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SOURCE-BASED NOMENCLATURE FOR NON-LINEAR MACROMOLECULES AND MACROMOLECULAR ASSEMBLIES

(IUPAC Recommendations 1997)

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Source-based nomenclature for non-linear macromolecules and macromolecular assemblies (IUPAC Recommendations 1997)

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Abstract: A source-based nomenclature for non-linear macromolecules and macromolecular assemblies is proposed. Source-based or structure-based names for linear regular (single-strand and double-strand) and irregular macromolecules can be derived using rules published previously. In contrast, the present document deals with the source-based naming of non-linear macromolecules and assemblies of macromolecules. The former comprise branched, graft, comb, star, cyclic and network macromolecules; the latter comprise polymer blends, interpenetrating polymer networks and polymer-polymer complexes. The names of non-linear macromolecules are formed by citing source-based name(s) of the constituent linear chains(s) and denoting their mode(s) of combination by prefixes and connectives. Specification of molecular weight, composition or branch-point functionality(ies) of the macromolecule or its constituents may be given in parentheses.

INTRODUCTION

The recommendations for macromolecular nomenclature published so far (1) have dealt with regular single-strand organic macromolecules (2,3), regular single-strand and quasi-single-strand inorganic and coordination macromolecules (4), copolymer macromolecules (5), regular double-strand organic macromolecules (6) and irregular single-strand organic macromolecules (7). As far as possible, the established principles of organic and inorganic nomenclature have been followed (8-10). The present document is intended to extend the system to non-linear macromolecules such as branched and cyclic macromolecules, micronetworks, polymer networks, and to macromolecular assemblies held together by non-covalent bonds or forces, such as polymer blends, interpenetrating polymer networks, and polymer complexes.

Conventionally, the word 'polymer' as a noun is ambiguous in meaning. It is commonly used 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 (11). 'Polymer' may also be employed unambiguously as an adjective according to accepted usage, e.g. 'polymer blend', 'polymer molecule'.

For non-linear macromolecules, the skeletal structure should be reflected in the name. Non-linear macromolecular structures and macromolecular assemblies are classified using the following terms:

Cyclic
Branched
  Short-branched
  Long-branched
Micronetwork
Network
Blend
Semi-interpenetrating polymer network
Interpenetrating polymer network
Polymer - polymer complex

Definitions of some of the terms used in this document can be found in previous nomenclature reports [11,12].

1 DEFINITIONS

1.1 chain

The whole or part of a macromolecule, an oligomer molecule, or a block, comprising a linear or branched sequence of constitutional units between two boundary constitutional units, each of which may be either an end-group, a branch point, or an otherwise-designated characteristic feature of the macromolecule.

Note 1 Except in linear single-strand macromolecules, the definition of the chain may be somewhat arbitrary.

Note 2 A cyclic macromolecule has no end-groups but may nevertheless be regarded as a chain.

Note 3 Any number of branch points may be present between the boundary units.

Note 4 Where appropriate, definitions relating to "macromolecule" may also be applied to "chain".

1.2 linear chain

A chain with no branch points intermediate between the boundary units.

1.3 branched chain

A chain with at least one branch point intermediate between the boundary units.

1.4 main chain

backbone

That linear chain to which all other chains, long or short 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.

1.5 subchain

An arbitrarily chosen contiguous sequence of constitutional units in a chain.

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

1.6 side chain

branch

pendant chain

An oligomeric or polymeric offshoot from a macromolecular chain.

Note 1 An oligomeric side chain may be termed a short-chain branch.

Note 2 A polymeric side chain may be termed a long-chain branch.

1.7 branch unit

A constitutional unit containing a branch point.

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.

1.8 branch point

A point on a chain at which a branch is attached.

Note 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.

Note 2 A branch point in a network may be termed a junction point.

1.9 crosslink

A small region in a macromolecule from which at least four chains emanate, and which is formed by reactions involving sites or groups on *existing* macromolecules or by interactions between *existing* macromolecules.

Note 1 The small region can be an atom, a group of atoms, or a number of branch points connected by bonds, groups of atoms, or oligomeric chains.

Note 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.

1.10 network

A highly ramified macromolecule in which essentially each constitutional unit is connected to each other constitutional units 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 coextensive with the macromolecule.

Note 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.

Note 2 If the permanent paths through the structure of a network are all formed by covalent bonds, the term covalent network may be used.

Note 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 molecules or macromolecules or a non-network macromolecule.

1.11 micronetwork

A highly ramifed macromolecule containing cyclic structures and of colloidal dimensions.

