2: Stereochemical Definitions and Notations Relating to Polymers

CONTENTS
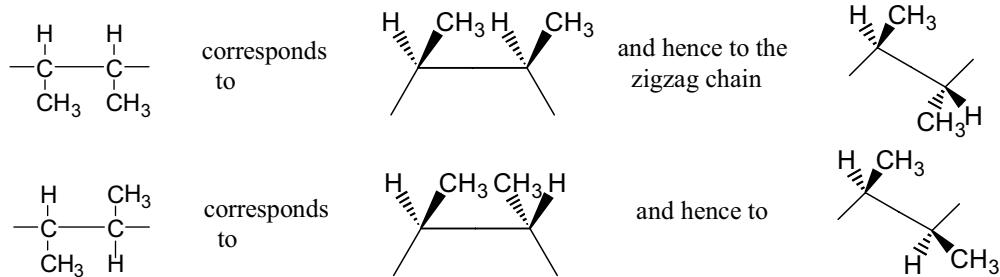
## PREAMBLE

A report entitled 'Nomenclature Dealing with Steric Regularity in High Polymers' was issued in 1962 by the Committee on Nomenclature of the Commission on Macromolecules of the IUPAC [1]. Since then, the development of increasingly sophisticated techniques for structure determination has greatly enlarged the field of polymer stereochemistry and this, in turn, has revealed the need for a detailed knowledge of molecular conformations in order to correlate chemical structure with physical properties. The terminology and nomenclature relating to the constitution and configuration of macromolecules has been refined, using structure-based concepts, in documents of this Commission [2,3], while an IUPAC paper [4] on the graphical representation of stereochemical configuration of organic molecules and an IUPAC-IUB document [5] on abbreviations and symbols to be used for the description of the conformations of polypeptide chains have appeared as definitive publications. The present statement is intended to bring up to date the nomenclature of features corresponding to stereoregularity in polymers; it employs the definitions prescribed in [2] and takes into account all the previously elaborated material cited above; it also introduces new concepts dealing with the microstructure of polymer chains, and it proposes a set of definitions and notations for the description of the conformations of polymer molecules. Consistency with documents [4] and [5] has been maintained as far as is possible.

Throughout this document, stereochemical formulae for polymer chains are shown as Fischer projections rotated through 90°, i.e., displayed horizontally rather than vertically, (at variance with [1]) or as hypothetical extended zigzag chains.

The use of rotated Fischer projections corresponds to the practice of using horizontal lines to denote polymer backbone bonds, but it is most important to note that this does not give an immediately visual impression of the zigzag chain. In the projections as used in this document, *at each individual backbone carbon atom* the horizontal lines represent bonds directed below the plane of the paper from the carbon atom while the vertical lines project above the plane of the paper from the carbon atom. Thus, the rotated Fischer projection
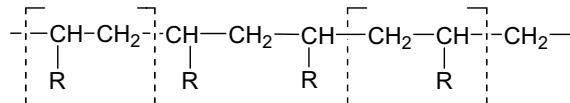

The use of rotated Fischer projections has been retained in the present edition in order to provide a link with, and an explanation of, the bulk of existing published polymer literature, although the present common practice [4] is to depict main-chain bonds in planar, extended zigzag (*all-trans*) conformations, together with a stereochemical representation of side-groups at tetrahedrally-bonded atoms.

Unless otherwise stated, the drawings of configurational base units, configurational repeating units, stereorepeating units, etc., provide information regarding *relative* configurations.

In a polymer molecule, the two portions of the main chain attached to any constitutional unit are, in general, non-identical; consequently, a backbone carbon atom that also bears two different side-groups is considered to be a chiral centre.

The absence from a formula of any one of the horizontal or vertical lines at a chiral or prochiral carbon atom (as in examples on pages 27 and 32), or of *E* or *Z* designations[*] at double bonds, indicates that the configuration of that stereoisomeric centre is not known. Also, as in our previous document [2], the convention of orienting polymer structures (and the corresponding constitutional and configurational units) from left to right is used. Thus, the two bracketted constitutional units in

are regarded as different, even though the repetition of either one of them would give the same regular polymer. Some of the definitions presented also appear in a previous paper of this Commission [2], but they are repeated here (with minor grammatical improvement) in order to provide a complete set of stereochemical definitions in a single document.

In order to present clear concepts it is necessary that idealized definitions be adopted but it is recognized that the realities of polymer science must be faced. Deviations from ideality arise with polymers at both molecular and bulk levels in ways that have no parallel with the ordinary small molecules of organic or inorganic chemistry. Although such deviations are not explicitly taken into account in the definitions below, the nomenclature recommended can usefully be applied to the predominant structural features of real polymer molecules, if necessary with self-explanatory, if imprecise, qualifications such as 'almost completely isotactic' or 'highly syndiotactic'. Although such expressions lack the rigour beloved by the purist, every experienced polymer scientist knows that communication in this discipline is impossible without them.

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[*] With regard to the arrangement of substituents at double bonds (double-bond configuration), it is recommended that *E* and *Z* stereodescriptors rather than *cis* and *trans* stereodescriptors be used throughout.

1 BASIC DEFINITIONS

1.1 configurational unit
Constitutional unit having one or more sites of defined stereoisomerism.

1.2 configurational base unit
Constitutional repeating unit in a regular macromolecule, a regular oligomer molecule, a regular block, or a regular chain, the configuration of which is defined at least at one site of stereoisomerism in the main chain.
Note: In a regular polymer, a configurational base unit corresponds to the constitutional repeating unit.

1.3 configurational repeating unit
Smallest set of successive *configurational base units* that prescribes configurational repetition at one or more sites of stereoisomerism in the main chain of a regular macromolecule, a regular oligomer molecule, a regular block, or a regular chain.
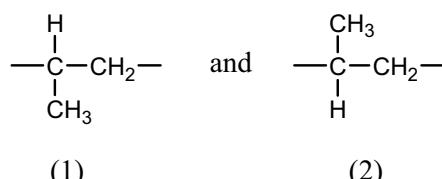
1.4 stereorepeating unit
Configurational repeating unit having defined configurations at all sites of stereoisomerism in the main chain of a regular macromolecule, a regular oligomer molecule, a regular block, or a regular chain.
Note: Two *configurational units* that correspond to the same constitutional unit are considered to be *enantiomeric* if they are non-superposable mirror images. Two non-superposable *configurational units* that correspond to the same constitutional unit are considered to be *diastereomeric* if they are *not* mirror images.
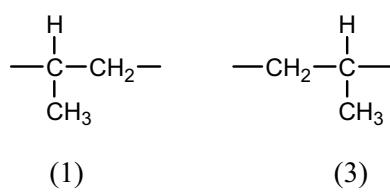
Examples:
In the regular polymer molecule $-[CH(CH_3)-CH_2-]_n$, polypropene, the constitutional repeating unit is $-CH(CH_3)-CH_2-$ and the corresponding *configurational base units* are
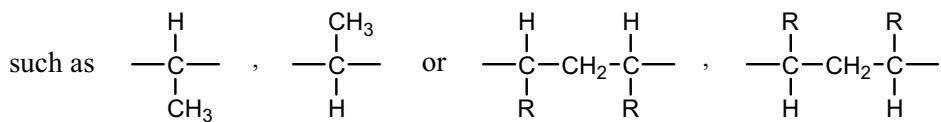

(1) and (2)

   The *configurational base units* (1) and (2) are enantiomeric, while the *configurational units* (1) and (3) cannot be enantiomeric because the constitutional units are different species, according to this nomenclature.


