline gels of iPS.

**Figure 1.46.** Maps of the conformational energy of the chains of various isotactic polymers as a function of the backbone torsion angles θ₁ and θ₂. Isotactic polystyrene (A), polypropylene (B), poly(1-butene) (C), and poly(4-methyl-1-pentene) (D). The conformational energy has been calculated under the constraint of the equivalent principle, assuming a σ(M/N) symmetry of the chains and a succession of torsion angles . . . θ,θ,θ,θ . . . (Fig. 1.30A), for fixed values of the bond angles τ₁ = 113° and τ₂ = 111°, as defined in Figure 1.30. As in the chain model in Figure 1.30A, the two bonds adjacent to the methine carbon atom, corresponding to the torsion angles θ₁ and τ₂, have (−) and (+) configurational signs, respectively. The isoe nergetic curves are reported every 10 (A,C,D) or 5 kJ/mol of monomeric units (B) with respect to the absolute minimum of each map assumed as zero. (Reproduced with permission from Reference 4. Copyright 2003 by Wiley Interscience.)
Figure 1.47. Details of the maps of the conformation energy of iP4MP (A) and iP4MP (B) as a function of \( \theta_1 \) and \( \theta_2 \) in the region of the helical conformation \( \theta_1 \approx T \) and \( \theta_2 \approx G \) (106-108). The conformational energy has been calculated under the constraint of the equivalent principle, assuming a \( s(M/N) \) symmetry of the chains and a succession of torsion angles \( \ldots \theta_0 \theta_1 \theta_2 \ldots \) (Fig. 1.30A), for fixed values of the bond angles \( \tau_1 = 113^\circ \) and \( \tau_2 = 111^\circ \). The curves are reported at intervals of 2 kJ/mol of monomeric units (A) and 5 kJ/mol of monomeric units (B) with respect to the absolute minimum of the map assumed as zero. The values of the energies corresponding to the minima (+) are also indicated. The continuous (A) and dashed (B) lines correspond to the loci of points for which the values of the unit twist are equal to \( \tau = 120^\circ, 98^\circ, \) and \( 90^\circ \), corresponding to the helical symmetries 3/1, 11/3, and 4/1, respectively, for iP (A) and \( \tau = 120^\circ, 102.8^\circ, \) and \( 90^\circ \), corresponding to the helices 3/1, 7/2, and 4/1, respectively, for iP4MP (B). In the map of iP4MP (B), the points corresponding to pairs of torsion angles \( \theta_1 \) and \( \theta_2 \), relative to the experimental 7/2 (□), 4/1 (▲), and 3/1 (○) helical conformations of the chains observed in form I, forms II and III, and form IV of iP4MP, respectively, are also shown.

(110), characterized by a succession along the chain of sequences in 3\( _1 \) helical conformation of opposite hands (right-handed and left-handed) connected by short sequences in trans-planar conformation (110). This energy minimum is absent for iP, iP, and iP4MP because of the greater repulsions between the nonplanar side groups (Fig. 1.46).

The regions of the maps in Figure 1.46C and D of the helical conformation (TG) for iP and iP4MP are reported in Figure 1.47 in enlarged scales of \( \theta_1 \) and \( \theta_2 \). In the energy map of iP, the energy minimum in the region of the helical conformation (TG) is split into two minima (Fig. 1.46C and Fig. 1.47A). The absolute minimum corresponds to the 3/1 helix (\( \theta_1 = 180^\circ, \theta_2 = 60^\circ \)) that has been observed for the conformation of the chains in the most stable form I of iP (111). The second minimum of higher energy is at values of \( \theta_1 \) and \( \theta_2 \) higher than 180\( ^\circ \) and 60\( ^\circ \), respectively (Fig. 1.47A), and is close to both the 11/3 and 4/1 helical conformations, which have been found for the chains of forms II and III of iP, respectively (105-107,112,113). These helical (T'G'\( _n \)) conformations are, therefore, characterized by values of the torsion angles \( \theta_1 \) and \( \theta_2 \) slightly deviated from the exact trans (180\( ^\circ \)) and gauche (60\( ^\circ \)) values typical of the 3/1 helix due to the steric interactions between the bulky side groups. These interactions induce a similar distortion of the two backbone torsion angles (114), \( \theta_1 = 180^\circ + \delta_1 \) and \( \theta_2 = 60^\circ + \delta_2 \), for a left-handed helix, \( \theta_1 = -60^\circ - \delta_1 \) and \( \theta_2 = 180^\circ - \delta_2 \) for a right-handed helix, with \( \delta_1 = \delta_2 \). These distorted helices have \( s(M/N) \) symmetries where the ratio \( M/N \) may have noninteger values. In general, for isotactic poly(\( \alpha \)-olefins) of the kind -(CH\( _2 \)-CH(R))\( _n \)-, the presence of side groups R bulkier than the methyl group induces slight distortions of the torsion angles \( \theta_1 \) and \( \theta_2 \) from the exact trans (180\( ^\circ \)) and gauche (60\( ^\circ \)) values typical of the 3/1 helix of iP due to the steric interaction between the bulkier side groups (114), producing helical conformation with values of the number of structural units per turn \( M/N \) between 3 and 4.

The presence of a second energy minimum in the region of the (TG) helical conformation, besides the absolute minimum of the 3/1 helix, is in agreement with the observed polymorphic behavior of iP that crystallizes in three forms characterized by different conformations of the chains (111-113). The 3/1, 11/3, and 4/1 helical conformations of the chains of the different polymorphic forms of iP are shown in Figure 1.48.

The same isodistortion of the torsion angles \( \theta_1 \) and \( \theta_2 \) is observed for iP4MP and is predicted by the energy
calculations (Fig. 1.46D and Fig. 1.47B). In this case, the distorted (T′G′)₆ helical conformations (with \( \theta_1 = 180° + \delta_1, \theta_2 = 60° + \delta_2 \)) are more stable than the 3/1 helix because of the increased bulkiness of the side groups. The absolute energy minimum is close to the 7/2 helical conformation, found in the most stable form I of iP4MP (81,115), and to the 4/1 helical conformation, found in form II (116–118) and form III of iP4MP (108,119,120) (Fig. 1.47B). The relative minimum of higher energy (Fig. 1.46D and Fig. 1.47B) corresponds to the 3/1 helical conformation (\( \theta_1 = 180°, \theta_2 = 60° \)), found in the less stable form IV of iP4MP (121,122). Also, in this case, the presence of an energy minimum corresponding to isodistorsion of the torsion angles is in agreement with the experimental observation of the conformational polymorphism of iP4MP. In particular, in the most stable form I of iP4MP with chains in 7/2 helical conformation, the torsion angles of the main chain are, on average, \( \theta_1 = 73° \) and \( \theta_2 = 192° \) (81,115) (see also Fig. 1.37) and deviate by 12°–15° from the exact staggered values of 60° and 180° of the 3/1 helix. In forms II and III with chains in 4/1 helical conformation, the torsion angles are \( \theta_1 = 82° \) and \( \theta_2 = 206° \) (108,117,119) with distortion by 22°–25° from the 3/1 helix. A greater distortion of the torsion angles occurs for the 4/1 helix, as revealed by the lower value of the unit height (1.97 Å for the 7/2 helix and 1.74 Å for the 4/1 helix) (108). The helical conformations of the chains of the polymorphic forms of iP4MP are shown in Figure 1.49.

