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PURE AND APPLIED CHEMISTRY

MACROMOLECULAR DIVISION
COMMISSION ON MACROMOLECULAR NOMENCLATURE

BASIC DEFINITIONS OF TERMS RELATING TO POLYMERS
1974

LONDON
BUTTERWORTHS

MACROMOLECULAR DIVISION
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PREAMBLE

In the growing field of polymer science, structure-based concepts have received increasing emphasis in the past decades. As a consequence, many of the basic definitions have required refinement.

This report updates and supersedes portions of the 1952 and later reports of the Sub-Commission on Nomenclature of the IUPAC Commission on Macromolecules[1a,b,c,d] as well as that of the present Commission[2].

The present report is intended to serve the needs of those working in the fundamental areas of polymer science, although the existence of a considerable overlap between the areas of fundamental and applied polymer science is recognized. For definitions in the field of plastics, readers are referred to the ISO Recommendations[3].

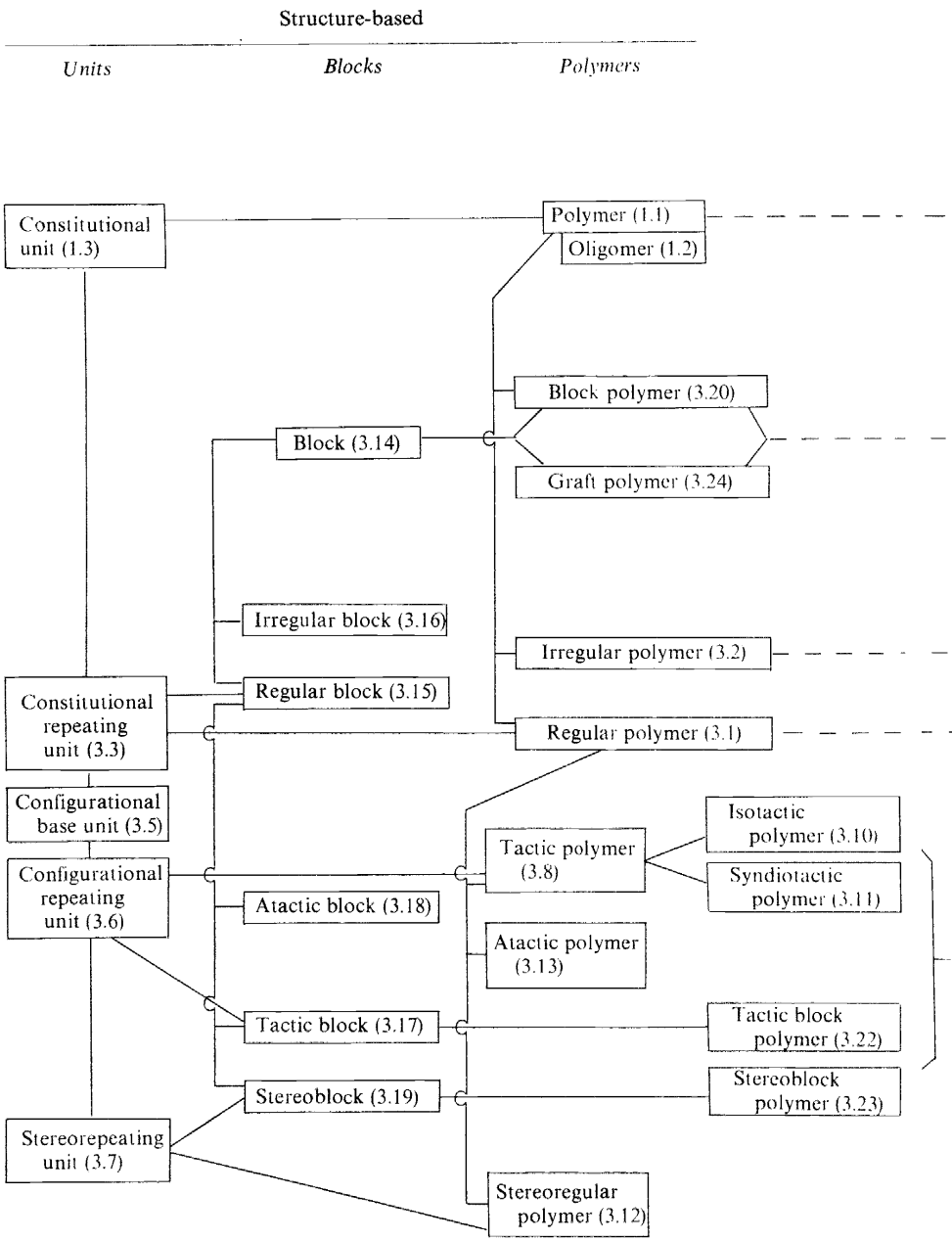
For the presentation of clear concepts, idealized definitions are required. At the same time, the realities of polymer science must be faced. Real polymers deviate more or less from ideality on the molecular as well as on the bulk levels. In these definitions, such deviations are neglected. Nevertheless, the definitions given here can be applied as well to the predominating structural features of real polymer molecules.