(1) (3)
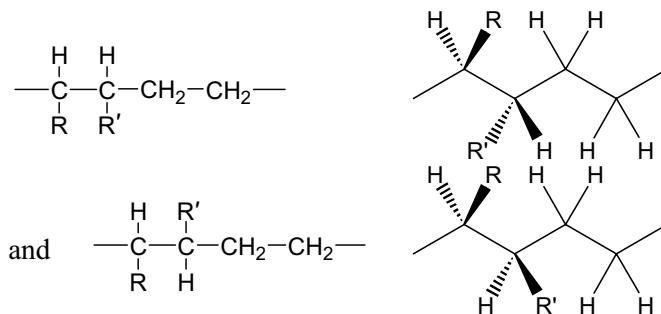
   It is immaterial whether (1) or (2) is taken as the *configurational repeating unit* and stereorepeating unit of isotactic polypropene (see Definition 1.7); this is so because the two infinite chains, one built up of identical *configurational units* (1) and the other built up of
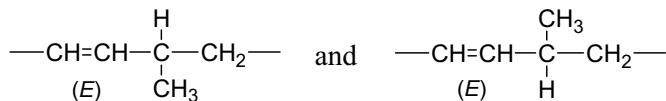
identical *configurational units* (2), are *not* enantiomeric and differ only in the chain orientation. Within each pair of units,

such as

$$\text{—}\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{—} \quad , \quad \text{—}\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\text{—} \quad \text{or} \quad \text{—}\overset{\text{H}}{\underset{\text{R}}{\text{C}}}\text{—CH}_2\text{—}\overset{\text{H}}{\underset{\text{R}}{\text{C}}}\text{—} \quad , \quad \text{—}\overset{\text{R}}{\underset{\text{H}}{\text{C}}}\text{—CH}_2\text{—}\overset{\text{R}}{\underset{\text{H}}{\text{C}}}\text{—}$$
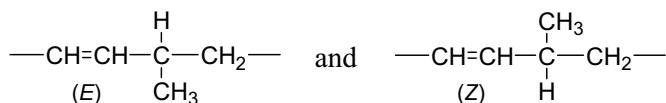
the components are enantiomeric since they are non-superposable mirror images, as defined above. However, with the constitutional unit –CHR–CHR'–CH_2–CH_2–, the two corresponding *configurational units*

$$\text{—}\overset{\text{H}}{\underset{\text{R}}{\text{C}}}\text{—}\overset{\text{H}}{\underset{\text{R'}}{\text{C}}}\text{—CH}_2\text{—CH}_2\text{—}$$

and

$$\text{—}\overset{\text{H}}{\underset{\text{R}}{\text{C}}}\text{—}\overset{\text{R'}}{\underset{\text{H}}{\text{C}}}\text{—CH}_2\text{—CH}_2\text{—}$$
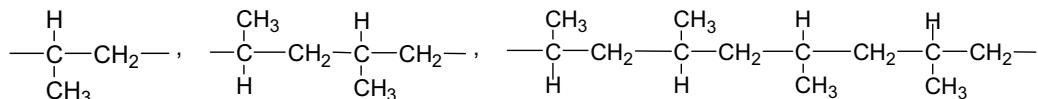
are diastereomeric. The units

$$\text{—CH=CH—}\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{—} \quad \text{and} \quad \text{—CH=CH—}\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\text{—CH}_2\text{—}$$
$$\quad (E) \qquad\qquad\qquad\qquad\qquad (E)$$

are enantiomeric. The units

$$\text{—CH=CH—}\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{—} \quad \text{and} \quad \text{—CH=CH—}\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\text{—CH}_2\text{—}$$
$$\quad (E) \qquad\qquad\qquad\qquad\qquad (Z)$$
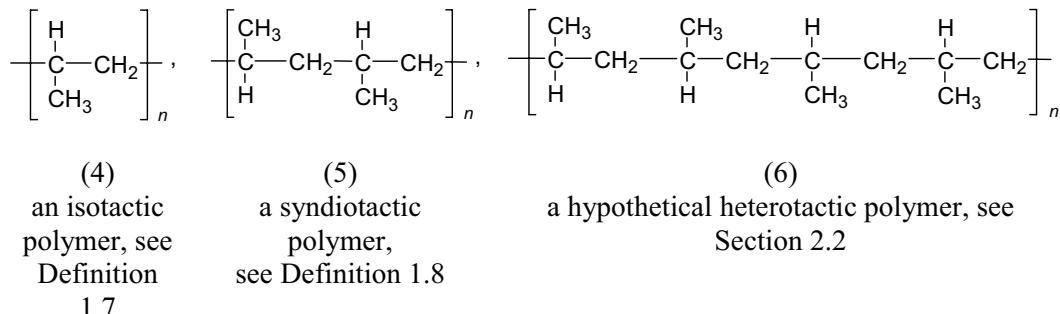
are not enantiomeric, but diastereomeric. The simplest possible stereorepeating units in a stereoregular polypropene are

$$\text{—}\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{—} \;,\; \text{—}\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\text{—CH}_2\text{—}\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{—} \;,\; \text{—}\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\text{—CH}_2\text{—}\overset{\text{CH}_3}{\underset{\text{H}}{\text{C}}}\text{—CH}_2\text{—}\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{—}\overset{\text{H}}{\underset{\text{CH}_3}{\text{C}}}\text{—CH}_2\text{—}$$

and the corresponding *stereoregular polymers* are

(4)	(5)	(6)
an isotactic polymer, see Definition 1.7	a syndiotactic polymer, see Definition 1.8	a hypothetical heterotactic polymer, see Section 2.2

1.5   tactic polymer
Regular polymer, the molecules of which have essentially all identical *configurational repeating units*.

1.6   tacticity
Orderliness of the succession of *configurational repeating units* in the *main chain* of a regular *macromolecule*, a regular *oligomer molecule*, a regular *block*, or a regular *chain*..
Note: For the definition of *degree of tacticity*, see Section 4.

1.7   isotactic polymer
Regular polymer, comprising tactic macromolecules having essentially only one species of *configurational base unit* which has chiral or prochiral atoms in the main chain in a unique arrangement with respect to its adjacent constitutional units.
Note 1: In an isotactic polymer, the *configurational repeating unit* is identical with the *configurational base unit*.
Note 2: An isotactic polymer consists of *meso* diads.