1.12 macrocycle

A cyclic macromolecule or a macromolecular cyclic portion of a macromolecule.

Note 1 See Note 2 to Definition 1.1.

Note 2 In the literature, the term "macrocycle" is sometimes used for molecules of low relative molecular mass that would not be considered 'macromolecules'.

1.13 comb macromolecule

A macromolecule comprising a main chain with multiple trifunctional branch points from each of which a linear side-chain emanates.

Note 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, the macromolecule is termed a regular comb macromolecule.

Note 2 If at least some of the branch points are of functionalities greater than three, the macromolecule may be termed a brush macromolecule.

1.14 star macromolecule

A macromolecule containing a single branch point from which linear chains (arms) emanate.

Note 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.

Note 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.

Note 3 If different arms of a star macromolecule are composed of different monomeric units, the macromolecule is termed a variegated star macromolecule.

1.15 polymer blend

A macroscopically homogeneous mixture of two or more different species of polymer.

Note 1 See Fig. 1a.

Note 2 In most cases, blends are homogeneous on scales larger than several times visual, optical wavelengths.

Note 3 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.

Note 4 The general use of the term "polymer alloy" as a synonym for a polymer blend is discouraged.

1.16 semi-interpenetrating polymer network (SIPN)

A polymer comprising one or more networks and one or more linear or branched polymers 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 1 See Figure 1b.

Note 2 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.

1.17 network polymer

A polymer composed of one or more networks.

1.18 interpenetrating polymer network (IPN)

A polymer comprising two or more networks 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 1 See Figure lc.

Note 2 A mixture of two or more pre-formed polymer networks is not an IPN.

1.19 polymer - polymer complex

A complex, at least two components of which are different polymers.

2 GENERAL PRINCIPLES

The following procedure is employed to name both non-linear macromolecules and macromolecular assemblies:

1. The topology of the structure of the non-linear macromolecule or modes of combination of the constituent species of macromolecules are ascertained.

2. For each constituent linear subchain in a non-linear macromolecule or for each species of macromolecule, a source-based name is assigned according to the rules for naming homopolymer or copolymer molecules [2,5].

3. The names of the constituent subchains in a non-linear macromolecule or those of the macromolecules are then combined together with the appropriate prefix or connective(s), or both.

The following italicized qualifiers can be used as both prefixes (e.g., *blend-*, *net-*) and connectives (e.g., *-blend-*, *-net-*), separated by (a) hyphen(s) from the constituent name(s), to designate the skeletal structure of non-linear macromolecules or macromolecular assemblies:

cyclic	*cyclo*
branched, unspecified	*branch*
short-chain-branched	*sh-bran*
long-chain-branched	*l-branch*
branched with branch points of functionality f	*f- branch* (f is given a numerical value)
comb(like)	*comb*
star	*star*
star with f arms	*f-star* (f is given a numerical value)
network	*net*
micronetwork	*μ-net*
polymer blend	*blend*
interpenetrating polymer network	*ipn*
semi-interpenetrating polymer network	*sipn*
polymer - polymer complex	*compl*

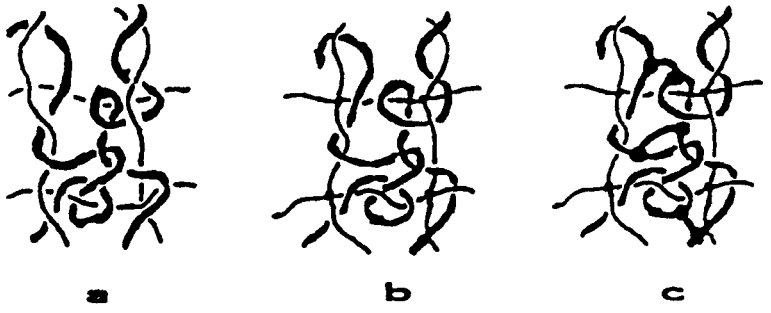

Fig. 1: Schematic representation of macromolecular assemblies —— polymer chain 1, ▬▬ polymer chain 2, ● branch point (a) polymer blend, (b) semi-interpenetrating polymer network, (c) interpenetrating polymer network

3 NON-LINEAR HOMOPOLYMER MOLECULES

Rule 1. In naming non-linear homopolymer molecules, the italicized prefix for the skeletal structure of the macromolecule is placed before the source-based name of the constituent linear chain.

Examples:

1.1 *sh-branch*-polyethylene

1.2 4-*star*-polystyrene

1.3 *cyclo*-poly(dimethylsiloxane)

1.4 *net*-polybutadiene

Rule 2. Crosslinks, the branch units of star macromolecules and other junction units [5] are optionally specified by their source-based names after the name of the macromolecule with the connective (Greek) ν, separated by hyphens.