Data of the chain conformations and crystal structures of isotactic polymers \(-\left(\text{CH}_2\right)_n\) are reported in Table 1.11. It is apparent from Table 1.11 that most of the isotactic polymers show conformational polymorphism. The data in Figure 1.46 and Figure 1.47 indicate that the crystallization of isotactic polymers in different polymorphic forms having different chain conformations is easily predicted by calculations of the conformational energy. In all the observed cases of chain conformation, the torsion angles do not deviate more than 20°–25° from the staggered (60° and 180°) values, and the number of monomeric units per turn \( M/N \) ranges between 3 and 4, depending on the bulkiness of the side group R (Fig. 1.50). Chains of 3-substituted polyolefins, like poly(3-methyl-1-butene), assume a 4/1 helical conformation (T′G′)₆ (123,124), while 4-substituted polyolefins, like poly(4-methyl-1-pentene), have less distorted helices with 7/2 symmetry (\( \text{T}'G' \))₉₅ (81). When the substituent on the side group is far from the chain atoms, like in poly(5-methyl-1-hexene), the...
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Chain Axis (Å)</th>
<th>Chain Symmetry</th>
<th>Unit Cell Parameters</th>
<th>Space Group</th>
<th>References</th>
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<td><em>i</em>-Polypropylene α-form</td>
<td>6.5</td>
<td>s(3/1)</td>
<td>a = 6.65 Å, b = 20.96 Å, c = 6.50 Å, β = 99.3°</td>
<td>P2₁/c - C2/c</td>
<td>(45,221,222)</td>
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<tr>
<td><em>i</em>-Polypropylene β-form</td>
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<td>s(3/1)</td>
<td>a = b = 11.03 Å, c = 6.5 Å</td>
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<td>(223-225)</td>
</tr>
<tr>
<td><em>i</em>-Polypropylene γ-form</td>
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<td>s(3/1)</td>
<td>a = 8.54 Å, b = 9.93 Å, c = 42.41 Å</td>
<td>Fddd</td>
<td>(226,227)</td>
</tr>
<tr>
<td><em>i</em>-Polypropylene trigonal form, in <em>i</em>-poly(propylene-co-pentene)</td>
<td>6.5</td>
<td>s(3/1)</td>
<td>a = b = 17.1 Å c = 6.5 Å, 30 mol % pentene</td>
<td>R3c - R3c</td>
<td>(228)</td>
</tr>
<tr>
<td><em>i</em>-Polypropylene trigonal form, in <em>i</em>-poly(propylene-co-hexene)</td>
<td>6.5</td>
<td>s(3/1)</td>
<td>a = b = 17.5 Å c = 6.5 Å, 26 mol % hexene</td>
<td>R3c - R3c</td>
<td>(229-231)</td>
</tr>
<tr>
<td><em>i</em>-Polybutene form I</td>
<td>6.5</td>
<td>s(3/1)</td>
<td>a = b = 17.7 Å, c = 6.5 Å</td>
<td>R3c - R3c</td>
<td>(111)</td>
</tr>
<tr>
<td><em>i</em>-Polybutene form II</td>
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<td>s(11/3)</td>
<td>a = b = 15.42 Å, c = 21.05 Å</td>
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<td>(112,232)</td>
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<tr>
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<td>s(4/1)</td>
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<td>(113)</td>
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<td><em>i</em>-Poly(3-methyl-1-butene)</td>
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<td>s(4/1)</td>
<td>a = 9.55 Å, b = 17.08 Å, c = 6.8 Å, γ = 116.5°</td>
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<td>–</td>
<td>(234)</td>
</tr>
<tr>
<td><em>i</em>-Poly((S)-3-methyl-1-pentene)</td>
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<td>s(4/1)</td>
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<tr>
<td><em>i</em>-Poly(4-methyl-1-pentene)</td>
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<td>s(4/1)</td>
<td>a = 10.49 Å, b = 18.89 Å, c = 7.13 Å, γ = 113.7°</td>
<td>P2₁/b, P2₁</td>
<td>(116-118)</td>
</tr>
<tr>
<td><em>i</em>-Poly(4-methyl-1-pentene) form II</td>
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<td>s(4/1)</td>
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<td>a = 22.17 Å, c = 6.69 Å</td>
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<tr>
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<td>s(7/2)</td>
<td>–</td>
<td>–</td>
<td>(235)</td>
</tr>
<tr>
<td><em>i</em>-Poly((S)-4-methyl-1-hexene) form I</td>
<td>13.5</td>
<td>s(7/2)</td>
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<td>(81a)</td>
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<tr>
<td><em>i</em>-Poly((S)-4-methyl-1-hexene) form II</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>(81a)</td>
</tr>
<tr>
<td><em>i</em>-Poly((R),(S)-4-methyl-1-hexene)</td>
<td>13.5</td>
<td>s(7/2)</td>
<td>a = b = 19.85 Å, c = 13.5 Å</td>
<td>P4</td>
<td>(81a)</td>
</tr>
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<td><em>i</em>-Poly(5-methyl-1-hexene)</td>
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<td>s(3/1)</td>
<td>a = 17.62 Å, b = 10.17 Å, c = 6.33 Å, or a = b = 17.62 Å, c = 6.33 Å, γ = 120°</td>
<td>P2₁ or P3₁</td>
<td>(125)</td>
</tr>
<tr>
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<td>s(3/1)</td>
<td>a = 18.40 Å, b = 10.62 Å, c = 6.36 Å</td>
<td>P2₁ or P3₁</td>
<td>(125b,c,146)</td>
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<td>(125b,c)</td>
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<td><em>i</em>-Polystyrene</td>
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<td>a = b = 21.9 Å, c = 6.65 Å</td>
<td>R3c - R3c</td>
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<tr>
<td><em>i</em>-Poly(α-methylstyrene)</td>
<td>8.1</td>
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<td>s(11/3)</td>
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<td>P₂₁/2, P₂₁</td>
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<td>s(4/1)</td>
<td>a = b = 21.9 Å, c = 6.5 Å</td>
<td>I₄₁</td>
<td>(238,239)</td>
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<td>a = b = 16.25 Å, c = 6.5 Å</td>
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<td>s(17/5)</td>
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<tr>
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<td>s(3/1)</td>
<td>a = 3.2b = 18.2 Å, c = 6.5 Å</td>
<td>Orthorhombic</td>
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### TABLE 1.11. (Continued)

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<th>Unit Cell Parameters</th>
<th>Space Group</th>
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<td>$\alpha$-Poly(t-butylacrylate)</td>
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</table>

(Continued)
Figure 1.50. Models for the conformations of the chains of isotactic polymers of the form \((\text{CH}_2-\text{CH}(R))_n\) with helical symmetries that depend on the bulkiness of the side group R and the distance of the substituents on the side group from the chain atoms. (Reproduced with permission from Reference 3. Copyright 1968 by Marcel Dekker.)
polymer crystallizes again with a threefold helical conformation (125) (Fig. 1.50 and Table 1.11).

Models of the chain conformations found for the polymorphic forms of various isotactic polymers are reported in Figure 1.51.

A similar analysis of the conformational energy has recently been performed also for various new syndiotactic polymers (4,93,126). The conformational energy maps of sPP (127), syndiotactic polystyrene (sPS) (128), poly(1-butene) (sPB) (91), and syndiotactic poly(4-methyl-1-pentene) (sP4MP) (92), calculated for chain models having the chirality of bonds as in Figure 1.30B, are reported in Figure 1.52. The calculations of the conformational energy have been performed on isolated syndiotactic macromolecules with fixed values of the bond angles $\tau_1 = 113^\circ$ and $\tau_2 = 111^\circ$ under the constraints imposed by the equivalence principle. As a consequence, a succession of backbone torsion angles $\ldots \theta, \gamma, \delta, \alpha, \beta, \ldots$ (Fig. 1.30B) has been assumed, corresponding to the assumption that the chains assume in the crystals regular helical conformation with line repetition symmetry $s(M/N)2$ (4,93) (Section 1.5.2).

All the maps in Figure 1.52 present energy minima into the regions corresponding to the highly extended trans-planar ($\theta_1 = \theta_2 = T = 180^\circ$) and helical conformations ($\theta_1 = 180^\circ, \theta_2 = 60^\circ$ or $\theta_1 = -60^\circ, \theta_2 = 180^\circ$). Also, in this case, the maps are symmetric with respect to the diagonal $\theta_1 = 360^\circ - \theta_2$, which separates equivalent energy minima corresponding to enantiomorphic helical conformations (right-handed and left-handed helices $s(M/N)2$).

In the case of sPS (Fig. 1.52A), the absolute minimum corresponds to the trans-planar conformation, while the relative minimum of higher energy at $\theta_1 = 180^\circ, \theta_2 = 60^\circ$ or $\theta_1 = -60^\circ, \theta_2 = 180^\circ$, corresponds to the twofold helical conformation (TTGG)$_2$, with $s(2/1)2$ symmetry. This is in agreement with the observed polymorphic behavior of sPS (129) that crystallizes in different polymorphic forms with chains in trans-planar or helical conformations. The most stable $\alpha$- and $\beta$-forms are, indeed, characterized by chains in trans-planar conformation (129–135), whereas the less stable $\gamma$- and $\delta$-forms present chains in the twofold helical conformation with $s(2/1)2$ symmetry (129,136–138). The same energy minima
Figure 1.52. Maps of the conformational energy of various syndioactic polymers as a function of the backbone torsion angles $\theta_1$ and $\theta_2$ (4,93). Syndiotactic polystyrene (A), polypropylene (B), poly(1-butene) (C), and poly(4-methyl-1-pentene) (D). The conformational energy has been calculated under the constraint of the equivalent principle assuming a $s(M/N)2$ symmetry of the chains and a succession of torsion angles $\ldots \theta_1, \theta_2, \theta_1, \theta_2, \theta_1, \theta_2, \ldots$, for fixed values of the bond angles $\tau_1 = 113^\circ$ and $\tau_2 = 111^\circ$, as defined in Figure 1.30B. As in the chain model in Figure 1.30B, the two bonds adjacent to the methine carbon atom, corresponding to the torsion angles $\theta_1$ and $\theta_2$, have $(-)$ and $(+)$ configurational signs, respectively. The isoenergetic curves are reported every 5 kJ/mol of monomeric units with respect to the absolute minimum of each map assumed as zero. The values of the energies corresponding to the minima ($\times$) are indicated. The experimental conformations observed for the different polymorphic forms of the polymers are indicated by triangles ($\triangleright$). (Reproduced with permission from Reference 93. Copyright 1992 by the Società Chimica Italiana.)

corresponding to trans-planar and twofold helical conformations are present in the map of sPP (Fig. 1.52B). The absolute minimum corresponds to the twofold helical conformation, found by X-ray diffraction in forms I and II of sPP (46,47,49,64), and the relative minimum to the trans-planar conformation, found in the less stable form III of sPP (48,49,65). A helical conformation of sPP with sequence $(T,G,T,G)_n$, made of portions of chain in the regular 2/1 helical $T_6G_7$ conformation and portions in trans-planar conformation $T_n$, has been found in the metastable form IV of sPP (139). The conformations of the chains of the different polymorphic forms of sPP and sPS are shown in Figure 1.53 and Figure 1.54, respectively.