1.8   syndiotactic polymer
Regular polymer, comprising tactic macromolecules having alternating enantiomeric *configurational base units*, which have chiral or prochiral atoms in the main chain in a unique arrangement with respect to their adjacent constitutional units.
Note 1: In a syndiotactic macromolecule, the *configurational repeating unit* consists of two *configurational base units* that are enantiomeric.
Note 2: A syndiotactic macromolecule consists of racemo diads.

1.9   stereoregular polymer
Regular polymer, the molecules of which essentially comprise only one species of stereorepeating unit
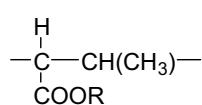
1.10   atactic polymer
Regular polymer, the molecules of which have equal numbers of the possible *configurational base units* in a random sequence distribution.
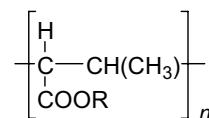
Examples:
For the polymer $-[CH(COOR)CH(CH_3)]_n$, if only the ester-bearing main-chain site in each constitutional repeating unit has defined stereochemistry, the *configurational repeating unit* is (7) and the corresponding *isotactic polymer* is (8).

$$-\underset{\underset{\text{COOR}}{|}}{\overset{\overset{\text{H}}{|}}{C}}-\text{CH(CH}_3)-$$

(7)

$$\left[\underset{\underset{\text{COOR}}{|}}{\overset{\overset{\text{H}}{|}}{C}}-\text{CH(CH}_3)\right]_n$$
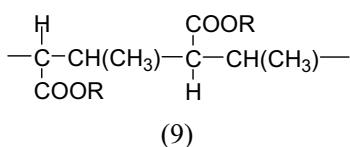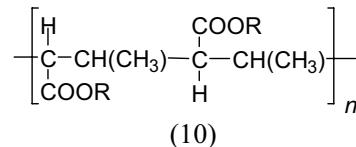
(8)

In the corresponding syndiotactic case, the *configurational repeating unit* is (9) and the *syndiotactic polymer* is (10):

$$-\underset{\underset{\text{COOR}}{|}}{\overset{\overset{\text{H}}{|}}{C}}-\text{CH(CH}_3)-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{COOR}}{|}}{C}}-\text{CH(CH}_3)-$$

(9)

$$\left[\underset{\underset{\text{COOR}}{|}}{\overset{\overset{\text{H}}{|}}{C}}-\text{CH(CH}_3)-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{COOR}}{|}}{C}}-\text{CH(CH}_3)\right]_n$$
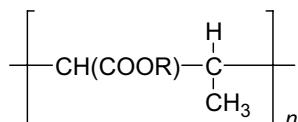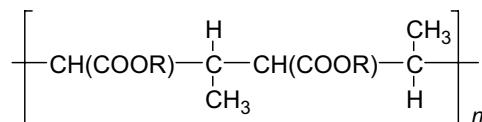
(10)

As the definition of a *stereoregular polymer* (see Definitions 1.4 and 1.9) requires that the configuration be defined at all sites of stereoisomerism, structures (8) and (10) do not represent *stereoregular polymers*. The same is true of (11) and (12), which differ from (8) and (10) in that the sites of specified and unspecified configuration have been interchanged.

$$\left[-\text{CH(COOR)}-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{H}}{|}}{C}}-\right]_n$$

(11)

$$\left[-\text{CH(COOR)}-\underset{\underset{\text{CH}_3}{|}}{\overset{\overset{\text{H}}{|}}{C}}-\text{CH(COOR)}-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{CH}_3}{|}}{C}}-\right]_n$$
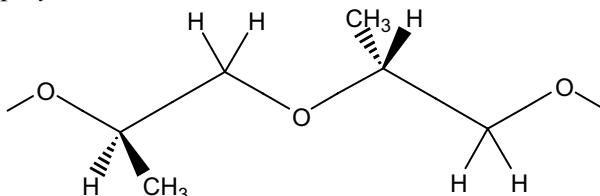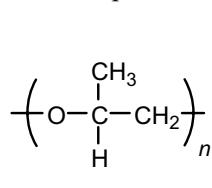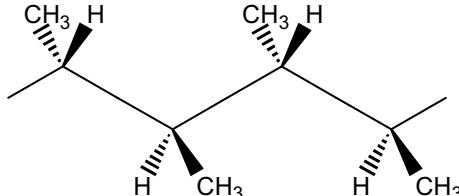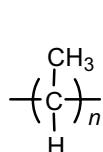
(12)

Examples (4), (5), (6), (8), (10), (11) and (12) are *tactic polymers*. A *stereoregular polymer* is always a *tactic polymer*, but a *tactic polymer* is not always stereoregular because a *tactic polymer* need not have all sites of stereoisomerism defined.

Further examples of *tactic polymers* are:

$$\left(-\text{O}-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{CH}_3}{|}}{C}}-\text{CH}_2\right)_n$$
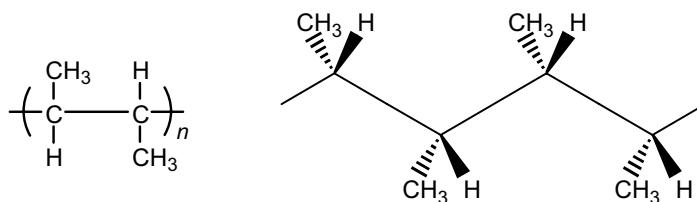
isotactic poly[oxy(1-methylethane-1,2-diyl)][*]

$$\left(-\underset{\underset{\text{H}}{|}}{\overset{\overset{\text{CH}_3}{|}}{C}}-\right)_n$$

isotactic poly(methylmethylene)

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[*] Formerly, the structure-based name, poly[oxy(1-methylethylene)], would have been acceptable for this molecule but longer is (see page 257 for an explanation of traditional names, structure-based names and source-based names of polymers).

syndiotactic poly(methylmethylene)
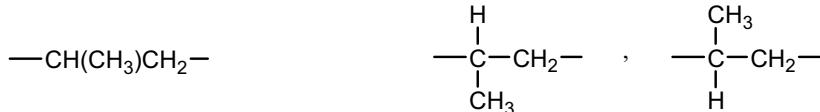
Note: Structure-based names of *tactic polymers* are formed before the application of adjectives designating *tacticity*; thus, 'syndiotactic poly(methylmethylene)' is preferred to 'syndiotactic poly(1,2-dimethylethane-1,2-diyl)' because a shorter repeating unit is identified, in conformity with the rules in Ref. 3.