Two broad sets of definitions are presented. One of these is based on the structure of polymer molecules and the other on the processes by which polymeric substances come into being. The first type of definition is termed 'structure-based' and the second 'process-based'. The primary definition of *polymer* is structure-based. The process-based set of definitions is linked to the primary definition of *polymer* through the definitions of the term *polymerization* and *monomer*. All other definitions are derived from these terms.

REFERENCES

1 [a] IUPAC, *J. Polymer Sci.* **8**, 257 (1952).
[b] M. L. Huggins, G. Natta, V. Desreux and H. Mark, *J. Polymer Sci.* **56**, 153 (1962).
[c] M. L. Huggins, G. Natta, V. Desreux and H. Mark, *Makromol. Chem.* **82**, 1 (1965) or *Pure Appl. Chem.* **12**, 645 (1966).
[d] M. L. Huggins, P. Corradini, V. Desreux, O. Kratky and H. Mark, *J. Polym. Sci.*, Part B. *Polymer Letters*, **6**, 257 (1968).
2 *IUPAC Information Bulletin*, Appendices on Tentative Nomenclature, Symbols, Units, and Standards, No. 13 (February 1971).
3 ISO Recommendation R 472 (1969).

† Those who have served on the Commission during the preparation of this document are K. L. Loening (*Chairman*), P. Corradini, L. C. Cross, R. B. Fox, V. V. Korshak, N. A. Platé, W. Ring, G. J. Smets, C. Suhr and T. Tsuruta. Serving as observers were N. Bikales, W. E. Cohn, G. Kline, C. Liébecq and O. Wichterle. Comments should be addressed to the Chairman, Chemical Abstracts Service, c/o Ohio State University, Columbus, Ohio 43210, USA.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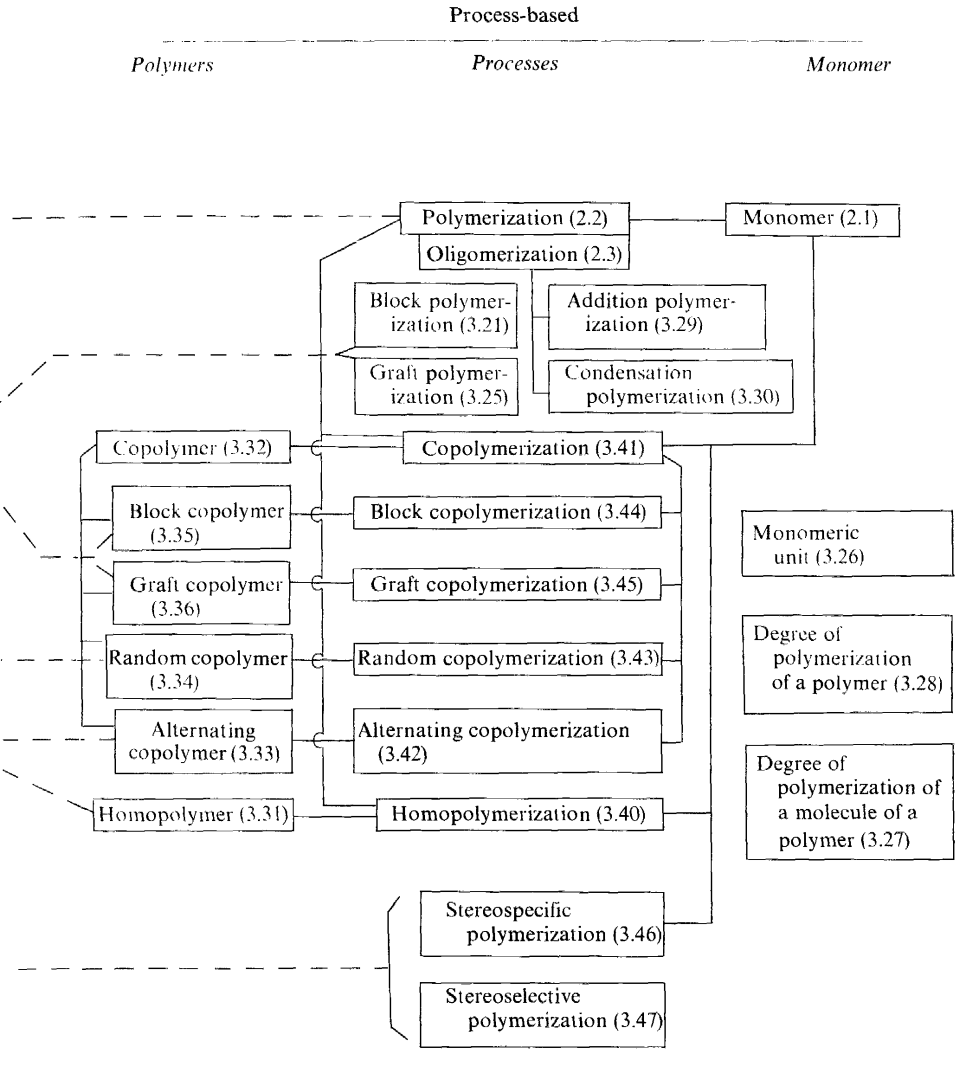
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Term	Definition
1—Primary Definitions	
1.1 Polymer	A substance composed of molecules characterized by the multiple repetition of one or more species of atoms or groups of atoms (constitutional units, see definition 1.3) linked to each other in amounts sufficient to provide a set of properties that do not vary markedly with the addition or removal of one or a few of the constitutional units. (structure-based)
1.2 Oligomer	A substance composed of molecules containing a few of one or more species of atoms or groups of atoms (constitutional units) repetitively linked to each other. The physical properties of an oligomer vary with the addition or removal of one or a few of the constitutional units from its molecules. (structure-based)
1.3 Constitutional unit	A species of atom or group of atoms present in a chain of a polymer or oligomer molecule. (structure-based)
2—Secondary Definitions	
2.1 Monomer	A compound consisting of molecules each of which can provide one or more constitutional units. (process-based)
