2: Stereochemical Definitions and Notations Relating to Polymers (1980)

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 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 stereochemistry 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.
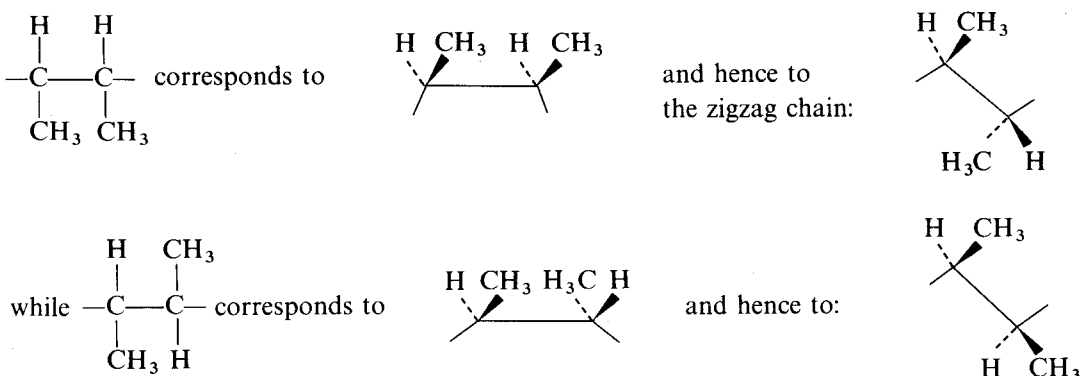
Throughout this document, stereochemical formulae for polymer chains are shown as Fischer projections rotated through 90° i.e. displayed horizontally rather than vertically, (at variance with [1]) or as hypothetical extended zigzag chains; the latter occasionally give a clearer indication of the three-dimensional arrangement. It is preferred that the hypothetical extended zigzag chains be consistently drawn with the backbone bond on the extreme left of the formula presented rising from left to right and with the interrupted line, on any given backbone carbon atom, drawn to the left of the full line.

The use of rotated Fischer projections corresponds to the common 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

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the plane of the paper from the carbon atom. Thus, the rotated Fischer projection

$$\begin{array}{cc} H & H \\ | & | \\ -C\!-\!\!-\!C- \\ | & | \\ CH_3 & CH_3 \end{array}$$
corresponds to

and hence to the zigzag chain:

$$\begin{array}{cc} H & CH_3 \\ | & | \\ -C\!-\!\!-\!C- \\ | & | \\ CH_3 & H \end{array}$$
while corresponds to

and hence to:

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 30 and 34), or of cis or trans 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

$$-\!\!\left[CH\!-\!CH_2\right]\!CH\!-\!CH_2\!-\!CH\!\left[CH_2\!-\!CH\right]\!CH_2\!- \\ \quad\;\; |\qquad\quad |\qquad\quad\; |\qquad\quad |\\ \quad\;\; R\qquad\quad R\qquad\quad R\qquad\quad R$$
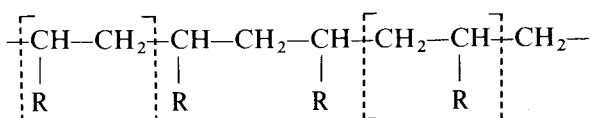
are regarded as different, even though the repetition of either one of them would give the same regular polymer. Some of the definitions presented also appear in a previous paper of this Commission [2], but they are repeated here (with minor grammatical improvement) in order to provide a complete set 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.

1 BASIC DEFINITIONS

Term	Definition
1.1 configurational unit	A constitutional unit having one or more sites of defined stereoisomerism.

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| *Term*	*Definition*
1.2 configurational base unit	A constitutional repeating unit, the configuration of which is defined at one or more sites of stereoisomerism in the main chain of a polymer molecule.

In a regular polymer, a configurational base unit corresponds to the constitutional repeating unit.

1.3 configurational repeating unit	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.
1.4 stereorepeating unit	A configurational repeating unit having defined configuration at all sites of stereoisomerism in the main chain of a polymer molecule.

*Note on enantiomeric and diastereoisomeric units*

Two configurational units (Definitions 1.1, 1.2, 1.3, 1.4 above) 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 *diastereoisomeric* if they are not mirror images.

Examples

In the regular polymer molecule $-[CH(CH_3)-CH_2]_n-$, poly(propylene), the constitutional repeating unit is $-CH(CH_3)-CH_2-$ and the corresponding configurational base units are
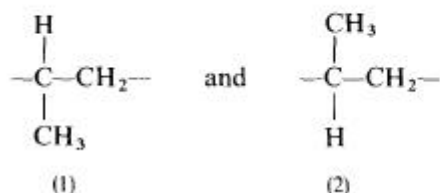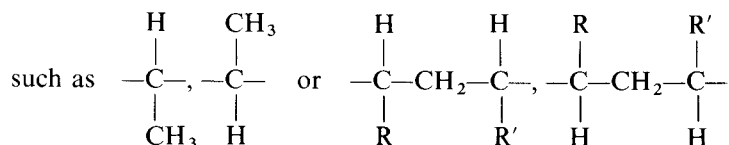

The configurational base units (1) and (2) are enantiomeric, while the configurational units (1) and (3) cannot be enantiomeric because the constitutional units are different species, according to this nomenclature.
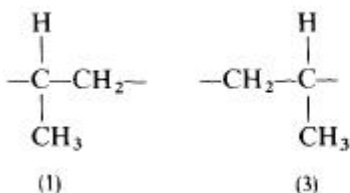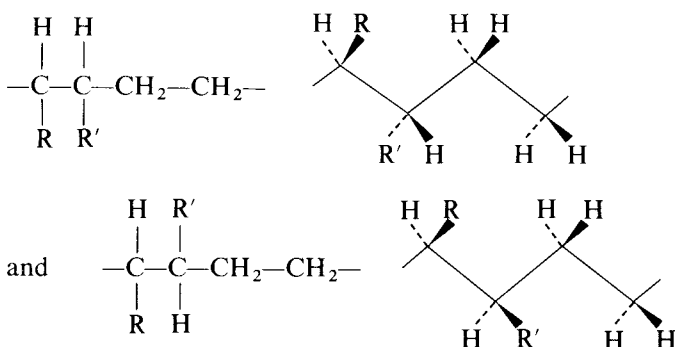

