

## Definitions Relating to Stereochemically Asymmetric Polymerizations

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**Abstract:** Asymmetric polymerization has been the interest of many academic and industrial polymer scientists but no reference has been made by IUPAC explicitly to definitions of reactions involving the asymmetric synthesis of polymers. Hence, this document presents definitions concerned with asymmetric and related polymerizations with examples included to clarify the meaning of the definitions. Asymmetric polymerizations embrace two main categories, “asymmetric chirogenic polymerizations” and “asymmetric enantiomer-differentiating polymerizations”.

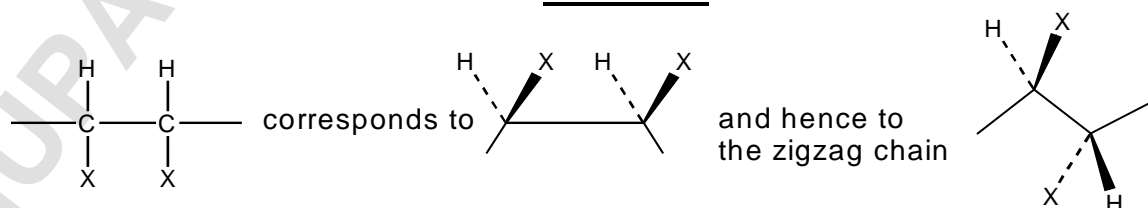
### Introduction

The working party would like to recognise the contribution of Professor Pierre Sigwalt to the conception of this document. He started the original work on it in 1981 and after discussion in the commission and with outside specialists in organic stereochemistry, the work was interrupted. The present document is a continuation of his original one with assistance from the Commission on Nomenclature of Organic Chemistry.

Basic definitions of terms relating to polymerization reactions (Refs. 1, 2 and 3) and stereochemical definitions and notations relating to polymers (Ref. 4) have been published, but no reference was made explicitly to reactions involving the asymmetric synthesis of polymers. It is the aim of the present document to recommend definitions relating to asymmetric polymerizations that may produce optically active polymers.

The rotated Fischer projection is used to denote a polymer backbone by a horizontal line, as mentioned in previous IUPAC documents (Refs. 1 and 4). Hence, *at each individual backbone carbon atom* the horizontal lines represent the bonds directed below the plane of the paper from the carbon atom while the vertical lines project above the plane of the paper from the carbon atom. Thus the rotated Fischer projection of

### Definitions



## 1. Asymmetric polymerization

A polymerization that proceeds in an unsymmetrical manner in terms of chirality under the influence of chiral features present in one or more components of the reaction system.

*Note 1.1:* Polymerization is defined as the process of converting a monomer or a mixture of monomers into a polymer (Refs. 1 and 2). Thus the definition of an asymmetric polymerization covers homopolymerization and copolymerization.

*Note 1.2:* Chiral features may be present in monomers, solvents, initiators, catalysts and supports.

*Note 1.3:* An asymmetric polymerization generally produces a polymer which contains centres of chirality of opposite configuration in unequal amounts.

*Note 1.4:* Some stereospecific polymerizations produce tactic polymers (Ref.4) that contain a mixture of pairs of enantiomeric polymer molecules in equal amounts. For example, in the case of a polymerization leading to an isotactic polymer the product consists of  $-(-R-)_i$ ,  $-(-R-)_{i+1}$ ,  $-(-R-)_{i+2}$ , ..... and their corresponding enantiomers  $-(-S-)_i$ ,  $-(-S-)_{i+1}$ ,  $-(-S-)_{i+2}$ , ..... in equal amounts; here, -R- and -S- represent enantiomeric configurational repeating units. The product can be considered a mixture of polymer racemates because a racemate is defined as an equimolar mixture of a pair of enantiomers (Ref. 5). Such polymerizations can be named by using the adjective "racemate-forming", as in "racemate-forming chirogenic polymerization" (see *Note 2.4*) and "racemate-forming enantiomer-differentiating polymerization" (see *Note 3.2*). Polymerizations of prochiral substituted-ethenes leading to atactic polymers usually give enantiomeric polymer molecules in equal amounts. However, use of the adjective "racemate-forming" is discouraged for such cases where a mixture of polymer racemates molecules with the same degree of polymerization consists of a large number of diastereomers.

## 2. Asymmetric chirogenic polymerization

An asymmetric polymerization in which the polymer molecules formed contain one (or more) new type(s) of elements of chirality not existing in the starting monomer(s).

