

REPORT ON NOMENCLATURE
DEALING WITH STERIC REGULARITY
IN HIGH POLYMERS

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Commission on Macromolecules*

PHYSICAL CHEMISTRY DIVISION

COMMISSION ON MACROMOLECULES

REPORT ON NOMENCLATURE DEALING WITH STERIC REGULARITY IN HIGH POLYMERS

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This report is an extension of the *Report on Nomenclature in the Field of Macromolecules*⁶, approved by the International Union of Pure and Applied Chemistry, September 15, 1951. It is based, to a considerable extent, on proposals of Natta and Danusso⁷ and Natta, Farina, and Peraldo⁸.

GENERAL IDEAS AND DEFINITIONS

We are concerned with the designation of steric regularity in high polymers—especially head-to-tail linear polymers. Difference in conformation between molecular structures, such that any one could hypothetically be transformed into any other by mere rotation around single bonds, are neglected. Moreover, although the terminology to be proposed is based on ideal structures (without chemical irregularities and neglecting chain ends), it will be understood to be applicable to real polymers substantially conforming to the definitions and rules presented.

Certain types of structures in a chain molecule permit alternative steric arrangements, hence isomerism. For example, steric isomerism results when two different atoms or groups (R, R') are attached (tetrahedrally) to a chain atom (C), if the two parts of the main chain which are attached to that atom are structurally non-equivalent (neglecting conformational differences):



Likewise, *cis-trans* isomerism can occur whenever a C=C double bond is incorporated in the chain:



* The authors constitute a subcommittee of the Commission on Macromolecules of the International Union of Pure and Applied Chemistry. This report, a modification of a preliminary version already published¹, was approved by the Commission on July 2, 1963. Correspondence concerning it should be addressed to Dr. M. L. Huggins, Stanford Research Institute, Menlo Park, California 94025, U.S.A. Italian², German³, French⁴ and Japanese⁵ translations of this report have been published.

Other types of isomerism occur when ring structures are incorporated in the chain. The same types of structure, leading to isomerism, can, of course, be present in side chains, but the classification of stereoregular polymers in this report is concerned only with steric isomerism in the main chains.

Asymmetric chain atoms, double bonds, rings of appropriate types, *etc.*, can be designated *sites of steric isomerism*. The *conventional base unit* of the polymer (defined with neglect of steric isomerism) may contain one or more sites of steric isomerism in the chain.

Steric order in the main chain can also be designated as *tacticity*. A *tactic polymer* is one in which there is an ordered structure with respect to the configurations around at least one main-chain site of steric isomerism per conventional base unit. A *holotactic* polymer is one in which the structure is ordered with respect to *all* main-chain sites of steric isomerism. *Monotactic*, *ditactic*, *etc.*, refer to ordering with respect to one, two, *etc.*, main-chain sites of steric isomerism per conventional base unit.

An *atactic polymer* is one in which there is complete randomness with regard to the configurations at all the main-chain sites of steric isomerism. Polymers with a low degree of order, having macroscopic properties practically indistinguishable from those of a strictly atactic polymer, are also customarily designated as atactic.

The terms *tactic*, *holotactic*, *monotactic*, *ditactic*, *atactic*, as well as *cis-tactic*, *trans-tactic*, *isotactic*, *syndiotactic*, *di-isotactic*, *etc.*, which will be introduced in the next section, are defined and used, in this and the next section with respect to polymers; however, these terms can also be applied with corresponding meanings, to molecular chains, segments, blocks, *etc.*, and to reactions of synthesis resulting in polymers of the indicated types.

The general term *stereospecific polymerization* refers to the formation of a tactic polymer from monomers (*e.g.*, vinyl compounds) theoretically capable of producing polymers containing sites of steric isomerism.

Stereoselective polymerization is the formation of a tactic polymer from a mixture of stereoisomeric monomers by selective addition of the different types to the growing polymer chain in a regular order.

SOME TYPES OF TACTIC POLYMERS

If there is a site of *cis-trans* isomerism in the conventional base unit of a polymer, it may be designated as *cis-tactic* or *trans-tactic*, provided that dispositions around all the double bonds are of the *cis* or *trans* type, respectively.

