

Nomenclature Relating to Polymers Having Sterically Ordered Structure

G. NATTA and F. DANUSSO, *Istituto Chimica Industriale del Politecnico, Milano, Italy*

(A) POLYMERS HAVING ORDERED STRUCTURE

A1. A linear polymer is considered as having an ordered structure when it is formed by macromolecules whose monomeric units follow one another along the chain with dispositions and/or configurations ordered according to some rule.

The rule which characterizes a partially or completely ordered arrangement, can be simple or composed by a few simple rules (and therefore periodical); it must not possess, in general, a random or statistical character.

Thus, by way of example, one can consider as a polymer with ordered structure: (a) a linear vinyl polymer with a complete head-to-tail arrangement; or (b) a linear polymer, ordered head-to-tail, and with the monomeric units all disposed in the same steric configuration along the chain; or (c) a linear polymer whose macromolecules are composed by a succession of blocks or big, equal repeating units, each of them composed by a certain number of base structural units disposed according to a certain rule (which is periodic with respect to the whole macromolecule).

In the first example we have an arrangement in relation only to the positional structure of the monomeric unit. In the second example we can think of two superimposed arrangements, one of positional structure, and the other of steric structure, or we can think of a unique arrangement of configuration.

Generally speaking, it is clear that an ordered arrangement can be composed by several arrangements which represent different steps of a partially or completely ordered arrangement.

The possibility of the existence of a plurality of arrangements finds its origin, first of all, in the possibility of existence of various isomeric structures, in the classical sense, of the monomeric units. In the case of monomeric units presenting some kind of asymmetry, the possibility also exists of different orientations of one monomeric unit with respect to an adjacent one or according to a selected direction along the chain (for instance head-to-tail arrangements or head-to-head—tail-to-tail arrangements).

This second possibility, however, can be considered in terms of positional isomery (of the substituents) of monomeric units or of base units.

In general, therefore, ordered structures in the polymers find their origins in the possibility of isomerism (positional, structural, geometric, steric, etc.) of the monomeric units or, in a more general way, of base units.

While in the past polymeric structures with arrangements related to positional or structural isomerism of the units were considered and obtained, only recently, owing to the discovery of particular processes of stereospecific polymerization, has it been found advisable to classify new polymers whose macromolecules are ordered also with regard to the steric configuration of the constitutive units.

It is interesting to note that the obtaining of arrangements of steric character needs such a regularity of mechanism of polymerization that, as for the cases until now examined, the polymers ordered by steric isomerism of the units are found to be ordered also by positional and/or structural isomerism.

The present nomenclature will be related, therefore, to linear polymers which, unless explicitly mentioned, are to be considered as having in any case positional and structural arrangement of the units.

(B) TACTICITY AND EUTACTICITY

B1. Linear tactic polymer* or simply *tactic polymer* is a polymer formed by macromolecules whose monomeric units (or base units) follow one another along the chain with steric configurations ordered according to some rule.

The rule, or *taxis*, which characterizes an arrangement partially or completely ordered, or *tacticity*, may be simple or composed by few simple rules, but it must not have in any case random or statistic character.

More complex tacticities can be originated not only by steric configuration of a few units, but also by the possibilities, theoretically very numerous, of programmatic arrangements of monomeric units having different configuration along the macromolecular chain (*programmatic tacticities* or *taxis*).

Eutactic polymer† is a tactic polymer whose monomeric units (or base units) are ordered according to such a number and kind of tacticities that its macromolecules are completely ordered.

In other words, an eutactic polymer is a tactic polymer which is completely devoid of any element of structural disorder along the chains of its molecules.

It is advisable that the definition of eutactic polymer be restricted to those cases in which the overall arrangement (*eutacticity*) is relatively simple, that is to say, when the repeating unit assumes relatively small dimensions (with a maximum of some monomeric units).

By way of example, a butadiene polymer is eutactic when all the mono-

* From the Greek verb "τάττω" I dispose, I order.