*Note 2.1:* The new elements of chirality generated in the course of the polymerization may be new types of centres of chirality in the polymer molecules (see *Notes 2.2, 2.4 and 2.5*) or

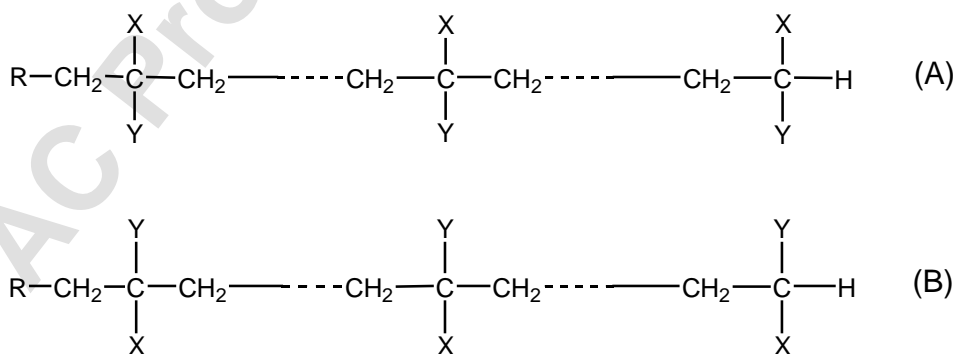
may arise from the helicity of the polymer molecules (see *Note 2.3*).

*Note 2.2:* In asymmetric chirogenic polymerizations of some prochiral monomers, such as Examples 2.1 and 2.2, at least one new type of centre of chirality in the main chain is (are) generated at each propagation step, which lead(s) to polymer molecules having the same configuration (R or S) at each corresponding centre of chirality. The resulting polymer is isotactic and optically active.

*Note 2.3:* Some asymmetric chirogenic polymerizations give helical polymer molecules of only one screw sense that usually show optical activity due to the helicity (see Examples 2.5, 2.6 and 2.7). The polymerizations may be termed asymmetric helix-chirogenic polymerizations.

*Note 2.4:* Some polymerizations produce enantiomeric polymer molecules in equal amounts; each polymer molecule contains only one type of centre of chirality in the main chain not existing in the starting monomer. The resulting polymer is optically inactive, and the polymerization is not an asymmetric chirogenic polymerization. Such a polymerization is termed a racemate-forming chirogenic polymerization. The polymerizations described in Examples 2.5, 2.6 and 2.7, carried out using an optically inactive initiator of the corresponding racemate, are examples of racemate-forming chirogenic polymerizations. Another example is the polymerization of penta-1,3-diene with an optically inactive initiator of the corresponding racemate (see Example 2.1), which leads to an isotactic product.

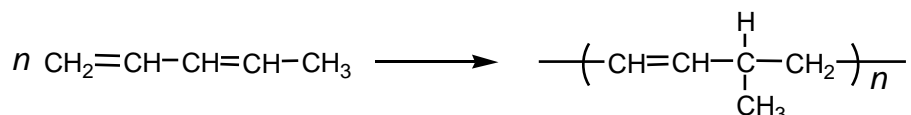
*Note 2.5:* In some polymerizations of vinyl monomers leading to isotactic polymers using an optically active initiator, stereorepeating units (Ref. 4) of one type of centre of chirality are formed at every propagation step. Hence, they give only one type of enantiomeric polymer molecule (A or B), and are asymmetric chirogenic polymerizations. Optical activities of the resulting isotactic polymers are usually very small or not detectable, because the polymer molecules can be regarded as having a plane of symmetry if their degrees of polymerization are so large that the presence of their end-groups is negligible.



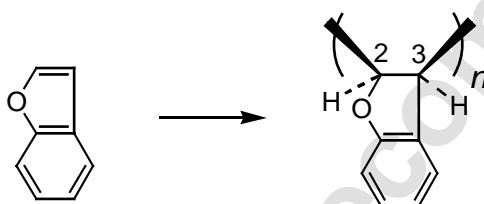
In usual polymerizations of vinyl monomers leading to isotactic polymers, the enantiomeric

polymer molecules (A) and (B) are formed in equal amounts, and the polymerizations are not asymmetric but racemate-forming chirogenic polymerizations.

Example 2.1: Polymerization of penta-1,3-diene by 1,4-addition with an optically active catalyst gives an optically active polymer comprising configurational repeating units with predominantly one type of centre of chirality.