An *isotactic polymer* is a tactic polymer, the base unit of which possesses, as a component of the main chain, a carbon atom* with two different lateral substituents, these atoms being so arranged that a hypothetical observer, advancing along the bonds constituting the main chain, finds each of these

* Here and elsewhere in this report, references to a carbon atom as a site of steric isomerism should be considered to be applicable also to other atoms, such as those of silicon, which are sterically similar to carbon atoms.

This carbon (or similar) atom need not be an asymmetric atom. Thus, a molecule of an ideal isotactic polymer $(\text{CH}_2\text{CHR})_n$ having a chain of *infinite* length does not contain asymmetric carbon atoms, since two chain portions are to be considered as equivalent. If one defines absolute configurations according to the conventions of Cahn, Ingold, and Prelog⁹ one-half of the asymmetric carbon atoms in an ideal isotactic vinyl polymer molecule of *finite* length have the *R* configuration and the other half the *S* configuration, provided differences between the terminal groups are either non-existent or neglected. According to their rule,

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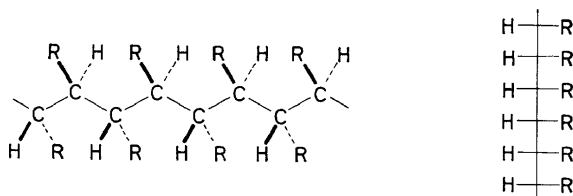
chain atoms with all of its substituents in the same steric order. (Here and in the definitions to follow, hydrogen is counted as a substituent.)

Alternatively, an *isotactic polymer* can be defined as a polymer, the molecules of which contain, at corresponding locations within each base unit, a carbon atom in the principal chain with two different lateral substituents, these being so located that in a Fischer projection the substituents of each type in successive base units are all indicated on the same side of the line representing the main chain.

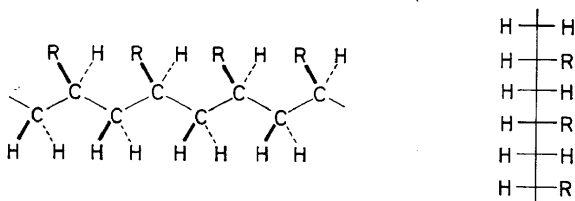
It may be noted that for an isotactic polymer the conventional base unit and the true base unit are identical.

For illustration, diagrams representing portions of the hypothetically extended zig-zag chains of three isotactic polymers, having one, two, and three chain atoms per base unit, respectively, are given here. In each case R denotes a methyl group. The corresponding Fischer projections are also given.

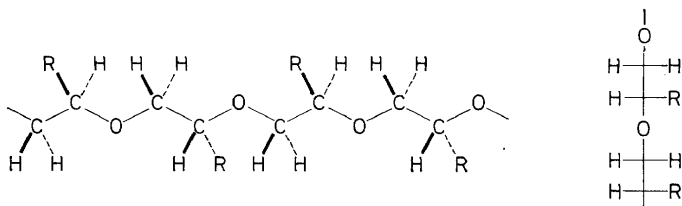
Isotactic polyethylidene or *isotactic poly(methyl)methamer*, $it\text{-}[\text{CH}(\text{CH}_3)]_n$:



Isotactic polypropylene or *isotactic poly(methyl)ethamer*, $it\text{-}[\text{CH}_2\text{CH}(\text{CH}_3)]_n$:

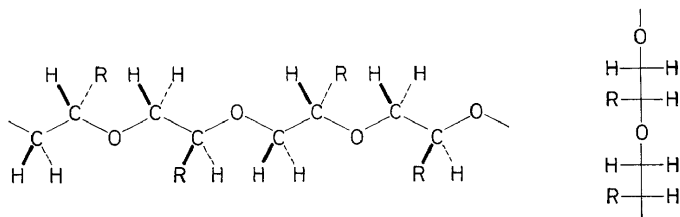


Isotactic poly(propylene oxide) or *isotactic poly(methyl)ethoxamer*, $it\text{-}[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]_n$:



the absolute configuration of an assemblage Xabcd is determined by the spatial configuration of this assemblage. The letters a, b, c, and d here designate atoms or groups attached to the central atom X, arranged in order of priority. This order is that of decreasing atomic numbers of the atoms attached directly to X. If two of these atoms have the same atomic number, the relative priority is determined by the atomic numbers of the atoms attached to them, *etc.*