† From the Greek prefix "ἐν" well, and the verb "τάττω" I dispose, I settle.

meric units have the same *trans*-1,4 configuration or all have the *cis*-1,4 configuration. A linear polyethylene is not to be called eutactic because, although it is formed by the ordered sequence of base units $-\text{CH}_2-$, these do not have any possibility of steric isomery.

An optical antipode oxyacid is the origin, by polycondensation, to an eutactic polycondensate. A mixture of isomers of an amino acid, on the other hand, gives by normal polycondensation a polymer which, in respect to the enchainment of the monomeric units, can be considered as positionally ordered but is not eutactic, because of the statistical disorder deriving from the steric isomery of the units.

Assuming the existence of a catalyst capable of polymerizing a mixture of stereoisomeric amino acids in such a way as to yield chains which were all formed by *l*-amino acid or by *d*-amino acid, the resulting polymer would be eutactic.

By radical polymerization of a vinyl monomer, one can obtain a polymer having some ordered chain, for instance, by head-to-tail enchainment; generally, however, the polymer will not be ordered from the point of view of the steric configuration (right or left in respect of one direction along the chain) of its units, and therefore it will not be an eutactic polymer. However, the same polymer can be obtained in an eutactic form through a polymerization method which is capable of disposing the monomeric units along the chain with the same steric configuration.

B2. It is likewise possible, as in the case of tactic polymers, to define *tactic macromolecules*, *tactic chains*, and *tactic blocks*; and in the case of eutactic polymers, to define *eutactic macromolecules*, *eutactic chains*, *eutactic blocks*, etc.

B3. *Tactic polymerization* is any polymerization producing a tactic polymer.

Eutactic polymerization is any polymerization producing an eutactic polymer. It is advisable, however, to restrict the significance of the term to the cases in which the formation of a tactic or eutactic polymer is the consequence of the particular polymerization mechanism and not simply of the structure of the monomer or of the monomeric unit.

(C) ATACTICITY

C1. *Atactic polymer** is a polymer whose macromolecules, although they have positional or structural arrangements, do not possess a steric order of the units or possess tacticities of such a complex character that cannot be understood by a simple intellect.

* From the Greek prefix "ἀ" non-, and the verb "τάττω" I put in order, I settle. The term "atactic" was first introduced by G. Natta during the meeting of the Gesellschaft Deutscher Chemiker at Bad Nauheim (Germany), on April 25, 1956 [*Angew. Chem.*, **68**, 393 (1956); *Chimica e industria (Milan)*, **38**, 751 (1956)]. It has a more general significance with respect to the original "anisotactic," proposed in the meeting of Accademia Nazionale dei Lincei in Rome (Italy) on December 11, 1954 [G. Natta and P. Corradini, *Atti accad. nazl. Lincei Mem.*, **4**, (8), 73 (1955)].

Therefore, *atacticity* must be considered as a structural state having steric character, but devoid of specific tacticities and, of course, also of eutacticities.

A vinyl polymer, for instance, obtained by conventional radical processes, is generally an atactic polymer; it may possess a head-to-tail arrangement, but it is disordered with regard to the steric configurations of the tertiary carbon atoms which follow each other along the main chains of the macromolecules.

C2. In a manner quite similar to atactic polymers, one can define *atactic macromolecules*, *atactic chains*, *atactic blocks*, etc.

C3. *Atactic polymerization* is any polymerization which leads to an atactic polymer.

(D) PARTICULAR TACTICITIES

In the chemistry of substances having low molecular weight, different kinds of steric isomerism are known, owing to differences of molecular configuration which are understandable only by spatial observation.

Steric isomerism often considered are, for instance, the isomerism due to the presence of asymmetric carbon atoms (isomerism usually indicated as optical); the ethylenic isomerism, due to the *cis* and *trans* configurations of two substituents, with respect to the double bond; *cis* and *trans* isomerism of more complex structures (sometimes also called geometric), etc.

Since steric isomerism is usually classified into different types, the classification of tactic polymers in various classes or categories may be justified.