On atactic polymers:
Note: As the definition above indicates, a regular polymer, the *configurational base units* of which contain one site of stereoisomerism only, is atactic if it has equal numbers of the possible types of *configurational base units* arranged in a random distribution. If the constitutional repeating unit contains more than one site of stereoisomerism, the polymer may be atactic with respect to only one type of site if there are equal numbers of the possible configurations of that site arranged in a random distribution.
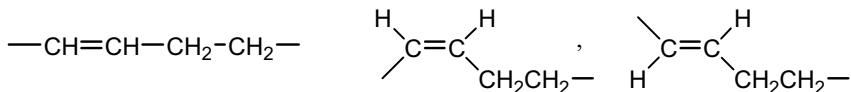
Examples:

constitutional repeating unit	*configurational base units* (randomly distributed in an *atactic polymer*)

constitutional repeating unit	*configurational base units* (randomly distributed in an *atactic polymer*)

A polymer such as ${-}$CH=CH–CH(CH$_3$)–CH$_2{-}_n$, which has two main-chain sites of stereoisomerism, may be atactic with respect to the double bond only, with respect to the chiral atom only or with respect to both centres of stereoisomerism. If there is a random distribution of equal numbers of units in which the double bond is *cis* and *trans*, the polymer is atactic with respect to the double bond, and if there is a random distribution of equal numbers of units containing the chiral atom in the two possible configurations, the polymer is atactic with respect to the chiral atom. The polymer is completely atactic when it contains, in a random distribution, equal numbers of the four possible *configurational base units* which have defined stereochemistry at both sites of stereoisomerism.

In addition to *isotactic, syndiotactic* and *atactic polymers* (and other well-defined types of *tactic polymers*), there exists the whole range of possible arrangements between the completely ordered and the completely random distributions of *configurational base units*,

and it is necessary to employ the concept of degree of *tacticity* (see Section 4) to describe such systems.
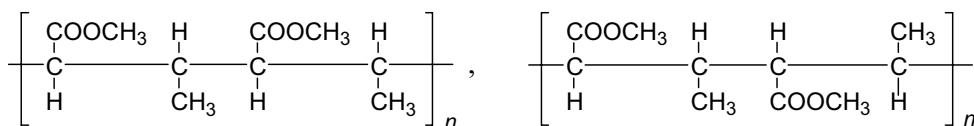
1.11 stereospecific polymerization

Polymerization in which a *tactic polymer* is formed. However, polymerization in which stereoisomerism present in the monomer is merely retained in the polymer is not to be regarded as stereospecific. For example, the polymerization of a chiral monomer, e.g., (*R*)-propylene oxide ((*R*)-methyloxirane), with retention of configuration is not considered to be a stereospecific reaction; however, selective polymerization, with retention, of one of the enantiomers present in a mixture of (*R*)- and (*S*)-propylene oxide molecules is so classified.

1.12 ditactic polymer

Tactic polymer that contains two sites of defined stereoisomerism in the main chain of the *configurational base unit*.
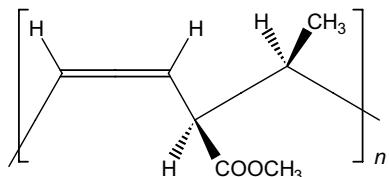
Examples:

are both ditactic.

1.13 tritactic polymer

Tactic polymer that contains three sites of defined stereoisomerism in the main chain of the *configurational base unit*.

Example:

poly[(*Z*)-(3S)-3-(methoxycarbonyl)-(4S)-4-methylbut-1-ene-1,4-diyl]

1.14 diisotactic polymer
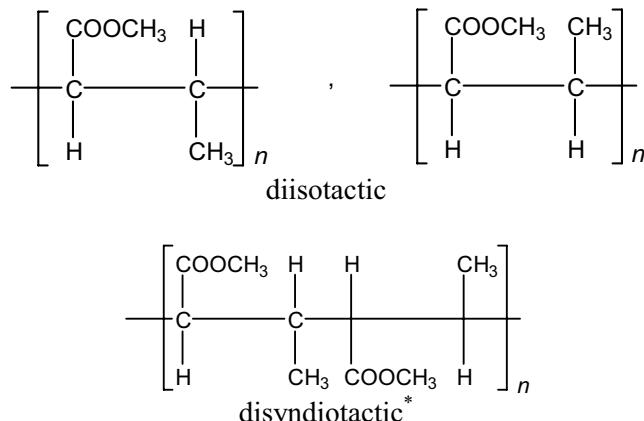
Isotactic polymer that contains two chiral or prochiral atoms with defined stereochemistry in the main chain of the *configurational base unit*.
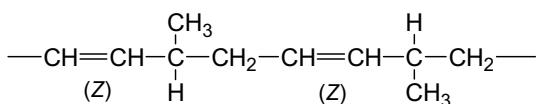
1.15 disyndiotactic polymer

Syndiotactic polymer that contains two chiral or prochiral atoms with defined stereochemistry in the main chain of the *configurational base unit*.

Examples:

diisotactic

disyndiotactic*

A polymer with the repeating unit

is ditactic and may be described as syndiotactic (see Definition 1.8), but it is not disyndiotactic.

The relative configuration of adjacent, constitutionally non-equivalent, carbon atoms can be specified as erythro or threo, as appropriate, by adding the required prefix to the terms 'diisotactic' and 'disyndiotactic', as necessary (see Section 2.2).

1.16 cistactic polymer
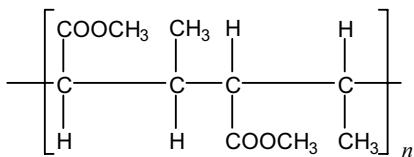
Tactic polymer in which the main-chain double bonds of the *configurational base units* are entirely in the *Z* configuration.

1.17 transtactic polymer

Tactic polymer in which the main-chain double bonds of the *configurational base units* are entirely in the *E* configuration.

Note 1: Terms referring to the *tacticity* of polymers (tactic, ditactic, tritactic, isotactic, cistactic, etc.) can also be applied with similar significance to chains, sequences, blocks, etc.

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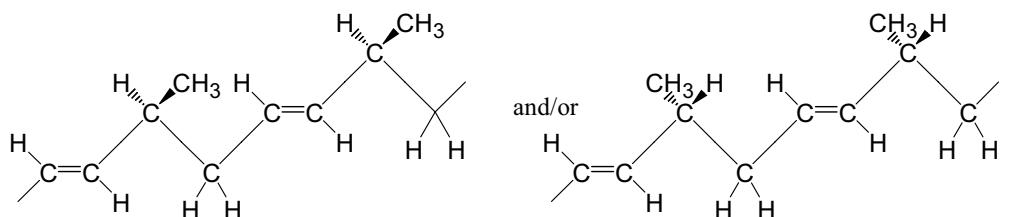
does not represent a different disyndiotactic polymer.
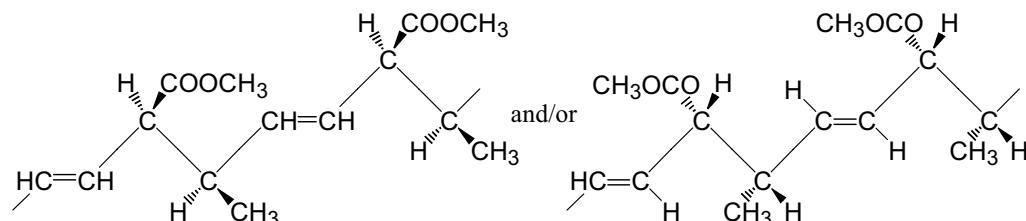
Note 2: Terms defining stereochemical arrangements are to be italicized only when they form part of the name of a polymer; the use of such terms as adjectives, even when immediately preceding names, does not require italics. This practice is illustrated in the examples below.