In the case of sPB and sP4MP, having bulkier side groups, deep energy minima are present only in the region of the helical conformation (TTGG), the minimum in the trans-planar region being of higher
energy due to repulsive interactions between bulky side groups. In Figure 1.52 it is immediately apparent the good agreement between the conformations experimentally found by X-ray diffraction from the values of \( h \) and \( r \) of the different polymorphic forms of these polymers (indicated by triangles in Figure 1.52), and minimum energy conformations obtained only on the basis of models of isolated chains. In particular, according to these calculations and the relative deepness of the energy minima present in the trans-planar and helical (TTGG) regions of the map, it was found that for sPS, the two crystalline forms with chains in the trans-planar conformation (\( \alpha \) - and \( \beta \)-forms) are the most stable ones (129), while the crystalline form of sPP with chains in the trans-planar conformation is metastable (48,49,65), and no crystalline forms with chains in trans-planar conformation have been observed for sPB (91) and sP4MP (92).

The energy maps of sPB and sP4MP in Figure 1.52C and D show that the energy minimum in the region of the helical conformations (=TTGG) is split into two minima of nearly equal energy, as occurs in the maps of the corresponding isotactic polymers (Fig. 1.46 and Fig. 1.47). The regions of the maps in Figure 1.52C and D of the helical conformation are reported in Figure 1.55 in enlarged scales of \( \theta _1 \) and \( \theta _2 \). The first energy minimum correspond to the twofold (TTGG), helical conformation \( s(2/1)z \), characterized by staggered values for the torsion angles \( \theta _1 = 180^\circ \) and \( \theta _2 = 60^\circ \). The second minimum corresponds to helical \( (T'T'G'G')_s \) conformations with \( s(M'/N) \) symmetry with \( M'/N \neq 2 \), characterized by values of torsion angles \( \theta _1 = T' = 180^\circ + \delta \), \( \theta _2 = G' = 60^\circ + \delta \) that deviate from the staggered values typical of the \( s(2/1)z \) helix (Fig. 1.55). For sPB, this energy minimum is close to the 5/3 helical conformation (Fig. 1.55A), whereas for sP4MP, it is close to the 12/7 helix.
Figure 1.55. Details of the maps of the conformation energy of sPB (A) (91) and sP4MP (B) (92) as a function of $\theta_1$ and $\theta_2$ in the region of the helical conformations $\theta_1 = \tau$ and $\theta_2 = G$. For each pair of backbone torsion angles $\theta_1$ and $\theta_2$, the torsion angles $\theta_3$ for sPB (A) and $\theta_3$ and $\theta_4$ for sP4MP (B) that define the conformation of the side groups (C) are scanned every 2.5° from 0 to 360° and the minimum value of the energy is reported. In (C) $R = CH_2$ for sPB and $CH(CH_2)_3$ for sP4MP. The torsion angles of the lateral groups $\theta_3$ and $\theta_4'$ of two consecutive monomeric units related by the binary axes perpendicular to the chain axis (C) are defined with respect to the same methylene group (indicated by an asterisk) (C). Torsion angles $\theta_3$ and $\theta_3'$ are defined with respect to the hydrogen atom of the methine group in the $CH(CH_2)_3$ group (C). The twofold axes crossing the methylene groups of the main chain for the $s(M/N)2$ symmetry impose $\theta_3 = \theta_3'$ and $\theta_4 = \theta_4'$ (C). The conformational energy has been calculated under the constraint of the equivalent principle assuming a $s(M/N)2$ symmetry of the chains and a succession of torsion angles ... $\theta_3, \theta_3, \theta_4, \theta_4, \theta_3$ ... (C) and for values of bond angles $\tau_1 = 113^\circ$ and $\tau_2 = 111^\circ$. The curves are reported at intervals of 4 kJ/mol of monomeric units (the first dashed curve correspond to 1 kJ/mol) (A) and 5 kJ/mol of monomeric units (B) with respect to the absolute minimum of the map assumed as zero. The values of the energies corresponding to the minima (●) are indicated. The pairs of torsion angles $\theta_3, \theta_4$ corresponding to conformations with symmetries $s(2/1)2$ (△), $s(5/3)2$ (●), and $s(5/2)2$ (◆) for sPB (A) and $s(12/7)2$ (▲) and $s(12/5)2$ (□) for sP4MP (B) are also indicated. The experimental conformations observed for the different polymorphic forms of sPB correspond to the symmetries $s(2/1)2$ (△), $s(5/3)2$ (●) (A), and that observed in sP4MP corresponds to the symmetry $s(12/7)2$ (▲) (B). Dotted and undotted regions in the map of sPB correspond to conformation for which the torsion angle $\theta_1$ is close to 60° and 180°, respectively (A).

(Fig. 1.55B). These calculations are in agreement with experimental observation of the polymorphic behavior of sPB (91) and sP4MP (92). In fact, two crystalline forms of sPB have been found (91,94,140); the most stable form I is characterized by chains in the $s(2/1)2$ helical conformation (91,140), whereas the metastable form II is characterized by chains in the helical conformation with $s(5/3)2$ symmetry (91,94). The only crystalline form found for sP4MP is characterized by chains in the helical conformation with $s(12/7)2$ symmetry (92,141), which corresponds to the absolute energy minimum in the maps in Figure 1.52D and Figure 1.55B. The 2/1 and 5/3 helical conformations of the chains of sPB in the forms I and II and the 12/7 helical conforma-
Figure 1.56. Chains of sPB in s(2/1)2 helical conformation (A) and s(5/3)2 helical conformation (B) that crystallize in form I (A) (91,140) and form II (91,94) of sPB, respectively.

Figure 1.57. Chain of sP4MP in s(12/7)2 helical conformation that crystallize in the only crystalline form found for sP4MP (92,141).

gives rise to a shortening of the unit height for isotactic polymers, it induces an increase of the unit height for syndiotactic polymers (93) and produces helical conformation (T'1'G'G'), with symmetries s(M/N)2 where the number of structural units per turn M/N may be noninteger. Data concerning the chain conformations of syndiotactic polymers are also reported in Table 1.11.

As discussed in Section 1.6, in the case of syndiotactic polymers, there exist two different kinds of helical conformations, characterized by the same s(M/N)2 symmetry but different values of the angle $\alpha$ between two consecutive binary axes perpendicular to the chain axis (Fig. 1.44). It is apparent from the map in Figure 1.55A that the s(5/3)2 helical conformation found by X-ray diffraction for the chains of form II of sPB ($\theta_1 = -164^\circ$, $\theta_2 = 74^\circ$, or $\theta_1 = 74^\circ$, $\theta_2 = -164^\circ$, $t = -144^\circ = 216^\circ$, and $\alpha = 108^\circ$, configuration (a') or (b') in Fig. 1.42B and Fig. 1.44) (91,94) corresponds to an energy minimum. The second possible helical conformation compatible with the observed unit height $h = 4$ Å and unit twist $t = 144^\circ$, resolution of sP4MP are shown in Figure 1.56 and Figure 1.57, respectively.

These data indicate that the principle of the similar distortions of the torsion angles of the main chain from the staggered values 60° and 180° ($\theta_1 = 180^\circ + \delta$, $\theta_2 = 60^\circ + \delta$), due to the bulkiness of the side groups and observed in various isotactic polyolefins (114), is also valid for the chain conformations of syndiotactic polymers. The 3/1 and 2/1 helical conformations of chains of isotactic and sPPs, respectively, corresponding to the staggered values of torsion angles $\theta_1 = 180^\circ$ and $\theta_2 = 60^\circ$ or $\theta_1 = -60^\circ$ and $\theta_2 = 180^\circ$, are the reference conformations for the more general cases of the conformations of isotactic and syndiotactic poly(\text{\ensuremath{$\alpha$}}-olefins) of the kind $-(\text{CH}_2-\text{CH}(\text{R}))_n-$. The presence of side groups R bulkier than the methyl group induces slight distortions of the torsion angles $\theta_1$ and $\theta_2$ from the exact trans (180°) and gauche (60°) values typical of the 3/1 helix of iPP and 2/1 helix of sPP due to the steric interaction between the bulkier side groups (114). While the isodistortion
with \( s(5/2)2 \) symmetry and \( \alpha = 72^\circ \) \( (\theta_1 = 147^\circ, \theta_2 = 72^\circ, \theta_3 = 147^\circ) \) for sPB (Fig. 1.55A) and \( s(3) \) for sPB (Fig. 1.55B) that define the conformation of the side groups (Fig. 1.55C) are scanned every 2.5° from 0° to 360° and the minimum value of the energy is reported. For sPB, the dotted regions of the map in Figure 1.55A corresponds to conformations for which the torsion angle \( \theta_1 \) is close to 60°, that is, the double gauche conformation of the lateral groups, whereas the undotted regions correspond to conformations for which \( \theta_1 \) is close to 180°. It is apparent that the conformation with \( \theta_1 = 60^\circ \) is favored for the \( s(2/1)2 \) helix of form I, whereas the conformation with \( \theta_1 = 180^\circ \) is favored for the \( s(5/3) \) helix of form II of sPB (91,93). This double gauche conformation has been, then, confirmed by the complete determination of the crystal structure of the form I of sPB (140) and by the solid state 13C NMR analysis of the form I (143).

It is worth noting that in both the \( s(5/3)2 \) helical conformation of form II of sPB (Fig. 1.56B) and the \( s(12/7)2 \) conformation of sP4MP (Fig. 1.57), and in all the helical conformations of the chains of iP in the three crystalline forms (3/1 in form I, 11/3 in form II, and 4/1 in form III, Fig. 1.48), the lateral groups always assume a conformation with \( \theta_1 = 180^\circ \), where the methyl carbon atoms are in gauche arrangement to one neighboring methylene carbon and in trans to the other methylene group (Fig. 1.58B).