2.2 Polymerization	The process of converting a monomer or a mixture of monomers into a polymer. (process-based).
2.3 Oligomerization	The process of converting a monomer or a mixture of monomers into an oligomer. (process-based)
3—Derived Definitions	
3.1 Regular polymer	A polymer whose molecules can be described by only one species of constitutional unit in a single sequential arrangement. (structure-based)
3.2 Irregular polymer	A polymer whose molecules cannot be described by only one species of constitutional unit in a single sequential arrangement. (structure-based)
3.3 Constitutional repeating unit	The smallest constitutional unit whose repetition describes a regular polymer. (structure-based)

Term	Definition
3.4 Configurational unit	A constitutional unit having one or more sites of defined stereoisomerism. (structure-based)
3.5 Configurational base unit	A constitutional repeating unit whose configuration is defined at least at one site of stereoisomerism in the main chain of a polymer molecule. Note 1: In a regular polymer, a configurational base unit corresponds to the constitutional repeating unit. Note 2: Two configurational base units are called enantiomeric when they are mirror images at the plane containing the main-chain bonds. (structure-based)
3.6 Configurational repeating unit	The smallest set of one, two or more successive configurational base units that prescribes configurational repetition at one or more sites of stereoisomerism in the main chain of a polymer molecule. (structure-based)
3.7 Stereorepeating unit	A configurational repeating unit having defined configuration at all sites of stereoisomerism in the main chain of a polymer molecule. (structure-based)
3.8 Tactic polymer	A regular polymer whose molecules can be described by only one species of configurational repeating unit in a single sequential arrangement. (structure-based)
3.9 Tacticity	The orderliness of the succession of configurational repeating units in the main chain of a polymer molecule. (structure-based)
3.10 Isotactic polymer	A regular polymer whose molecules can be described by only one species of configurational base unit (having chiral or prochiral atoms in the main chain) in a single sequential arrangement. Note: In an isotactic polymer molecule the configurational repeating unit is identical with the configurational base unit. (structure-based)
3.11 Syndiotactic polymer	A regular polymer whose molecules can be described by alternation of configurational base units that are enantiomeric. Note: In a syndiotactic polymer the configurational repeating unit consists of two configurational base units that are enantiomeric. (structure-based)

