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MACROMOLECULAR DIVISION
COMMISSION ON MACROMOLECULAR NOMENCLATURE*

GLOSSARY OF BASIC TERMS IN POLYMER SCIENCE

(IUPAC Recommendations 1996)

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Glossary of basic terms in polymer science (IUPAC Recommendations 1996)

Abstract: The clear and unambiguous definition of basic terms in a field of science has special significance. Subsequent nomenclature must refer back to these basic terms, and the utmost care is, therefore, required in preparing and revising them. In 1974 , the Commission published a document entitled "Basic Definitions of Terms Relating to Polymers (1974)", that appeared in *Pure Appl. Chem.* **1974**, *40*, 479–491. These definitions have been the foundation for the Commission's work and, building on this basis, the Commission has developed a number of further nomenclature documents. The vast majority of terms in the basic document serve their purpose well. Progress in polymer science and the need for new definitions, the proper wording of which would have been incompatible with some of the basic terms, made it increasingly apparent that some change was needed in the basic terms. Approximately twenty years since the publication of the first document, the Commission now issues a revised and enlarged set of basic terms. The new glossary of terms has been formulated by the Commission with the additional input and aid of several well-known researchers and journal editors.

PREAMBLE

In order to present clear concepts it is necessary that idealized definitions be adopted but it is recognized that the realities of polymer science must be faced. Deviations from ideality arise with polymers at both molecular and bulk levels in ways that have no parallel with the ordinary small molecules of organic or inorganic chemistry. Although such deviations are not explicitly taken into account in the definitions below, the nomenclature recommended can usefully be applied to the *predominant* structural features of real polymer molecules, if necessary with self-explanatory, if imprecise, qualifications such as "essentially ...", "almost completely ...", or "highly ...". Although such expressions lack the rigour beloved by the purist, every experienced polymer scientist knows that communication in this discipline is impossible without them.

Conventionally, the word *polymer* used as a noun is ambiguous; it is commonly employed to refer to both polymer substances and polymer molecules. Henceforth, *macromolecule* is used for individual molecules and *polymer* is used to denote a substance composed of macromolecules. *Polymer* may also be employed unambiguously as an adjective, according to accepted usage, e.g. *polymer blend, polymer molecule*.

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1 - MOLECULES AND MOLECULAR STRUCTURE

1.1 macromolecule
polymer molecule

A molecule of high relative molecular mass, the structure of which essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass.

Notes
1. In many cases, especially for synthetic polymers, a molecule can be regarded as having a high relative molecular mass if the addition or removal of one or a few of the units has a negligible effect on the molecular properties. This statement fails in the case of certain macromolecules for which the properties may be critically dependent on fine details of the molecular structure.
2. If a part or the whole of the molecule has a high relative molecular mass and essentially comprises the multiple repetition of units derived, actually or conceptually, from molecules of low relative molecular mass, it may be described as either **macromolecular** or **polymeric**, or by **polymer** used adjectivally.

1.2 oligomer molecule

A molecule of intermediate relative molecular mass, the structure of which essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass.

Notes
1. A molecule is regarded as having an intermediate relative molecular mass if it has properties which do vary significantly with the removal of one or a few of the units.
2. If a part or the whole of the molecule has an intermediate relative molecular mass and essentially comprises a small plurality of units derived, actually or conceptually, from molecules of lower relative molecular mass, it may be described as **oligomeric**, or by **oligomer** used adjectivally.

1.3 monomer molecule

A molecule which can undergo polymerization (see Definition 3.1), thereby contributing constitutional units (see Definition 1.14) to the essential structure of a macromolecule (see Definition 1.1).

1.4 regular macromolecule

A macromolecule (see Definition 1.1), the structure of which essentially comprises the repetition of a single constitutional unit (see Definition 1.14) with all units connected identically with respect to directional sense.

1.5 irregular macromolecule

A macromolecule (see Definition 1.1), the structure of which essentially comprises the repetition of more than one type of constitutional unit (see Definition 1.14), or a macromolecule the structure of which comprises constitutional units not all connected identically with respect to directional sense.

1.6 linear macromolecule

A macromolecule (see Definition 1.1), the structure of which essentially comprises the multiple repetition in linear sequence of units derived, actually or conceptually, from molecules of low relative molecular mass.

1.7 regular oligomer molecule

An oligomer molecule (see Definition 1.2), the structure of which essentially comprises the repetition of a single constitutional unit (see Definition 1.14) with all units connected identically with respect to directional sense.

1.8 monomeric unit
monomer unit
mer

The largest constitutional unit (see Definition 1.14) contributed by a single monomer molecule (see Definition 1.3) to the structure of a macromolecule (see Definition 1.1) or oligomer molecule (see Definition 1.2).

Note
The largest constitutional unit contributed by a single monomer molecule to the structure of a macromolecule or oligomer molecule may be described as either **monomeric**, or by **monomer** used adjectivally.

1.9 macromonomer molecule

A macromolecule (see Definition 1.1) that has one end-group which enables it to act as a monomer molecule (see Definition 1.3), contributing only a single monomeric unit (see Definition 1.8) to a chain of the final macromolecule.