### 1.8 HELICAL CONFORMATION AND OPTICAL ACTIVITY

An isotactic chain of a vinyl polymer is chiral as long as the chain ends are different. Isotactic polylefins are generally not optically active because in a very long polymer chain, the chain ends are indistinguishable (24). The manifestation of the chirality, such as the optical activity, is precluded by the high molecular weight of polymers, which makes the chain ends an unimportant part of the chain structure. Isotactic polymers belong, therefore, to a class of molecules in which the chirality is buried (24), leading to a cryptochiral state (144,145).

Optical activity may be produced in these polymers in another manner. One possibility is the presence of chiral, nonracemic lateral groups (146), as in the case of isotactic poly[(S)-3-methyl-1-pentene] (iP(S)3MP) (147). It has been shown that the conformation of the chain is influenced not only by the steric hindrance of the lateral group (as shown in Fig. 1.47 and Fig. 1.55) but also by its configuration. The conformational energy maps of iP(S)3MP in the regions of the minimum energy right-handed G T' and left-handed TG' helical conformations are reported in Figure 1.59 (105). The two
\[ \theta_1 = C1-C2-C3-C4 \quad \theta_4 = C2-C3-C6-C7 \]
\[ \theta_2 = C2-C3-C4-C5 \quad \theta_4 = C3-C6-C7-C8 \]

**Left-handed helix**

**Right-handed helix**

**Figure 1.59.** Maps of the conformational energy, as a function of the backbone torsion angles \( \theta_1 \) and \( \theta_2 \), of a chain of isotactic poly((S)-3-methyl-1-pentene) for the left-handed helix (A and B) and the right-handed helix (C) (105), and projection along the chain axis of the chain of isotactic poly((S)-3-methyl-1-pentene) in the conformation of left-handed 4/1 helix found in the crystal structure (D) (147). In the energy maps, for each pair of \( \theta_1 \) and \( \theta_2 \), the reported energy corresponds to the minimum obtained by varying the torsion angles of the lateral group \( \theta_3 \) and \( \theta_4 \). The curves are reported at intervals of 0.5 kcal/mol of monomeric unit. The values of the energies corresponding to the minima are also indicated. In the molecular model D, the white balls and the dashed lines indicate the two statistical positions of the methyl carbon atom, corresponding to the two possible low energy conformations of the side groups with \( \theta_4 \approx 60 \) and 180°. (A–C: Reproduced with permission from Reference 105, Copyright 1976 by Elsevier Science. D: Reproduced with permission from Reference 147, Copyright 1972 by Elsevier Science.)
energy minima present in each map correspond to the 3/1 and 4/1 helical conformations, the latter being the conformation found in the crystal structure (147). Because of the chirality of the lateral group, right- and left-handed helices of iP(S)3MP are not equivalent, as instead generally occurs for isotactic polymers. In fact, two low energy conformations of the chiral lateral group, with $\theta_1 = 60$ and $180^\circ$, are possible for the left-handed helix (Fig. 1.59A,B), while only one low energy conformation, with $\theta_1 = 180^\circ$, is possible for the right-handed helix (Fig. 1.59C). The left-handed helix of iP(S)3MS is, therefore, favored over the right-handed one. In the crystal structure, the chains of iP(S)3MP assume a 4/1 helical conformation (147) and only left-handed helices are included in the tetragonal unit cell, with the lateral groups that may take statistically both conformations of minimum energy (105). Therefore, the chirality of the lateral groups induces the crystallization of isochiral helices.

The chirality of the lateral group influences the conformation of the chain not only in the crystalline state. The experimental observation that vinyl polymers having optically active lateral groups show optical activity also in solution, and that the optical activities show nonlinear relationships between the configurational enantiomeric characteristics of the monomeric units and the optical activity of the derived polymer (146), suggests that a prevailing spiralization sense of the helical chains is present in solution. In the case of iP(S)3MP in solution or in the melt, a local left-handed helical conformation should prevail in length over the right-handed one for entropic reason (148) because of the higher numbers of possible low energy conformational states accessible to the lateral groups when the helical chains are left-handed.

### 1.9 Alternating Copolymers

Chains of copolymers may keep a regular constitution when the different monomeric units alternate along the chain. One of the monomeric units may present stereoisomeric centers, and also in this case, crystalline alternating copolymers having regular configurations, and hence regular conformations, have been synthesized with Ziegler–Natta catalysts (149) and, more recently, with the new homogeneous metallocene catalysts (150).

Alternating copolymers of ethylene with olefins containing double bonds in the cis configuration, like cis-2-butene, cyclopentene, cycloheptene (149), and norbornene (150) have been described. In addition, copolymers of carbon monoxide with styrene and styrene derivatives, having syndiotactic (151) and isotactic (152) configurations, have also been synthesized and characterized.

In the case of the alternating copolymer of ethylene with cis-2-butene (E2B), prepared with Ziegler–Natta catalysts, the presence of slight crystallinity was taken as indicative of a regularity of the chemical and steric structure (149). This copolymer may be also regarded as corresponding to the regular enchainment head-to-head, tail-to-tail of propylene monomeric units. For this alternating copolymer, four different regular configurations, shown in Figure 1.60, are possible according to the relative meso or racemo configurations of two adjacent tetrahedral stereoisomeric centers, and the relative configuration, isotactic or syndiotactic, of successive monomeric units along the chain (153) (see also Fig. 1.11). The four possible configurations have been defined threo-isotactic and -syndiotactic, and erythro-isotactic and -syndiotactic (153). As shown in Figure 1.11, the terms threo and erythro must be used to define the relative configurations in monomeric units containing two adjacent tetrahedral stereoisomeric centers bound to different substituents (CHA CHB) (21d). In the case of E2B alternating copolymers, the stereoisomeric centers are bound to two methyl groups; therefore, the possible configurations should be defined racemo-isotactic and -syndiotactic, and meso-isotactic and -syndiotactic (21d) (Fig. 1.60).

Meso and racemo configurations correspond to a cis and trans opening of the internal double bond of a cis-olefin, respectively. The experimental chain axis of 9.10 Å, determined by X-ray fiber diffraction of E2B, and a periodicity per structural unit of 2.27 Å, evaluated from the presence of a strong meridional reflection in the X-ray fiber tilted diffraction pattern, have indicated that two structural units, composed of two ethylene and two 2-butene units, are included in the identity period (153). Although it was already recognized that the catalytic species could possibly act through a cis opening of the double bond (153), none of the four limiting maximum order microstructures in Figure 1.60 was discarded from the X-ray diffraction analysis. Simple considerations based on the application of the equivalence postulate and of the principle that the chains in the crystalline state adopt regular conformations corresponding to the minimum energy for the isolated chain (Sections 1.5.1 and 1.5.2) led to assume a conformation of the chains characterized by a succession of torsion angles (TTTG.TTTG’), and a 4i symmetry (Fig. 1.61) (153). This conformation accounts for the experimental chain axis $c = 9.10$ Å and is compatible with a meso-diisotactic configuration of the chain, as found in the crystal structure (153), and corresponds to a succession along the chain of enantiomorphic structural units related by an inversion center (Fig. 1.61).

Conformational energy calculations on models of chains have indicated that, at least in principle, all four limit order microstructures in Figure 1.60 may adopt in
the crystalline state the conformation \((T,T,G,T,G)\), at a low cost of conformational energy (110). This conformation corresponds to the \(ti\) symmetry for the meso-diisotactic structure and a \(tci\) symmetry for the racemo-disyndiotactic structure. The complete determination of the crystal structure by X-ray diffraction has indicated that the chains of the E2B copolymer have a meso-diisotactic structure and are characterized by the \((T,G,T,G)\), conformation in Figure 1.61 (153). This structure is the first case in which an isotactic polymer is characterized by a chain conformation in the crystalline state corresponding to a regular succession of enantiomorphous structural units, related by an inversion center, instead of a helical conformation characterized by a repetition of isomorphous structural units.

A similar conformation has been proposed for the alternating ethylene-cis-2-butene copolymer (ECP) (149,153–155). Only preliminary data concerning the chain conformation in the crystalline state and the dimensions of the unit cell were reported for samples prepared by Ziegler–Natta catalysts (149,153). A complete determination of the chain conformation and the crystal structure has recently been reported (154,155) from X-ray diffraction analysis on a highly crystalline strictly alternating meso-diisotactic ECP, prepared by ring opening metathesis polymerization (ROMP) of bicyclo[3.2.0]hept-6-ene using a chiral molybdenum carbene complex and successive hydrogenation of the unsaturated polymer (156). A value of the chain axis of 9.0 Å has been evaluated from the X-ray fiber diffraction data (153–155). Geometric and conformational energy analyses have shown that the meso-isotactic chains assume nearly extended conformations, shown in Figure 1.62, having \(ti\) symmetry and a succession of torsion angles \((T,\theta,1,\theta)\) (Fig. 1.62A), or twofold helical \(s(2/1)m\) symmetry and a succession of torsion angles \((T,\text{cis})\) (Fig. 1.62B), corresponding to a repetition of antiparallel enantiomorphic structural units along the chain (154,155). A high degree of conformational disorder is present in the crystalline state related to the conformational freedom of the cyclopentene rings, which may assume twist \((C_2\text{-symmetric})\) and envelope \((C_1\text{-symmetric})\) conformations interconverting with a low energy barrier. For the \(ti\) conformation, the torsion

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**Figure 1.60.** Four possible configurations of the chain of the alternating ethylene-cis-2-butene copolymer. The inherent asymmetry of the skeletal bonds is represented with the configurational (+) and (−) signs. Note that in Reference 153, the relative configurations racemo and meso were defined as threo and erythro, respectively. (Reproduced with permission from Reference 4. Copyright 2003 by Wiley Interscience.)
angle $\theta$ is variable in the range $-50$° to $+50$° depending on the conformation of the cyclopentene ring (154,155).
 Both $(T_1;\theta T_2;\theta)_n$ and $(T_3;\text{cis})_n$ conformations account for the experimental chain axis of 9.0 Å, and chains with sequences in both conformations may be present in the crystals due to the presence of dynamic conformational disorder (154,155).