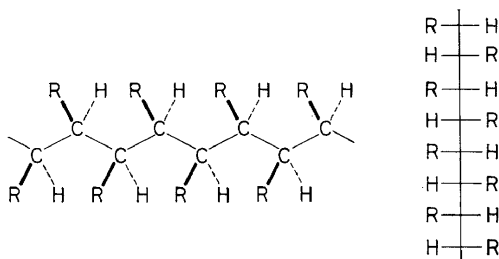
and/or



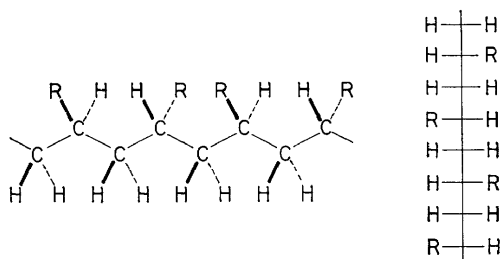
A *syndiotactic polymer* is a tactic polymer in which the conventional base unit possesses, as a component of the main chain, a carbon atom with two different lateral substituents, these substituents being so arranged that a hypothetical observer advancing along the bonds constituting the main chain finds opposite steric configurations around these chain atoms in successive conventional base units. (The true base unit is thus twice the size of the conventional base unit.)

For example:

Syndiotactic polyethylidene or *syndiotactic* poly(methyl)methamer, st -[CH-(CH₃)]_n:



Syndiotactic polypropylene or *syndiotactic* poly(methyl)ethamer, st -[CH₂-CH(CH₃)]_n:



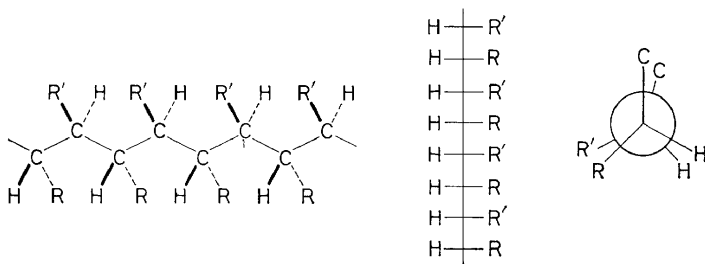
A *di-isotactic polymer* is a polymer, the conventional base unit of which possesses, as components of the main chain, two carbon atoms each having two different lateral substituents, with the steric orientations in successive units such as to make the molecule isotactic with respect to the configuration around corresponding chain atoms of either type, considered separately.

There exist two types of di-isotactic polymers, differing with regard to the steric configurations around these two types of carbon atoms. To distinguish between them we make use of the *threo-erythro* terminology already applied to low molecular weight organic compounds.

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An *erythro-di-isotactic* polymer is a di-isotactic polymer in which the configurations at the two main-chain sites of steric isomerism in the conventional base unit are alike. In a hypothetically extended (zig-zag conformation) molecule of an *erythro-di-isotactic* polymer of general formula $(\text{CHRCHR}')_n$, the substituents of one kind (R) are all on one side of the plane containing the chain atoms and the substituents of the other kind (R') are all on the other side. In a Fischer projection, all R and R' substituents are on the same side of the line representing the main chain. In a Newman representation¹⁰ of an eclipsed formation of two consecutive chain atoms and their attached atoms or groups, in which the next succeeding chain atom is superimposed over the next preceding chain atom, R is superimposed over R' and H over H. For example:

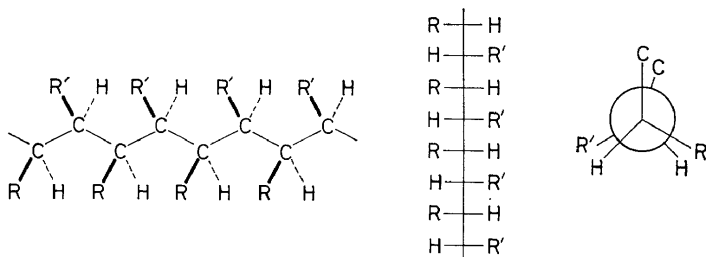
Erythro-di-isotactic poly-2-pentene or *erythro-di-isotactic* poly(1-ethyl)(2-methyl)ethamer, *eit*- $[\text{CH}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)]_n$:



(Here and in other examples to follow, R' denotes an ethyl group; R represents a methyl group, as in the preceding examples.)

A *threo-di-isotactic* polymer is a di-isotactic polymer in which the configurations at the two main-chain sites of steric isomerism in each conventional base unit are opposite. In a hypothetically extended (zig-zag conformation) molecule of a *threo-di-isotactic* polymer of general formula $(\text{CHRCHR}')_n$, the substituents of both kinds, R and R', are all on the same side of the plane containing the chain atoms. In a Fischer projection, R and R' are on opposite sides of the line representing the main chain. In a Newman representation of an eclipsed formation of two consecutive chain atoms and their attached atoms or groups, in which the next succeeding chain atom is superimposed over the next preceding chain atom, R is superimposed over H and H over R'. For example:

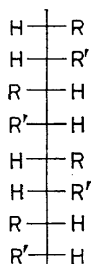
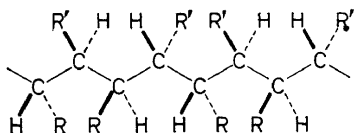
Threo-di-isotactic poly-2-pentene or *threo-di-isotactic* poly(1-ethyl)(2-methyl)ethamer, *tit*- $[\text{CH}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)]_n$:



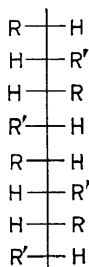
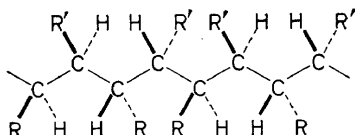
A *di-syndiotactic polymer* is a polymer, the conventional base unit of which possesses, as components of the main chain, two carbon atoms each having two different lateral substituents, with the steric orientations in successive units such as to make the molecule syndiotactic with respect to the configuration around corresponding chain atoms of either type, considered separately.

Erythro-di-syndiotactic and *threo-di-syndiotactic* polymers can be defined, described, and represented in a manner analogous to that used for the corresponding types of *di-isotactic* polymers, except that the steric arrangement cannot be represented, for each type, by a single formula of the Newman type, since the representation for the second half of the true base unit is opposite to that for the first half. For example:

Erythro-di-syndiotactic poly-2-pentene or *erythro-di-syndiotactic* poly(1-ethyl(2-methyl) ethamer, *est*-[CH(CH₃)CH(C₂H₅)]_n:



Threo-di-syndiotactic poly-2-pentene or *threo-di-syndiotactic* poly(1-ethyl(2-methyl) ethamer, *tst*-[CH(CH₃)CH(C₂H₅)]_n:



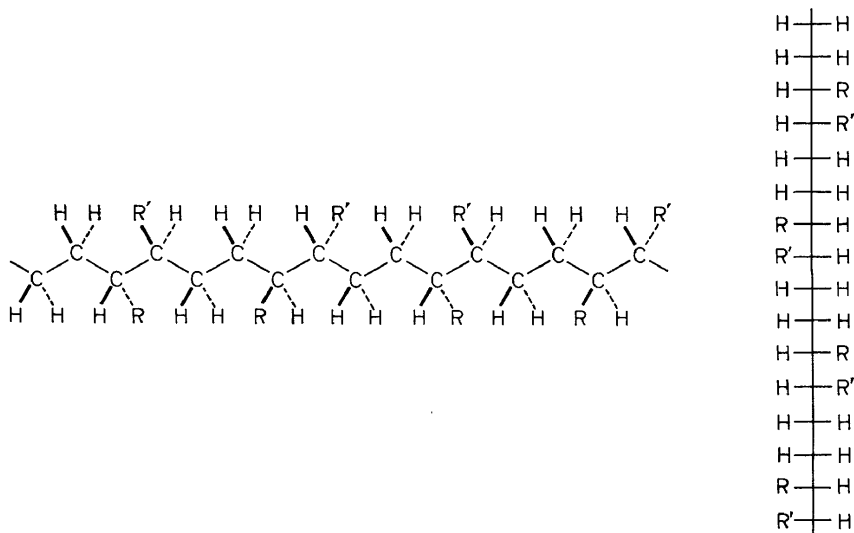
It should be noted that these two polymers are identical, except for the end groups, the choice of terminology depending only on an arbitrary choice of the boundaries of the mer and the relation between the direction of the chain and the numbering of the substituents. Polymerization of 2-pentene in such a way that the two carbon atoms of each monomer which are connected to the remainder of the chain have the *same* steric orientations and polymerization in such a way that these two carbon atoms have *opposite* orientations give the same polymer, if one requires that the orientations of corresponding atoms in consecutive mers are reversed (*i.e.*, that the structure is *syndiotactic*). It should be sufficient, for most purposes, to designate these polymers, prepared by either method, as *di-syndiotactic*, with the abbreviation *st*. The additional prefix, *erythro-* or *threo-* can be used if it is desired to specify the relative orientations at the two atoms in each mer, with a given sequence of atoms, which are directly connected to the rest of the chain. (This specification is useless, however, if these relative orientations

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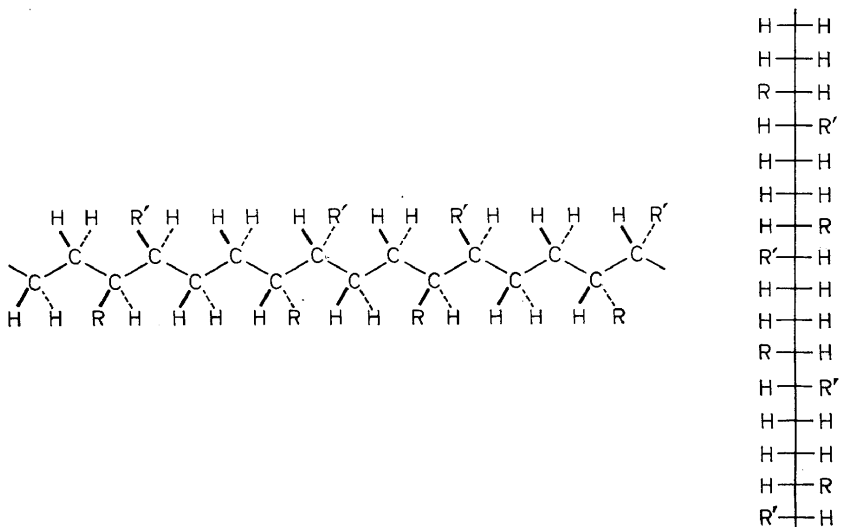
cannot be determined.) A similarly indeterminate situation exists if successive asymmetric chain atoms are separated by other chain atoms when the separating moieties are all alike and nondirectional.

If the moiety between an asymmetric chain atom of one type (*A*) and one of the other type (*B*) differs from that between *B* and *A*, proceeding in the same direction along the chain, an *erythro*- or *threo*- prefix is needed to avoid ambiguity. It is required, for example, for an alternating syndiotactic copolymer of 2-pentene and ethylene:

Erythro-di-syndiotactic poly(2-pentene-co-ethylene) or
erythro-di-syndiotactic poly(1-ethyl)(2-methyl)butamer:



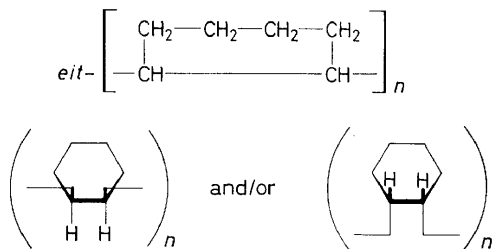
Threo-di-syndiotactic poly(2-pentene-co-ethylene) or
threo-di-syndiotactic poly(1-ethyl)(2-methyl)butamer:



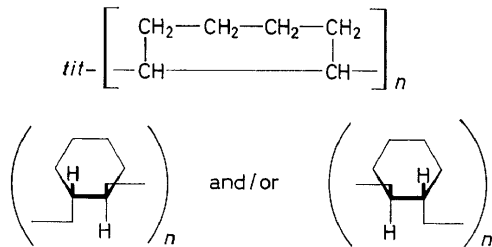
The tacticity of a stereoregular polymer in which rings are incorporated into the main chain, with asymmetric atoms at the points where the chain enters and leaves each ring, can be indicated and classified as for other *ditactic* polymers without rings. Considering the chain as passing around the ring by the shorter path (if the two possible paths are unequal), the two ring atoms which are not included in this chain but are bonded directly to atoms in it can, for this purpose, be treated as lateral substituents. The simplest types of stereoregular asymmetric ring polymers can thus be designated as *erythro-* and *threo-di-isotactic* and *erythro-* and *threo-di-syndiotactic* polymers. In the *erythro* types the main chain bonds entering and leaving the ring have *cis* orientations: *i.e.*, they are on the same side of the median plane of the ring. In the *threo* types the entering and leaving bonds have *trans* orientations.

For example (*cf.* the third and fifth examples following *Rule 16* of reference 6):

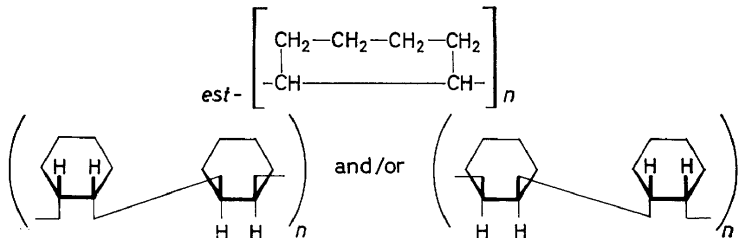
Erythro-di-isotactic polycyclohexylene or *erythro-di-isotactic* polycyclohexyl-enamer-2:



Threo-di-isotactic polycyclohexylene or *threo-di-isotactic* polycyclohexyl-enamer-2:

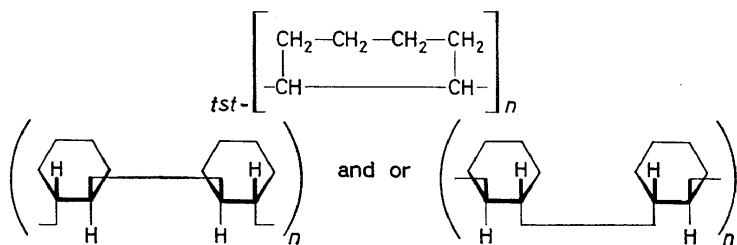


Erythro-di-syndiotactic polycyclohexylene or *erythro-di-syndiotactic* polycyclohexylenamer-2:



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Threo-di-syndiotactic polycyclohexylene or *threo-di-syndiotactic* polycyclohexylenamer-2:



STRUCTURE NAMES AND FORMULAE

A linear polymer can be named and designated by a formula in either of two ways: (i) on the basis of its real or hypothetical method of preparation from a monomer, or (ii) in terms of the base unit of the molecule (*cf.* reference 6, p. 272). Thus, a polymer composed of molecules having the composition of high molecular weight normal paraffins can be designated as (linear) polyethylene, $(\text{CH}_2\text{CH}_2)_n$, or as polymethamer, $(\text{CH}_2)_n$. Linear polypropylene, $[\text{CH}_2\text{CH}(\text{CH}_3)]_n$, can also be called poly(methyl)ethamer, with the same formula*.

To provide for the systematic designation of stereoregularity in high polymers, we propose the following rules, to be added to those previously adopted.