It is immaterial whether (1) or (2) is taken as the configurational repeating unit and stereorepeating unit of isotactic poly(propylene) (see Definition 1.7); this is so because the two infinite chains, one built up of identical configurational units (1) and the other built up of identical configurational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

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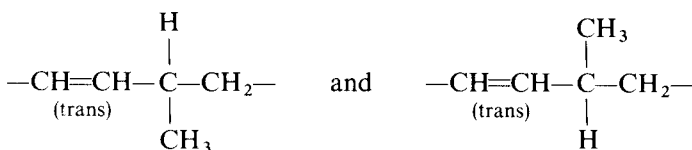each pair of units,

$$\text{such as } -\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-,\ -\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\quad \text{or}\quad -\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-,\ -\overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-$$
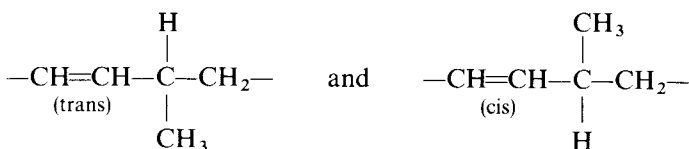
the components are enantiomeric since they are non-superposable mirror images, as defined above. However, with the constitutional unit $-CHR-CHR'-CH_2-CH_2-$, the two corresponding configurational units
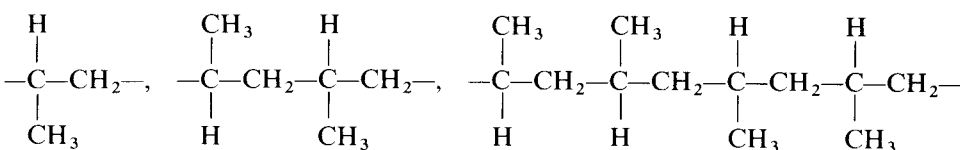
$$-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}}-CH_2-CH_2-$$

$$\text{and}\quad -\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-\overset{\overset{\displaystyle R'}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-CH_2-$$

are diastereoisomeric. The units

$$-CH{=}CH-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-CH_2-\quad\text{and}\quad -CH{=}CH-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-$$
$$\text{(trans)}\qquad\qquad\qquad\text{(trans)}$$

are enantiomeric, while the units

$$-CH{=}CH-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-CH_2-\quad\text{and}\quad -CH{=}CH-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-CH_2-$$
$$\text{(trans)}\qquad\qquad\qquad\text{(cis)}$$
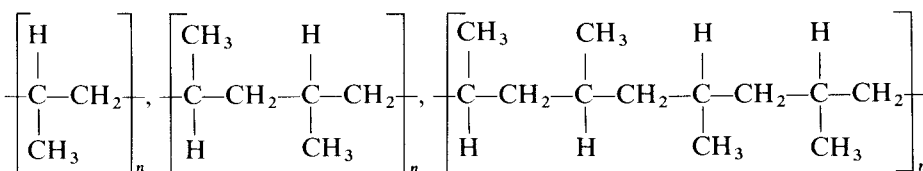
are not enantiomeric, but diastereoisomeric. The simplest possible stereorepeating units in a stereoregular poly(propylene) are

$$-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-,\quad -\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-,\quad -\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-$$

and the corresponding stereoregular polymers are

$$\left[\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2\right]_n,\quad \left[\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2\right]_n,\quad \left[\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-CH_2\right]_n$$

(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

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Term	Definition
1.5 tactic polymer	A regular polymer, the molecules of which can be described in terms of only one species of configurational repeating unit in a single sequential arrangement.
1.6 tacticity	The orderliness of the succession of configurational repeating units in the main chain of a polymer molecule. (For the definition of degree of tacticity, see Section 4)
1.7 isotactic polymer	A regular polymer, the molecules of which 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. *Note* In an isotactic polymer, the configurational repeating unit is identical with the configurational base unit.
1.8 syndiotactic polymer	A regular polymer, the molecules of which can be described in terms of alternation of configurational base units that are enantiomeric. *Note* In a syndiotactic polymer, the configurational repeating unit consists of two configurational base units that are enantiomeric.
1.9 stereoregular polymer	A regular polymer, the molecules of which can be described in terms of only one species of stereorepeating unit in a single sequential arrangement.
1.10 atactic polymer	A 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).

(7)   (8)
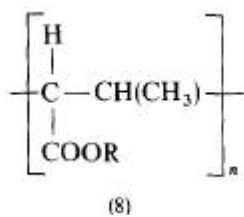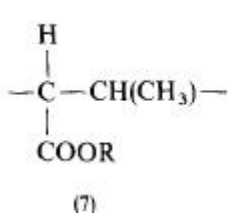
In the corresponding syndiotactic case, the configurational repeating unit is (9) and the

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syndiotactic polymer is (10):

$$
\begin{array}{cc}
\text{H} & \text{COOR} \\
| & | \\
-\text{C}-\text{CH(CH}_3)-\text{C}-\text{CH(CH}_3)- \\
| & | \\
\text{COOR} & \text{H}
\end{array}
\qquad
\left[
\begin{array}{cc}
\text{H} & \text{COOR} \\
| & | \\
-\text{C}-\text{CH(CH}_3)-\text{C}-\text{CH(CH}_3)- \\
| & | \\
\text{COOR} & \text{H}
\end{array}
\right]_n
$$

(9)   (10)
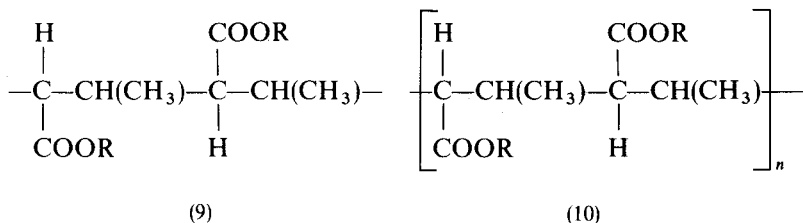
As the definition of a stereoregular polymer (see Definitions 1.4 and 1.9) requires that the configuration be defined at all sites of stereoisomerism, structures (8) and (10) do not represent stereoregular polymers. The same is true of (11) and (12), which differ from (8) and (10) in that the sites of specified and unspecified configuration have been interchanged.