Term	Definition
3.12 Stereoregular polymer	A regular polymer whose molecules can be described by only one species of stereorepeating unit in a single sequential arrangement. (structure-based)
3.13 Atactic polymer	A regular polymer whose molecules have a random distribution of equal numbers of the possible configurational base units. (structure-based)
3.14 Block	A portion of a polymer molecule comprising many constitutional units, that has at least one constitutional or configurational feature not present in the adjacent portions. Note: The definitions that relate to polymer can also be applied to block. (structure-based)
3.15 Regular block	A block that can be described by only one species of constitutional repeating unit in a single sequential arrangement. (structure-based)
3.16 Irregular block	A block that cannot be described by only one species of constitutional repeating unit in a single sequential arrangement. (structure-based)
3.17 Tactic block	A regular block that can be described by only one species of configurational repeating unit in a single sequential arrangement. (structure-based)
3.18 Atactic block	A regular block that has a random distribution of equal numbers of the possible configurational base units. (structure-based)
3.19 Stereoblock	A regular block that can be described by one species of stereorepeating unit in a single sequential arrangement. (structure-based)
3.20 Block polymer	A polymer whose molecules consist of blocks connected linearly. The blocks are connected directly or through a constitutional unit that is not part of the blocks. (structure-based)
3.21 Block polymerization	Polymerization in which a block polymer is formed. (process-based)
3.22 Tactic block polymer	A polymer whose molecules consist of tactic blocks connected linearly. (structure-based)
3.23 Stereoblock polymer	A polymer whose molecules consist of stereoblocks connected linearly. (structure-based)

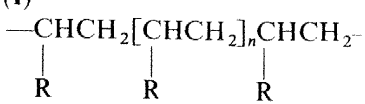
Term	Definition
3.24 Graft polymer	A polymer whose molecules have one or more species of block connected to the main chain as side chains, these side chains having constitutional or configurational features different from the constitutional units comprising the main chain, exclusive of junction points. (structure-based)
3.25 Graft polymerization	Polymerization in which a graft polymer is formed. (process-based)
3.26 Monomeric unit Mer	The largest constitutional unit contributed by a single monomer molecule in a polymerization process. (process-based)
3.27 Degree of polymerization of a molecule of a polymer	The number of monomeric units in a molecule of a polymer. (process-based)
3.28 Degree of polymerization of a polymer	The average value of the degree of polymerization of the molecules of a polymer. Note: The method of averaging must be stated: for example, number-average degree of polymerization. (process-based)
3.29 Addition polymerization	Polymerization by a repeated addition process. (process-based)
3.30 Condensation polymerization; polycondensation	Polymerization by a repeated condensation process (i.e. with elimination of simple molecules). (process-based)
3.31 Homopolymer	A polymer derived from one species of monomer. (process-based)
3.32 Copolymer	A polymer derived from more than one species of monomer. (process-based)
3.33 Alternating copolymer	A copolymer in whose molecules two species of monomeric units are distributed in alternating sequence. (process-based)
3.34 Random copolymer	A copolymer in whose molecules two or more species of monomeric units are distributed in random sequence. (process-based)
3.35 Block copolymer	A block polymer derived from more than one species of monomer. (process-based)
3.36 Graft copolymer	A graft polymer derived from more than one species of monomer. (process-based)

Term	Definition
3.37 Bipolymer	A polymer derived from two species of monomer. (process-based)
3.38 Terpolymer	A polymer derived from three species of monomer. (process-based)
3.39 Quaterpolymer	A polymer derived from four species of monomer. (process-based)
3.40 Homopolymerization	Polymerization in which a homopolymer is formed. (process-based)
3.41 Copolymerization	Polymerization in which a copolymer is formed. (process-based)
3.42 Alternating copolymerization	Polymerization in which an alternating copolymer is formed. (process-based)
3.43 Random copolymerization	Polymerization in which a random copolymer is formed. (process-based)
3.44 Block copolymerization	Polymerization in which a block copolymer is formed. (process-based)
3.45 Graft copolymerization	Polymerization in which a graft copolymer is formed. (process-based)
3.46 Stereospecific polymerization	Polymerization in which a tactic polymer is formed. (process-based)
3.47 Stereoselective polymerization	Polymerization in which a polymer molecule is formed from a mixture of stereoisomeric monomer molecules by incorporation of only one stereoisomeric species. (process-based)

