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DEFINITIONS RELATING TO STEREOCHEMICALLY ASYMMETRIC POLYMERIZATIONS

(IUPAC Recommendations 2001)

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Definitions relating to stereochemically asymmetric polymerizations

(IUPAC Recommendations 2001)

Abstract: Asymmetric polymerization has been of interest to many academic and industrial polymer scientists, but no reference has been made by IUPAC explicitly to classification and definitions of reactions involving the asymmetric synthesis of polymers. 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”.

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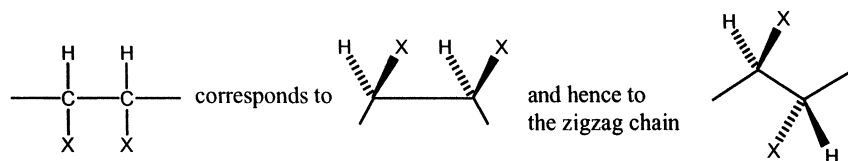
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INTRODUCTION

The working party would like to recognize the contribution of Prof. Pierre Sigwalt to the conception of this document. He started working on it in 1981, but originally there was no agreement within the Commission and with outside specialists in organic chemistry. The current document reflects the continuation of this work with assistance from the IUPAC Commission on Nomenclature of Organic Chemistry.

Basic definitions of terms relating to polymerization reactions [1–3] and stereochemical definitions and notations relating to polymers [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 classification and 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 [1,4]. 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



*Usually, in Fischer projections the carbon atoms of the main chain are omitted [5]. In general, in the area of macromolecular chemistry, element symbols are not omitted in the backbone and are usually shown in the rotated Fischer projection [4].

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 An asymmetric polymerization generally produces a polymer that contains chirality centers of opposite configuration in unequal amounts.

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

Note 1.3 Polymerization is defined as the process of converting a monomer or a mixture of monomers into a polymer [1,2]. Thus, the definition of an asymmetric polymerization covers homopolymerization and copolymerization.

Note 1.4 Some stereospecific polymerizations produce tactic polymers [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 to be a mixture of polymer racemates because a racemate is defined as an equimolar mixture of enantiomers [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).

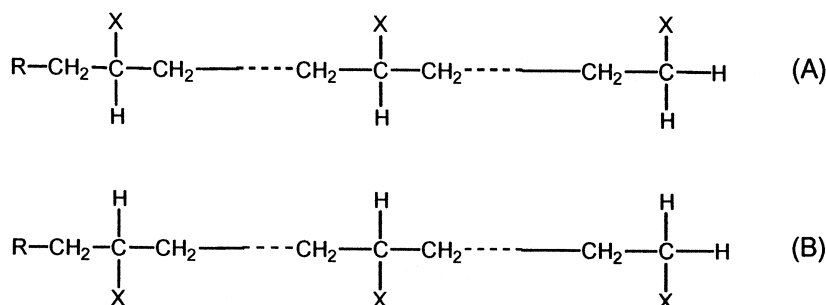
Note 2.1 The new elements of chirality generated in the course of the polymerization may be new types of chirality centers in the polymer molecules (see Notes 2.2, 2.4, and 2.5) or may arise from the helicity of the polymer molecules (see Note 2.3).

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 chirality center in the main chain is generated at each propagation step, which lead to polymer molecules having the same configuration (*R* or *S*) at each corresponding chirality center. 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 are termed “asymmetric helix-chirogenic polymerizations”.

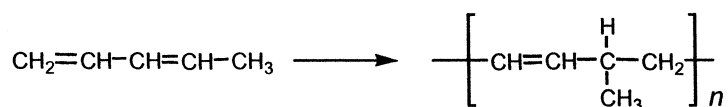
Note 2.4 Some polymerizations produce enantiomeric polymer molecules in equal amounts; each polymer molecule contains, in its main chain, a single type of chirality center that does not exist in the starting monomer. The resulting polymer is optically inactive, and the polymerization is not an asymmetric 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 [4] of one type of chirality center 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.

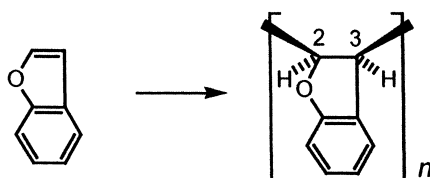


In usual polymerizations of vinyl monomers leading to isotactic polymers, the enantiomeric polymer molecules (A) and (B) are formed in equal amounts, and the polymerizations are not asymmetric but racemate-forming chirogenic polymerizations.