$$
\left[
\begin{array}{c}
\text{H} \\
| \\
-\text{CH(COOR)}-\text{C}- \\
| \\
\text{CH}_3
\end{array}
\right]_n
\qquad
\left[
\begin{array}{cc}
\text{H} & \text{CH}_3 \\
| & | \\
-\text{CH(COOR)}-\text{C}-\text{CH(COOR)}-\text{C}- \\
| & | \\
\text{CH}_3 & \text{H}
\end{array}
\right]_n
$$

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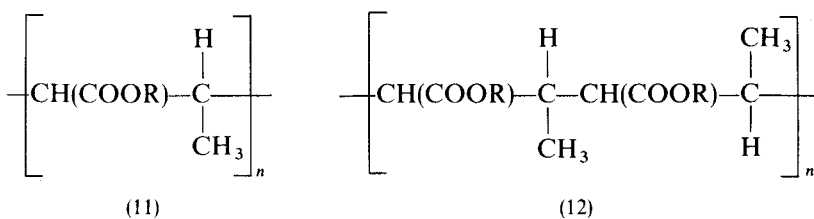
Examples (4), (5), (6), (8), (10), (11) and (12) are tactic polymers. A stereoregular polymer is always a tactic polymer, but a tactic polymer is not always stereoregular because a tactic polymer need not have all sites of stereoisomerism defined.

Further examples of tactic polymers are:

$$
\left[
\begin{array}{c}
\text{CH}_3 \\
| \\
-\text{O}-\text{C}-\text{CH}_2- \\
| \\
\text{H}
\end{array}
\right]_n
$$
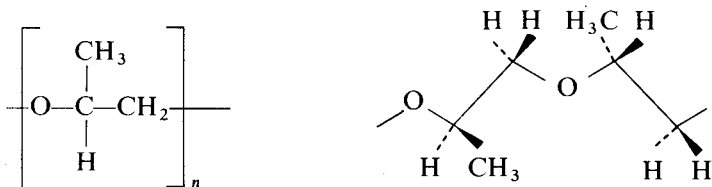
isotactic poly(oxypropylene)

$$
\left[
\begin{array}{c}
\text{CH}_3 \\
| \\
-\text{C}- \\
| \\
\text{H}
\end{array}
\right]_n
$$

isotactic poly(ethylidene)

$$
\left[
\begin{array}{cc}
\text{CH}_3 & \text{H} \\
| & | \\
-\text{C}-\text{C}- \\
| & | \\
\text{H} & \text{CH}_3
\end{array}
\right]_n
$$

syndiotactic poly(ethylidene)

30
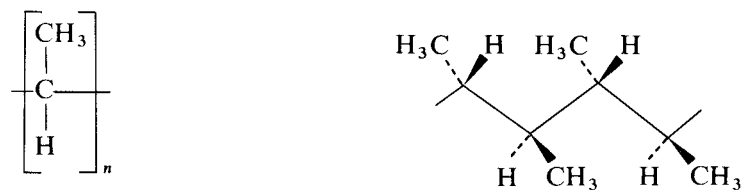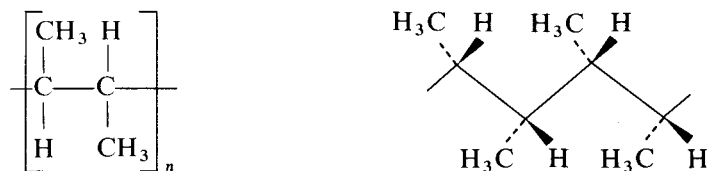
Note

Structure-based names of tactic polymers are formed before the application of adjectives designating tacticity; thus, 'syndiotactic poly(ethylidene)' is preferred to 'syndiotactic poly(1,2-dimethylethylene)' because a shorter repeating unit is identified, in conformity with the rules in Reference [3].

Note on atactic polymers

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)
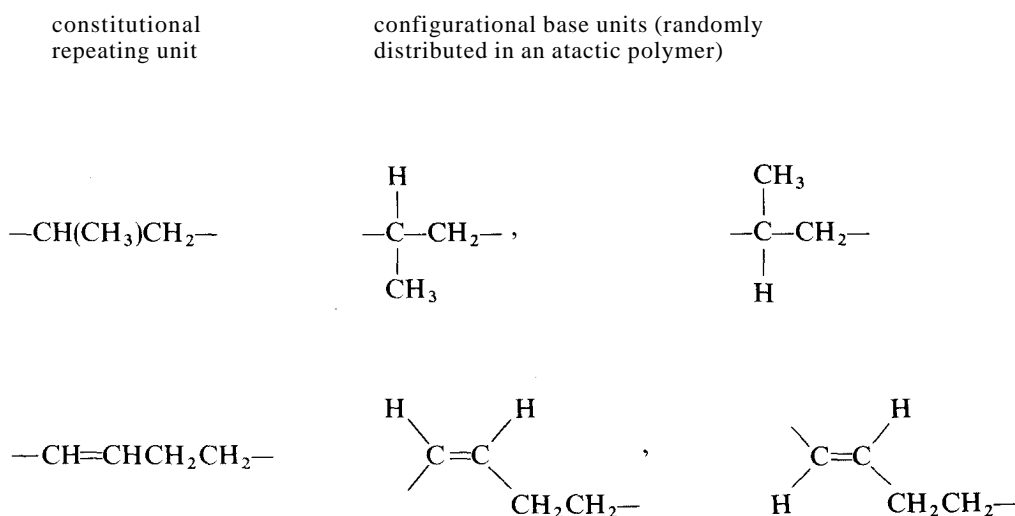
A polymer such as $+CH=CH-CH(CH3)-CH2+_n$, which has two main-chain sites of stereoisomerism, may be atactic with respect to the double bond only, with respect to the chiral atom only or with respect to both centres of stereoisomerism. If there is a random distribution of equal numbers of units in which 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.

