

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

MACROMOLECULAR DIVISION
COMMISSION ON MACROMOLECULAR NOMENCLATURE*

**GRAPHIC REPRESENTATIONS (CHEMICAL
FORMULAE) OF MACROMOLECULES**

(IUPAC Recommendations 1994)

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Graphic representations (chemical formulae) of macromolecules (IUPAC Recommendations 1994)

Ubi materia, ibi geometria,
J. Kepler (1571–1630)

Synopsis. The unambiguous graphic representation of molecules is specially important for macromolecules, which often exhibit a larger number of structural features than do molecules of low molecular weight. For example, the formula of a copolymer should immediately imply if it is meant to present a block copolymer or a copolymer with an unspecified sequence of monomeric units. Thus, a two-block copolymer consisting of a block containing p monomeric units A and a block comprising q monomeric units B is represented by the formula $\text{-(A)}_p\text{-(B)}_q$ whereas the corresponding random copolymer is represented by the formula -(A- / -B-)_n where $p + q = n$.

Overall, the document provides rules and examples for the graphic representation of constitutional repeating units and monomeric units, regular and irregular polymers of simple as well as complex structures, including organic and inorganic homopolymers, alternating and periodic copolymers, statistical, random and unspecified copolymers, block copolymers and graft copolymers, including star polymers. The proposed graphic representations of chemical formulae for polymers are suitable for presentation through graphics computer programs.

Preamble

Graphic representations (chemical formulae) of macromolecules are used extensively in the scientific literature on polymers including IUPAC documents on macromolecular nomenclature (Ref. 1). This document establishes rules for the unambiguous representation of macromolecules by chemical formulae. The rules apply principally to synthetic macromolecules. Insofar as is possible, these rules are consistent with the formulae given in IUPAC documents (Refs. 1–5) and they also cover the presentation of formulae for irregular macromolecules (Ref. 6), copolymer molecules (Refs. 1, 2, 7), and star macromolecules.

In comparison with chemical formulae of low-molecular-weight compounds, chemical formulae of polymers must additionally reflect the multiplicity of constitutional units in a macromolecule and the various possibilities for connecting the constitutional units in a macromolecule.

Throughout the text the term *constitutional unit* (Ref. 2) is taken to include both *constitutional repeating unit* (Ref. 2) and *monomeric unit* (Ref. 2); one of these types of unit should be used wherever possible and appropriate.

As a general rule, chemical formulae for macromolecules should be written only in those cases where the structures of the constitutional units are known. A given structure may, however, be written in various ways to emphasize specific structural features; such alternative structures need not necessarily reflect the order of citation dictated by structure-based nomenclature (Ref. 3).

1. General Rules

Rule 1.1: The formula representation of constitutional units shall be in accordance with usage in organic (Ref. 8) and inorganic (Ref. 9) chemistry, and with IUPAC rules for the nomenclature of polymers (Refs. 1–7).

Rule 1.2: Consistent with the structure of the macromolecule, the order of citation of constitutional units within the formulae is arbitrary and, hence, need not comply with that given in Ref. 3.

Rule 1.3: To make the formulae more concise, dashes representing chemical bonds may be omitted. At the ends of constitutional repeating units and monomeric units, dashes must be attached.

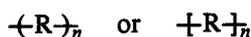
Note 1.3: The absence of one or more of the dashes from a chiral or prochiral atom, or of dashes from atoms linked by a double bond, signifies lack of knowledge about the configuration of the corresponding site of stereoisomerism or lack of intention to specify it (Refs. 1, 2, 4).