EXAMPLES

Constitutional unit

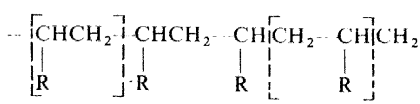
The polymer chain (**1**)



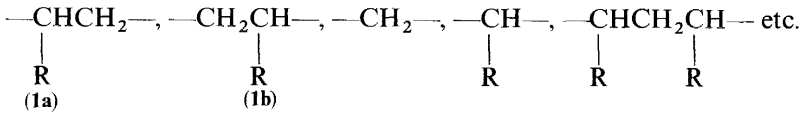
(**1**)

can provide the *constitutional units**

* The convention of orienting polymer structures (and the corresponding constitutional and configurational units) from left to right is used in this document. Thus, the bracketed constitutional units in



are regarded as different, even though their repetition leads to the same regular polymer.



Only the first two constitutional units (**1a** and **1b**) are the smallest ones completely describing this polymer chain.

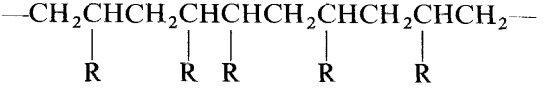
Constitutional repeating unit

Regular polymer

Either of the constitutional units (**1a**) or (**1b**) is a *constitutional repeating unit*, and the polymer whose molecules can be described by (**1**) is a *regular polymer*.

Irregular polymer

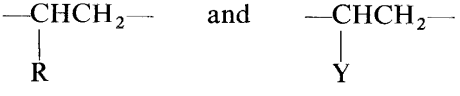
The fragment (**2**)



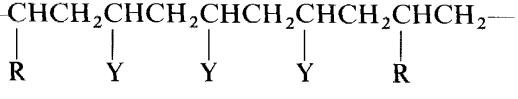
(2)

of a polymer molecule cannot be described by only one constitutional unit, such as (**1a**) or (**1b**), in a single sequential arrangement. The polymer whose molecules consist of a random arrangement of (**1a**) and (**1b**), as in (**2**) is an *irregular polymer*.

A polymer whose molecules consist of a random arrangement of

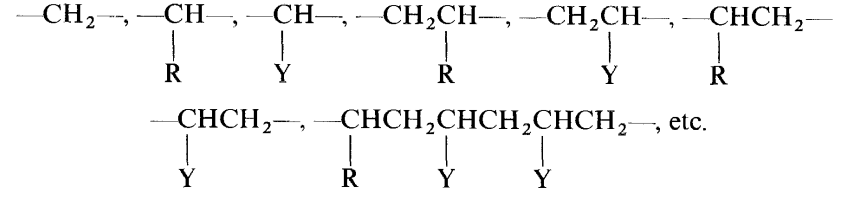


units provides fragments like (**3**):



(3)

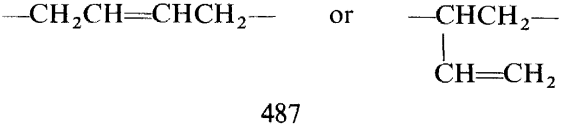
In this fragment there are the constitutional units

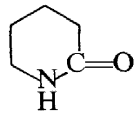


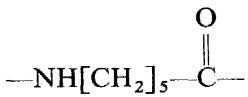
The constitution of (**3**) cannot be described by any one of these constitutional units alone. Therefore, the polymer molecules corresponding to (**3**) are those of an irregular polymer.