1.10 macroradical

A macromolecule (see Definition 1.1) which is also a free radical.

1.11 pre-polymer molecule

A macromolecule (see Definition 1.1) or oligomer molecule (see Definition 1.2) capable of entering, through reactive groups, into further polymerization (see Definition 3.1), thereby contributing more than one monomeric unit (see Definition 1.8) to at least one chain of the final macromolecule.

Note
A pre-polymer molecule capable of entering into further polymerization through reactive end-groups (see Definition 1.35), often deliberately introduced, is known as a **telechelic molecule**.

1.12 macromonomeric unit
macromonomer unit

The largest constitutional unit (see Definition 1.14) contributed by a single macromonomer molecule (see Definition 1.9) to the structure of a macromolecule (see Definition 1.1).

1.13 degree of polymerization

The number of monomeric units (see Definition 1.8) in a macromolecule (see Definition 1.1) an oligomer molecule (see Definition 1.2), a block (see Definition 1.62), or a chain (see Definition 1.30).

1.14 constitutional unit

An atom or group of atoms (with pendant atoms or groups, if any) comprising a part of the essential structure of a macromolecule (see Definition 1.1), an oligomer molecule (see Definition 1.2), a block (see Definition 1.62), or a chain (see Definition 1.30).

1.15 constitutional repeating unit (CRU)

The smallest constitutional unit (see Definition 1.14), the repetition of which constitutes a regular macromolecule (see Definition 1.4), a regular oligomer molecule (see Definition 1.7), a regular block (see Definition 1.62), or a regular chain (see Definition 1.30).

1.16 configurational unit

A constitutional unit (see Definition 1.14) having at least one site of defined stereoisomerism.

1.17 configurational base unit

A constitutional repeating unit (see Definition 1.15) in a regular macromolecule (see Definition 1.4), a regular oligomer molecule (see Definition 1.7), a regular block (see Definition 1.62), or a regular chain (see Definition 1.30), the configuration of which is defined at least at one site of stereoisomerism in the main chain (see Definition 1.34).

1.18 configurational repeating unit

The smallest set of successive configurational base units (see Definition 1.17) that prescribes configurational repetition at one or more sites of stereoisomerism in the main chain (see Definition 1.34) of a regular macromolecule (see Definition 1.4), a regular oligomer molecule (see Definition 1.7), a regular block (see Definition 1.62), or a regular chain (see Definition 1.30).

1.19 stereorepeating unit

A configurational repeating unit (see Definition 1.18) having defined configuration at all sites of stereoisomerism in the main chain (see Definition 1.34) of a regular macromolecule (see Definition 1.4), a regular oligomer molecule (see Definition 1.7), a regular block (see Definition 1.62), or a regular chain (see Definition 1.30).

1.20 tacticity

The orderliness of the succession of configurational repeating units (see Definition 1.18) in the main chain (see Definition 1.34) of a regular macromolecule (see Definition 1.4), a regular oligomer molecule (see Definition 1.7), a regular block (see Definition 1.62), or a regular chain (see Definition 1.30).

1.21 tactic macromolecule

A regular macromolecule (see Definition 1.4) in which essentially all the configurational (repeating) units (see Definitions 1.16 and 1.18) are identical.

1.22 stereoregular macromolecule

A regular macromolecule (see Definition 1.4) essentially comprising only one species of stereorepeating unit (see Definition 1.19).

1.23 isotactic macromolecule

A tactic macromolecule (see Definition 1.21), essentially comprising only one species of configurational base unit (see Definition 1.17), which has chiral or prochiral atoms in the main chain (see Definition 1.34) in a unique arrangement with respect to its adjacent constitutional units (see Definition 1.14).

Notes
1. In an isotactic macromolecule, the configurational repeating unit (see Definition 1.16) is identical with the configurational base unit.
2. An isotactic macromolecule consists of meso diads (see Definition 1.64).

1.24 syndiotactic macromolecule

A tactic macromolecule (see Definition 1.21), essentially comprising alternating enantiomeric configurational base units (see Definition 1.17), which have chiral or prochiral atoms in the main chain (see Definition 1.34) in a unique arrangement with respect to their adjacent constitutional units (see Definition 1.14).

Notes
1. In a syndiotactic macromolecule, the configurational repeating unit consists of two configurational base units that are enantiomeric.
2. A syndiotactic macromolecule consists of racemo diads (see Definition 1.64).

1.25 atactic macromolecule

A regular macromolecule (see Definition 1.4) in which the configurational (base) units (see Definitions 1.16 and 1.17) are not all identical.

1.26 block macromolecule

A macromolecule (see Definition 1.1) which is composed of blocks (see Definition 1.62) in linear sequence.

1.27 junction unit

A non-repeating atom or non-repeating group of atoms between blocks in a block macromolecule (see Definition 1.26).