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*With regard to isomerism about double bonds, it is recommended that the *E* and *Z* designations [4] be used, where appropriate, in describing side-chain configurations and in the names of monomers used in source-based polymer nomenclature. In structure-based polymer names and in descriptions of configuration about double bonds in polymer main chains, the use of cis and trans is preferred.

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DEFINITIONS

Term	Definition
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. D-propylene oxide (D-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 D- and L-propylene oxide molecules is so classified.
1.12 ditactic polymer	A tactic polymer that contains two sites of defined stereoisomerism in the main chain of the configurational base unit.
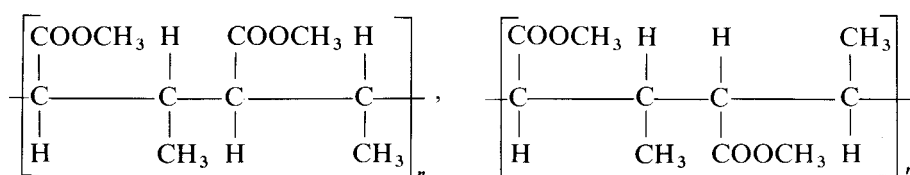
Examples

are both ditactic.

Term	Definition
1.13 tritactic polymer	A tactic polymer that contains three sites of defined stereoisomerism in the main chain of the configurational base unit.

Example
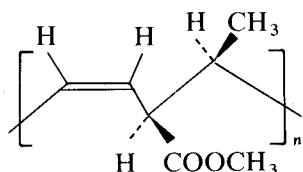
poly[3-(methoxycarbonyl)-4-methyl-*cis*-1-butenylene]

Term	Definition
1.14 diisotactic polymer	An 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	A syndiotactic polymer that contains two chiral or prochiral atoms with defined stereochemistry in the main chain of the configurational base unit.

Examples

Diisotactic

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$$\left[\begin{array}{cccc} \overset{\displaystyle COOCH_3}{\underset{\displaystyle H}{|}} & \overset{\displaystyle H}{\underset{\displaystyle CH_3}{|}} & \overset{\displaystyle H}{\underset{\displaystyle COOCH_3}{|}} & \overset{\displaystyle CH_3}{\underset{\displaystyle H}{|}} \\ -C\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-C\!\!-\!\!-C\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-C\!\!- \end{array}\right]_n$$
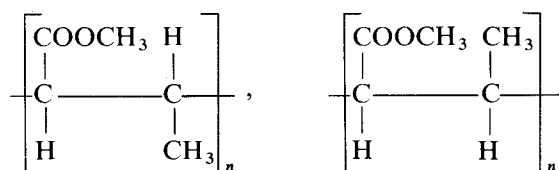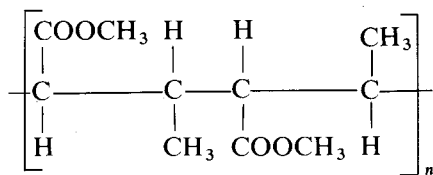
disyndiotactic*

A polymer with the repeating unit

$$-CH\!=\!CH\!-\!\overset{\displaystyle CH_3}{\underset{\displaystyle H}{C}}\!-\!CH_2\!-\!CH\!=\!CH\!-\!\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C}}\!-\!CH_2-$$
(cis)   (cis)
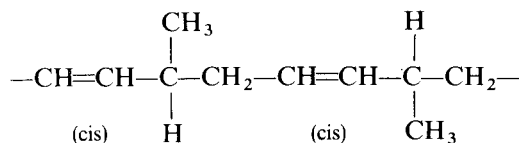
is ditactic and may be described as syndiotactic (see Definition 1.8), but it is not disyndiotactic.

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).

Term	Definition
1.16 cistactic. polymer	A tactic polymer in which the main-chain double bonds of the configurational base units are entirely in the cis arrangement.
1.17 transtactic polymer	A tactic polymer in which the main-chain double bonds of the configurational base units are entirely in the trans arrangement.

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.

Note
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(3-methyl-trans-l-butenylene)
transisotactic poly(3-methyl-l-butenyllene)†

and/or

$$^*\left[\begin{array}{cccc} \overset{\displaystyle COOCH_3}{\underset{\displaystyle H}{|}} & \overset{\displaystyle CH_3}{\underset{\displaystyle H}{|}} & \overset{\displaystyle H}{\underset{\displaystyle COOCH_3}{|}} & \overset{\displaystyle H}{\underset{\displaystyle CH_3}{|}} \\ -C\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-C\!\!-\!\!-C\!\!-\!\!\!-\!\!\!-\!\!\!-\!\!\!-C\!\!- \end{array}\right]_n$$ does *not* represent a different disyndiotactic polymer.

†Structure-based name; either may be used.