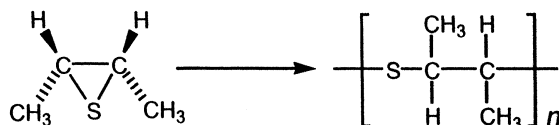
Example 2.1 Polymerization of penta-1,3-diene by 1,4-addition with an optically active catalyst gives an optically active polymer comprising configurational repeating units with predominantly one type of chirality center.



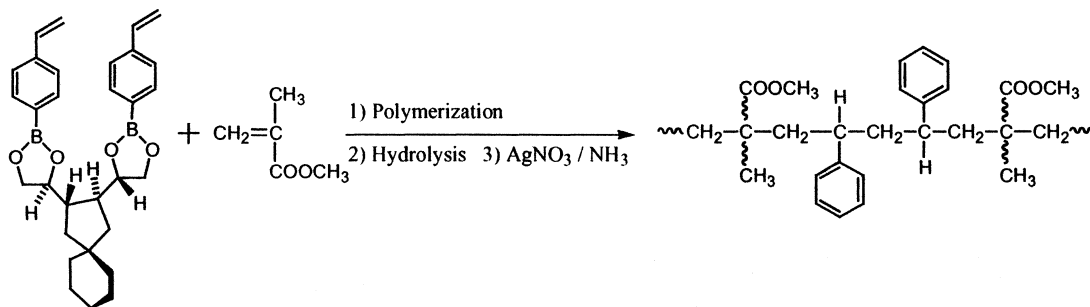
Example 2.2 Polymerization of benzofuran with an optically active initiator gives the optically active polymer, poly[(2*R*,3*S*)-2,3-dihydrobenzofuran-2,3-diyl], containing predominantly one type of stereorepeating unit.



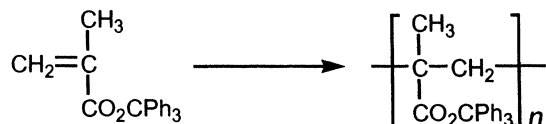
Example 2.3 Polymerization of *cis*-2,3-dimethylthiirane with an optically active initiator results in an optically active polymer, poly[(*R,R*)-sulfanediy(1,2-dimethylethylene)], containing predominantly *RR* configurational repeating units. Inversion of configuration occurs on ring opening, which gives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



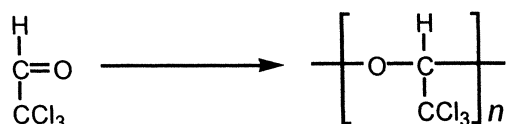
Example 2.4 Copolymerization of a monomer having two styrene moieties attached to a chiral template molecule with a comonomer (e.g., methyl methacrylate) gives copolymers with strong optical activity after removal of the template molecules. In this case, styrene diads of an *S,S* configuration separated from other styrene diads by comonomeric units are responsible for the optical activity.



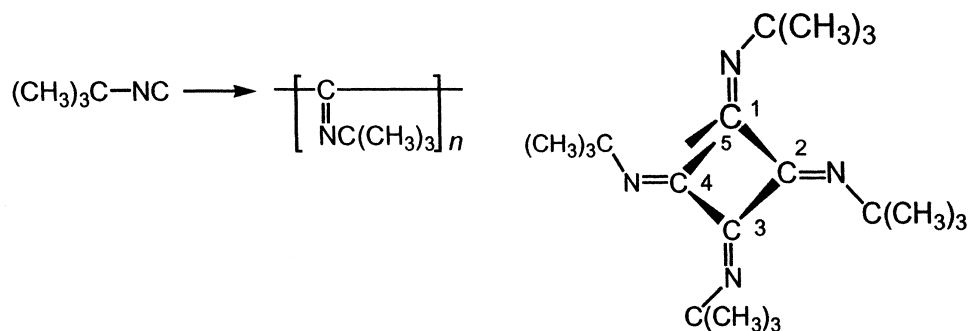
Example 2.5 A polymerization of a bulky methacrylate ester (e.g., triphenylmethyl methacrylate) using an optically active anionic initiator can give an isotactic polymer, poly{1-methyl-1-[(triphenylmethoxy)carbonyl]ethylene}, of high optical activity owing to the formation of helical polymer molecules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