- Rule 1.4: Side-groups or substituents written on the same line as the backbone of the macromolecule and consisting of more than one atom symbol are set between enclosing marks, usually parentheses.
- Rule 1.5: Enclosing marks together with subscript letters denote multiplicity of the enclosed constitutional units. The enclosing marks are parentheses (round brackets) or (square) brackets and can be used at random, except for inorganic polymers, for which exclusive use of parentheses is recommended for this purpose, in order to avoid confusion with (square) brackets, which denote coordination structures.
- Rule 1.6: The subscript letters *n*, *p*, *q*, *r*, etc. denote multiplicities of polymeric sequences, whereas the subscript letters *a*, *b*, *c*, etc. denote multiplicities of oligomeric sequences. The subscripts should be printed in italic type or, in the absence of italics, underlined.
- Rule 1.7: The formulae of end groups, if known, may be attached to the bonds at the ends of the constitutional units, but placed outside the enclosing marks.
- Rule 1.8: Specifications about mass fractions (*w*), mole fractions (*x*), molar masses (*M*), relative molecular masses (*M_r*), degrees of polymerization (DP), or the average values of the latter three quantities, may be expressed by placing the corresponding values in parentheses after the formula of the macromolecule in a manner analogous to that recommended for the naming of copolymers (Ref. 7).

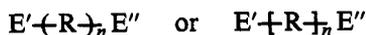
Applications of the general rules are illustrated in the following sections.

2. Regular Polymers

Rule 2.1: The formula of a **regular polymer** (Ref. 2, Definition 3.1) with the **constitutional repeating unit** (Ref. 2, Definition 3.3) —R— is given as:



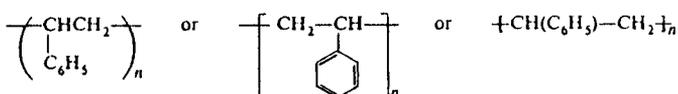
and in cases where the end groups E' and E'' are known:



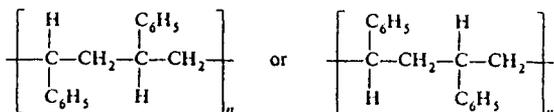
Note 2.1: The chemical bonds connecting the constitutional repeating units are represented by dashes drawn across the enclosing marks.

Examples^{a, b)}

2-E1: poly(1-phenylethylene)
polystyrene



2-E2: syndiotactic poly(1-phenylethylene)
syndiotactic polystyrene

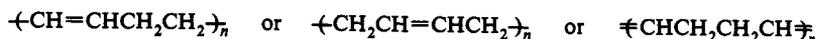


Note: Analogous formulae can be drawn for other tactic macromolecules (Ref. 4)

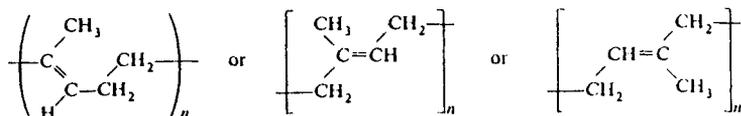
^{a)} Systematic structure-based names (Refs. 1, 3–5, 10) are given first, followed by source-based, semisystematic or trivial names (Refs. 1, 3–5, 10), if these exist. (See "A Guide to IUPAC Nomenclature of Organic Compounds (Recommendations 1993)" for changes since publication of Ref. 8).

^{b)} The formulae of the constitutional repeating units depicted are understood to be non-exclusive.

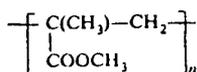
- 2-E3: poly(but-1-ene-1,4-diyl)
1,4-polybutadiene



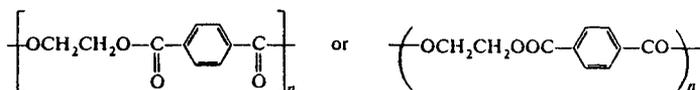
- 2-E4: poly(1-methyl-*trans*-but-1-ene-1,4-diyl)
trans-1,4-polyisoprene



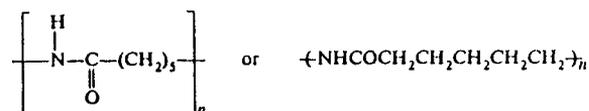
- 2-E5: poly[1-(methoxycarbonyl)-1-methylethylene]
poly(methyl methacrylate)



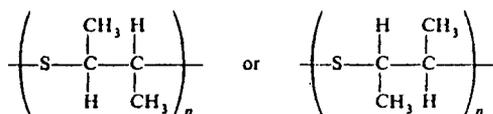
- 2-E6: poly(oxyethyleneoxyterephthaloyl)
poly(ethylene terephthalate)



- 2-E7: poly[imino-(1-oxohexane-1,6-diyl)]
poly(ϵ -caprolactam)

