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## Report on Nomenclature Dealing with Steric Regularity in High Polymers

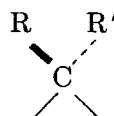
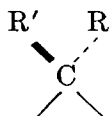
M. L. HUGGINS, G. NATTA, V. DESREUX, and H. MARK\*

This report is an extension of the Report on Nomenclature in the Field of Macromolecules,<sup>1</sup> 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 Danusso<sup>2</sup> and Natta, Farina, and Peraldo.<sup>3</sup>

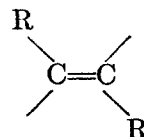
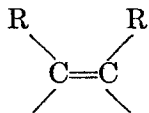
### General Ideas and Definitions

We are concerned with the designation of steric regularity in high polymers—especially head-to-tail linear high polymers. Differences 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 nonequivalent (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 was approved by the Commission on July 28, 1961 for a one-year trial. Criticisms and suggestions for changes should be sent to Dr. M. L. Huggins, Stanford Research Institute, Menlo Park, Calif., U.S.A.

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 the 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 lat-

\* 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 con-

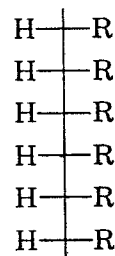
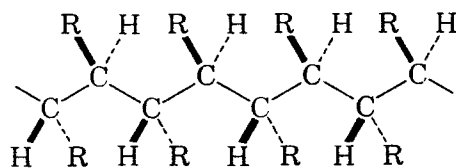
eral substituents, these atoms being so arranged that a hypothetical observer, advancing along the bonds constituting the main chain, finds each of these chain atoms with all of its substituents in the same steric order. (Here and in the definitions to follow, hydrogen is counted as a substituent.)

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.

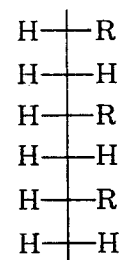
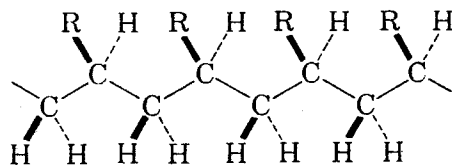
It may be noted that for an isotactic polymer the conventional base unit and the true base unit are identical.

For illustration, diagrams representing portions of the hypothetically extended zigzag 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*-[CH-(CH<sub>3</sub>)]<sub>n</sub>:

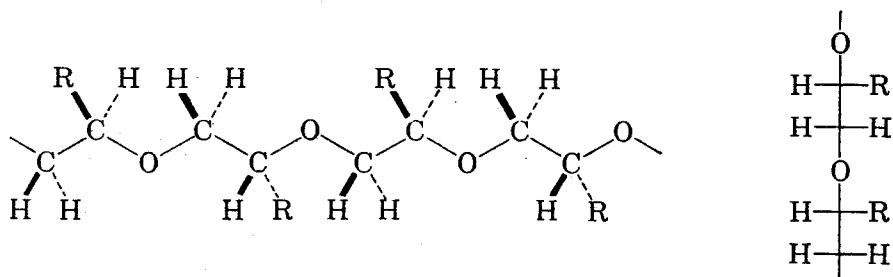


*isotactic* polypropylene or *isotactic* poly(methyl)ethamer, *it*-[CH<sub>2</sub>CH-(CH<sub>3</sub>)]<sub>n</sub>:

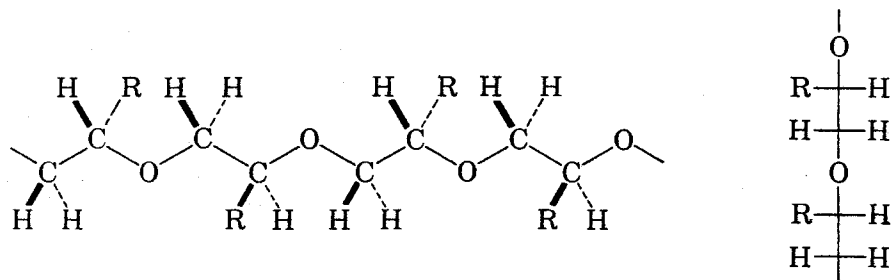


tain asymmetric carbon atoms, since the two chain portions are to be considered as equivalent. If one defines absolute configurations according to the conventions of Cahn, Ingold, and Prelog,<sup>4</sup> one-half of the asymmetric carbon atoms in an ideal isotactic vinyl polymer molecule of *finite* length have the *R* configuration and the other half the *S* configuration, provided differences between the terminal groups are either nonexistent or neglected. According to their rule, 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.