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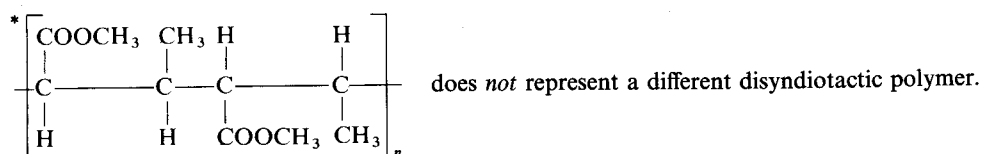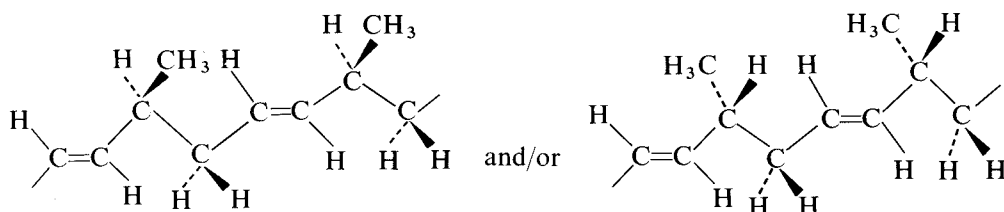
diisotactic poly[*threo*-3-(methoxycarbonyl)-4-methyl-*trans*-1-butenylene]
transthreodiisotactic poly[3-(methoxycarbonyl)-4-methyl-1-butenylene]*
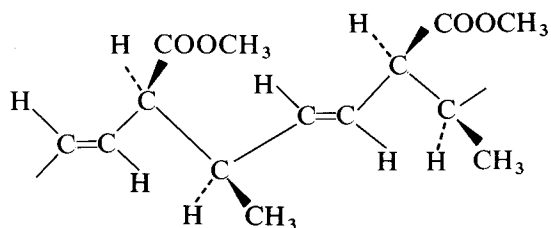
and/or
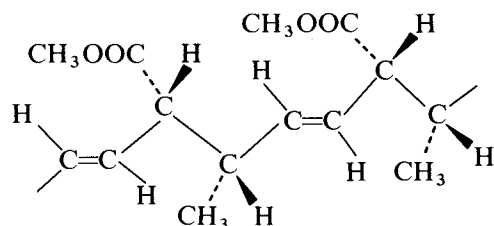
Term	*Definition*
1.18 block	A portion of a polymer molecule, comprising many constitutional units, that has at least one constitutional or configurational feature which is not present in the adjacent portions.
1.19 tactic block	A regular block that can be described by only one species of configurational repeating unit in a single sequential arrangement.
1.20 atactic block	A regular block that has equal numbers of the possible configurational base units in a random sequence distribution.
1.21 stereoblock	A regular block that can be described by one species of stereorepeating unit in a single sequential arrangement.
1.22 tactic block polymer	A polymer, the molecules of which consist of tactic blocks connected linearly.
1.23 stereoblock polymer	A polymer, the molecules of which consist of stereoblocks connected linearly.

Examples
Tactic block polymer

$$-A_k-B_l-A_m-B_n-$$
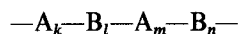
where A and B are, for example,

(A)   (B)
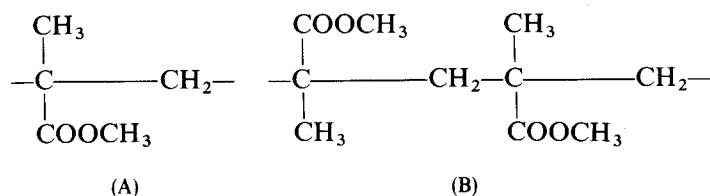
*Structure-based name; either may be used.

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 following example of a regular poly(propylene) 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 (see Definitions 1.21 and 2.1.3).
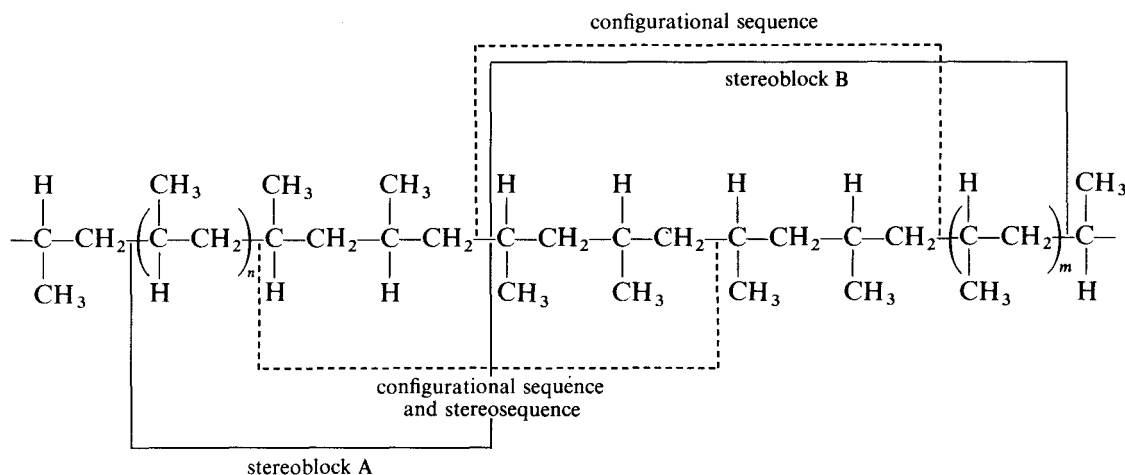
The configurational sequence and stereosequence coincide in this particular case because there is only one site of stereoisomerism in each constitutional repeating unit (compare Definitions 2.1.3 and 2.1.4).

2 SEQUENCES

2.1 Constitutional and configurational sequences

The description of polymer structure revealed by studies of physical properties focuses attention on the distribution of local arrangements present in the molecules, and terms useful in this context are defined below. (The terms defined here in relation to complete polymer molecules can also be applied to sequences and to blocks, as in Reference [2], Definition 3.14.)

Term	Definition
2.1.1 constitutional sequence	A defined portion of a polymer molecule comprising constitutional units of one or more species.

Example

$$-CH_2-CH_2-CH_2-CH(CH_3)- \quad -CH_2-CH(CH_3)-CH_2-CH(CH_3)-$$
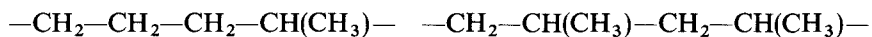
Term	Definition
2.1.2 constitutional homosequence	A constitutional sequence which contains constitutional units of only one species and in one sequential arrangement.

Example

$$-CH(CH_3)-CH_2-CH(CH_3)-CH_2- \quad -[CH(CH_3)-CH_2]_6$$

35
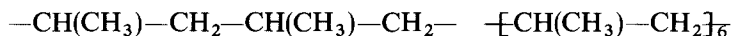
In these two cases, the constitutional unit $-CH(CH_3)-CH_2-$ can be called the constitutional repeating unit of the homosequence.

Term	Definition
2.1.3 configurational sequence	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. (See example following Definition 1.23)
2.1.4 stereosequence	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.
2.1.5 configurational homosequence	A 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	A 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
The relative configuration at two contiguous carbon atoms in the main chain bearing, respectively, substituents a and b (a≠b), is designated by the prefix 'erythro' or 'threo', as appropriate, by analogy with the terminology for carbohydrate systems* in which the substituents are –OH.