Rule 17

The type of stereoregularity in an isotactic, syndiotactic, *erythro*-di-isotactic *threo*-di-isotactic, *erythro*-di-syndiotactic, or *threo*-di-syndiotactic polymer or the absence of stereoregularity in an atactic polymer can be indicated in the name by the appropriate adjective, italicized, and in the formula by the corresponding italicized prefix: *it-*, *st-*, *eit-*, *tit-*, *est-*, *tst-*, or *at-*. The base units to be used for syndiotactic and atactic polymers are the "conventional base units", defined with neglect of the steric configurations, even though the true base unit of a syndiotactic polymer is twice this size and there is, strictly, no true base unit for an atactic polymer.

Examples of names and formulae conforming to this rule have been given in the preceding section.

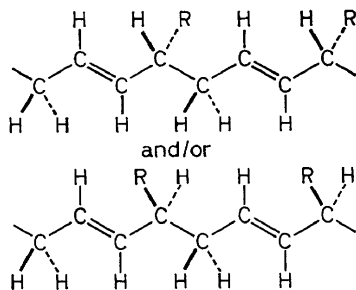
Rule 18

If a polymer exhibits tacticity with regard to stereoisomerism of both the tetrahedral atom type and the *cis-trans* type, the former type is specified first, in both name and formula.

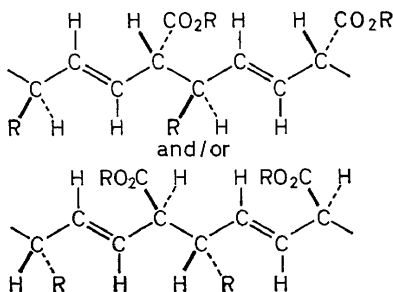
Examples:

Iso-trans-tactic poly(1-methyl)but-2-enamer, *it*-[*trans*- $\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3)$] $_n$:

* In the previous report⁶ a large number of base units was designated in the formula by the subscript p . We here use the subscript n , to conform to common usage.



Erythro-di-iso-trans-tactic poly(1-methoxycarbonyl) (4-methyl)but-2-enamer
ait-[*trans*-CH(CH₃)CH=CHCH(CO₂CH₃)]_n:



Rule 19

The tacticity of a stereoregular polymer in which rings are incorporated into the main chain, with asymmetric atoms at the points where the chain enters and leaves each ring, can be indicated and classified as for other *ditactic* polymers. Considering the chain as passing around the ring by the shorter path (if the two possible paths are unequal), the bond connecting each asymmetric ring-chain-junction atom to a ring atom which is not included in the chain is to be treated, for the purpose of designating tacticity, as if it connected the chain to a lateral substituent.

Examples are given in the preceding section.

Rule 20

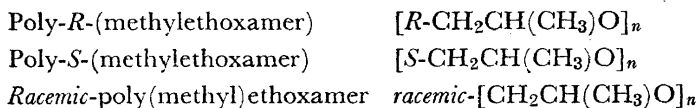
If the tacticity of an isotactic polymer is due to asymmetric atoms with a covalency not greater than 4 (the asymmetry of which is a result of differences between neighbouring atoms or atomic groups, rather than differences between the lengths of the main chain in the two directions or differences between the chain ends), the absolute steric configurations of these atoms can be determined and indicated by the italic letters *R* and *S* (or *r* and *s* in the case of pseudo-asymmetric atoms), according to the rules proposed by Cahn, Ingold, and Prelog⁹.

These designations are not advantageously applicable to simple isotactic or syndiotactic vinyl polymers, because of the absence of *locally* asymmetric atoms. Also, they cannot properly be applied (without further qualification)