Note When the content of the crosslinking monomer is high, the macromolecule is treated as a copolymer molecule.

Examples:

2.1 *net*-polybutadiene-ν-sulfur

(polybutadiene vulcanized with sulfur)

2.2 *net*-polystyrene-ν-divinylbenzene

(polystyrene crosslinked with divinylbenzene to form a network)

2.3 *branch*-polystyrene-ν-divinylbenzene

(polystyrene crosslinked with divinylbenzene, insufficient to cause a network to form)

2.4 *l-branch*-poly(ethyl acrylate)-ν-(ethylene dimethacrylate)

2.5 3-*star*-polystyrene-ν-methyltrichlorosilane

4 NON-LINEAR COPOLYMER MOLECULES

4.1 Copolymer molecules comprising a single species of linear chain

Rule 3. In naming non-linear copolymer molecules comprising linear subchains of the same monomeric units in a single type of skeletal structure, the italicized prefix for the skeletal structure is placed before the source-based name of the constituent linear subchains. In the case of star macromolecules with block copolymer arms, the block named first after the prefix emanates from the branch point.

Examples:

3.1 *cyclo*-poly(styrene-*stat*-α-methylstyrene)

3.2 *star*-(polystyrene-*block*-poly(methyl methacrylate))

(each arm of the star macromolecule is a block copolymer chain with a polystyrene block attached to the central unit)

3.3 *μ-net*-poly[styrene-*stat*-(vinyl cinnamate)]

(crosslinked copolymeric micronetwork)

3.4 *net*-poly(phenol-*co*-formaldehyde)

3.5 *comb*-poly(styrene-*stat*-acrylonitrile)

(both the main chain and side chains are statistical copolymer chains of styrene and acrylonitrile)

3.6 *net*-poly[(hexane-1,6-diyl diisocyanate)-*alt*-glycerol]

3.7 *net*-poly[styrene-*alt*-(maleic anhydride)]-*v*-(ethylene glycol)

(alternating copolymer of styrene and maleic anhydride crosslinked with ethylene glycol to form a network)

3.8 *star*-(polyA-*block*-polyB-*block*-polyC)

(star copolymer molecule, each arm of which consists of the same block-copolymer chain, see Figure 2a).

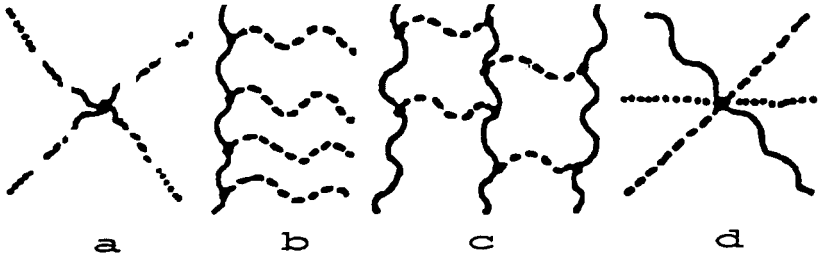

Fig. 2: Schematic representation of non-linear copolymer molecules——— polymer chain 1, - - - - polymer chain 2, ···· polymer chain 3, ● branch point (a), (d) star macromolecules, (b) comb macromolecule, (c) network macromolecule

4.2 Copolymer molecules comprising a variety of species of chains

Rule 4. In naming non-linear copolymer molecules having linear subchains of two or more types, the italicized connective for the skeletal structure is placed between the source-based names of the types of constituent linear subchains. In the case of branched and comb-like macromolecules, the linear chain named before the connective is that which forms the main chain, whereas that (those) named after the connective forms (form) the side chain(s). The names of different species of side chain are separated by semicolons. In the case of variegated star macromolecules the prefix is placed before the name of the macromolecule with the different species of arms separated by semicolons.

Examples:

4.1 polystyrene-*comb*-polyacrylonitrile

(equivalent to polystyrene-*graft*-polyacrylonitrile, see Figure 2b; *-graft-* is recommended for these cases. However, *comb* cannot be replaced by *graft* if the former is a prefix, cf. Example 3.5)

4.2 polystyrene-*comb*-[polyacrylonitrile; poly(methyl methacrylate)]

(a comb macromolecule with polyacrylonitrile and poly(methyl methacrylate) side chains)

4.3 poly[(ethylene glycol)-*alt*-(maleic anhydride)]-*net*-oligostyrene

(unsaturated polyester cured with styrene, see Figure 2c)

4.4 poly(methyl methacrylate)-*net*-poly(ethylene oxide)

4.5 *star*-(polyA; polyB; polyC)

(a variegated star copolymer molecule consisting of arm(s) of polyA, arm(s) of polyB and arm(s) of polyC, see Figure 2d)

Rule 5. The name of a crosslinking monomer molecule having two or more different types of polymerizable groups, each serving as a monomeric unit for one of two or more different linear chains, is cited with the name of each of the chains with the symbol ν.