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

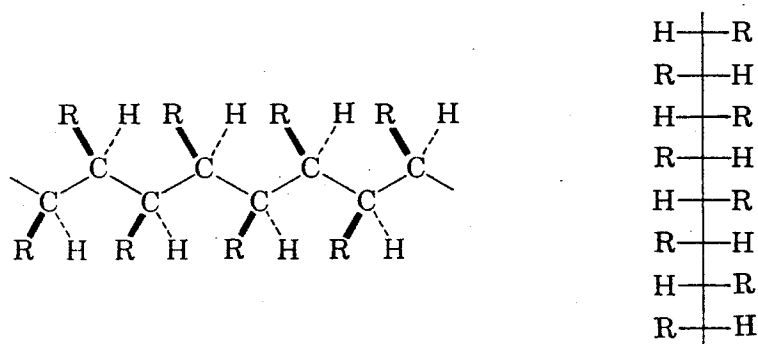


and/or

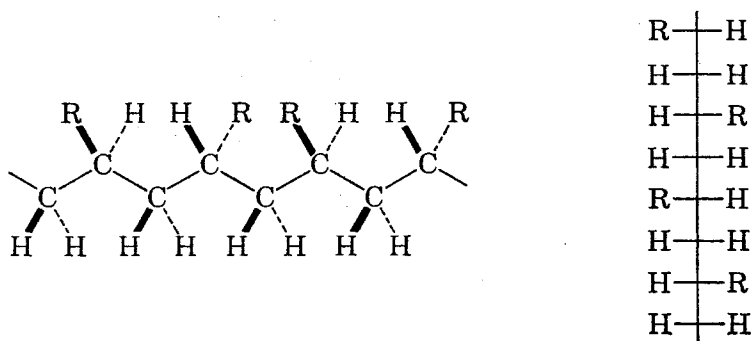


A *syndiotactic polymer* is a tactic polymer in which the conventional base unit possesses, as a component of the main chain, a carbon atom with two different lateral substituents, these substituents being so arranged that a hypothetical observer advancing along the bonds constituting the main chain 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,  $st\text{-}[\text{CH}(\text{CH}_3)]_n$ :



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

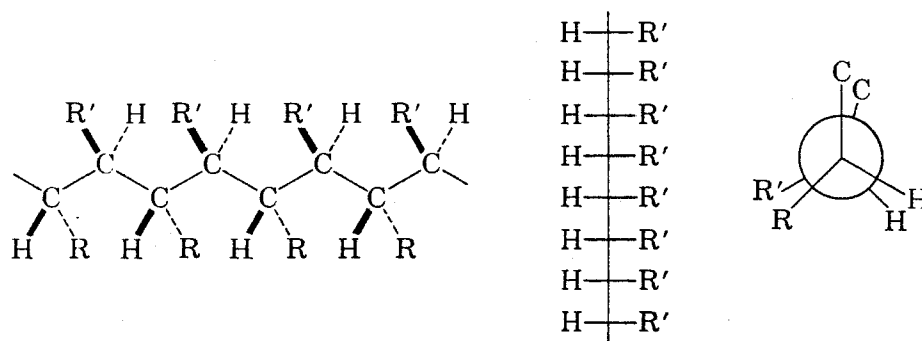


A *di-isotactic polymer* is a polymer, the base unit of which possesses, as components of the main chain, two carbon atoms each having two different lateral substituents, with the steric orientations in successive units such as to make the molecule isotactic with respect to the configuration around corresponding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

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 base unit are alike. In a hypothetically extended (zigzag 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 representation<sup>5</sup> 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:

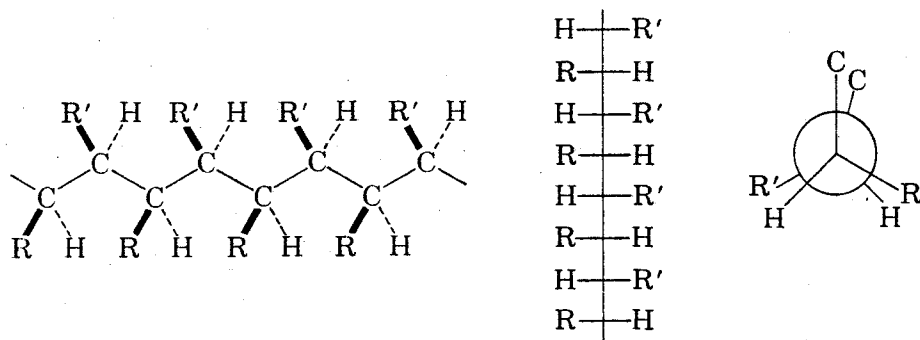
*erythro-di-isotactic* poly-2-pentene or *erythro-di-isotactic* poly(1-ethyl)(2-methyl)ethamer, *et*- $[\text{CH}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)]_n$ :