In the present report we will define three types of tacticities relating to macromolecular structures which have been practically obtained and identified up to now. For these, some terms have already entered in current use, and we will specify them in three separate paragraphs, with actual observations about their ordinary significances.

(a) Isotacticity

Def. In the case of polymers whose monomeric units (or base units) may exist in two enantiomorphous configurations (the one being the specular image of the other), either intrinsically or because of their position in the chain, tacticities due to configurations of asymmetrically substituted carbon atoms may occur. We will regard the units of such a kind of polymers as *asymmetric units*.

*Isotactic** is a polymer whose monomeric units (or base units) are asym-

* From the Greek terms "*ισος*," the same, equally, and "*τάττω*," I put in order. The term "isotactic" was first introduced by Giulio Natta during a meeting of the "Accademia Nazionale dei Lincei" in Rome (Italy) on December 11, 1954. G. Natta, *Atti accad. nazl. lincei, Mem.*, **8** [4], 61 (1955). G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti, and G. Moraglio, *J. Am. Chem. Soc.*, **77**, 1708 (1955). G. Natta, *J. Polymer Sci.*, **16**, 143 (1955). See also: G. Natta, P. Pino, and G. Mazzanti, *Gazz. chim. ital.*, **87**, 528 (1957).

metric units, ordered in such a way that when passing along a single chain from one monomeric unit (or base unit) to the subsequent one, one finds repetition of the unit configuration. In geometric terms, when considering two successive monomeric units (or two base units), by translation and rotation of one of them one can obtain the superimposition of the two units (this can take place also by rotation of single groups around internal bonds).

An isotactic polymer is usually eutactic. The corresponding arrangement, or *isotacticity*, can be resumed in a simple rule (*isotaxis*), which is the *repetition* of the configuration of the monomeric units along a single chain.

It follows that all the arrangements which may compose the isotacticity must be only repetitive arrangements.

Thus, for instance, a polymer of a vinyl monomer or of a vinylidene asymmetrically substituted monomer is isotactic when it is both positionally ordered by a head-to-tail enchainment and tactic, having all its monomeric units with the same steric configuration along the chain.

A hypothetical polyisoprene having 1-2 enchainment, and therefore a structural order, could be isotactic only if it also had a positional head-to-tail arrangement and a steric arrangement, with repetition of the spatial configuration of the quaternary carbon atom.

The polymer obtained by polycondensation from a *d*-amino acid is, according to the above definition, an isotactic polymer. Isotactic is the crystalline polymer obtainable by a particular polymerization method from racemic propylene oxide.* It is to be noted that the different sterical configurations of a monomeric unit may also derive from more than one site or center of asymmetry. Thus, from a vinyl monomer, the substituent of which contains, e.g., one asymmetric carbon atom, one can obtain a truly isotactic polymer only if the following repetition arrangements are realized: (a) positional (head-to-tail), (b) steric along the main chain, and (c) steric because of the configuration of the substituents.

Leaving out tacticity (c), one could have isotacticity limited to the main chain and the tacticities of the side chains could be considered separately. Thus one could perhaps distinguish, using different words, between *main chain isotacticity* and *side chain* (or *substituent group*) *isotacticity*.

Unless explicitly mentioned, we will refer only to isotacticities of the main chain.

Note. Originally the definition of "isotactic polymer" had been introduced to indicate briefly (avoiding the use of long explicative phrases) those polymers of monomers of the $\text{CH}_2=\text{CHR}$ type in the macromolecules of which all the tertiary carbon atoms have, at least for long chain portions, the same steric configuration.

* C. C. Price, M. Osgam, R. E. Hughes, and C. Shamberlan, *J. Am. Chem. Soc.*, **78**, 690 (1956); G. Natta, P. Corradini, and G. Dall'Asta, *Atti. accad. nazl. Lincei*, **8**, 20, 408 (1956).

To make things simpler, an isotactic macromolecule deriving from a $\text{CH}_2=\text{CHR}$ monomer was defined as the one in which, supposing the main chain fully stretched in a plane, all the R substituents find themselves on one side of the plane, while the hydrogen atoms linked to the tertiary carbon atoms are on the other side of the plane. Each tertiary carbon atom of the main chain is comprised in these polymers between two $-\text{CH}_2-$ groups.