1.28 graft macromolecule

A macromolecule (see Definition 1.1) with one or more species of block (see Definition 1.62) connected to the main chain (see Definition 1.34) as side-chains (see Definition 1.53), these side-chains having constitutional or configurational features that differ from those in the main chain.

1.29 stereoblock macromolecule

A block macromolecule (see Definition 1.26) composed of stereoregular, and possibly non-stereoregular, blocks (see Definition 1.62).

1.30 chain

The whole or part of a macromolecule (see Definition 1.1), an oligomer molecule (see Definition 1.2), or a block (see Definition 1.62), comprising a linear or branched sequence of constitutional units (see Definition 1.14) between two boundary constitutional units, each of which may be either an end-group (see Definition 1.35), a branch point (see Definition 1.54), or an otherwise-designated characteristic feature of the macromolecule.

Notes
1. Except in linear single-strand macromolecules (see Definition 1.39), the definition of a chain may be somewhat arbitrary.
2. A cyclic macromolecule has no end-groups but may nevertheless be regarded as a chain.
3. Any number of branch points may be present between the boundary units.
4. Where appropriate, definitions relating to *macromolecule* may also be applied to *chain*.

1.31 subchain

An arbitrarily chosen contiguous sequence of constitutional units (see Definition 1.14) in a chain (see Definition 1.30).

Note
The term *subchain* may be used to define designated subsets of the constitutional units in a chain.

1.32 linear chain

A chain (see Definition 1.30) with no branch points (see Definition 1.54) intermediate between the boundary units.

1.33 branched chain

A chain (see Definition 1.30) with at least one branch point (see Definition 1.54) intermediate between the boundary units.

1.34 main chain
backbone

That linear chain (see Definition 1.32) to which all other chains, long (see Definition 1.36) or short (see Definition 1.37) or both, may be regarded as being pendant.

Note
Where two or more chains could equally be considered to be the main chain, that one is selected which leads to the simplest representation of the molecule.

1.35 end-group

A constitutional unit (see Definition 1.14) that is an extremity of a macromolecule (see Definition 1.1) or oligomer molecule (see Definition 1.2).

Note
An end-group is attached to only one constitutional unit of a macromolecule or oligomer molecule.

1.36 long chain

A chain (see Definition 1.30) of high relative molecular mass.

Note
See Note 1 to Definition 1.1.

1.37 short chain

A chain (see Definition 1.30) of low relative molecular mass.

Note
See Note 1 to Definition 1.2.

1.38 single-strand chain

A chain (see Definition 1.30) that comprises constitutional units (see Definition 1.14) connected in such a way that adjacent constitutional units are joined to each other through two atoms, one on each constitutional unit.

1.39 single-strand macromolecule

A macromolecule (see Definition 1.1) that comprises constitutional units (see Definition 1.14) connected in such a way that adjacent constitutional units are joined to each other through two atoms, one on each constitutional unit.

1.40 double-strand chain

A chain (see Definition 1.30) that comprises constitutional units (see Definition 1.14) connected in such a way that adjacent constitutional units are joined to each other through three or four atoms, two on one side and either one or two on the other side of each constitutional unit.

1.41 double-strand macromolecule

A macromolecule (see Definition 1.1) that comprises constitutional units (see Definition 1.14) connected in such a way that adjacent constitutional units are joined to each other through three or four atoms, two on one side and either one or two on the other side of each constitutional unit.

1.42 spiro chain

A double-strand chain (see Definition 1.40) consisting of an uninterrupted sequence of rings, with adjacent rings having only one atom in common.

Note
A spiro chain is a double-strand chain (see Definition 1.40) with adjacent constitutional units (see Definition 1.14) joined to each other through three atoms, two on one side and one on the other side of each constitutional unit.

1.43 spiro macromolecule

A double-strand macromolecule (see Definition 1.41) consisting of an uninterrupted sequence of rings, with adjacent rings having only one atom in common.

Note
A spiro macromolecule is a double-strand macromolecule (see Definition 1.41) with adjacent constitutional units (see Definition 1.14) joined to each other through three atoms, two on one side and one on the other side of each constitutional unit.

1.44 ladder chain

A double-strand chain (see Definition 1.40) consisting of an uninterrupted sequence of rings, with adjacent rings having two or more atoms in common.

Note
A ladder chain is a double-strand chain (see Definition 1.40) with adjacent constitutional units (see Definition 1.14) joined to each other through four atoms, two on one side and two on the other side of each constitutional unit.

1.45 ladder macromolecule

A double-strand macromolecule (see Definition 1.41) consisting of an uninterrupted sequence of rings, with adjacent rings having two or more atoms in common.

Note
A ladder macromolecule is a double-strand macromolecule (see Definition 1.41) with adjacent constitutional units (see Definition 1.14) joined to each other through four atoms, two on one side and two on the other side of each constitutional unit.

1.46 multi-strand chain

A chain (see Definition 1.30) that comprises constitutional units (see Definition 1.14) connected in such a

way that adjacent constitutional units are joined to each other through more than four atoms, more than two on at least one side of each constitutional unit.