The sequence of configurations of tertiary carbon atoms in consecutive cyclopentene rings may be (RS)$_n$ or (SR)$_n$, yielding a projection along the chain axis characterized by a Z- or S-shape (Fig. 1.62). The crystal structure is characterized by high degree of structural disorder in the conformation and in the packing of the chains. The conformational disorder is related to the interconversion between twist and envelope forms of the cyclopentene rings, whereas the packing disorder is due to the statistical substitution of chains having S- and Z-shapes in each site of the crystalline lattice (155).

Similar to the E2B alternating copolymer (Fig. 1.61), the ECP alternating copolymer represents an example of an isotactic polymer that assumes in the crystalline state a conformation that does not correspond to a helical repetition of isoclinic, isomorphous structural units (154,155).

The synthesis of linear alternating copolymers of styrene and carbon monoxide, using soluble organometallic palladium catalysts, has been recently described (151). Depending on the catalyst, isotactic or syndiotac-

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**Figure 1.61.** Side view and projection along the chain axis of the chain of alternating ethylene-cis-2-butene copolymer in the $(T_1;G'T_1;G')_n$ conformation with $t$ symmetry (110,153). The inversion centers (○) placed at the center of the CH$_2$-CH$_2$ bonds of the ethylene units are indicated. (Reproduced with permission from Reference 110. Copyright 2004 by Wiley-VCH.)

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**Figure 1.62.** Chains of $\text{meso-diisotactic}$ alternating ethylene-cyclopentene copolymer in $(T_1;G'T_1;G')_n$ conformation with $t$ symmetry (A) and $(T_3;\text{cis})_n$ conformation with helical $s(2/1)m$ symmetry (B). The sequence of configurations of tertiary carbon atoms in consecutive cyclopentene rings may be (RS)$_n$ or (SR)$_n$, yielding a projection along the chain axis characterized by a Z or S shape. (Reproduced with permission from References 154,155. Copyright 2005 by the American Chemical Society.)
tic configurations of the styrene units have been obtained. With achiral ligands, a chain end control of the polymerization was considered to be operative (157) and a syndiotactic configuration of the copolymer was assigned by X-ray diffraction (157). Chiral ligands switch the chain end control to yield the isotactic optically active copolymer (152). The relatively low molecular mass of the samples prevented the observation of stretched oriented fibers and the determination of the chain axis from the X-ray fiber diffraction. The conformation of the chains and the complete crystal structures of both syndiotactic (157–159) and isotactic copolymers (160,161) have been determined by simple application of the equivalence principle and by the analysis of the X-ray powder diffraction profile.

The constitution of isotactic (iSTCO) and syndiotactic (sSTCO) alternating styrene–carbon monoxide copolymers makes the two directions of the chain intrinsically nonequivalent (Fig. 1.63) so that inversion centers, binary axes, and mirror planes perpendicular to the chain axis can be excluded for both copolymers. For the isotactic copolymer, a glide plane parallel to the chain axis can be excluded because it is incompatible with the isotactic configuration. Therefore, the only possible line repetition group for the isotactic copolymer is the helical s(M/N) (Fig. 1.63A). For the syndiotactic copolymer, the helical s(M/N) symmetry can be excluded because it is incompatible with the configuration, and the only possible line repetition group is the glide plane tc with a glide plane c containing the chain axis (Fig. 1.63B).

According to the equivalence principle, the helical repetition s(M/N) occurs in the case of the isotactic configuration with the same succession of values of the bond angles and with a sequence of torsion angles \( \theta_1, \theta_4, \theta_2, \theta_7, \theta_3 \) . . . (Fig. 1.63A). In the case of the syndiotactic copolymer, the tc symmetry imposes the sequence of torsion angles \( \theta_1, \theta_4, \theta_2, \theta_7, \theta_3 \) . . . (Fig. 1.63B). Similar values of the chain axes \( c = 7.5–7.6 \) Å have been assumed for both syndiotactic (157–159) and isotactic copolymers (160,161), in analogy with the chain axis of the crystalline alternating ethylene–carbon monoxide copolymer (poly(1-oxotrimethylene)) (162). This value indicates nearly extended conformations for the chains of both copolymers.

According to the chain models in Figure 1.63, highly extended chains with a chain axis of 7.5–7.6 Å are obtained for both iSTCO and sSTCO with a nearly trans-planar conformation and a repeating unit composed of two monomeric units -\((\text{CH}_2=\text{CH}(\text{C}_2\text{H}_5))\)- included in the chain axis. This may occur with a s(2/1) helix repeating after two monomeric units for iSTCO (160,161) and with a glide plane symmetry tc for sSTCO (157–159). The condition of identical repetition after two monomeric units implies that only two of the three torsion angles \( \theta_1, \theta_4, \theta_2, \theta_7, \theta_3 \) can be varied independently in order to obtain a given unit height (74). According to the methods described in Section 1.5.4, it is possible to calculate the values of torsion angles and the combination of the three torsion angles that give the period per monomeric unit of \((7.5–7.6)/2 = 3.7–3.8 \) Å and the twofold helical repetition for iSTCO, or a glide plane repetition for sSTCO. These calculations can be performed varying \( \theta_1 \) and \( \theta_4 \) and determining the occurring value of \( \theta_2 \) that gives the required helical s(2/1) or glide plane repetition. The calculations can be simplified assuming that \( \theta_1 = \theta_4 (157,158,161) \) This assumption arises from qualitative energy considerations that indicate that bonds of opposite intrinsic chirality having opposite configurational signs (+) and (−) adjoining a tertiary carbon atom (Fig. 1.63) may have opposite slight deviations from the staggered (180°) conformation (principle of isodistorsion of torsion angles discussed in Section 1.7.2) (3,4,114). The value of the torsion angle \( \theta_2 \) that gives the helical s(2/1) repetition or the glide plane repetition tc, and the corresponding identity period \( c = 7.5–7.6 \) Å are reported in Figure 1.64 as a function of the torsion angle \( \theta_1 = -\theta_4 \) (161).

![Figure 1.63](image-url) Sequences of torsion angles in the chains of the isotactic (A) and syndiotactic (B) alternating styrene–CO copolymers, according to the s(M/N) and tc symmetries, respectively. (Reproduced with permission from Reference 4. Copyright 2003 by Wiley Interscience.)
It is apparent that for iSTCO for every value of $\theta_1$, near to 180°, the helical s(2/1) symmetry is obtained when $\theta_1 = 180°$ (Fig. 1.64A). A highly extended chain conformation with $c = 7.5$–7.6 Å is obtained for a helical s(2/1) symmetry, when $\theta_1$ and $\theta_2$ are in the range 180° ± $\delta$, with $\delta = 25°$ + 30°. The condition that $\theta_3 = 180°$ in order to have a s(2/1) symmetry under the assumption $\theta_2 = \theta_1$ can be interpreted considering that nearly trans-planar chains with helical s(2/1) symmetry are obtained when the torsion angles $\theta_1$, $\theta_2$, and $\theta_3$ have slight deviations from 180°, but their average value must remain approximately 180°. The assumption $\theta_2 = \theta_1$ satisfies this condition for a positive deviation of $\theta_1$ from 180° ($\theta_1 = 180° + \delta$), there is a negative deviation of $\theta_2$ ($\theta_2 = 180° - \delta$). Since the succession of torsion angles is $\ldots \theta_1\theta_1\theta_1\theta_1\theta_1\ldots$, the assumption $\theta_2 = \theta_1$ imposes that $\theta_3 = 180°$ because any deviation of $\theta_3$ from 180° is propagated along the chain and the average value of the torsion angles becomes very different from 180° (161).

In the case of sSTCO in Figure 1.64B, it is apparent that a highly extended chain conformation with $c = 7.5$–7.6 Å can be obtained, for a glide plane symmetry, when $\theta_1$ and $\theta_2$ are in the range 180° ± $\delta$, $\theta_1 = 180° + \delta$ with $\delta = 30°$, and the torsion angle $\theta_3$ that gives the tc glide plane repetition may also have great deviation from 180° (158). In fact, since the succession of torsion angles for the syndiotactic copolymer is $\ldots \theta_1\theta_1\theta_1\theta_1\theta_1\ldots$, the highly extended chains and a tc repetition are obtained when the average value of the torsion angles along the chain is nearly 180°. Therefore, under the assumption $\theta_2 = \theta_1$, the torsion angle $\theta_3$ can be even different from 180° because for any deviation of $\theta_3$ from 180°, there is an opposite deviation of $\theta_3$ in the successive monomeric unit (Fig. 1.63B) (158,161).