Therefore, for each tertiary carbon atom the possibility of existence of two steric configurations is determined by a difference in the endgroups and/or by a different length and different configuration of the two main chain segments linked to it.

The first examples of these polymers were the isotactic polymers of propylene, of butene, of several other α -olefins, and of styrene, i.e., of substances which, at the state of monomer, do not contain asymmetric carbon atoms.

Subsequently a strong tendency was shown by many authors to extend the definition to other cases. Thus, for instance, polymers derived from monomers formerly containing asymmetric carbon atoms were also called "isotactic" (e.g., Price et al., loc. cit.). In this Report we intend to favor this tendency which, under certain aspects, simplifies the terminology and which, on the other hand, follows the etymological significance.

The broader definition may, however, lead to some discussions. Thus, for instance, the polymer obtained by polycondensation from a *d*-amino acid is, according to the extended definition, an isotactic polymer. This is, however, one of the cases in which the term "isotactic" is not strictly necessary since the polymer can be clearly identified, in its eutactic character, by the term "poly(*d*-amino acid)."

The crystalline polymers, which are now obtainable from propylene oxide, can similarly be defined in their structure as "poly(*l*-propylene oxide)" or as "poly(*d*-propylene oxide)" when obtained from an optically active monomer, and as "racemic poly(propylene oxide)" when obtained from a racemic monomer.

A *non*-crystalline polymer obtained by conventional polymerization of racemic propylene oxide can be defined by the term "poly(*d* + *l*)-propylene oxide" or, more simply, "polypropylene oxide."

Similar considerations can be made for the syndiotactic polymers, for which a broader or more restricted definition can be given, while as for the atactic polymers, the definition given in the present Report corresponds to the original one.

Da2. In a similar way one can define *isotactic macromolecules, isotactic chains, isotactic blocks*, etc.

Da3. *Isotactic polymerization* is any polymerization which, owing to a particular mechanism, produces an isotactic polymer.

This term is of significance either when one starts from a monomer which does not admit of steric isomers (such as, e.g., α -olefins) or when one starts from a monomer which does admit of them. For the sake of

clarity one should distinguish between the two cases of isotactic polymerization which can be defined by the following two more general types of polymerization having a steric effect:

(a) *Stereotactic (or stereospecific) polymerization* occurs when from a single monomer, which can be the origin to two stereoisomeric monomeric units, one obtains a tactic polymer.

(b) *Stereolectic* (or stereoelective) polymerization* occurs when from a mixture of stereoisomeric monomers, each of which can be the origin of a unique type of monomeric unit, one obtains a tactic polymer.

In the case of the formation of isotactic polymers, one may thus distinguish between *stereoisotactic polymerization* (e.g., the one of α -olefins) and *stereoisolectic polymerization* (e.g., the one of random propylene oxide). It is interesting to note that in the case of stereoisolectic polymerization, the macromolecules formed by one of the monomeric stereoisomers are optically active, but the total polymer may be inactive because there can be present, in equal number, enantiomorphous molecules formed by the second monomeric stereoisomer. On the other hand, in the case of stereoisotactic polymerization generally, the macromolecules (e.g., in vinyl polymers) formed by monomeric units of one type (e.g., left) may be practically identical with those formed by monomeric units of the other type (e.g., right), because for polymers of high molecular weight the asymmetry due to endgroups can be neglected.

(b) Syndiotacticity

Db1. A *syndiotactic*[†] polymer is a polymer formed by macromolecules whose monomeric units (or base units) are asymmetric and ordered in such a way that, when passing along the chain from one unit to the subsequent one, one finds a repetition of position (of the substituents) and of structure, but inversion of the steric configuration.

In geometric terms, when considering two successive monomeric units (or two base units) and by translation and rotation of one of them (and, if necessary, by rotation around single internal bonds), one cannot obtain the superimposition of the two units, but each of them may only become the specular image of the other.