(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 base unit are opposite. In a hypothetically extended (zigzag 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, *tt*-[CH(CH<sub>3</sub>)CH(C<sub>2</sub>H<sub>5</sub>)]<sub>n</sub>:



### Structure Names and Formulas

A linear polymer can be named and designated by a formula in either of two ways: (1) on the basis of its real or hypothetical method of preparation from a monomer, or (2) in terms of the base unit of the molecule (Cf. ref. 1, pp. 272-273). Thus, a polymer composed of molecules having the composition of high molecular weight normal paraffins can be designated as (linear) polyethylene, (CH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>, or as polymethamer, (CH<sub>2</sub>)<sub>n</sub>. Linear polypropylene, [CH<sub>2</sub>CH(CH<sub>3</sub>)]<sub>n</sub>, 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.

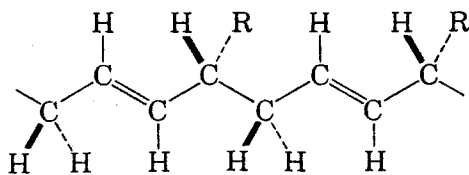
*Rule 17.* The type of stereoregularity in an isotactic, syndiotactic, *erythro*-di-isotactic, or *threo*-di-isotactic polymer or the absence of stereoregularity in an atactic polymer can be indicated in the name by the appropriate adjective, italicized, and in the formula by the corresponding italicized prefix: *it*-, *st*-, *et*-, *tt*-, 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 formulas conforming to this rule have been given in the preceding section.

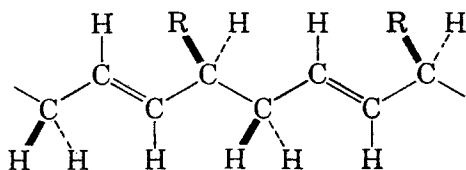
*Rule 18.* If a polymer exhibits tacticity with regard to stereoisomerism of both the tetrahedral atom type and the *cis-trans* type, the former type is specified first, in both name and formula.

*Examples:*

*iso-trans-tactic* poly(1-methyl)but-2-enamer, *it*-[*trans*-CH<sub>2</sub>CH=CHCH(CH<sub>3</sub>)]<sub>n</sub>:

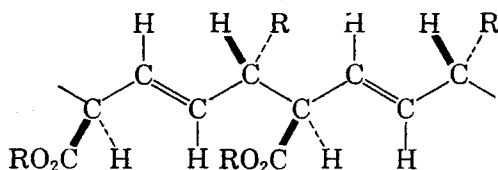


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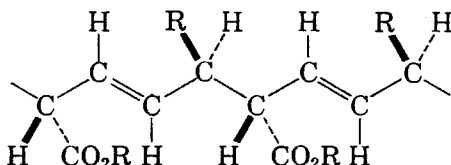


\* In the previous report,<sup>1</sup> a large number of base units was designated in the formula by the subscript *p*. We here use the subscript *n*, to conform to common usage.

*erythro-di-iso-trans-tactic* poly(1-methoxycarbonyl) (4-methyl)but-2-enamer, *et*-[*trans*-CH(CH<sub>3</sub>)CH=CHCH(CO<sub>2</sub>CH<sub>3</sub>)]<sub>n</sub>



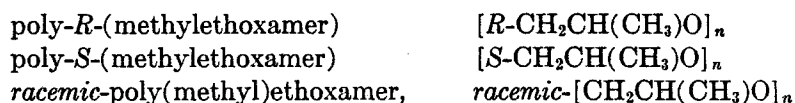
and/or



*Rule 19.* 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 neighboring 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 Prelog.<sup>4</sup>

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) 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 formulas 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.

poly-*R-trans*-(1-methyl)but-2-enamer, [ *R-trans*-CH<sub>2</sub>CH=CHCH(CH<sub>3</sub>) ]<sub>n</sub>