More general relations between $\theta_1$, $\theta_2$, and $\theta_3$ can be obtained if the simplifying assumption $\theta_2 = \theta_1$ is removed (161,163). Calculations may be performed with $\theta_2 \neq \theta_1$, by varying $\theta_2$ and determining the outcome value of $\theta_3$ that gives the helical s(2/1) or the tc symmetries, for various values of $\theta_1$ in the most significant range, $\theta_1 = 180°$ ± 40° (161). Extended chains are obtained if $\theta_1$, $\theta_2$, and $\theta_3$ are near to 180°, that is, $\theta_1 = 180° + \delta$, with small values of $\delta$, and in order to have a helical s(2/1) conformation of a highly extended chain, it must be $\delta_1 + \delta_2 + \delta_3 = 0$ (161). Indeed, under this condition, for a succession of torsion angles $\ldots \theta_1\theta_1\theta_1\theta_1\theta_1\ldots$, the average value of the torsion angles along the chain remains about 180°. For instance, for a chain with $\tau_1 = \tau_2 = 111°$ and $\tau_3 = 117°$, if $\theta_1 = 162°$ and $\theta_2 = -153°$, then $\theta_3 = 169.3°$ (with $\delta_1 = -18°$, $\delta_2 = 27°$, and $\delta_3 = -10.7°$, i.e., $\delta_1 + \delta_2 + \delta_3 = 0$) and the chain axis is 7.45 Å (161). In the particular case of $\theta_1 = 180°$ and $\tau_1 = \tau_2$, $\tau_3 = -\tau_2$, the identity period $c = 7.5$–7.6 Å is obtained for a s(2/1) helical symmetry for $\theta_3 = 180° + \delta$ with $\delta = 20–25°$ (161). Slightly different trends are obtained, for each value of $\theta_1$, for different values of $\tau_1$ and $\tau_2$ in the range 110°–114° (161).

Similar geometric relations between $\theta_1$, $\theta_2$, and $\theta_3$ have been reported for the syndiotactic copolymer (163). Highly extended conformations with $c = 7.5$–7.6 Å can be obtained, for a glide plane symmetry, when $\theta_1$, $\theta_2$, and $\theta_3$ are slightly deviated from 180°, in the range $180° \pm \delta$ with $\delta = 25–30°$ (158).

These slight deviations of the torsion angles of the main chain from the staggered conformation are feasi-
ble because of the low value of the barrier energy in the torsional potential energy around the bond C–CO (161,163) and are suitable in order to relax nonbonded interactions between atoms appended to the chain.

The complete determinations of the crystal structure of both iSTCO (160) and sSTCO (157,158), performed only by using the limited data from the X-ray powder diffraction profiles, have confirmed the previsions of the conformations obtained from the above-mentioned geometric analysis and the simple application of the equivalence principle (158,161). For the syndiotactic copolymer, the experimental values of the torsion angles found in the crystal structure (157,158) are, indeed, \( \theta_1 = 170^\circ, \theta_2 = 162^\circ, \text{and} \theta_3 = 150^\circ \). Similar values have been found by conformational energy calculations (163). For the isotactic polymer, the experimental values of the torsion angles found in the crystal structure (160) are \( \theta_1 = 161.5^\circ, \theta_2 = 155.3^\circ, \text{and} \theta_3 = 171.4^\circ \). Similar values have been found by conformational energy calculations (161). Models of the chain conformations of iSTCO and sSTCO are reported in Figure 1.65.

### 1.10 POLYDIENES

Double bonds present along a polymer chain are stereoisomeric centers, which may have a cis or trans configuration. Polymers of 1,3-dienes with 1,4 additions of the monomeric units contain double bonds along the chains and may contain up to two stereoisomeric tetrahedral centers. Stereoregular polymers can be cis- or trans-tactic, isotactic or syndiotactic, and diisotactic or disyndiotactic if two stereoisomeric tetrahedral centers are present. In the latter case, erythro and threo structures are defined depending on the relative configurations of two chiral carbon atoms (3).

All the possible line repetition groups for cis- and trans-polydienes compatible with the isotactic or syndiotactic configurations are reported in Figure 1.66 (4,126,164). In order to consider only the possible conformations assumed in the crystalline state, the torsion angle of the central single bond is assumed to be 180° (trans) in both the cis- and trans-polydienes. This condition produces conformations sufficiently extended to be packed in a crystalline lattice for each value of the torsion angles \( \theta_1 \) and \( \theta_2 \) (Fig. 1.66).

The line repetition group \( s(M/N) \) is general for cis- and trans-polydienes, whichever the A and B substituents, and corresponds to a succession of torsion angles (\( \theta_1,\text{cis}\theta_2,T \)), and (\( \theta_1,\text{trans}\theta_2,T \)). When A = A' and B = B', the cis polymer may present mirror planes or binary axes perpendicular to the chain axis in correspondence of the double bonds, whereas inversion centers and binary axes may be present in the trans polymer. Inversion centers in the center of the CHA–CHA' single bond or binary axes crossing the same bond and

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**Figure 1.65.** Side views and projections along the chain axis of the conformations of the chains in isotactic (160,161) and syndiotactic (157,158) alternating styrene–CO copolymers, with helical \( s(2/1) \) and glide plane \( t \) symmetries, respectively. (Reproduced with permission from Reference 4. Copyright 2003 by Wiley Interscience.)
perpendicular to the chain axis may be also present in both cis and trans polymers (Fig. 1.66). As a consequence, line repetition groups s(2/1)m, s(M/N)2, and tci are possible for cis-polydiene, whereas s(M/N)2, ti, and tci line repetition groups are possible for trans-polydienes (126,164–166). When A = A' ≠ H, line repetition groups s(2/1)m and s(M/N)2 are compatible for cis-isotactic chains, while s(M/N)2 and ti symmetries are compatible for trans-isotactic polydienes, and only the tci line repetition group is possible for syndiotactic-cis or trans polymers. In these cases, only one torsion angle (θ in Fig. 1.66) in the backbone is independent for each line repetition group (126). In the case of cis polymers, if mirror planes perpendicular to the chain axis, bisect-
ing the double bonds, and binary axes perpendicular to the chain axis, crossing the CHA-CHA′ single bond, are both present, a conformation of the kind (θ cis-θ T = θ cis θ T)ₜ, is produced and the chain degenerates in a cycle (126,165).

When A ≠ A′ or B ≠ B′, the symmetry is lower and the only possible line repetition groups are s(M/N) and tc for isotactic and syndiotactic polymers, respectively, in both cis and trans configurations. In these cases, two independent torsion angles in the main chain define the regular conformation (θ₁ and θ₂ in Fig. 1.66).

Also, for polydiene, the actual conformation assumed by the chain under the constraint of the equivalence principle is determined by energetic factors as defined by the principle of the minimum conformational energy. The torsion angles of single bonds adjacent to double bonds preferentially assume values equal to 120° or 120°. In fact, the intrinsic torsional energy may be still described by a threefold function, but the energy minima are at values of the torsion angles 120°, 120°, and 0° (antialcinal A″ and A′; and cis) (Fig. 1.29, Section 1.5.3). The minima are separated by a barrier energy lower than that in the torsional energy function of single bonds adjacent to single bonds. For these reasons, in polydiene, deviations from the equilibrium torsion angles are possible at a lower cost of energy; moreover, the packing energy may play an important role in determining the chain conformation in the crystalline state.

The conformational energy maps as a function of the torsion angles θ₁ and θ₂ of the two single bonds adjacent to the double bonds, for θ₁ = T = 180°, for cis-1,4-poly(1,3-butadiene) (cisPBD) (165), trans-1,4-poly(1,3-butadiene) (transPBD) (166), cis-1,4-poly(isoprene) (cisPi) (164), trans-1,4-poly(isoprene) (transPi) (167), cis-1,4-poly(2,3-dimethyl-1,3-butadiene) (cisPMBD) (164), and trans-1,4-poly(2,3-dimethyl-1,3-butadiene) (transPMBD) (164) are reported in Figure 1.67. These polymers are representative examples of polydiene with A = A′ = H and B or B′ equal to H or CH₃ and show the effect of the presence of the methyl groups adjacent to the double bonds on the conformational energy. The maps present various energy minima for values of θ₁ and θ₂ close to the torsional minima A″, A′, and cis (120°, −120° and 0°). The conformations found in the crystals, corresponding to a succession of the torsion angles θ₁ and θ₂ in the torsional minima A″, A′, and cis, according to the symmetries in Figure 1.66, and the values of the chain axes are reported in Table 1.12.

In the case of cisPBD (A = B = H), (Fig. 1.67A), the absolute minimum is localized in the two equivalent regions (A′cisA′T) = (A cis A′T), while two nearly isoenergetic minima were found in the regions (A′transA′T) = (A trans A′T) and (A′transA′T) = (A trans A′T) in the case of the transPBD (Fig. 1.67B). On the basis of the minima present in the map of the cis polymer, the possible conformations corresponding to the line repetition groups s(2/1)m, tci, and s(M/N)2 are characterized by the succession of torsion angles (A′cisAT)ₜ, (A′cisAT1A cis A′T)ₜ, and (A′cisAT′)ₜ, respectively (165). The periodicity of the tci conformation (A′cisAT)ₜ, corresponds to the chain axis c = 8.6 Å found in the crystalline form of cisPBD (50,53) (Table 1.12).

For transPBD, the possible conformations corresponding to the s(M/N)2, tci, and s(M/N) symmetries are (A′transAT)ₜ, (A′transAT)ₜ, and (CtransAT)ₜ, respectively (166). The tci conformation (A′transAT)ₜ, corresponds to that found in the stable polymorphic form of transPBD (form I) with a chain periodicity c = 4.83 Å (19,51,52,168).