Note
A chain that comprises constitutional units joined to each other through *n* atoms on at least one side of each constitutional unit is termed an ***n*-strand chain**, e.g., three-strand chain. If an uncertainty exists in defining *n*, the highest possible number is selected.

1.47 multi-strand macromolecule

A macromolecule (see Definition 1.1) that comprises constitutional units (see Definition 1.14) connected in such a way that adjacent constitutional units are joined to each other through more than four atoms, more than two on at least one side of each constitutional unit.

Note
A macromolecule that comprises constitutional units joined to each other through *n* atoms on at least one side of each constitutional unit is termed an ***n*-strand macromolecule**, e.g., three-strand macromolecule. If an ambiguity exists in defining *n*, the highest possible number is selected.

1.48 skeletal structure

The sequence of atoms in the constitutional unit(s) (see Definition 1.14) of a macromolecule (see Definition 1.1), an oligomer molecule (see Definition 1.2), a block (see Definition 1.62), or a chain (see Definition 1.30), which defines the essential topological representation.

1.49 skeletal atom

An atom in a skeletal structure (see Definition 1.48).

1.50 skeletal bond

A bond connecting two skeletal atoms (see Definition 1.49).

1.51 star macromolecule

A macromolecule (see Definition 1.1) containing a single branch point (see Definition 1.54) from which linear chains (see Definition 1.32) (arms) emanate.

Notes
1. A star macromolecule with *n* linear chains (arms) attached to the branch point is termed an ***n*-star macromolecule**, e.g., five-star macromolecule.
2. If the arms of a star macromolecule are identical with respect to constitution and degree of polymerization, the macromolecule is termed a **regular star macromolecule**.
3. If different arms of a star macromolecule are composed of different monomeric units, the macromolecule is termed a **variegated star macromolecule**.

1.52 comb macromolecule

A macromolecule (see Definition 1.1) comprising a main chain (see Definition 1.34) with multiple

trifunctional branch points (see Definition 1.54) from each of which a linear side-chain (see Definition 1.53) emanates.

Notes
1. If the subchains between the branch points of the main chain and the terminal subchains of the main chain are identical with respect to constitution and degree of polymerization, *and* the side chains are identical with respect to constitution and degree of polymerization (see Definition 1.13), the macromolecule is termed a **regular comb macromolecule**.
2. If at least some of the branch points are of functionality greater than three, the macromolecule may be termed a **brush macromolecule**.

1.53 branch
side-chain
pendant chain

An oligomeric (see Definition 1.2) or polymeric (see Definition 1.1) offshoot from a macromolecular (see Definition 1.1) chain (see Definition 1.30).

Notes
1. An oligomeric branch may be termed a **short-chain branch**.
2. A polymeric branch may be termed a **long-chain branch**.

1.54 branch point

A point on a chain (see Definition 1.30) at which a branch (see Definition 1.53) is attached.

Notes
1. A branch point from which f linear chains emanate may be termed an ***f*-functional branch point**, e.g., five-functional branch point. Alternatively, the terms **trifunctional**, **tetrafunctional**, **pentafunctional**, etc. may be used, e.g., pentafunctional branch point.
2. A branch point in a network may be termed a **junction point**.

1.55 branch unit

A constitutional unit (see Definition 1.14) containing a branch point (see Definition 1.54).

Note
A branch unit from which f linear chains emanate may be termed an ***f*-functional branch unit**, e.g., five-functional branch unit. Alternatively, the terms **trifunctional**, **tetrafunctional**, **pentafunctional**, etc. may be used, e.g., pentafunctional branch unit.

1.56 pendant group
side-group

An offshoot, neither oligomeric (see Definition 1.2) nor polymeric (see Definition 1.1), from a chain (see Definition 1.30).

1.57 macrocycle

A cyclic macromolecule (see Definition 1.1) or a macromolecular cyclic portion of a macromolecule.

Notes
1. See Note 2 to Definition 1.30.
2. In the literature, the term *macrocycle* is sometimes used for molecules of low relative molecular mass that would not be considered *macromolecules* as specified in Definition 1.1.

1.58 network

A highly ramified macromolecule (see Definition 1.1) in which essentially each constitutional unit (see Definition 1.14) is connected to each other constitutional unit and to the macroscopic phase boundary by many permanent paths through the macromolecule, the number of such paths increasing with the average number of intervening bonds; the paths must *on the average* be co-extensive with the macromolecule.

Notes
1. Usually, and in all systems that exhibit rubber elasticity, the number of distinct paths is very high, but, in most cases, some constitutional units exist which are connected by a single path only.
2. If the permanent paths through the structure of a network are all formed by covalent bonds, the term **covalent network** may be used.
3. The term **physical network** may be used if the permanent paths through the structure of a network are not all formed by covalent bonds but, at least in part, by physical interactions, such that removal of the interactions leaves individual macromolecules or a macromolecule that is not a network.

1.59 crosslink

A small region in a macromolecule (see Definition 1.1) from which at least four chains (see Definition 1.30) emanate, and formed by reactions involving sites or groups on existing macromolecules or by interactions between existing macromolecules.