Note When the proportion of the crosslinking monomer having two or more different polymerizable groups is a significant fraction of the total, the constituent chains are treated as copolymer chains.

Examples:

5.1 [poly(butyl vinyl ether)-ν-(2-vinyloxyethyl methacrylate)]-*net*-[poly-(methyl methacrylate)-ν-(2-vinyloxyethyl methacrylate))

(poly(butyl vinyl ether) and poly(methyl methacrylate) chains crosslinked mutually with 2-vinyloxyethyl methacrylate to form a network)

5.2 poly[(butyl vinyl ether)-*co*-(2-vinyloxyethyl methacrylate)]-*net*-poly-[(methyl methacrylate)-*co*-(2-vinyloxyethyl methacrylate)]

(a copolymer of butyl vinyl ether and 2-vinyloxyethyl methacrylate formed into a network with a copolymer of methyl methacrylate and 2-vinyloxyethyl methacrylate)

5.3 [*branch*-poly(butyl vinyl ether)-ν-(2-vinyloxyethyl methacrylate)]-ν-[*branch*-poly(methyl methacrylate)-ν-(2-vinyloxyethyl methacrylate)]

(poly(butyl vinyl ether) and poly(methyl methacrylate) chains crosslinked mutually with 2-vinyloxyethyl methacrylate, insufficient to cause a network to form)

5 MACROMOLECULAR ASSEMBLIES

Assemblies of macromolecules include polymer blends, semi-interpenetrating polymer networks, network polymers, interpenetrating polymer networks, and polymer - polymer complexes.

Rule 6. Assemblies of macromolecules held together by non-covalent bonds are named by combination of the names of the constituent macromolecules together with an italicized connective between them.

Examples:

6.1 polystyrene-*blend*-poly(2,6-dimethylphenol)

6.2 (*net*-polystyrene)-*blend*-(*net*-polybutadiene)

(blend of two networks)

6.3 (*net*-polystyrene)-*sipn*-poly(vinyl chloride)

(SIPN of a polystyrene network and a linear poly(vinyl chloride), see Figure 1b)

6.4 (*net*-polybutadiene)-*ipn*-(*net*-polystyrene)

(IPN of two networks, see Figure 1c)

6.5 [*net*-poly(styrene-*stat*-butadiene)]-*ipn*-[*net*-poly(ethyl acrylate)]

(IPN of two networks)

6.6 poly(acrylic acid)-*compl*-poly(4-vinylpyridine)

(complex of two species of linear macromolecules)

6.7 poly[(methyl methacrylate)-*stat*-(methacrylic acid)]-*compl*-poly(*N*-vinyl-2-pyrrolidone)

(complex of statistical copolymer and homopolymer molecules)

6 QUANTITATIVE SPECIFICATIONS

Quantitative characteristics of a macromolecule or an assembly of macromolecules, such as mass and mole fractions or percentages as well as the degrees of polymerization and molar masses, may be expressed by placing corresponding figures after the complete name. The order of citation is the same as for the monomer species in the name. Some characteristics cannot be defined for all types of macromolecules and assemblies dealt with in this document, e.g., molar mass of a network.

Rule 7. Mass or mole fractions or percentages of the monomeric units are placed in parentheses after the name of the macromolecule or assembly of macromolecules in parentheses after the name of the macromolecule or assembly of macromolecules with the symbol '*w*', or '*x*', respectively, followed by the mass or mole fractions or percentages. The order of citation in the parentheses is the same as that of the monomers in the name; the individual values are separated by colons. Unknown quantities can be designated by *a*, *b*, etc., or hyphens.

Note For examples, see Rule 8.1 of ref. 5.

Rule 8. For simple systems, the molar mass, relative molecular mass or degree of polymerization may be included in the scheme of Rule 7 by the symbol M, M_r or DP, respectively, followed by the corresponding numerical values, separated by colons. Symbols are qualified if quantities refer to parts of macromolecules or assemblies, e.g., M (block), M_r (arm), M (network chain), etc.