In the case of cisPi (A = A′ = H and B = CH₃ and B′ = H), the two conformations corresponding to the two nonequivalent energy minima in the map in Figure 1.67C (164), (A′cisAT)ₜ, (s(2/1) symmetry), and (A′cisAT1A cis A′T)ₜ, (tc symmetry), correspond to the conformations of the chains in the crystal structure of cisPi proposed by Nyburg (169), and Bunn (60), respectively. The X-ray diffraction data are, however, better accounted for by a disordered conformation, proposed by Corradini (50,53,170), characterized by a statistical succession of monomeric units, which assume these two energy minimum conformations.

For transPi, among the possible s(M/N) conformations, (A′transAT)ₜ, (A′transAT)ₜ, and (CtransAT)ₜ, the succession (A′transAT)ₜ, with c = 4.72 Å and tci symmetry, corresponds to the conformation found in the β-form of transPi (51,60). The three possible tci conformations (A′transAT1A trans A′T)ₜ, (A′transAT trans A′T)ₜ, and (CtransAT1CtransAT)ₜ, give chain periodicities similar to the experimental chain axis of 8.77 Å of the α-form of transPi (61), but the conformation (CtransAT1CtransAT)ₜ, gives the best packing in the proposed space group (167), as actually found in the crystal structure (61).

In the case of cisPMBD and transPMBD (A = A′ = H and B = B′ = CH₃), the maps present narrow minima in correspondence to θ₁ and θ₂ close to 90°. The tci and tci conformations were found in the crystals of cisPMBD (171) and transPMBD (172), respectively (Table 1.12). The values of the torsion angles lower than 120° are in agreement with the lower values of the chain axes in both cisPMBD (7.0 Å (171)) and transPMBD (4.35 Å (172)) with respect to those of cis and trans poly(1,3-butadiene) and poly(isoprene).

The calculations in Figure 1.67 indicate some features of the conformations of polydiene. Minima in the region of the torsional cis minimum (θ₁ and θ₂ = 0) are present in the maps of the trans polymers (Fig. 1.67B,D) but disappear in the map of the cis polymers.
regions in the case of cis and trans poly(1,3-butadiene) (Fig. 1.67A,B) become narrow in poly(isoprene) (Fig. 1.67C,D) and poly(2,3-dimethylbutadiene) (Fig. 1.67E,F) due to the presence of the bulky methyl groups. For the same reason, some of these minima disappear because of the repulsive nonbonded interactions arising between the atoms in Figure 1.68 (164). The same nonbonded interactions induce slight deviations from the exact anticlinal torsional minimum for the cis polymers. Moreover, the large energy minimum in the case of cis and trans-1,4-poly(1,3-butadiene) (A), trans-1,4-poly(1,3-butadiene) (B), cis-1,4-poly(isoprene) (C), trans-1,4-poly(isoprene) (D), cis-1,4-poly(2,3-dimethyl-1,3-butadiene) (E), trans-1,4-poly(2,3-dimethyl-1,3-butadiene) (F). The isoenergetic curves are reported every 2 kJ/mol of monomeric units with respect to the absolute minimum of each map assumed as zero. (Reproduced with permission from Reference 164. Copyright 1986 by the Società Chimica Italiana.)
### TABLE 1.12. Structural Data of Polydienees

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Energy Minima</th>
<th>Conformation in the Crystalline State</th>
<th>Chain Symmetry</th>
<th>Space Group</th>
<th>References</th>
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<tr>
<td>cis-1,4-Poly(1,3-butadiene)</td>
<td>A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;; A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>tci</td>
<td>C&lt;sup&gt;2&lt;/sup&gt;c</td>
<td>(50)</td>
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<td>(19,52,166,260,261)</td>
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<td>(A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
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<td>t&lt;sub&gt;c&lt;/sub&gt;</td>
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<td>it-cis-1,4-Poly(2-methyl-1,3-pentadiene) α form</td>
<td>A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;; A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;</td>
<td>7.87</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>s(2/1)</td>
<td>Pbc&lt;sub&gt;a&lt;/sub&gt;</td>
</tr>
<tr>
<td>it-cis-1,4-Poly(2-methyl-1,3-pentadiene) β form</td>
<td>A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;; A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;</td>
<td>7.90</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>s(2/1)</td>
<td>P&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;1&lt;/sup&gt;/&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;1&lt;/sub&gt;</td>
</tr>
<tr>
<td>it-trans-1,4-Poly(2-methyl-1,3-pentadiene)</td>
<td>A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;; A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;</td>
<td>4.82</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>t&lt;sub&gt;i&lt;/sub&gt;</td>
<td>P&lt;sub&gt;2&lt;/sub&gt;/&lt;sub&gt;c&lt;/sub&gt;</td>
</tr>
<tr>
<td>it-cis-1,4-Poly(3-methyl-1,3-pentadiene)</td>
<td>A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;; A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;</td>
<td>8.0</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>s(2/1)</td>
<td>–</td>
</tr>
<tr>
<td>it-trans-1,4-Poly(1,3-hexadiene)</td>
<td>A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;; A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;</td>
<td>8.6</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>t&lt;sub&gt;c&lt;/sub&gt;</td>
<td>–</td>
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<tr>
<td>it-cis-1,4-Poly(1,3-hexadiene)</td>
<td>4.85</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>t&lt;sub&gt;i&lt;/sub&gt;</td>
<td>P&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;1&lt;/sup&gt;/&lt;sub&gt;2&lt;/sub&gt;&lt;sub&gt;1&lt;/sub&gt;</td>
<td>(264)</td>
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<tr>
<td>it-cis-1,4-Poly(1,3-hexadiene)</td>
<td>8.0</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; cis A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>s(2/1)</td>
<td>–</td>
<td>(265)</td>
</tr>
<tr>
<td>it-trans-erythro-Poly(methylsorbate)</td>
<td>A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;; A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;</td>
<td>4.8</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>t&lt;sub&gt;i&lt;/sub&gt;</td>
<td>–</td>
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<td>it-trans-threo-Poly(methylsorbate)</td>
<td>A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;; A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;</td>
<td>9.4</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>s(M/N)</td>
<td>–</td>
</tr>
<tr>
<td>trans-Polypentanamer</td>
<td>11.9</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>s(2/1)m</td>
<td>–</td>
<td>(56a)</td>
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<tr>
<td>trans-Polyheptanamer</td>
<td>17.1</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>s(2/1)m</td>
<td>–</td>
<td>(56a)</td>
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<tr>
<td>trans-Polyoctenamer</td>
<td>9.85</td>
<td>(A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>t&lt;sub&gt;i&lt;/sub&gt;</td>
<td>–</td>
<td>(56a)</td>
</tr>
<tr>
<td>trans-Polydodecenamer</td>
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<td>(A&lt;sup&gt;c&lt;/sup&gt; trans A&lt;sup&gt;T&lt;/sup&gt;)&lt;sub&gt;n&lt;/sub&gt;</td>
<td>t&lt;sub&gt;i&lt;/sub&gt;</td>
<td>–</td>
<td>(56a)</td>
</tr>
</tbody>
</table>

<sup>it</sup>, isotactic; <sup>st</sup>, syndiotactic
in the energy maps of isotactic and syndiotactic poly(1,3-pentadienes) (with A = H and A’ = CH$_3$) (173–175) and substituted poly(1,3-pentadienes) (with B or B’ = CH$_3$) (176–180) (Table 1.12).

According to the conformational energy minima, isotactic trans-1,4-poly(1,3-pentadiene) (51,52,181–185) and trans-1,4-poly(2-methyl-1,3-pentadiene) (186) are characterized by chains in the conformation (A transA’T)$_n$ (t1 symmetry), and chain axes c = 4.85 Å and 4.82 Å, respectively. The conformation (A cisA’T)$_n$ with s(2/1) symmetry characterizes the chains in the structures of isotactic cis-1,4-poly(1,3-pentadiene) (187–189) and cis-1,4-poly(2-methyl-1,3-pentadiene) (176).

For the syndiotactic polymers, experimental data and energy calculations have been reported for cis-1,4-poly(1,3-pentadiene) (174,190,191) and cis-1,4-poly(3-methyl-1,3-pentadiene) (178). In both cases, energy minima are obtained for the tc conformation (A cisA TA’cisA’T)$_n$ (126,174,178), according to the observed chain axes of 8.5 and 8.6 Å (178,190).

Examples of ditactic polydienes are provided by a class of crystalline polymers derived from the alkyl esters of the trans–trans isomer of sorbic acid (192,193). For example, trans-poly(methyl sorbate) (–CH(CH$_3$)–CH=CH–CH=CH(CH$_3$)$_2$)$_n$ presents two asymmetric carbon atoms (A = CH$_3$, A’ = COOCH$_3$, B = B’ = H). Polymers with prevalently erythro or threo configurations have been obtained with different catalytic systems (193). Polymers with erythro configuration show a chain axis of c = 4.8 Å (194,195), while polymers with threo configuration present a chain preredicity of c = 9.4 Å (193). X-ray diffraction analysis (195) and conformational energy calculations (196) have shown that the polymers with trans–erythro configuration are disisotactic with a t1 conformation, characterized by a succession of torsion angles (A transA’T)$_n$, whereas polymers with trans–threo configuration are disisotactic but with conformation (A’transA TA transA’T)$_n$.