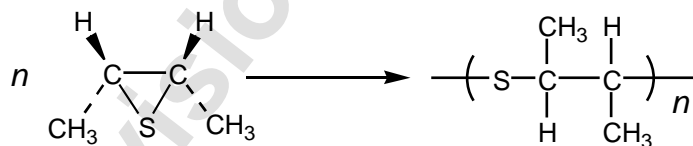


Example 2.2: Polymerization of benzofuran with an optically active initiator gives the optically active polymer, poly[(2*R*,3*S*)-2,3-dihydrobenzofuran-2,3-diyl], containing predominantly one type of stereorepeating unit.

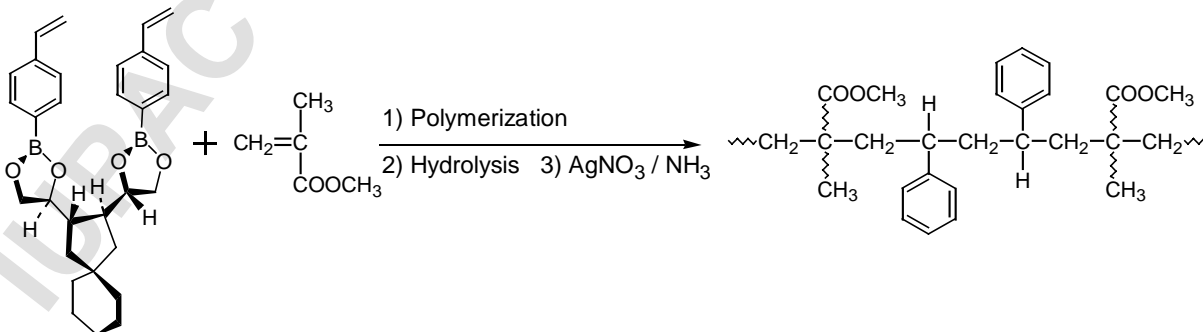


Example 2.3: Polymerization of *cis*-2,3-dimethylthiirane with an optically active initiator results in an optically active polymer, poly[(*R,R*)-thio-1,2-dimethylethylene], containing predominantly *RR* configurational repeating units. Inversion of configuration occurs on ring opening, which gives contiguous monomer units with two identical centres of chirality.

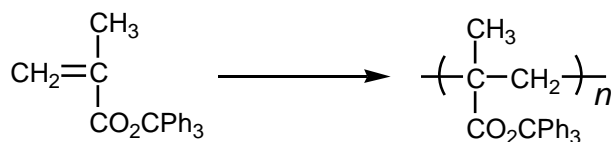
Example 2.4: Copolymerization of a monomer having two styrene moieties attached to a



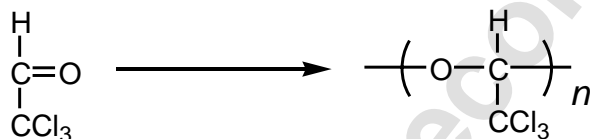
chiral template molecule with a comonomer (e.g., methyl methacrylate) gives copolymers with strong optical activity after removal of the template molecules. In this case styrene diads of an (*S,S*) configuration separated from other styrene diads by comonomeric units are responsible for the optical activity.



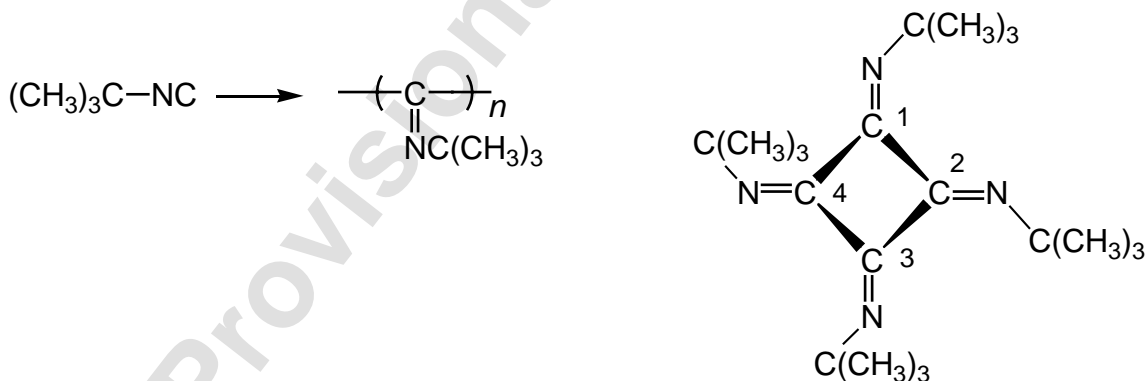
Example 2.5: A polymerization of a bulky methacrylate ester (e.g. triphenylmethyl methacrylate) using an optically active anionic initiator can give an isotactic polymer, poly{1-methyl-1-[(triphenylmethoxy)carbonyl]ethylene}, of high optical activity owing to the formation of helical polymer molecules with units of predominantly one chiral sense.