Notes
1. The small region may be an atom, a group of atoms, or a number of branch points connected by bonds, groups of atoms, or oligomeric chains.
2. In the majority of cases, a crosslink is a covalent structure but the term is also used to describe sites of weaker chemical interactions, portions of crystallites, and even physical interactions and entanglements.

1.60 micronetwork

A highly ramified macromolecule (see Definition 1.1) that contains cyclic structures and is of colloidal dimensions.

1.61 loose end

A chain (see Definition 1.30), only one point of which is attached to a network (see Definition 1.58).

1.62 block

A portion of a macromolecule (see Definition 1.1), comprising many constitutional units (see Definition 1.14), that has at least one feature which is not present in the adjacent portions.

Note
Where appropriate, definitions relating to *macromolecule* may also be applied to *block*.

1.63 constitutional sequence

The whole or part of a chain (see Definition 1.30) comprising one or more species of constitutional unit(s) (see Definition 1.14) in defined sequence.

Note
Constitutional sequences comprising two constitutional units are termed **diads**, those comprising three constitutional units **triads**, and so on. In order of increasing sequence lengths they are called **tetrads**, **pentads**, **hexads**, **heptads**, **octads**, **nonads**, **decads**, **undecads**, etc.

1.64 configurational sequence

The whole or part of a chain (see Definition 1.30) comprising one or more species of configurational unit(s) (see Definition 1.16) in defined sequence.

Note
Configurational sequences comprising two configurational units are termed **diads**, those with three such configurational units **triads**, and so on. In order of increasing sequence lengths they are called **tetrads**, **pentads**, **hexads**, **heptads**, **octads**, **nonads**, **decads**, **undecads**, etc.

1.65 polyelectrolyte molecule

A macromolecule (see Definition 1.1) in which a substantial portion of the constitutional units (see Definition 1.14) have ionizable or ionic groups, or both.

1.66 ionomer molecule

A macromolecule (see Definition 1.1) in which a small but significant proportion of the constitutional units (see Definition 1.14) have ionizable or ionic groups, or both.

Note
Some protein molecules may be classified as ionomer molecules.

2 - SUBSTANCES

2.1 monomer

A substance composed of monomer molecules (see Definition 1.3).

2.2 polymer

A substance composed of macromolecules (see Definition 1.1).

2.3 oligomer

A substance composed of oligomer molecules (see Definition 1.2).

Note
An oligomer obtained by telomerization (see Definition 3.2) is often termed a **telomer**.

2.4 homopolymer

A polymer (see Definition 2.2) derived from one species of (real, implicit or hypothetical) monomer (see Definition 2.1).

Notes
1. Many polymers are made by the mutual reaction of complementary monomers. These monomers can readily be visualized as reacting to give an "implicit monomer", the homopolymerization of which would give the actual product, which can be regarded as a homopolymer. Common examples are poly(ethylene terephthalate) and poly(hexamethylene adipamide).
2. Some polymers are obtained by the chemical modification of other polymers such that the structure of the macromolecules that constitute the resulting polymer can be thought of as having been formed by the homopolymerization of a hypothetical monomer. These polymers can be regarded as homopolymers. Example: poly(vinyl alcohol).

2.5 copolymer

A polymer (see Definition 2.2) derived from more than one species of monomer (see Definition 2.1).

Note
Copolymers that are obtained by copolymerization (see Definition 3.4) of two monomer species are sometimes termed **bipolymers**, those obtained from three monomers **terpolymers**, those obtained from four monomers **quaterpolymers**, etc..

2.6 pseudo-copolymer

An irregular polymer (see Definition 2.16), the molecules of which are derived from only one species of monomer (see Definition 2.1) but which display a variety of structural features more appropriate for description in copolymer (see Definition 2.5) terms.

Note
Where appropriate, adjectives specifying the types of *copolymer* may be applied to *pseudo-copolymer*. The term **statistical pseudo-copolymer**, for instance, may be used to describe an irregular polymer in the molecules of which the sequential distribution of configurational units obeys known statistical laws (see Definition 2.9).

2.7 co-oligomer

An oligomer (see Definition 2.3) derived from more than one species of monomer (see Definition 2.1).

2.8 pseudo-co-oligomer

An irregular oligomer (see Definition 2.3), the molecules of which are derived from only one species of monomer (see Definition 2.1) but which display a variety of structural features more appropriate for description in co-oligomer (see Definition 2.7) terms.

2.9 statistical copolymer

A copolymer (see Definition 2.5) consisting of macromolecules (see Definition 1.1) in which the sequential distribution of the monomeric units (see Definition 1.8) obeys known statistical laws.

Note
An example of a statistical copolymer is one consisting of macromolecules in which the sequential distribution of monomeric units follows Markovian statistics.

2.10 random copolymer

A copolymer (see Definition 2.5) consisting of macromolecules (see Definition 1.1) in which the probability of finding a given monomeric unit (see Definition 1.8) at any given site in the chain (see Definition 1.30) is independent of the nature of the adjacent units.