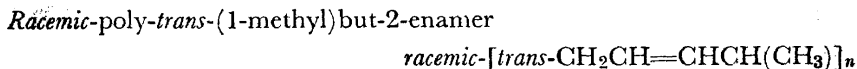
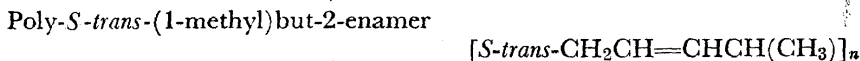
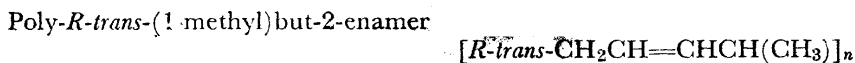
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unless the absolute configurations of corresponding atoms in each base unit are identical throughout each polymer chain and in all the polymer molecules. Following custom in cases of low molecular compounds, however, a racemic mixture of equal numbers of molecules of the two enantiomorphous forms can be indicated in the name and the formula by use of the designations of both forms. These should be placed before "poly" in the name and before the bracket enclosing the formula of the base unit, since otherwise it might be mistakenly assumed that an atactic polymer is meant. It is recommended, however, that for polymers having only a single site of *R-S* isomerism per base unit, the italicized prefix *racemic* be used instead of the designation *RS*.

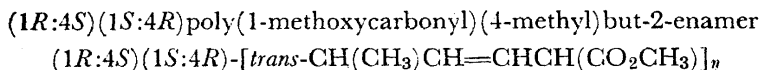
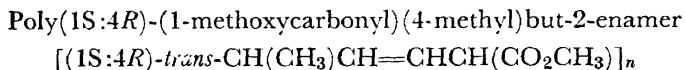
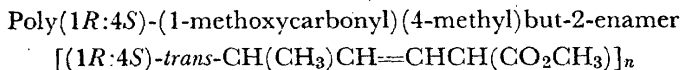
Examples:



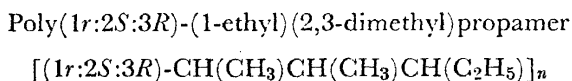
These names and formulae represent, respectively, a polymer composed exclusively of molecules having the structure indicated by the first diagram given above for isotactic poly(propylene oxide), a polymer composed exclusively of molecules having the structure indicated by the second diagram, and a polymer composed of equal numbers of macromolecules of these two kinds.

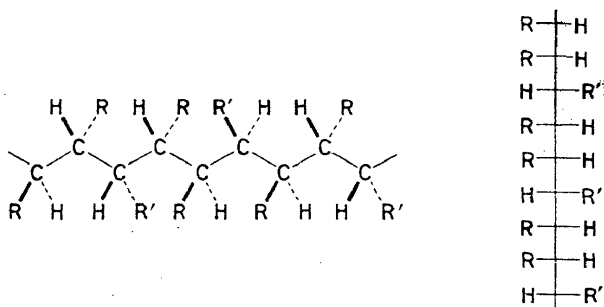


These refer, respectively, to the two polymers represented by the first pair of diagrams in the examples for Rule 18 and to a racemic mixture of these two.

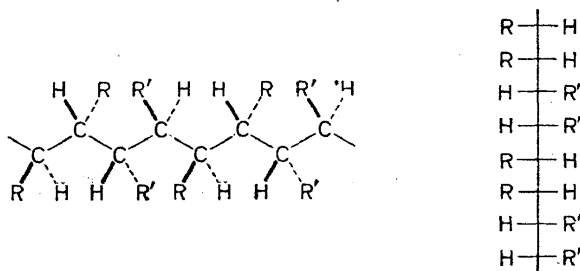


These denote, respectively, the polymers represented by the second pair of diagrams in the examples for Rule 18 and a racemic mixture of the two.





Poly(1S:2R:3S:4R)-(1,2-diethyl)(3,4-dimethyl)butamer
 $[(1S:2R:3S:4R)-CH(CH_3)CH(CH_3)CH(C_2H_5)CH(C_2H_5)]_n$



References

- ¹ M. L. Huggins, G. Natta, V. Desreux, and H. Mark. *J. Polymer Sci.* **56**, 153 (1962).
- ² M. L. Huggins, G. Natta, V. Desreux, and H. Mark. *Chim. Ind. (Milan)* **46**, 536 (1964).
- ³ M. L. Huggins, G. Natta, V. Desreux, and H. Mark. *Makromol. Chem.* **82**, 1 (1965).
- ⁴ M. L. Huggins, G. Natta, V. Desreux, and H. Mark. *Bull. Soc. Chim. France*, **2127** (1965).
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