Syndiotacticity is the corresponding arrangement. We can think of it as composed of positional and structural arrangements identical to those of isotacticity (repetition arrangements) and of a tacticity opposite to that of isotacticity (inversion tacticity).

For example, a butadiene polymer formed through 1-2, head-to-tail enchainment, the successive monomeric units of which have alternatively

* From the Greek verb "λέγω," I pick up, I choose.

† From the Greek terms "σύν," together; "δύο," two; "τάττω," I put in order. The term "syndiotactic" was first introduced by Giulio Natta during a meeting of the Accademia Nazionale dei Lincei in Rome (Italy) on November 12, 1955. G. Natta and P. Corradini, *Atti. accad. nazl. Lincei*, **8**, 19, 229 (1955); *J. Polymer Sci.*, **20**, 251 (1956).

right and left configuration along the chain in respect of a selected direction, is a syndiotactic polymer.

In a similar way a polymer derived from a vinyl monomer or from a vinylidene asymmetrically substituted monomer can also be syndiotactic.

Db2. In a similar way one can define *syndiotactic macromolecules*, *syndiotactic chains*, *syndiotactic blocks*, etc.

Db3. *Syndiotactic polymerization* is any polymerization producing a syndiotactic polymer. As in the case of isotactic polymerization, one could, in addition to *stereosyndiotactic polymerization*, foresee a *stereosyndiolectic polymerization*, depending on whether the polymerization is stereotactic or stereoelectic.

It is interesting to note that the syndiotactic macromolecules, obtainable through the second type of polymerization, are always identical to each other in their structure and are not formed by a mixture of enantiomorphous macromolecules as is the case with isotactic polymers.

(c) *cis*-Tacticity and *trans*-Tacticity

Dc1. When a polymer contains a double bond or a bond or group with an equivalent structural result in its monomeric unit, two tacticities may occur which regulate the *cis* and *trans* configuration of the involved groups.

cis-Tactic polymer or *trans-tactic polymer* is any polymer whose macromolecules are formed by monomeric units (or base units) susceptible to *cis* and *trans* isomery, and which follow each other all with the same *cis* or *trans* configuration along the chains. Typical examples of these polymers have been obtained from diolefins (*cis* and *trans* polybutadienes or polyisoprenes).

The following terms can be defined in a similar way:

Dc2. *cis-Tactic* and *trans-tactic macromolecules*, *chains*, *blocks*, etc.

Dc3. *cis-Tactic* and *trans-tactic polymerization*.

(E) STEREOCOPOLYMERS

E1. *Stereocopolymers* are polymers with macromolecules which are formed by monomeric units (or base units) which are chemically identical (homopolymers), and which are ordered through positional and structural arrangements (possibly also through tacticities), but which do not have a unitary steric structure.

An atactic polymer is, for instance, a stereocopolymer.

E2. A stereocopolymer is eutactic only when the sterically differentiated units are ordered according to taxis. A simple case of eutactic stereocopolymer is the syndiotactic polymer.

More generally, a stereocopolymer is eutactic whenever the realization of a programmatic tacticity is achieved (for instance, the alternation of blocks having uniform dimensions and presenting two different eutacticities).

E3. *Stereoblock-polymers* (or *stereoblock-homopolymers*) are stereoco-

polymers with molecules which are formed either by tactic blocks of at least two types, or by tactic and atactic blocks.

It is preferable to limit this denomination to the cases in which the blocks have a relatively large average size (for instance, a size not smaller than the one necessary to impart a crystallinity detectable by x-rays or infrared rays).

Otherwise a stereocopolymer will be an atactic polymer, which could be considered as an atactic stereocopolymer.

Note

The text presented at the Macromolecules Commission of IUPAC attributed to the term "tacticity" the broadest significance of "arrangement" in general. Following the opinion expressed by some members of the same Commission, we thought it advisable to modify the significance of tacticity, as expressed in the present reprint, by limiting it to the unique case of arrangement of steric configurations.