Note
In a random copolymer, the sequence distribution of monomeric units follows Bernoullian statistics.

2.11 alternating copolymer

A copolymer (see Definition 2.5) consisting of macromolecules (see Definition 1.1) comprising two species of monomeric units (see Definition 1.8) in alternating sequence.

Note
An alternating copolymer may be considered as a homopolymer derived from an implicit or hypothetical monomer; see Note 1 to Definition 2.4.

2.12 periodic copolymer

A copolymer (see Definition 2.5) consisting of macromolecules (see Definition 1.1) comprising more than two species of monomeric units (see Definition 1.8) in regular sequence.

2.13 uniform polymer
monodisperse polymer

A polymer (see Definition 2.2) composed of molecules uniform with respect to relative molecular mass and constitution.

Notes
1. A polymer comprising a mixture of linear (see Definition 1.32) and branched (see Definition 1.33) chains, all of uniform relative molecular mass, is not uniform.
2. A copolymer comprising linear molecules of uniform relative molecular mass and uniform elemental composition but different sequential arrangements of the various types of monomeric units (see Definition 1.8), is not uniform (e.g., a copolymer comprising molecules with a random arrangement as well as a block arrangement of monomeric units).
3. A polymer uniform with respect only to *either* relative molecular mass *or* constitution may be termed **uniform**, provided a suitable qualifier is used (e.g., "a polymer uniform with respect to relative molecular mass").
4. The adjectives *monodisperse* and *polydisperse* are deeply rooted in the literature, despite the former being non-descriptive and self-contradictory. They are in common usage and it is recognized that they will continue to be used for some time; nevertheless, more satisfactory terms are clearly desirable. After an

extensive search for possible replacements, the terms *uniform* and *non-uniform* have been selected and they are now the preferred adjectives.

2.14 non-uniform polymer
polydisperse polymer

A polymer (see Definition 2.2) comprising molecules non-uniform with respect to relative molecular mass or constitution or both.

Note
See Notes 3 and 4 to Definition 2.13.

2.15 regular polymer

A polymer composed of regular macromolecules (see Definition 1.4), regular star macromolecules (see Definition 1.51), or regular comb macromolecules (see Definition 1.52).

Note
A polymer consisting of star macromolecules with arms identical with respect to constitution and degree of polymerisation is considered to be regular; see Note 2 to Definition 1.51. Analogously, a polymer consisting of comb macromolecules with the sub-chains between the branch points of the main chain and the terminal sub-chains of the main chain identical with respect to constitution and degree of polymerisation and the side-chains identical with respect to constitution and degree of polymerisation is considered to be regular; see Note 1 to Definition 1.52.

2.16 irregular polymer

A polymer composed of irregular macromolecules (see Definition 1.5).

2.17 tactic polymer

A polymer composed of tactic macromolecules (see Definition 1.21).

2.18 isotactic polymer

A polymer composed of isotactic macromolecules (see Definition 1.23).

2.19 syndiotactic polymer

A polymer composed of syndiotactic macromolecules (see Definition 1.24).

2.20 stereoregular polymer

A polymer composed of stereoregular macromolecules (see Definition 1.22).

2.21 atactic polymer

A polymer composed of atactic macromolecules (see Definition 1.25).

2.22 block polymer

A polymer composed of block macromolecules (see Definition 1.26).

2.23 graft polymer

A polymer composed of graft macromolecules (see Definition 1.28).

2.24 block copolymer

A copolymer (see Definition 2.5) that is a block polymer (see Definition 2.22).

Note
In the constituent macromolecules of a block copolymer, adjacent blocks are constitutionally different, i.e., adjacent blocks comprise constitutional units (see Definition 1.14) derived from different species of monomer (see Definition 2.1) or from the same species of monomer but with a different composition or sequence distribution of constitutional units.

2.25 graft copolymer

A copolymer (see Definition 2.5) that is a graft polymer (see Definition 2.23).

Note
In the constituent macromolecules of a graft copolymer, adjacent blocks in the main chain or side-chains, or both, are constitutionally different, i.e., adjacent blocks comprise constitutional units (see Definition 1.14) derived from different species of monomer (see Definition 2.1) or from the same species of monomer but with a different composition or sequence distribution of constitutional units.

2.26 stereoblock polymer

A polymer composed of stereoblock macromolecules (see Definition 1.29).

2.27 linear polymer

A polymer (see Definition 2.2) composed of linear macromolecules (see Definition 1.6).

2.28 linear copolymer

A copolymer (see Definition 2.5) composed of linear macromolecules (see Definition 1.6).

2.29 single-strand polymer

A polymer (see Definition 2.2), the macromolecules (see Definition 1.1) of which are single-strand macromolecules (see Definition 1.39).

2.30 double-strand polymer

A polymer (see Definition 2.2), the macromolecules (see Definition 1.1) of which are double-strand macromolecules (see Definition 1.41).

Notes
1. A polymer, the macromolecules of which are spiro macromolecules (see Definition 1.43), is termed a **spiro polymer**.
2. A polymer, the macromolecules of which are ladder macromolecules (see Definition 1.45), is termed a **ladder polymer**.