Monomer

The *monomer* molecule $CH_2{=}CHCH{=}CH_2$ can provide the constitutional units:



The monomer molecule CH_2N_2 can provide the constitutional unit $-CH_2-$. The monomer molecule  can provide the constitutional unit



By a condensation process, the monomer molecules $H_2N(CH_2)_6NH_2$ and $ClCO(CH_2)_4COCl$ can lead to the regular polymer molecule

$$\text{-}[\text{-}NH(CH_2)_6NHCO(CH_2)_4CO\text{-}]_n$$

which contains the constitutional units

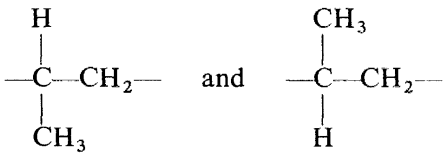
$$-NH(CH_2)_6NH- \quad \text{and} \quad -CO(CH_2)_4CO-$$

Configurational base unit

In the regular polymer molecule

$$-[CH(CH_3)CH_2]_n- \qquad \text{poly(propylene)}$$

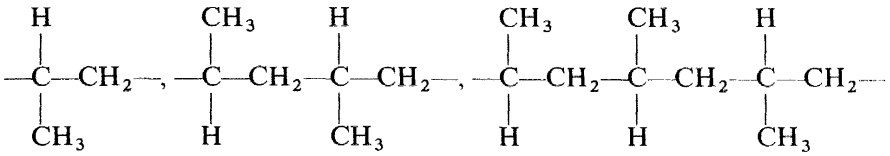
the constitutional repeating unit is $-CH(CH_3)CH_2-$ and the configurational base units are*



These two configurational base units are enantiomeric to each other.

Stereorepeating unit

In a stereoregular poly(propylene), possible *stereorepeating units* are:

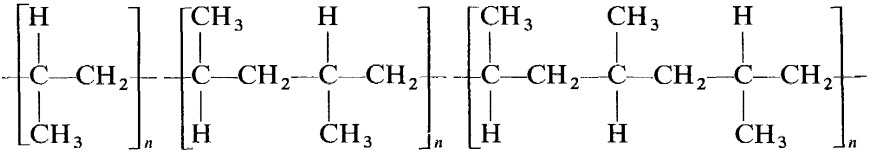


* In the drawing of configurations horizontal bonds are below the plane of the paper and vertical bonds above [See IUPAC Rules on Fundamental Stereochemistry, *J. Org. Chem.* **35**, 2849 (1970), **Rule E-7.1**, note 2]. The main-chain bonds of polymer molecules are drawn as horizontal bonds. Unless otherwise stated the drawings of a configurational base unit, configurational repeating unit, stereorepeating unit, etc. provide information concerning *relative* configurations.

The absence in a formula of any one of the horizontal and/or vertical bonds at a chiral or prochiral carbon atom, or of the *cis* and *trans* designations, means lack of knowledge about the configuration of the corresponding stereoisomeric center.

Stereoregular polymer

The corresponding *stereoregular polymers* are:



(4) (an isotactic polymer) (5) (a syndiotactic polymer) (6)

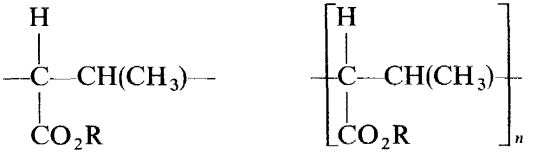
Configurational repeating unit

Tactic polymer

Isotactic polymer

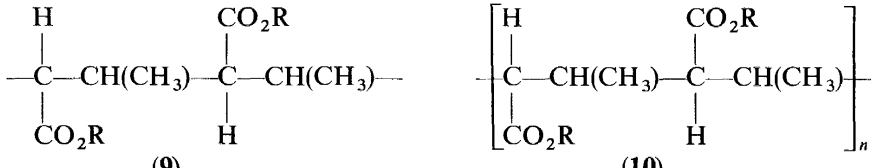
Syndiotactic polymer

In the polymer $-[-CH(CO_2R)CH(CH_3)-]_n$, if only one main-chain stereoisomeric site of each constitutional repeating unit is defined, as in (7):



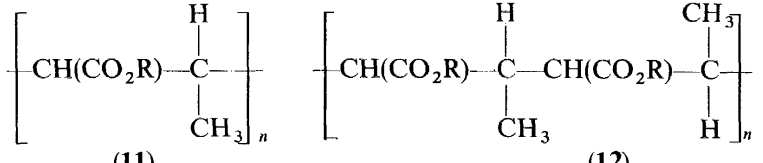
(7) (8)

then (7) is a *configurational repeating unit* and the corresponding polymer (8) is a *tactic* (*isotactic*) *polymer*. Another example of a configurational repeating unit is (9):