Examples:

isotactic poly[(*E*)-3-methylbut-1-ene-1,4-diyl];
transisotactic poly(3-methylbut-1-ene-1,4-diyl)[*]

diisotactic poly[*threo*-(*E*)-3-(methoxycarbonyl)-4-methylbut-1-ene-1,4-diyl];
transthreodiisotactic poly[3-(methoxycarbonyl)-4-methylbut-1-ene-1,4-diyl][*]

1.18 block
Portion of a *macromolecule*, comprising many *constitutional units*, that has at least one constitutional or configurational feature which is not present in the adjacent portions.

1.19 tactic block
Regular block that can be described by only one species of *configurational repeating unit* in a single sequential arrangement.

1.20 atactic block
Regular block that has equal numbers of the possible *configurational base units* in a random sequence distribution.

1.21 stereoblock
Regular block that can be described by one species of stereorepeating unit in a single sequential arrangement.

1.22 tactic block polymer
Polymer, the molecules of which consist of tactic blocks connected linearly.

[*] Structure-based name; either may be used.
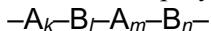
1.23   stereoblock polymer
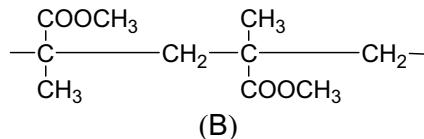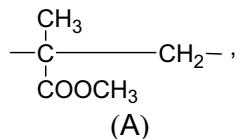
Polymer, the molecules of which consist of stereoblocks, and possibly some non-stereoregular blocks.

Examples:
Tactic block polymer
$-A_k-B_l-A_m-B_n-$
where A and B are, for example,
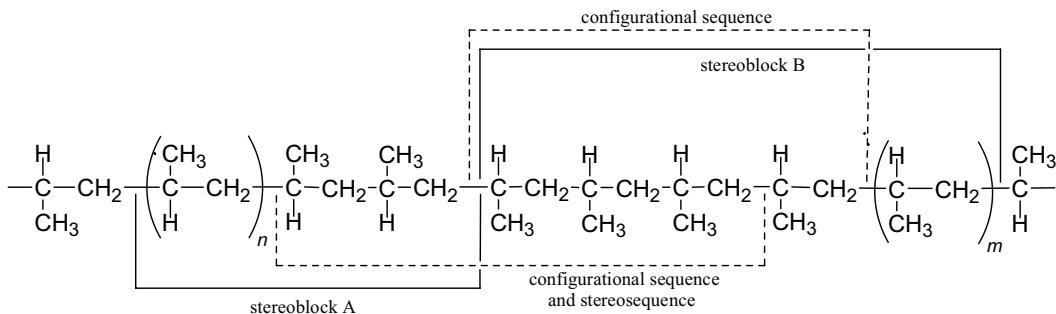
(A)   (B)

In this case the blocks are stereoblocks but the block polymer is not a block copolymer because all the units derive from a single monomer.

In the folowing example of a regular polypropene chain, the stereoblocks are denoted by |‾‾‾| . Here, the sequence of identical relative configurations of adjacent units that characterizes the stereoblock is terminated at each end of the block. Note that ¦‾‾‾‾¦ represents a *configurational sequence*, which may or may not be identical with a *stereoblock*.

The *configurational sequence* and *stereosequence* coincide in this particular case because there is only one site of stereoisomerism in each constitutional repeating unit (compare Definitions 2.1.3 and 2.1.4).

2   SEQUENCES
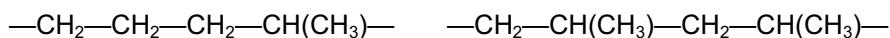
2.1   Constitutional and Configurational Sequences

Descriptions of polymer structures revealed by studies of physical properties focus attention on the distribution of local arrangements present in the molecules, and terms useful in this context are defined in this section. (The terms defined here in relation to complete polymer molecules can also be applied to sequences and to blocks, as in Ref. 2, Definition 3.14.)

2.1.1   constitutional sequence

Whole or part of a chain comprising one or more species of constitutional unit(s) in defined sequence.

Example:

$$—CH_2—CH_2—CH_2—CH(CH_3)— \qquad —CH_2—CH(CH_3)—CH_2—CH(CH_3)—$$
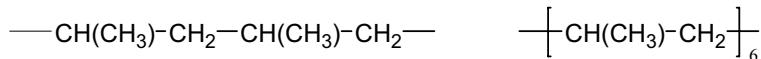
Note: Constitutional sequences comprising two constitutional units are termed diads, those comprising three constitutional units triads, and so on. In order of increasing sequence lengths they are called tetrads, pentads, hexads, heptads, octads, nonads, decads, undecads, etc.

2.1.2   constitutional homosequence
Constitutional sequence which contains constitutional units of only one species and in one sequential arrangement.

Example:

$$—CH(CH_3)\text{-}CH_2—CH(CH_3)\text{-}CH_2— \qquad \left[CH(CH_3)\text{-}CH_2\right]_6$$

In these two cases, the constitutional unit –CH(CH$_3$)–CH$_2$– can be called the constitutional repeating unit of the homosequence.

2.1.3   configurational sequence
Whole or part of a chain comprising one or more species of *configurational unit(s)* in defined sequence.
Note 1: See examples following Definition 1.23.
Note 2: Configurational sequences comprising two configurational units are termed diads, those with three such configurational units triads, and so on. In order of increasing sequence lengths they are called tetrads, pentads, hexads, heptads, octads, nonads, decads, undecads, etc.

2.1.4   stereosequence
Configurational sequence in which the relative or absolute configuration is defined at all sites of stereoisomerism in the main chain of a polymer molecule.

2.1.5   configurational homosequence
Constitutional homosequence 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.

2.1.6   stereohomosequence
Configurational homosequence in which the relative or absolute configuration is defined at all sites of stereoisomerism in the main chain of a polymer molecule.
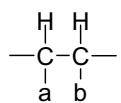
## 2.2   Description of Relative Configurations

erythro and threo structures
Relative configurations at two contiguous carbon atoms in main chains bearing, respectively, substituents a and b (a ≠ b), are designated by the prefix *erythro or threo,* as appropriate, by analogy with the terminology for carbohydrate systems [6] in which the substituents are –OH.
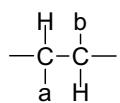
Examples:

```
   H  H                    H  b
   |  |                    |  |
 — C — C —              — C — C —
   |  |                    |  |
   a  b                    a  H
```
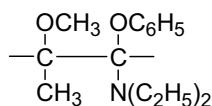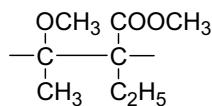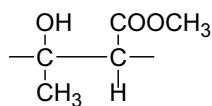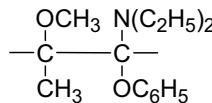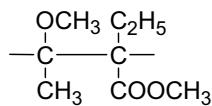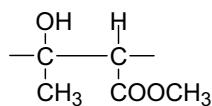
  erythro   *threo*