1.11 NONHELICAL CHAIN CONFORMATIONS OF ISOTACTIC POLYMERs

In the previous sections, it has been demonstrated that isotactic vinyl polymers generally assume a helical (TG), conformation in the crystalline state according to the basic principles of equivalence and of minimum conformational internal energy (Sections 1.5.2 and 1.5.3) and calculations of the conformational energy (Section 1.7.2). The number of monomeric units per pitch ranges in all observed cases between 3.0 and 4.0, and the internal rotation angles do not deviate, in general, more than 20° from staggered values. This rule is widely applicable to the vast majority of head-to-tail stereoregular crystallizable polymers, with an isotactic configuration because the s(M/N) helical symmetry of isotactic vinyl polymers is compatible with the regular repetition along the chain axis of isomorphous isoctlined units (3,4,43). However, at least two cases where an isotactic polymer chain does not adopt a helical conformation in the crystalline state have already been described in Section 1.9. The first case is represented by the alternating ethylene-cis-butene-2 copolymer, which adopts a (T,G’1,G’) conformation with t1 symmetry in the crystalline state (Fig. 1.61) (110,153), and the second example is provided by the alternating meso-disisotactic ethylene–cyclopentene copolymer (ECP), which may assume both the (T,G’T,G’) conformation with t1 symmetry and the (T,cis) conformation with helical s(2/1)m symmetry (Fig. 1.62) (154,155) due to dynamic conformational disorder. In these examples, the chain conformation does not correspond to a helical repetition of isoclinic, isomorphous structural units but corresponds to a succession of enantiomorphous anticlinal structural units (for the t1 symmetry).

Another example of nonhelical conformation is represented by iP5 in the polymorphic form that crystallizes in gels (110). iP5 forms with a variety of solvents thermoreversible crystalline gels (197–201) that present structural features quite different from those of the stable crystalline form of iP5, which is characterized by chains in the 3/1 helical conformation (Fig. 1.51). irrespective of the used solvent, the X-ray diffraction patterns of stretched dry gels of iP5 present the most intense reflection on the meridian at 5.1 Å on the sixth layer line, corresponding to a chain repeat length of $d = 5.1 \times 6 = 30.6$ Å (197–201). The presence of the superperiodicity of 5.1 Å has been a puzzle for long time and for which a simple explanation has been found only recently (110). In fact, various conflicting models for the chain conformation of iP5 in gels have been proposed in the attempt to explain the presence of the meridional reflection at 5.1 Å in the stretched dry gels (Fig. 1.69) (197–199,202–208).
The conformation of iPS chains in the gels should reconcile the apparent conflict between two sets of experimental data: the X-ray diffraction patterns of stretched dry gels, with the strong meridional reflection at 5.1 Å on the sixth layer line, which should simply correspond to trans-planar sequences (199) that for iPS may be energetically feasible (205,209), and the Fourier transform infrared (FTIR) experimental data of wet (206) and dry (207) stretched gels that indicate that the chain conformation is virtually the same as in the stable crystalline form; that is, the chains must present long and regular sequences of dihedral angles in the 3/1 helical conformation (206–208,210–214).

On the basis of these data, the model of chain conformation of the almost extended 12 helix of sixfold symmetry (per dimeric unit) in Figure 1.69A, with unit height \( h = 5.1 \) Å and periodicity \( c = 30.6 \) Å (Fig. 1.69A) (198,199,202–204), should be ruled out, and one has to accept that in nascent and stretched dry gels, the chains present long and regular sequences of dihedral angles in the (TG) \( _n \) conformation. Based on this assumption and on neutron diffraction data, Guenet (208) has proposed a ladderlike model for the nascent gel (Fig. 1.69C), where chains of iPS in basically 3/1 helical conformation are able to host molecules of solvent in cavities generated by the side benzene rings and the solvent molecules are considered to be responsible for the reflection at 5.1 Å (208).

Chatani and Nakamura (207) proposed a coiled-coil molecular model in which the chains are assumed to have locally basically the same 3/1 helical structure as the conformation in the crystalline form, but the axis of

![Figure 1.69](image-url)
the 3/1 helix describes itself a larger helix having a long pitch of 30.6 Å (Fig. 1.69B). Six turns of the 3/1 helix (for a total of 18 monomeric units) would be comprised in one turn of the large helix. Since the radius of such large helix would be 4.08 Å, the axis of the 3/1 helix tilts by 40° from the direction of the axis of the large helix with the result that the asymmetric unit (comprising three monomeric units in one turn of the original 3/1 helix) produces an axial length of 5.1 Å (=6.65 × cos 40°) (Fig. 1.69B). This subperiodicity would account for the strong meridional reflection at 5.1 Å as well as for the chain repetition length c = 30.6 Å (207).

An alternative and simpler model has been recently proposed (110) on the basis of the studies that suggest the presence in the crystalline gels of chains in a nearly 3/1 helical conformation (206–208,210–214) and of simple considerations about the conformational statistics of polymer chains in solution (215). In this model, it has been hypothesized that the chain conformation in the nascent gel should not be too much different from that one in solution (110), according to the studies of Guenet et al. (208,210–214). The chain conformation of iPS in the stretched dry gels is hence derived from the conformation of chains present in solution, in a rather straightforward manner (110).

The chains of highly isotactic vinyl polymers in solution present, indeed, sequences in helical conformation of the kind (TG)n, or (G–T)n, where the symbols T and G' denote dihedral angles in the ranges 180 ± 30°, +60 ± 30°, and −60 ± 30°, and the equivalence principle does not hold true as for the crystalline state (3,215,216). These sequences may rapidly interconvert at sufficiently high temperatures and along the same chain, short spiral sequences with opposite chirality may alternate (Fig. 1.70). The conformational energy cost of these helix reversals, indeed, is not high (215,216) and reversals could occur in solution (in the isomeric rotational model approximation) (209,217) with a frequency of 1 every 5–10 monomeric units slightly above room temperature. The same considerations are valid for syndiotactic vinyl polymers (3,215).

In the case of iPS, Bruckner et al. (218) have demonstrated that, for two spiralized stems of a chain of opposite handedness linked according to the scheme . . . (G–T)(G–T)(T–T)(G–T)(G–T)(G–T) . . . (i = 0, 1, 2 . . . n), the cost of the conformational energy is zero when n = 0 and increases with increasing n (218). Therefore, models of conformation of iPS in solution may be built assuming the presence of 3/1 helical sequences and of reversals in the helical hand along the chains (218). It has been assumed that the inversion of spirals of the kind . . . (G–T)(G–T)(G–T) . . . to spirals of the kind . . . (G–T)(G–T)(G–T) . . . takes place only for n = 0, as shown in the model in Figure 1.71A (110). For an inversion in the sense of spiralization after a sequence of the kind . . . (TG)n(TG)n(TG)n . . . instead, the cost of conformational energy would be in any case higher than zero (218). For junctions involving two dihedral angles according to the scheme . . . (TG)n(TG)n(TG)n(TG)n(TG)n(TG)n(TG)n(TG)n . . . , a possible minimum energy conformation is shown in Figure 1.71B (110).

The chain conformation of iPS in solution may be described in terms of sequences of the kind . . . (G–T),n(θ,θi,θn) (G–T)n(θ,θi,θn) (G–T)n(θ,θi,θn) . . . (m, n, 1, 2, 3, 4, . . . , k), where the solution with n = 0 and q = 1 is at the lowest cost of conformational energy (218). In solution, the subscripts m, n, 1, 2, 3, 4, . . . , k vary in time (215), whereas in the gel state, the helical portions become more regular and rigid, and the conformational transitions are suppressed or occur on a longer timescale (110). Extensive studies performed by Guenet et al. (208,210–214) have, indeed, indicated that the nascent gels of iPS comprise long and rigid stems in the 3/1 helical conformation and the chain conformation is virtually the same as in solution in the pregel state (i.e., at temperatures above the melting temperature of the gel).

Upon stretching procedures of dry gels, the conformational order, as well as the order in the lateral packing
of the chains, increases. A possible conformational model of minimum energy of the chains of iPS chains in the ordered regions of the stretched dry gels is shown in Figure 1.71C (110). The model corresponds to sequences of the kind . . . (G T)₃₉(G T')₃₂(T T')₂₀(G T)₃₇(T G')₇ₙ . . . , that is, helical stems of opposite chirality follow each other along the chain linked through the junctions of the kind shown in Figure 1.71A and B, alternatively. Isochiral helical stems run parallel each other, and it is possible to define a chain axis, assumed parallel to z as in Figure 1.71C (110). In this model, the axes associated to the 3/1 helical portions are inclined by 40° with respect to the chain axis, resulting in a chain subperiodicity of 5.1 Å (= 6.65 × cos 40°) (Fig. 1.71C), in agreement with the presence of the X-ray meridional reflection at 5.1 Å in the fiber diffraction pattern of iPS dry gels (110). Since this chain possibly includes mainly short helical stems, that is, comprising 3, 6, 9, or 12 monomeric units, at chance, the average periodicity results 30.6 Å, and a period would comprise 16 monomeric units on average. This explains the main features of the X-ray diffraction patterns of the stretched dry gels (110). It is worth noting that longer helical stems would be also occasionally present in the ordered regions of the stretched dry gels, but if they were prevalent, the normal crystal form of iPS would set in (110).

The conformation of the chains of iPS in crystalline gels is, therefore, an example of nonhelical conformation even though the whole chain is built up of regular helical blocks that are, however, of opposite handedness alternating along the chain. The equivalence principle is, indeed, not valid, and the conformation does not correspond to a regular repetition along the chain axis of isomorphous isoaxial units.

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