2.31 double-strand copolymer

A copolymer (see Definition 2.5), the macromolecules (see Definition 1.1) of which are double-strand macromolecules (see Definition 1.41).

2.32 star polymer

A polymer composed of star macromolecules (see Definition 1.51).

2.33 comb polymer

A polymer composed of comb macromolecules (see Definition 1.52).

Note
See the Notes to Definitions 1.52 and 2.15

2.34 branched polymer

A polymer (see Definition 2.2), the molecules of which are branched chains (see Definition 1.33).

2.35 macromonomer

A polymer composed of macromonomer molecules (see Definition 1.9).

2.36 mesogenic monomer

A monomer (see Definition 2.1) which can impart the properties of liquid crystals to the polymers (see Definition 2.2) formed by its polymerization (see Definition 3.1).

2.37 pre-polymer

A polymer or oligomer composed of pre-polymer molecules (see Definition 1.11).

2.38 polyelectrolyte

A polymer composed of polyelectrolyte molecules (see Definition 1.65).

2.39 ionomer

A polymer composed of ionomer molecules (see Definition 1.66).

2.40 polymer blend

A macroscopically homogeneous mixture of two or more different species of polymer (see Definition 2.2).

Notes
1. In most cases, blends are homogeneous on scales smaller than several times visual optical wavelengths.
2. For polymer blends, no account is taken of the miscibility or immiscibility of the constituent polymers, i.e., no assumption is made regarding the number of phases present.
3. The use of the term *polymer alloy* for a polymer blend is discouraged.

2.41 network polymer
polymer network

A polymer composed of one or more networks (see Definition 1.58).

2.42 semi-interpenetrating polymer network (SIPN)

A polymer (see Definition 2.2) comprising one or more networks (see Definition 1.58) and one or more linear (see Definition 1.32) or branched (see Definition 1.33) polymer(s) characterized by the penetration on a molecular scale of at least one of the networks by at least some of the linear or branched macromolecules.

Note
Semi-interpenetrating polymer networks are distinguished from interpenetrating polymer networks because the constituent linear or branched polymers can, in principle, be separated from the constituent polymer network(s) without breaking chemical bonds; they are polymer blends.

2.43 interpenetrating polymer network (IPN)

A polymer (see Definition 2.2) comprising two or more networks (see Definition 1.58) which are at least partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken.

Note
A mixture of two or more pre-formed polymer networks is not an IPN.

2.44 polymer-polymer complex

A complex, at least two components of which are different polymers (see Definition 2.2).

3 - REACTIONS

3.1 polymerization

The process of converting a monomer (see Definition 2.1) or a mixture of monomers into a polymer (see Definition 2.2).

3.2 oligomerization

The process of converting a monomer (see Definition 2.1) or a mixture of monomers into an oligomer (see Definition 2.3).

Note
An oligomerization by chain reaction carried out in the presence of a large amount of chain-transfer (see Definition 3.24) agent, so that the end-groups (see Definition 1.35) are essentially fragments of the chain-transfer agent, is termed **telomerization**.

3.3 homopolymerization

Polymerization (see Definition 3.1) in which a homopolymer (see Definition 2.4) is formed.

3.4 copolymerization

Polymerization (see Definition 3.1) in which a copolymer (see Definition 2.5) is formed.

3.5 co-oligomerization

Oligomerization (see Definition 3.2) in which a co-oligomer (see Definition 2.7) is formed.

3.6 chain polymerization

A chain reaction in which the growth of a polymer (see Definition 1.1) chain (see Definition 1.30) proceeds exclusively by reaction(s) between monomer(s) (see Definition 2.1) and reactive site(s) on the polymer chain with regeneration of the reactive site(s) at the end of each growth step.

Notes
1. A chain polymerization consists of initiation and propagation reactions, and may also include termination and chain transfer (see Definition 3.24) reactions.
2. The adjective *chain* in *chain polymerization* denotes a chain reaction rather than a polymer chain.
3. Propagation in chain polymerization usually occurs without the formation of small molecules. However, cases exist where a low-molar-mass by-product is formed, as in the polymerization of oxazolidine-2,5-diones derived from amino acids (commonly termed amino-acid *N*-carboxy anhydrides). When a low-molar-mass by-product is formed, the adjective *condensative* is recommended to give the term **condensative chain polymerization**.
4. The growth steps are expressed by

$$P_x + M \rightarrow P_{x+1}\ (+\,L)\ \{x\} \in \{1, 2, \ldots \infty\}$$

where P_x denotes the growing chain of degree of polymerization x, M a monomer, and L a low-molar- mass by-product formed in the case of condensative chain polymerization.
5. The term *chain polymerization* may be qualified further, if necessary, to specify the type of chemical reactions involved in the growth step, e.g., ring-opening chain polymerization, cationic chain polymerization.
6. There exist, exceptionally, some polymerizations that proceed *via* chain reactions that, according to the definition, are not chain polymerizations. For example, the polymerization

$$HS\text{-}X\text{-}SH + H_2C{=}CH\text{-}Y\text{-}CH{=}CH_2 \rightarrow S\text{-}X\text{-}S\text{-}CH_2\text{-}CH_2\text{-}Y\text{-}CH_2\text{-}CH_2$$

proceeds *via* a radical chain reaction with intermolecular transfer of the radical center. The growth step,

however, involves reactions between molecules of all degrees of polymerization and, hence, the polymerization is classified as a polyaddition (see Definition 3.8). If required, the classification can be made more precise and the polymerization described as a chain-reaction polyaddition.