Similar systems in which a higher level of substitution exists may be treated analogously if the *erythro* or *threo* designation is employed to denote the relative placements of those two substituents, one for each backbone carbon atom, which rank highest according to the Sequence Rule. Thus, the following hypothetical examples would be designated as indicated:

Examples:

erythro

```
   OH     COOCH3
   |      |
 — C ———— C —
   |      |
   CH3    H
```

```
   OCH3   COOCH3
   |      |
 — C ———— C —
   |      |
   CH3    C2H5
```

```
   OCH3   OC6H5
   |      |
 — C ———— C —
   |      |
   CH3    N(C2H5)2
```

threo

```
   OH     H
   |      |
 — C ———— C —
   |      |
   CH3    COOCH3
```

```
   OCH3   C2H5
   |      |
 — C ———— C —
   |      |
   CH3    COOCH3
```

```
   OCH3   N(C2H5)2
   |      |
 — C ———— C —
   |      |
   CH3    OC6H5
```
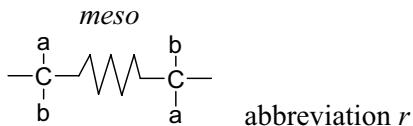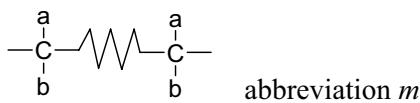
This novel extension of the *erythro/threo* terminology, especially its conjunction with the Sequence Rule, is specifically proposed solely to cope with the problems incurred in describing the steric structures of macromolecules.
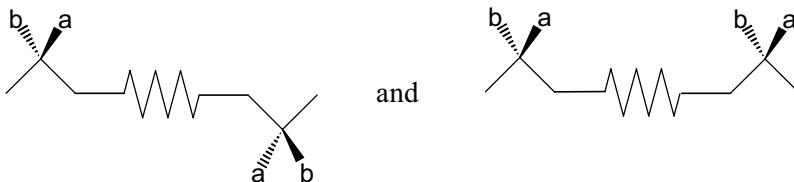
meso and racemo structures

Relative configurations of consecutive, but not necessarily contiguous, constitutionally equivalent carbon atoms that have a symmetrically constituted connecting group (if any) are designated as *meso* or *racemo*, as appropriate.


abbreviation *m*

meso

abbreviation *r*
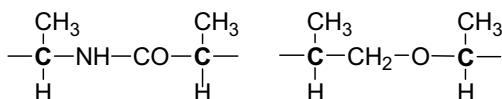
racemo

(The symbol –/\/\/– represents a symmetrically constituted connecting group, such as –CH_2–, –CH_2–CH_2–, or –CR_2–CH_2–CR_2–.)

Note: The structures

        and
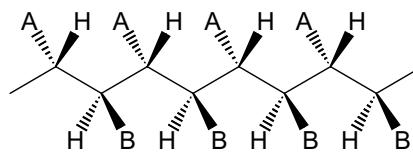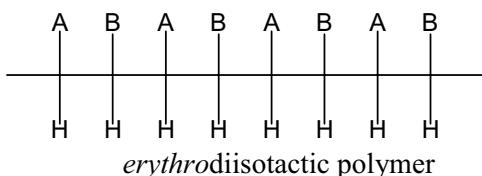
both have the *meso* relative configuration but the boldly printed carbon atoms in each of the formulae below cannot be considered as in a *meso* arrangement because the connecting group lacks the necessary symmetry.
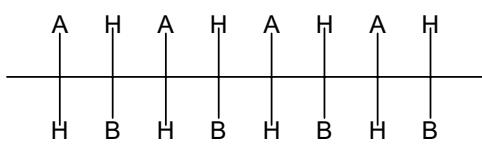

The term '*racemo*' is introduced here as the logical prefix for the designation of an arrangement that is analogous to racemic, in the sense defined above. It is unfortunate that the meaning of the term 'racemic' current in organic chemistry is not directly applicable to polymers, but the use of the prefix '*racemo*' proposed here should not cause confusion because of the special context. To achieve a full configurational description, it may be necessary to preface the name of a polymer with a compound adjective that combines a term such as *erythro*, *threo*, *meso* or *racemo* with a term such as 'diisotactic' or 'disyndiotactic'.
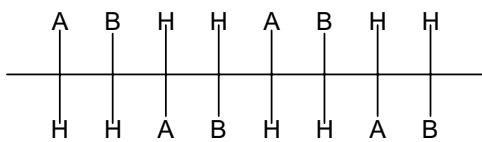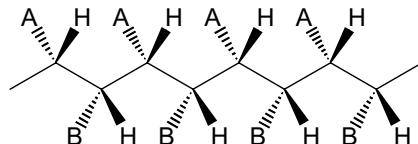
Examples:
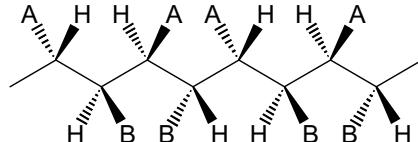

*erythro*diisotactic polymer
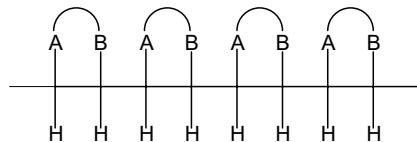
*threo*diisotactic polymer
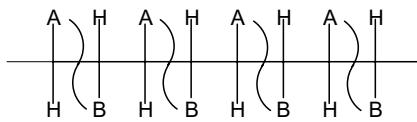
disyndiotactic polymer[*]

Polymers with chiral centres arising from rings linking adjacent main-chain carbon atoms can be included in this nomenclature:
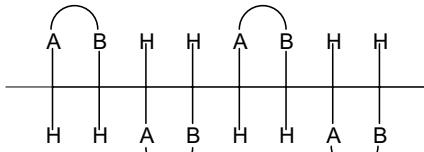

*erythro*diisotactic polymer
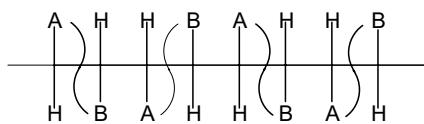
*threo*diisotactic polymer

In the last two cases, the chiralities of the asymmetric centres should be designated *R*- or *S*-, if known.
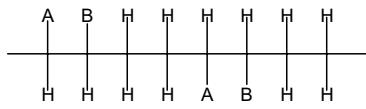

*erythro*disyndiotactic polymer
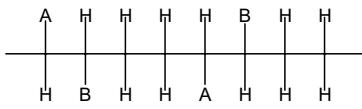
*threo*disyndiotactic polymer

---

[*] This polymer cannot be expressed as erythrodisyndiotactic or as threodisyndiotactic. Instead:
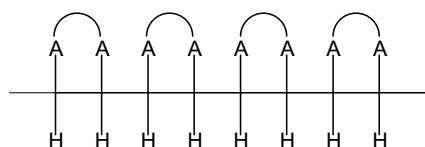