Note 1 Average quantities are denoted by the symbol $\overline{M}$, $\overline{M}_r$ or $\overline{\mathrm{DP}}$.

Note 2 M (network chain) is often denoted M_c. Similarly, M_r (network chain) would be denoted $M_{r,c}$.

Examples:

8.1 net-polystyrene-ν-divinylbenzene (*w* 98:2%)

(polystyrene crosslinked with 2% divinylbenzene)

8.2 *star*-(polyacrylonitrile; polystyrene) (M_r 100 000:20 000)

(star macromolecule consisting of arms of polyacrylonitrile of a total M_r =100 000 and arms of polystyrene of a total M_r = 20 000)

8.3 *star*-(polyacrylonitrile; polystyrene) (M_r (arm) 50 000:10 000)

(star macromolecule consisting of arms of polyacrylonitrile each of M_r = 50 000 and arms of polystyrene each of M_r = 10 000; the macromolecule could be identical to that of example 8.2 with two arms of polyacrylonitrile and two arms of polystyrene)

Rule 9. The functionality of a monomer, oligomer or polymer molecule (or their mixtures) or of a branch point may be included in the scheme of Rule 7 by adding the symbol '*f*' and the figure corresponding to the functionality in parentheses after the name of the monomer, oligomer or polymer molecule or branch point.

Note If a mixture of monomer, oligomer or polymer molecules is present with components of the mixture bearing the same type of chemical functionality, an average value of f for the mixture may be quoted in parentheses following the list of components in the mixture.

Examples:

9.1 *net*-poly[glycerol; pentaerythritol (*f* 3.5)-*co*-(dimethylphenylene diisocyanate)]

(network formed by the reaction of the glycerol/pentaerythritol mixture of average functionality 3.5 with dimethylphenylene diisocyanate)

9.2 *star*-polystyrene-ν-methyltrichlorosilane (*f* 2.8)

9.3 6-*star*(polyacrylonitrile (*f* 3); polystyrene (*f* 3)) (M_r (arm) 50 000 : 10 000)

(a six-armed star macromolecule consisting of three arms of polyacrylonitrile, each of M_r = 50 000, and three arms of polystyrene, each of M_r =10 000)

9.4 4-*star*-(polyacrylonitrile-*block*-polystyrene) (M_r (arm) 50 000)

(a four-armed star macromolecule, each arm of which consists of the same copolymeric block of M_r = 50 000)

9.5 *net*-polystyrene ($\overline{M}_{r,c}$ 10 000)

(network chains of average M_r =10 000)

7 REFERENCES

1 IUPAC. *Compendium of Macromolecular Nomenclature*. Blackwell Scientific Publications, Oxford (1991).

2 IUPAC. Nomenclature of regular single-strand organic polymers. *Pure Appl. Chem.* **48**, 373-385 (1976). Reprinted as Chapter 5 in ref. 1.

3 IUPAC. A classification of linear single-strand polymers. *Pure Appl. Chem.* **61**, 243-254 (1989). Reprinted as Chapter 8 in ref. 1.

4 IUPAC. Nomenclature for regular single-strand and quasi-single-strand inorganic and coordination polymers. *Pure Appl. Chem.* **57**, 149-168 (1985). Reprinted as Chapter 6 in ref. 1.

5 IUPAC. Source-based nomenclature for copolymers. *Pure Appl. Chem.* **57**, 1427-1440 (1985). Reprinted as Chapter 7 in ref. 1.

6 IUPAC. Nomenclature of regular double-strand (ladder and spiro) organic polymers. *Pure Appl. Chem.* **65**, 1561-1580 (1993).

7 IUPAC. Structure-based nomenclature for irregular single-strand organic polymers. *Pure Appl. Chem.* **66**, 873-889 (1994).

8 IUPAC. *Nomenclature of Organic Chemistry*, Sections A, B, C, D, E, F and H, Pergamon Press, Oxford (1979).

9 IUPAC. *A Guide to IUPAC Nomenclature of Organic Compounds*. Blackwell Scientific Publications, Oxford (1994).

10 IUPAC. *Nomenclature of Inorganic Chemistry*, 3rd Edn., Blackwell Scientific Publications, Oxford (1990).

11 IUPAC. Basic definitions of terms relating to polymers. *Pure Appl. Chem.* **40**, 479-491 (1974). Reprinted as Chapter 1 in ref. 1. Currently under revision.

12 IUPAC. Definitions of terms relating to individual macromolecules, their assemblies, and dilute polymer solutions. *Pure Appl. Chem.* **61**, 211-241 (1989). Reprinted as Chapter 3 in ref. 1.