Examples

```
    H   H
    |   |
 —C———C——
    |   |
    a   b
```

erythro

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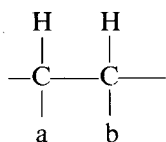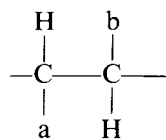
threo

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

*See Rule 4.11 of Reference [4].

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Rule. Thus, the following hypothetical examples would be designated as indicated:

Examples

erythro

$$\begin{array}{c} OH \\ | \\ -C- \\ | \\ CH_3 \end{array} \begin{array}{c} COOCH_3 \\ | \\ C- \\ | \\ H \end{array}$$

$$\begin{array}{c} OCH_3 \\ | \\ -C- \\ | \\ CH_3 \end{array} \begin{array}{c} COOCH_3 \\ | \\ C- \\ | \\ C_2H_5 \end{array}$$

$$\begin{array}{c} OCH_3 \\ | \\ -C- \\ | \\ CH_3 \end{array} \begin{array}{c} OC_6H_5 \\ | \\ C- \\ | \\ N(C_2H_5)_2 \end{array}$$

threo

$$\begin{array}{c} OH \\ | \\ -C- \\ | \\ CH_3 \end{array} \begin{array}{c} H \\ | \\ C- \\ | \\ COOCH_3 \end{array}$$

$$\begin{array}{c} OCH_3 \\ | \\ -C- \\ | \\ CH_3 \end{array} \begin{array}{c} C_2H_5 \\ | \\ C- \\ | \\ COOCH_3 \end{array}$$

$$\begin{array}{c} OCH_3 \\ | \\ -C- \\ | \\ CH_3 \end{array} \begin{array}{c} N(C_2H_5)_2 \\ | \\ C- \\ | \\ OC_6H_5 \end{array}$$
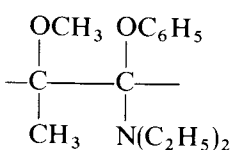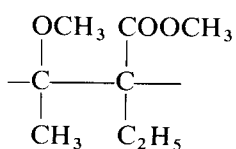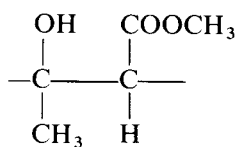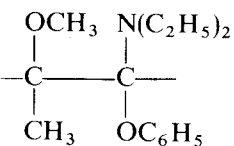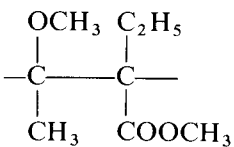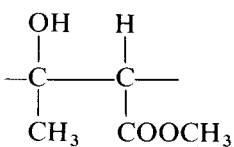
This novel extension of the erythro/threo terminology, especially its conjunction with the Sequence Rule, is specifically proposed solely to cope with the problems incurred in describing the steric structures of macromolecules.

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.

Examples

$$\begin{array}{c} a \\ | \\ -C-\wedge\wedge\wedge-C- \\ | \qquad\qquad | \\ b \qquad\qquad b \end{array} \qquad \begin{array}{c} a \\ | \\ \\ \\ \end{array}$$

abbreviation *m*

meso

DEFINITIONS

abbreviation *r*
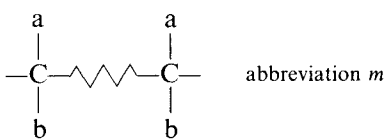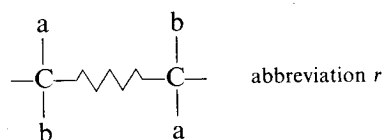
racemo

(The symbol —$\wedge\wedge\wedge$— 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
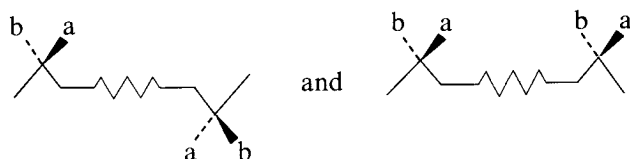
both have the meso relative configuration but the boldly printed carbon atoms in each of the formulae below cannot be considered as in a meso arrangement because the connecting group lacks the necessary symmetry.
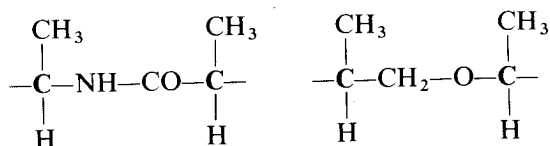

The term 'racemo' is introduced here as the logical prefix for the designation of an arrangement that is analogous to racemic, in the sense defined above. It is unfortunate that the meaning of the term 'racemic' current in organic chemistry is not directly applicable to polymers, but the use of the prefix '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 'racerno' with a term such as 'diisotactie' or 'disyndiotactic'.

Examples

erythrodiisotactic polymer

threodiisotactic polymer

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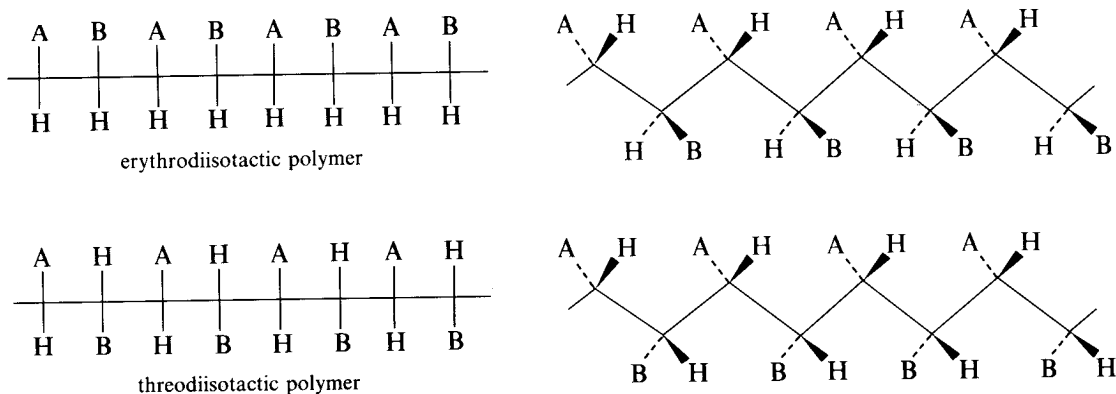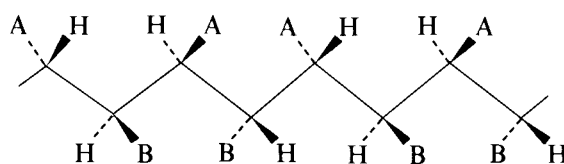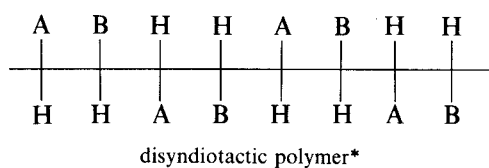
Polymers with chiral centres arising from rings linking adjacent main-chain carbon atoms can be included in this nomenclature:

erythrodiisotactic polymer

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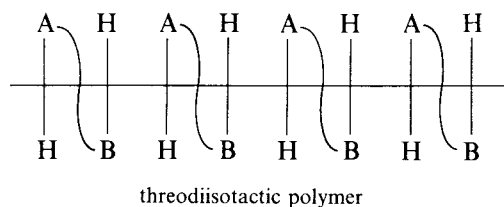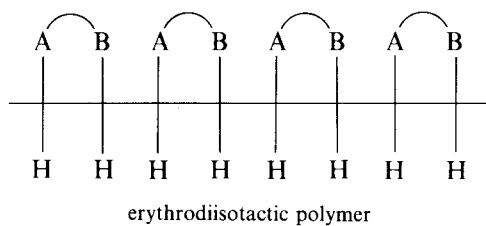
In the last two cases, the chiralities of the asymmetric centres should be designated R- or S-, if known.

erythrodisyndiotactic polymer
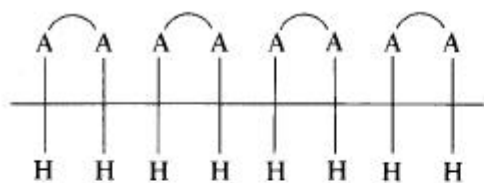

threodisyndiotactic polymer
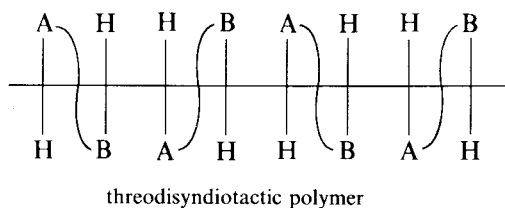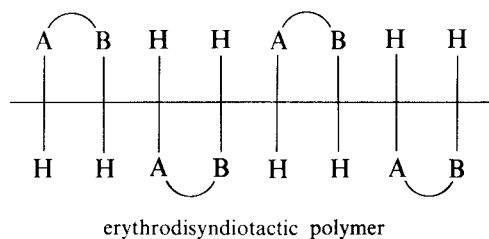
*This polymer cannot be expressed as erythrodisyndiotactic nor as threodisyndiotactic.

erythrodisyndiotactic

threodisyndiotactic

39
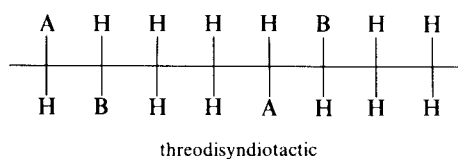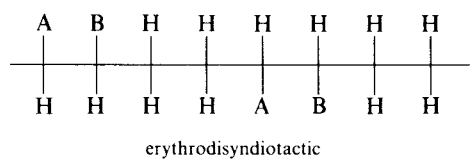
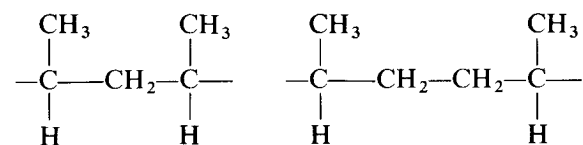If the rings are symmetrical:

mesodiisotactic

racemodiisotactic

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 mesc, *(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 *-m m m m m m-,* whereas a syndiotactic vinyl polymer consists entirely of *r* diads, corresponding to the sequence *-r r r r r r-.* Similarly, a vinyl polymer consisting entirely of *mr (=rm)* triads is called a heterotactic polymer.
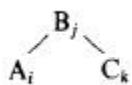
3 CONFORMATIONS

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.
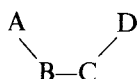
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Bond angles

is written $\tau(A_i, B_j, C_k)$ which may be abbreviated, if there is no ambiguity, to $\tau(B_j)$, $\tau_j{}^B$, $\tau B(j)$ 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 $q(A_i, B_j, C_k, D_l,)$, which may be abbreviated, if there is no ambiguity, to $q(B_j, C_k)$, $q(B_j)$ or $q_j{}^B$, etc. In the eclipsed conformation in which the projections of A–B and C–D coincide, q is given the value 0° (synperiplanar conformation). A torsion angle is considered positive *(+q)* or negative *(-q)* 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° < q < + 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 ô, can be used to denote torsion angles; q or w 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 $q(A, B, C, D)$, 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. ~ + 60°, ~ – 60° (or ~ + 120°, ~ –120°). The notation G, $\bar{G}$; A, $\bar{A}$; (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 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 (~), as in the following examples: G(~); $\bar{G}$ (~); G^+(~); G^-(~).

*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* on pages 42 and 43.

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Examples

The chain conformation of isotactic poly(propylene) in the crystalline state is:

... TGTGTGTG ...

The chain conformation of syndiotactic poly(propylene) 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 symbols (cis) and (trans) may be used to designate rigid dihedral angles such as those occurring with double bonds.

The chain conformation of crystalline poly(l, 1-difluoroethylene), modification 2, is:

... TGT$\bar{G}$ TGT$\bar{G}$ ...

The chain conformation of crystalline poly(*trans*- 1 -methyl- 1 -butenylene) in the á-form is:

... (trans) CTA(trans) CT$\bar{A}$ ...

The chain conformation of isotactic vinyl polymers in the crystalline state is:

... T(~)G(~)T(~)G(~) ...