*erythro*disyndiotactic
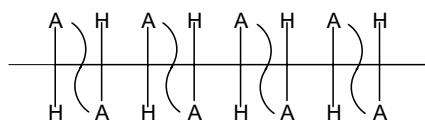
*threo*disyndiotactic

If the rings are symmetrical:

*meso*diisotactic
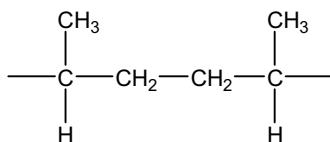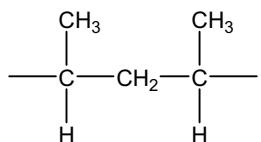
*racemo*diisotactic

Stereosequences
Stereosequences terminating in tetrahedral stereoisomeric centres at both ends, and which comprise two, three, four, five, etc., consecutive centres of that type, may be called diads, triads, tetrads, pentads, etc., respectively.
    Typical diads are:

When it is necessary to specify the internal stereochemistry of the group, a prefix is required. In vinyl polymers there are meso *(m)* and racemic *(r)* diads and *mm, mr, rr* triads. The latter may be called isotactic, heterotactic and syndiotactic triads, respectively. *Stereoregular* vinyl polymers can be defined in terms of the regular sequences of diads; thus an isotactic vinyl polymer consists entirely of *m* diads, i.e., it corresponds to the following succession of relative configuration -*mmmmmm-,* whereas a syndiotactic vinyl polymer consists entirely of *r* diads, corresponding to the sequence –*rrrrrrr-.* Similarly, a vinyl polymer consisting entirely of *mr (= rm)* triads is called a heterotactic polymer.


3   CONFORMATIONS
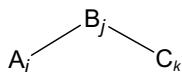
3.1   Designation of conformation of polymer molecules

Bond lengths
If a specific A–B bond is denoted as A_i–B_j, the bond length is written $b(A_i, B_j)$. Abbreviated notations, such as b_i, may be used if this meaning is clarified by a diagram.

Bond angles
The bond angle formed by three consecutive atoms
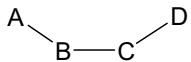
is written $\tau(A_i, B_j, C_k)$ which may be abbreviated, if there is no ambiguity, to $\tau(B_j)$, τ_j^B, $\tau B(j)$, or τ_j.

Torsion angles
If a system of four consecutive atoms

is projected onto a plane normal to bond B–C, the angle between the projection of A–B and the projection of C–D is described as the torsion angle of A and D about bond B–C; this angle may also be described as the angle between the plane containing A, B and C and the plane containing B, C and D. The torsion angle is written in full as $\theta\,(A_i, B_j, C_k, D_l,)$, which may be abbreviated, if there is no ambiguity, to $\theta\,(B_j, C_k)$, $\theta\,(B_j)$ or θ_j^B, etc. In the eclipsed conformation in which the projections of A–B and C–D coincide, θ is given the value 0° (synperiplanar conformation). A torsion angle is considered positive *(+θ)* or negative *(-θ)* depending on whether, when the system is viewed along the central bond in the direction B–C (or C–B), the bond to the front atom A (or D) requires the smaller angle of rotation to the right or to the left, respectively, in order that it may eclipse the bond to the rear atom D (or A); note that it is immaterial whether the system be viewed from one end or the other. According to this definition, a sequence of consecutive positive torsion angles generates a right-handed helix (Helix sense, p. 43). It is to be noted that:

1. torsion angles are measured in the range -180° < θ < + 180° rather than from 0° to 360°, so that the relationship between enantiomeric configurations or conformations can be readily appreciated;
2. any Greek letter from the end of the alphabet, except τ, can be used to denote torsion angles; θ or ω of are recommended;
3. abbreviated notations are preferably restricted to bond lengths, bond angles and torsion angles related to main-chain atoms.

Conformations referring to torsion angles θ (A, B, C, D), where A, B, C, D are main-chain atoms, can be described as: *cis* or *synperiplanar* (C); *gauche* or *synclinal* (G); *anticlinal* (A); and *trans* or *antiperiplanar* (T), corresponding to torsion angles within ±30° of, respectively, 0°, ±60°, ± 120° and ± 180°. The letters shown in parentheses (upper case C, G, A, T) are the recommended abbreviations.[*]
The symbols G^+, G^- (or A^+, A^-, for example) refer to torsion angles of similar type but opposite known sign, i.e., $\sim + 60°$, $\sim - 60°$ (or $\sim + 120°$, $\sim -120°$). The notation G, $\overline{G}$; A, $\overline{A}$; (and T, $\overline{T}$; C, $\overline{C}$ whenever the torsion angles are not exactly equal to 180º and 0º respectively) is reserved for the designation of enantiomorph conformations, i.e., conformations of opposite but unspecified sign. Where necessary, a deviation from the proper value of the torsion angle can be indicated by the sign ($\sim$), as in the following examples: G($\sim$); $\overline{G}$($\sim$); G^+($\sim$); G^-($\sim$).

Examples:

The chain conformation of isotactic polypropene in the crystalline state is:
... TGTGTGTG ...

_____

[*] Different authors variously use upper and lower case letters in this context. The desire for uniformity necessitates an arbitrary choice between the alternatives, and the upper case has been selected in the belief that it conflicts less with other designations, for example, the use of *c* and *t* in Section 3.2

The chain conformation of syndiotactic polypropene in the crystalline state is:
... TTGGTTGG ... or ... TTTTTTTT ...
The chain conformation of a right-handed α-helix is:
... G⁻G⁻(*trans*) G⁻G⁻(*trans*) ...
or ... G⁻(~)G⁻(~)(*trans*)G⁻(~)G⁻(~)(*trans*) ...

The *cis* and *trans* notation may be used to designate rigid dihedral angles such as those occurring with double bonds.
The chain conformation of crystalline poly(1,1-difluoroethene), modification 2, is:
... TGTG̅TGT ...
The chain conformation of crystalline poly[(*Z*)-1-methylbut-1-ene-1,4-diyl] in the α-form is:
... (*trans*) CTA(*trans*) CTA̅ ...
The chain conformation of isotactic vinyl polymers in the crystalline state is:
... T(~)G(~)T(~)G(~) ...
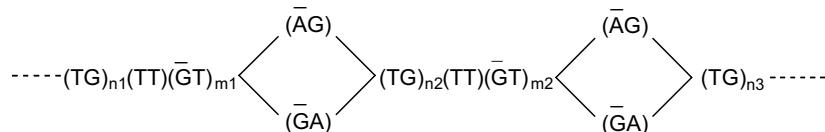
A possible conformation of isotactic polypropene in the melt can be described as:

3.2 Specific terminology for crystalline polymers
The crystallographic identity period parallel to the chain axis should preferably be designated *c* in descriptions of macromolecular crystallography.