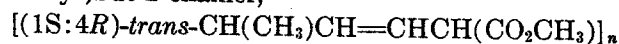
poly-*S-trans*-(1-methyl)but-2-enamer, [ *S-trans*-CH<sub>2</sub>CH=CHCH(CH<sub>3</sub>) ]<sub>n</sub>

*racemic*-poly-*trans*-(1-methyl)but-2-enamer, *racemic*-[ *trans*-CH<sub>2</sub>CH=CHCH(CH<sub>3</sub>) ]<sub>n</sub>

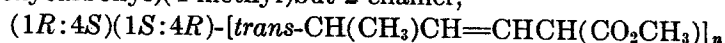
These refer, respectively, to the two polymers represented by the first pair of diagrams in the examples for Rule 18 and to a racemic mixture of these two.

poly(1*R*:4*S*)-(1-methoxycarbonyl)(4-methyl)but-2-enamer,  
[(1*R*:4*S*)-*trans*-CH(CH<sub>3</sub>)CH=CHCH(CO<sub>2</sub>CH<sub>3</sub>)]<sub>n</sub>

poly(1*S*:4*R*)-(1-methoxycarbonyl)(4-methyl)but-2-enamer,

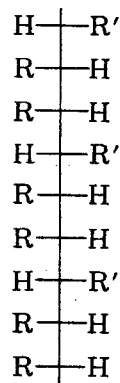
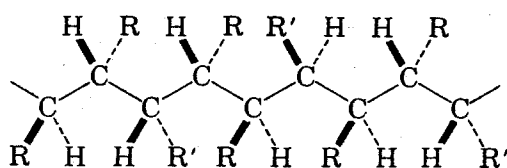
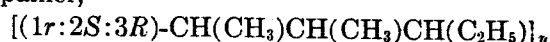


(1*R*:4*S*)(1*S*:4*R*)poly(1-methoxycarbonyl)(4-methyl)but-2-enamer,

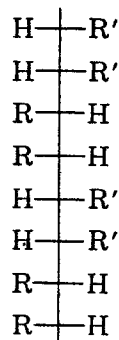
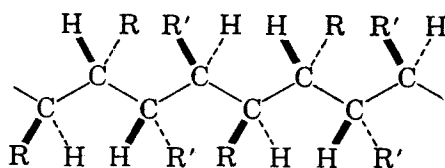
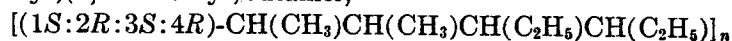


These denote, respectively, the polymers represented by the second pair of diagrams in the examples for Rule 18 and a racemic mixture of the two.

poly(1*r*:2*S*:3*R*)-(1-ethyl)(2,3-dimethyl)propamer,



poly(1*S*:2*R*:3*S*:4*R*)-(1,2 diethyl)(3,4 dimethyl)butamer,



## References

1. *J. Polymer Sci.*, **8**, 257 (1952). A French translation was published as a supplement to the *Bulletin de la Société Chimique de France* in 1952; for the corresponding report in the German language, see *Makromol. Chem.*, **38**, 1 (1960).
2. Natta, G., and F. Danusso, *J. Polymer Sci.*, **34**, 3 (1959).
3. Natta, G., M. Farina, and M. Peraldo, Report to the International Commission on Macromolecules at Wiesbaden, October 1959; *Chim. e ind. (Milan)*, **42**, 255 (1960); *J. Polymer Sci.*, **43**, Issue No. 142 (April, 1960); *Makromol. Chem.*, **38**, 13 (1960).
4. Cahn, R. S., C. K. Ingold, and V. Prelog, *Experientia*, **12**, 81 (1956).
5. Newman, M. S., *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, p. 10.

## Synopsis

This report deals with the classification and naming of high polymers composed of molecules possessing steric regularity, and with related problems of nomenclature. It has been tentatively approved, for one year, by the Commission on Macromolecules of the International Union of Pure and Applied Chemistry.



### Résumé

Ce rapport traite de la classification et de la désignation de hauts polymères composés de molécules stéréoréguliers, ainsi que des problèmes relatifs à la nomenclature. Il a été approuvé à l'essai, pour un an, par la Commission sur les Macromolécules de l'Union Internationale de Chimie Pure et Appliquée.

### Zusammenfassung

Der vorliegende Bericht befasst sich mit der Klassifizierung und Benennung von Hochpolymeren, die aus sterisch regelmässig angeordneten Molekülen bestehen, und mit verwandten Nomenklaturproblemen. Er wurde von der Kommission für Makromoleküle der internationalen Union für reine und angewandte Chemie probeweise für ein Jahr approbiert.

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