Example 2.6: Polymerization of trichloroacetaldehyde in bulk using an optically active initiator gives an isotactic polymer, poly{oxy[(trichloromethyl)methylene]}, of high optical activity owing to the formation of the helical polymer molecules with units of predominantly one chiral sense.



Example 2.7: Polymerization of *tert*-butyl isocyanide using an optically active initiator gives an optically active polymer comprising helical polymer molecules with units of predominantly one chiral sense.



poly[(*tert*-butylimino)methylene]  
(view of the right-handed helix along  
the helical axis; unit 5 is below unit 1)

### 3. Asymmetric enantiomer-differentiating polymerization

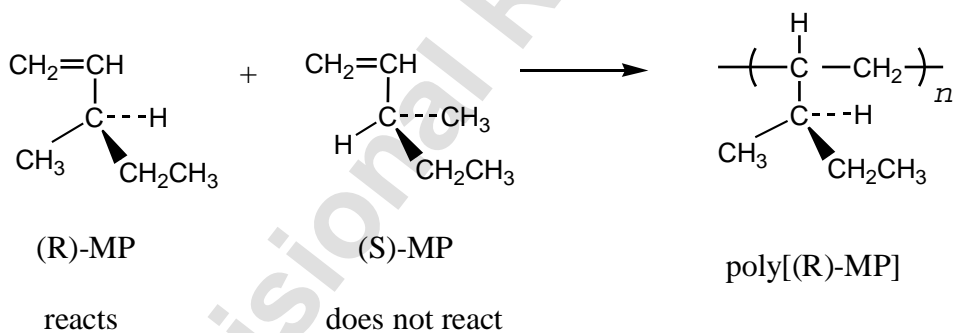
An asymmetric polymerization in which, starting from a mixture of enantiomeric monomer

molecules, only one type of enantiomer is polymerized.

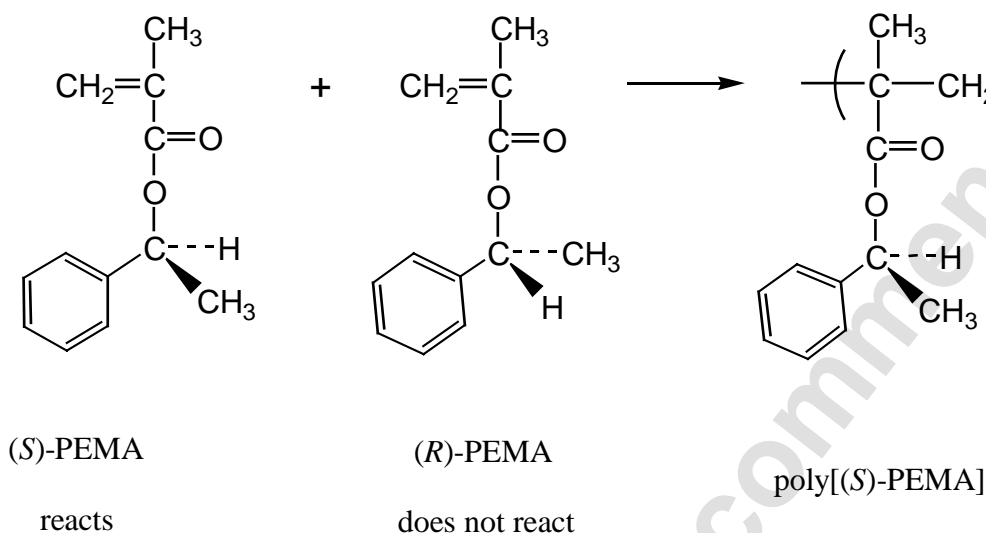
*Note 3.1:* A stereoselective polymerization is defined as "a polymerization in which a *polymer molecule* is formed from a mixture of stereoisomeric monomer molecules by the incorporation of only one stereoisomeric species" (Ref. 1). Thus, an asymmetric enantiomer-differentiating polymerization is a stereoselective polymerization, in which *all the polymer molecules* are formed by the incorporation of only one type of stereoisomeric species.