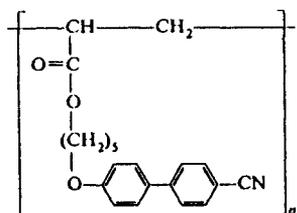


- 2-E8: poly[thio-(*R,R*)-1,2-dimethylethylene] or poly[thio-(*S,S*)-1,2-dimethylethylene]
poly[*cis*-(*R,S*)-2,3-dimethylthiirane]

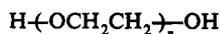


Note: Enantioselective polymerization of *cis*-(*R,S*)-2,3-dimethylthiirane can produce poly[thio-(*R,R*)-1,2-dimethylethylene] or its enantiomer.

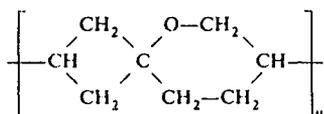
- 2-E9: poly{1-[5-(4'-cyanobiphenyl-4-yloxy)pentyl]oxy}carbonyl}ethylene}



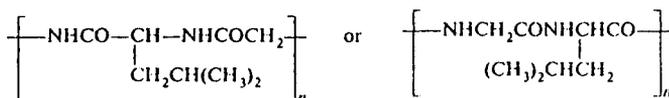
2-E10: α -hydro- ω -hydroxypoly(oxyethylene)
poly(ethylene glycol)



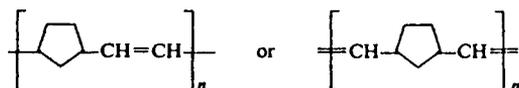
2-E11: poly(5-oxaspiro[3.5]nonane-2,7-diyl)



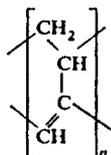
2-E12: poly[imino(2-isobutyl-1-oxoethylene)imino(1-oxoethylene)]
poly(glycylleucine)



2-E13: poly(cyclopentane-1,3-diylvinylene)
polynorbornene or poly(8,9,10-trinorborn-2-ene)

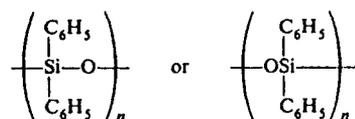


2-E14: poly(but-1-ene-1,4:3,2-tetrayl) (Ref. 10)
ladder-poly(methyl vinyl ketone) (Ref. 10)

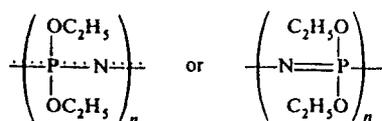


Note: The source-based name identifies the starting monomer of this ladder polymer, the synthesis of which comprises a multistep reaction involving condensation and cyclization.

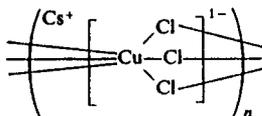
2-E15: *catena*-poly[(diphenylsilicon)- μ -oxo] (Ref. 5) or poly[oxy(diphenylsilylene)] (Ref. 3) or poly[oxy(diphenylsilanediy)] (Refs. 3, 8)
poly(diphenylsiloxane)



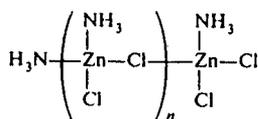
2-E16: *catena*-poly[(diethoxyphosphorus)- μ -nitrido] (Ref. 5) or poly[nitrilo(diethoxyphosphoranylidyne)] (Ref. 3)
poly(diethoxyphosphazene)



- 2-E17: *catena*-poly[caesium [cuprate-tri- μ -chloro](1-)] or
catena-poly[caesium [cuprate(II)-tri- μ -chloro]]

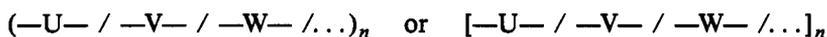


- 2-E18: α -ammine- ω -(amminedichlorozinc)-*catena*-poly[(amminechlorozinc)- μ -chloro]



3. Irregular Polymers (Refs. 2, 6)

Rule 3.1: The formula of an **irregular polymer** (Ref. 2, Definition 3.2) or **irregular block** (Ref. 2, Definition 3.16) comprised of the constitutional units —U—, —V—, —W—, etc., is given as:



Note 3.1.1: The sequence of dots denotes the presence of further constitutional units.