3.7 polycondensation

A polymerization (see Definition 3.1) in which the growth of polymer (see Definition 1.1) chains (see Definition 1.30) proceeds by condensation reactions between molecules of all degrees of polymerization (see Definition 1.13).

Notes

1. The growth steps are expressed by

$$P_x + P_y \rightarrow P_{x+y} + L \quad \{x\} \in \{1, 2, \ldots \infty\}; \{y\} \in \{1, 2, \ldots \infty\}$$

where P_x and P_y denote chains of degree of polymerization x and y, respectively, and L a low-molar- mass by-product.

2. The earlier term *polycondensation* was synonymous with *condensation polymerization.* It should be noted that the current definitions of polycondensation and condensative chain polymerization were both embraced by the earlier term *polycondensation.*

3.8 polyaddition

A polymerization (see Definition 3.1) in which the growth of polymer (see Definition 1.1) chains (see Definition 1.30) proceeds by addition reactions between molecules of all degrees of polymerization (see Definition 1.13).

Notes

1. The growth steps are expressed by

$$P_x + P_y \rightarrow P_{x+y} \quad \{x\} \in \{1, 2, \ldots \infty\}; \{y\} \in \{1, 2, \ldots \infty\}$$

where P_x and P_y denote chains of degrees of polymerization x and y, respectively.

2. The earlier term *addition polymerization* embraced both the current concepts of *polyaddition* and *chain polymerization,* but did not include *condensative chain polymerization.*

3.9 statistical copolymerization

A copolymerization (see Definition 3.4) in which a statistical copolymer (see Definition 2.9) is formed.

3.10 random copolymerization

A copolymerization (see Definition 3.4) in which a random copolymer (see Definition 2.10) is formed.

3.11 alternating copolymerization

A copolymerization (see Definition 3.4) in which an alternating copolymer (see Definition 2.11) is formed.

3.12 periodic copolymerization

A copolymerization (see Definition 3.4) in which a periodic copolymer (see Definition 2.12) is formed.

3.13 ring-opening polymerization

A polymerization (see Definition 3.1) in which a cyclic monomer (see Definition 2.1) yields a monomeric unit (see Definition 1.8) which is acyclic or contains fewer cycles than the monomer.

Note
If the monomer is polycyclic, the opening of a single ring is sufficient to classify the reaction as a ring-opening polymerization.

3.14 ring-opening copolymerization

A copolymerization (see Definition 3.4) which is a ring-opening polymerization (see Definition 3.13) with respect to at least one monomer (see Definition 2.1).

3.15 radical polymerization

A chain polymerization (see Definition 3.6) in which the kinetic-chain carriers are radicals.

Note
Usually, the growing chain end bears an unpaired electron.

3.16 radical copolymerization

A copolymerization (see Definition 3.4) which is a radical polymerization (see Definition 3.15).

3.17 ionic polymerization

A chain polymerization (see Definition 3.6) in which the kinetic-chain carriers are ions or ion-pairs.

Note
Usually, the growing chain ends are ions.

3.18 ionic copolymerization

A copolymerization (see Definition 3.4) which is an ionic polymerization (see Definition 3.17).

3.19 anionic polymerization

An ionic polymerization (see Definition 3.18) in which the kinetic-chain carriers are anions.

3.20 cationic polymerization

An ionic polymerization (see Definition 3.18) in which the kinetic-chain carriers are cations.

3.21 living polymerization

A chain polymerization from which chain transfer and chain termination are absent.

Note
In many cases, the rate of chain initiation is fast compared with the rate of chain propagation, so that the number of kinetic-chain carriers is essentially constant throughout the polymerization.

3.22 living copolymerization

A copolymerization (see Definition 3.4) which is a living polymerization (see Definition 3.21).

3.23 cyclopolymerization

A polymerization (see Definition 3.1) in which the number of cyclic structures in the constitutional units (see Definition 1.14) of the resulting macromolecules (see Definition 1.1) is larger than in the monomer molecules (see Definition 1.3).

3.24 chain scission

A chemical reaction resulting in the breaking of skeletal bonds (see Definition 1.50).

3.25 depolymerization

The process of converting a polymer (see Definition 2.2) into a monomer (see Definition 2.1) or a mixture of monomers.

Note
Unzipping is depolymerization occurring by a sequence of reactions, progressing along a macromolecule (see Definition 1.1) and yielding products, usually monomer molecules (see Definition 1.3), at each reaction step, from which macromolecules similar to the original can be regenerated.

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