A possible conformation of isotactic poly(propylene) in the melt can be described as:
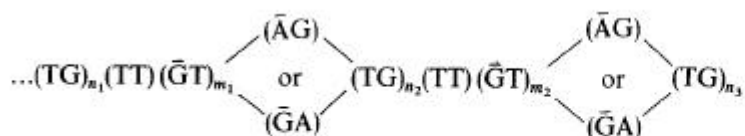
3.2 Specific terminology for crystalline polymers

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:

$n = M/N$

$h = c/M$

$t = 2\pi N/M$

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For isotactic poly(propylene), 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 poly(propylene) 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 poly(propylene) are isomorphous.

Isotactic poly(propylene) chains of the ...TG⁻TG⁺TG⁺... and ...G⁻TG⁻TG⁻T ... types are mutually enantiomorphous.
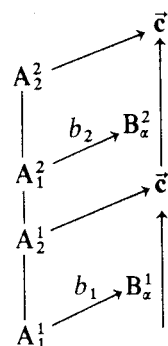
Isoclined and anticlined structures
With regard to orientation, consider a repeating side group originating at atom $A_1{}^i$, the first atom of the side group being $B_\alpha{}^i$. For certain chain symmetries (helical, for instance) the bond vectors

$$\vec{b}(A_1^i, B_\alpha^i)$$

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
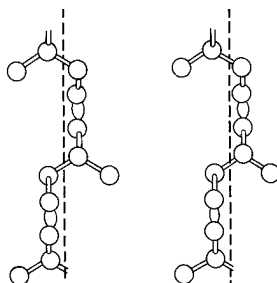
DEFINITIONS

isoclined; two equivalent chains having bond vectors along *c* of the same magnitude but opposite sign are designated *anticlined*.
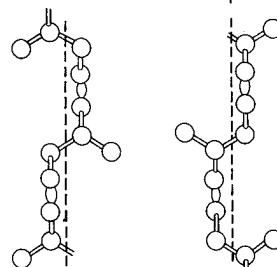
Examples

1. Isotactic poly(3-methyl-*cis*-l-butenylene)

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 poly(propylene)

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
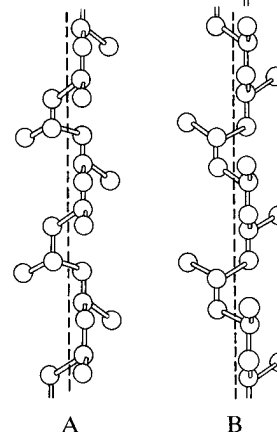
Line repetition groups and symmetry elements
To designate linear chain conformations in the crystalline state, the use of line repetition groups [6] is recommended.

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(ll/3) or s(3.67 ± 0.02).]

Second and further symbols. The symmetry elements required to define the line repetition group are suggested in Reference [7]. Possible symmetry elements are:

i centre of symmetry
m plane of symmetry perpendicular to the chain axis

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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 process-based name second, in each case.)

Table 2.1 Chain symmetry of some crystalline polymers

Line repetition group	Polymer
t1	poly(1-methyl-*trans*-l-butenylene)
	trans- 1,4-polyisoprene
s(*M/N*)1	isotactic poly(propylene) (*M/N*=3/1)
	isotactic polypropene (*M/N*=3/1)
s(*M/N*)2	syndiotactic poly(propylene) (*M/N*=2/1) (helical modification)
	syndiotactic polypropene (*M/N*=2/1) (helical modification)
t*m*	Poly[imino(1,7-dioxoheptamethylene)iminoheptamethylene]
	poly(heptamethylene pimelamide)
t*c*	Poly(1,1-difiuoroethylene) (modification 2)
	Poly(1,1-difluoroethylene) (modification 2)
t*i*	Diisotactic poly(1,2-dimethyltetramethylene)
	diisotactic alternating copolymer of ethylene and *cis*-2-butene
s(2/1)*m*	poly(1-pentenylene)
	poly(cyclopentene)
s(2/1)*d*	poly(iminoadipoyliminohexamethylene)
	poly(hexamethylene adipamide)
t*dm*	—
t*id*	—
t*cm*	syndiotactic poly(1-vinylethylene)
	syndiotactic 1,2-poly(1,3-butadiene)
s(2/1)*dm*	poly(methylene)
	polyethylene

4 SUPPLEMENTARY DEFINITIONS*

Term		*Definition*
4.1	degrees of triad isotacticity, syndiotacticity and heterotacticity	The fractions of triads in a regular vinyl polymer that are of the *mm, rr* and *mr=rm* types, respectively. 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.

*Tacticity in side chains will be treated in a later document.

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Term	Definition
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	This is defined as the fraction of the bulk polymer that consists of regions showing long-range three-dimensional order.
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.

REFERENCES

1 M.L. Huggins, G. Natta, V. Desreux and H. Mark (for IUPAC Commission on Macromolecules). Report on nomenclature dealing with steric regularity in high polymers. *J. Polym. Sci.* **56**, 153-161 (1962); *Pure Appl. Chem.* **12**, 643-656 (1966).

2 IUPAC. Basic definitions of terms relating to polymers 1974. *Pure Appl. Chem.* **40**, 477-491 (1974). Reprinted as Chapter 1, this volume.

3 IUPAC. Nomenclature of regular single-strand organic polymers (rules approved 1975). *Pure Appl. Chem.* **48**, 373-385 (1976). Reprinted as Chapter 5, this volume.

4 IUPAC. Rules for the nomenclature of organic chemistry. Section E: stereochemistry (recommendations 1974). *Pure Appl. Chem.* **45**, 11 (1976).

5 IUPAC-IUB. Abbreviations and symbols for the description of the conformation of polypeptide chains (rules approved 1974). *Pure Appl. Chem.* **40**, 291-308 (1974).

6 A. Klug, F.AC Crick and H.W. Wyckoff. *Acta Crystallogr.* **11**, 199 (1958).

7 P. Corradini. Chain conformation and crystallinity. In *Stereochemistry of Macromolecules* (Ed. A. Ketley). Marcel Dekker, New York, Part III, 1-60 (1968).