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

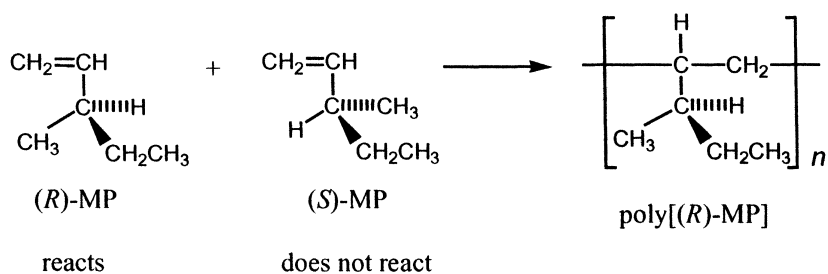
3. Asymmetric enantiomer-differentiating polymerization

An asymmetric polymerization in which, starting from a mixture of enantiomeric monomer molecules, only one enantiomer is polymerized.

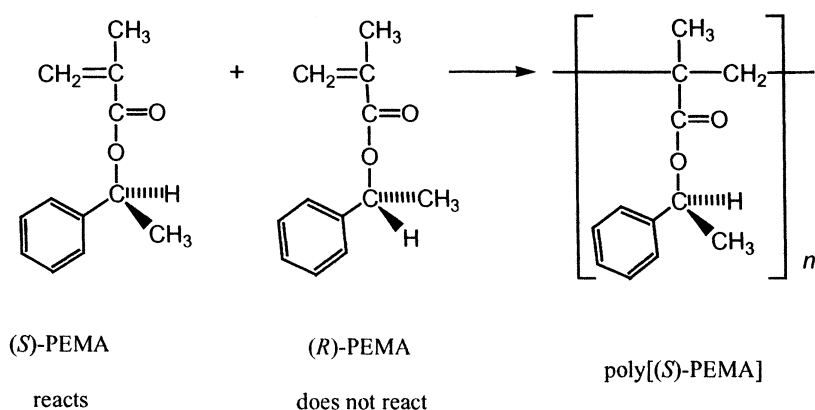
Note 3.1 A stereoselective polymerization is defined as “a polymerization in which a *polymer molecule* is formed from a mixture of stereoisomeric monomer molecules by the incorporation of only one stereoisomeric species” [1]. Thus, an asymmetric enantiomer-differentiating polymerization is a “stereoselective 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).

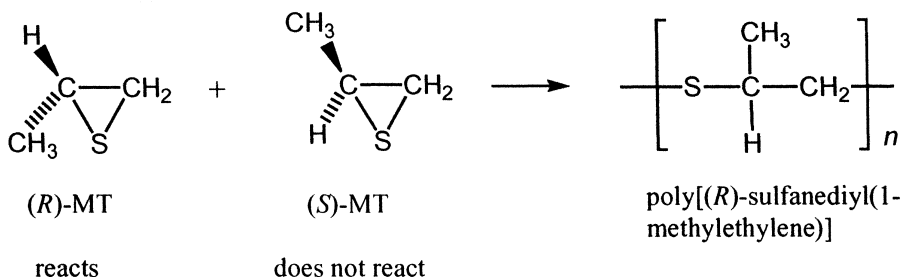
Example 3.1 Polymerization of racemic 3-methylpent-1-ene (MP) using an optically active catalyst may give an optically active polymer by a polymerization that is partially asymmetric; preferential consumption of one of the two enantiomers leaves a monomer mixture having optical activity.



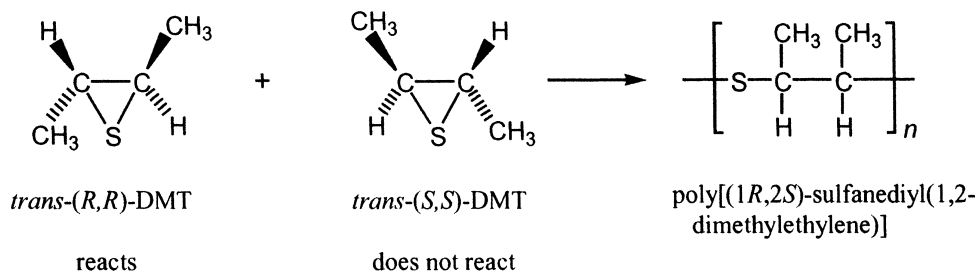
Example 3.2 Polymerization of racemic 1-phenylethyl methacrylate (PEMA) using a chiral complex of a Grignard reagent with a diamine as an initiator may proceed by reaction of only one of the two enantiomers to give an optically active polymer.



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 chirality center 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, nonchiral polymer molecules as a result of inversion of the configuration of the attacked carbon atom.



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