(9) (10)

and the corresponding polymer (10) is a *tactic* (*syndiotactic*) *polymer*. Examples (8) and (10) are not stereoregular because the configuration at the stereoisomeric center —$CH(CH_3)$— is not defined. Similarly, (11) and

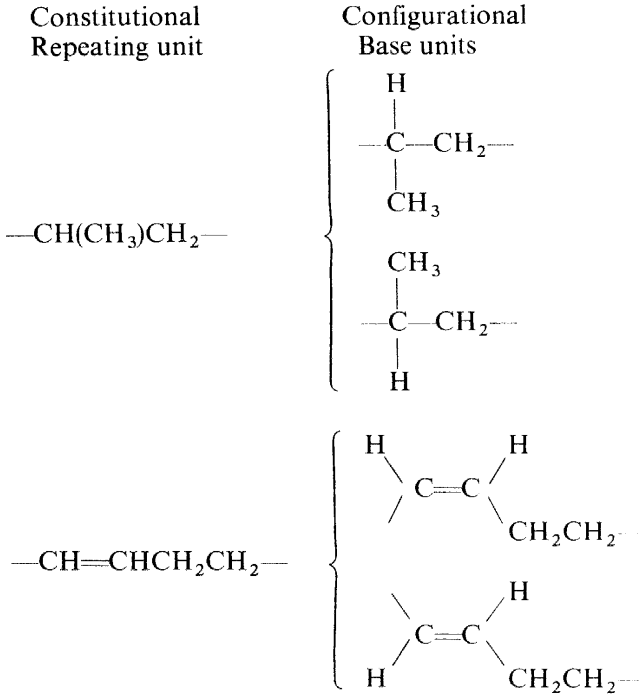


(11) (12)

(12) are not stereoregular because of lack of knowledge about the stereoisomeric center —$CH(CO_2R)$—. Examples (4), (5), (6), (8), (10), (11) and (12) are *tactic polymers*. A stereoregular polymer is always a tactic polymer, but a tactic polymer is not always stereoregular, since a tactic polymer need not have every site of stereoisomerism defined.

Atactic polymer

A regular polymer that is *atactic* contains a *random* distribution of equal numbers of the possible configurational base units corresponding to the constitutional repeating unit. Some examples are:



Block

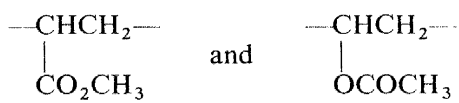
Regular block

Block polymer

In the polymer molecule

$$A_k—B_l—A_m—B_n \qquad (13)$$

A_k, B_l, A_m and B_n are *blocks*, and the individual blocks are *regular*. In the *block polymer* molecule **(13)**, A and B may be



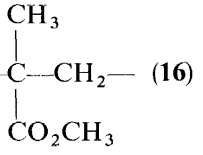
(14) **(15)**

Block copolymer

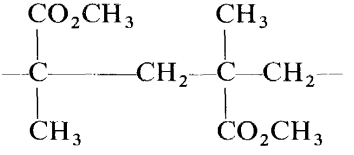
The block polymer whose molecules consist of **(14)** and **(15)** is a *block copolymer* because **(14)** and **(15)** arise from different monomer species.

Tactic block

In the block polymer molecule (**13**) A and B may be:



(**16**)



(**17**)

Stereoblock

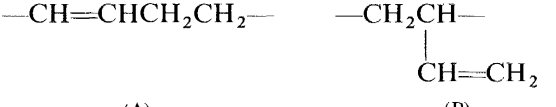
The blocks are *stereoblocks*. The block polymer whose molecules consist of (**16**) and (**17**) is not a block copolymer because (**16**) and (**17**) arise from the same monomer species.

Graft polymer

Graft copolymer

In the *graft polymer* molecule

the A-chain, B_m and B_n are regular blocks, the A-chain is the main chain, and B_m and B_n are the side-chain grafts. The —A— units are junction points and are considered to be part of the main chain. Where A and B are derived from the same monomer, as in



(A) (B)

the polymer is a graft polymer. The graft polymer whose molecules consist of A = (**14**) and B = (**15**) is a *graft copolymer*.