In the description of helices, the following parameters and symbols should be employed: *n* signifies the number of conformational repeating units per turn (the conformational repeating unit in a crystalline polymer is the smallest unit of given conformation that is repeated through symmetry operations which comprise a translation. In most cases it corresponds to the *configurational repeating unit*); *h* signifies the unit height, i.e., the translation along the helix axis per conformational repeating unit; *t* signifies the unit twist, i.e., the angle of rotation about the helix axis per conformational repeating unit.

Examples:
If the number of conformational repeating units along the identity period *c* is *M* and the number of turns is *N,* then:

$n = M/N$
$h = c/M$
$t = 2\pi N/M$

For isotactic polypropene, since *M* = 3*, N* = 1 and *c* = 6.50 Å,

$n = 3$
$h = 2.17$ Å
$t = 2\pi/3$
For poly(oxymethylene), since *M* = 9*, N* = 5 and *c* =17.39 Å,

$n = 1.8$
$h = 1.93$ Å
$t = 2\pi(5/9)$.

Helix sense
The right-handed sense of a helix traces out a clockwise rotation moving away from the observer; the left-handed sense of a helix traces out an anticlockwise rotation moving away from the observer, e.g., the ...TG$^+$TG$^+$TG$^+$... helix of isotactic polypropene is left-handed.

Isomorphous and enantiomorphous structures
In the crystalline state, polymer chains are generally parallel to one another but neighbouring chains of equivalent conformation may differ in chirality and/or orientation.

Chains of identical chirality and conformation are *isomorphous*. Chains of opposite chirality but equivalent conformation are *enantiomorphous*.
Examples:
Two ...TG$^+$TG$^+$TG$^+$... helices of isotactic polypropene are isomorphous.

Isotactic polypropene chains of the ...TG$^+$TG$^+$TG$^+$... and ...G$^-$TG$^-$TG$^-$T... types are mutually enantiomorphous.

*Isoclined and anticlined structures*
With regard to orientation, consider a repeating side-group originating at atom A_1^i, the first atom of the side-group being B_α^i. For certain chain symmetries (helical, for instance) the bond vectors
$$\vec{b}(A_1^i, B_\alpha^i)$$
have the same components (positive or negative)
$$\vec{b} \cdot \vec{c} / |\vec{c}|$$
along the *c* axis for every *i*.
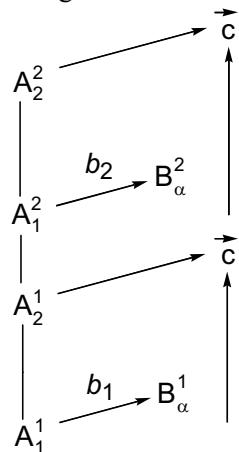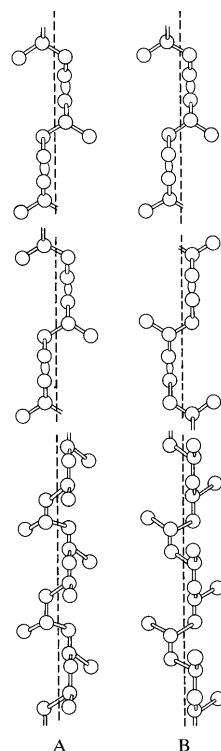
Two equivalent (isomorphous or enantiomorphous) chains in the crystal lattice, having identical components of the bond vectors along c, both positive or both negative, are designated *isoclined*; two equivalent chains having bond vectors along *c* of the same magnitude but opposite sign are designated *anticlined*.

Examples:
1. Isotactic poly[(*Z*)-3-methylbut-1-ene-1,4-diyl]

Isoclined isomorphous chains: the two chains have parallel axes and the same orientation of the pendant methyl groups.

Anticlined isomorphous chains: the two chains have parallel axes and opposite orientation of the pendant methyl groups.

2. Isotactic polypropene

Anticlined enantiornorphous chains: the conformation of A corresponds to a $(TG^-)_n$ bond succession (right-handed helix). The conformation of B corresponds to a $(G^+T)_n$ bond succession (left-handed helix).

A   B

Line repetition groups and symmetry elements
To designate linear chain conformations in the crystalline state, the use of line repetition groups [7] is recommended.

First symbol   t   translation
              s   screw repetition

[In this case of screw repetition, the number of conformational repeating residues per turn is included in parentheses, i.e.: s(11/3) or s(3.67 $\pm$ 0.02).]

Second and further symbols. The symmetry elements required to define the line repetition group are suggested in Reference [8]. Possible symmetry elements are:

i   centre of symmetry
m plane of symmetry perpendicular to the chain axis
c   glide plane parallel to the chain axis
d plane of symmetry parallel to the chain axis
2   two-fold axis of symmetry perpendicular to the chain axis

    The possible line repetition groups are listed below, with examples. (The structure-based name is given first, the source-based name second, in each case.)

Table 1. Chain symmetry of some crystalline polymers [9]

Line repetition group [a]	Polymer (source-based name, structure-based name)
t*l*	*trans*-1,4-polyisoprene, poly[(*E*)-2-methylbut-2-ene-1,4-diyl]]
s(A**M/N*)	isotactic polypropene, poly(1-methylethane-1,2-diyl) (*M/N*=3/1, A=2)
s(A**M/N*)2	syndiotactic polypropene, poly(1-methylethane-1,2-diyl) (*M/N*=2/l, A=4, helical modification)
t*m*	poly(heptane-1,7-diylheptanediamide), poly(iminoheptanedioyliminoheptane-1,7-diyl)
t*c*	poly(1,1-difluoroethene), poly(1,1-difluoroethane-1,2-diyl) (modification 2)
t*i*	diisotactic poly[ethene-*alt*-(*E*)-but-2-ene], diisotactic poly(1,2-dimethylbutane-1,4-diyl)
s(5*2/1)*m*	poly(cyclopentene), poly(cyclopentane-1,2-diyl)
s(14*2/1)*d*	poly(hexamethylene adipamide), poly(iminoadipoyliminohexane-1,6-diyl)
t*cm*	syndiotactic 1,2-polybuta-1,3-diene, poly(1-vinylethane-1,2-diyl)
s(1*2/1)*dm*	polyethene, poly(methylene), PE

[a] See the note, Definition 2.9 for explanation of symbols.

4   SUPPLEMENTARY DEFINITIONS

4.1   degrees of triad isotacticity, syndiotacticity and heterotacticity
Fractions of triads in a regular vinyl polymer that are of the *mm*, *rr* and *mr* = *rm* types, respectively.
Note: In cases where triad analysis is not attainable, the diad isotacticity and diad syndiotacticity may be defined as the fractions of diads in a regular-vinyl polymer that are of the *m* and *r* types, respectively.

4.2   degrees of cistacticity and transtacticity
For a regular polymer containing double bonds in the main chain of the constitutional repeating units, these are the fractions of such double bonds that are in the *cis* and *trans* configurations, respectively.

4.3   degree of crystallinity
Fractional amount of crystallinity in a polymer sample.

4.4   lateral order
Order in the side-by-side packing of the molecules of a linear polymer.

4.5   longitudinal order
Order in the atomic positions along the chains of a linear polymer.