Note 3.1.2: The order of the constitutional units in the formula is arbitrary.

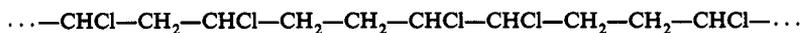
Note 3.1.3: The oblique stroke drawn between the constitutional units means that the sequential arrangement of these units is irregular or unknown.

Note 3.1.4: The dashes at each end of the formula are drawn fully inside the enclosing marks, because they do not necessarily denote terminal chemical bonds of the macromolecules.

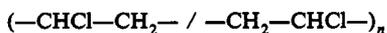
Note 3.1.5: The validity of the constitutional units selected should always be checked by arranging their formulae with repetition, thus forming formulae of longer sequences. In this way it is possible to exclude combinations of constitutional units that do not occur in the macromolecules.

Examples^{a)}

- 3-E1: poly(1-chloroethylene/2-chloroethylene)
(an irregular polymer derived from vinyl chloride, the units of which are joined both head-to-tail and head-to-head):



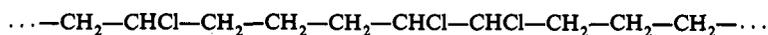
with monomeric units: $-\text{CHCl}-\text{CH}_2-$, $-\text{CH}_2-\text{CHCl}-$



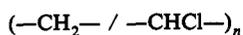
Note: The sequence of dots denotes the continuation of the macromolecular chain.

^{a)} Structure-based names are given first (Ref. 6) followed, if necessary, by an explanation (in parentheses) and a formula segment of the macromolecule. Then the monomeric or constitutional units necessary to describe the complete structure are given followed by the proposed formula. (See "A Guide to IUPAC Nomenclature of Organic Compounds (Recommendations 1993)" for changes since publication of Ref. 8).

- 3-E2: poly(chloromethylene/methylene)
(chlorinated polyethene that does not contain dichloromethylene units):

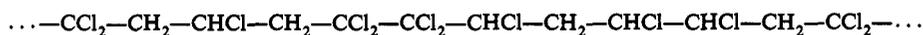


with constitutional units: $-\text{CH}_2-$, $-\text{CHCl}-$

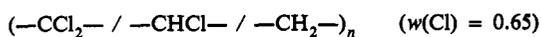


See note to 3-E1.

- 3-E3: poly(chloromethylene/dichloromethylene/methylene)
(chlorinated poly(vinyl chloride) with a mass fraction of chlorine of 0.65):

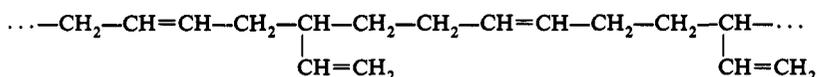


with constitutional units: $-\text{CCl}_2-$, $-\text{CH}_2-$, $-\text{CHCl}-$

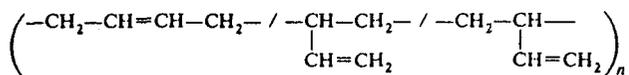


See note to 3-E1.

- 3-E4: poly(but-2-ene-1,4-diyl/1-vinylethylene/2-vinylethylene)
(irregular polymer comprising units derived from 1,4- and 1,2-additions in the polymerization of buta-1,3-diene):

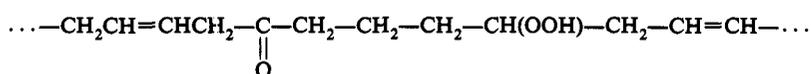


with monomeric units: $-\text{CH}_2 - \text{CH}=\text{CH} - \text{CH}_2-$, $-\underset{\text{CH}=\text{CH}_2}{\text{CH}} - \text{CH}_2-$

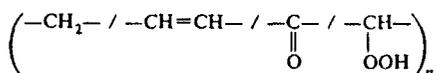


See note to 3-E1.