*Note 3.2:* A polymerization in which, starting from the racemate of a chiral monomer, two types of polymer molecules, each containing monomeric units derived from one of the enantiomers, form in equal amounts is termed racemate-forming enantiomer-differentiating polymerization. The resulting polymer is optically inactive (see *Note 2.4*).

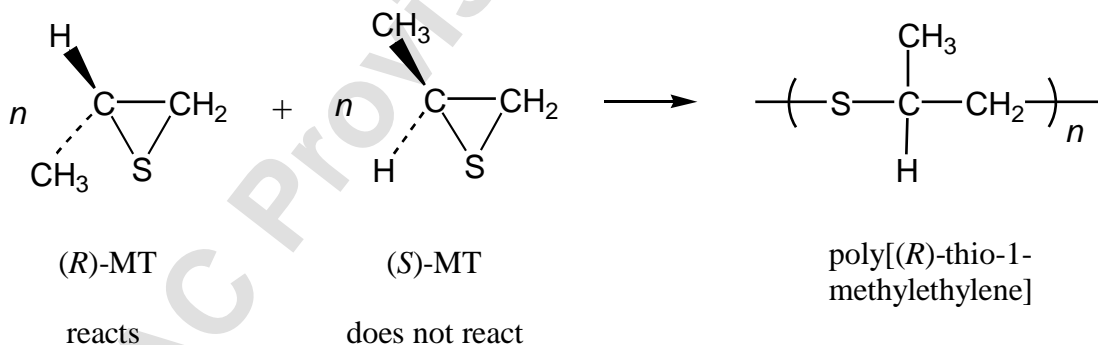
*Example 3.1:* Polymerization of racemic 3-methylpent-1-ene (MP) using an optically active catalyst may give an optically active polymer by a polymerization that is partially asymmetric; preferential consumption of one of the two enantiomers leaves a monomer mixture having optical activity.



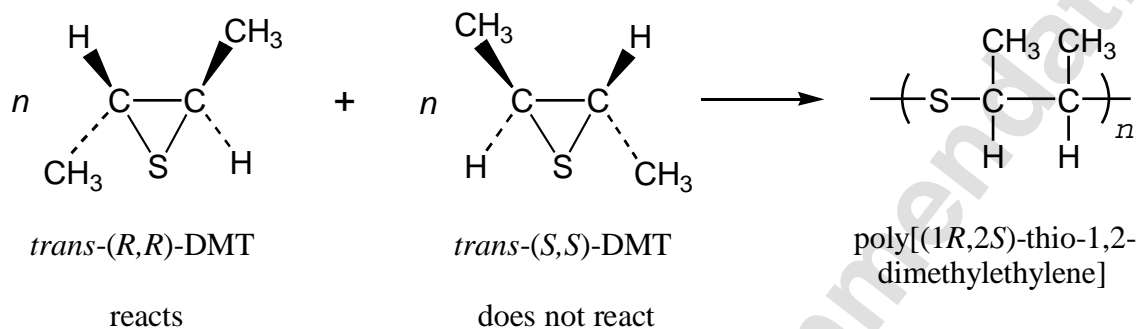
Example 3.2: Polymerization of racemic 1-phenylethyl methacrylate (PEMA) using a chiral complex of a Grignard reagent with a diamine as an initiator may proceed by reaction of only one of the two enantiomers to give an optically active polymer.



Example 3.3: Polymerization of racemic methylthiirane (MT) using an optically active initiator may proceed by reaction of only one of the two enantiomers to produce stereoregular polymer molecules, comprising only one type of configurational repeating unit, as a result of either complete retention or complete inversion of configuration at the centre of chirality of the monomer. The following equation represents the case of complete retention of monomer configuration in the polymer formed, which is optically active.



Example 3.4: Polymerization of racemic *trans*-2,3-dimethylthiirane (DMT) using an optically active initiator may proceed by reaction of only one of the two enantiomers to give stereoregular but optically inactive, non-chiral polymer molecules as a result of inversion of the configuration of the attacked carbon atom.



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MACROMOLECULAR DIVISION

COMMISSION ON MACROMOLECULAR NOMENCLATURE

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