- 3-E5: poly(carbonyl/hydroperoxymethylene/methylene/vinylene) (oxidized polyethene):

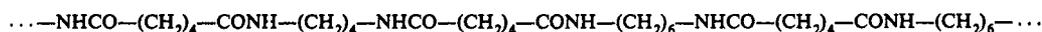


with constitutional units: $-\text{CH}_2-$, $-\text{CH}=\text{CH}-$, $-\overset{\text{O}}{\text{C}}-$, $-\text{CH}(\text{OOH})-$

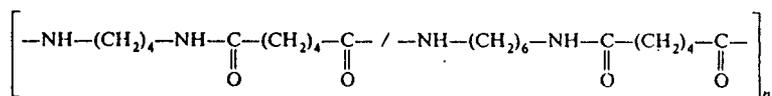


See note to 3-E1.

- 3-E6: poly(iminohexane-1,6-diyliminoadipoyl/iminobutane-1,4-diyliminoadipoyl)
(polyamide derived from adipoyl chloride and a mixture of hexane-1,6-diyl diamine and butane-1,4-diyl diamine):

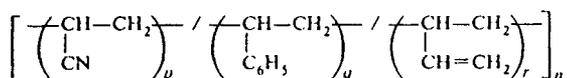


with constitutional units: $-\text{NH}-(\text{CH}_2)_4-\text{NHCO}-(\text{CH}_2)_4-\text{CO}-$,
 $-\text{NH}-(\text{CH}_2)_6-\text{NHCO}-(\text{CH}_2)_4-\text{CO}-$



See note to 3-E1.

- 3-E7: poly[poly(1-cyanoethylene)/poly(1-phenylethylene)/poly(1-vinylethylene)] (irregular polymer which consists of regular blocks of polyacrylonitrile, polystyrene and 1,2-polybutadiene with an unspecified sequential arrangement of the blocks $\text{+CH}(\text{CN})-\text{CH}_2\text{+}_p$, $\text{+CH}(\text{C}_6\text{H}_5)-\text{CH}_2\text{+}_q$ and $\text{+CH}(\text{CH}=\text{CH}_2)-\text{CH}_2\text{+}_r$):



Note: The choice of the constitutional units is dictated by Rule 1.1 and the rules of Refs. 1 and 3, e.g. 1-cyanoethylene is preferred to 2-cyanoethylene.

4. Copolymers

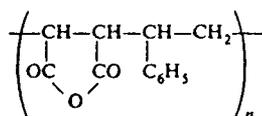
4.1 Alternating and Periodic Copolymers

Rule 4.1.1: Alternating and periodic copolymers, as far as possible, are treated as regular polymers.

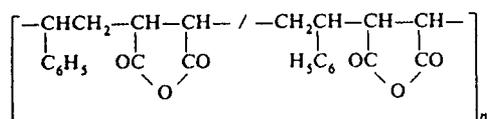
Rule 4.1.2: Pseudoperiodic copolymers, e.g., those in which only some of the constitutional units occur regularly, are treated as irregular polymers (see example 4.1-E1) or as unspecified copolymers (see example 4.1-E3).

Examples^{a)}

- 4.1-E1: poly[styrene-*alt*-(maleic anhydride)]
poly[(2,5-dioxotetrahydrofuran-3,4-diyl)(1-phenylethylene)]



Note: In cases in which both 1-phenylethylene and 2-phenylethylene units are present in measurable amounts, the formula for an irregular polymer is used:

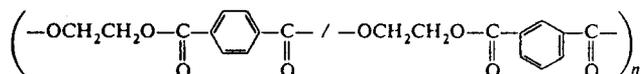


^{a)} Source-based (co)polymer names (Refs. 1, 3, 7) are given first, followed by systematic structure-based names (Refs. 1, 3), if these exist, before the proposed formula.

4.1-E2: poly[formaldehyde-*per*-(ethylene oxide)-*per*-(ethylene oxide)] or poly(1,3,6-trioxacyclooctane)
poly(oxymethyleneoxyethyleneoxyethylene)



4.1-E3: poly[(ethylene glycol)-*alt*-(terephthalic acid; isophthalic acid)]
poly[(ethylene terephthalate)-*co*-(ethylene isophthalate)]

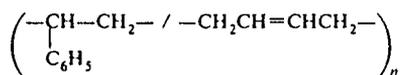


4.2 Statistical, Random and Unspecified Copolymers

Rule 4.2.1: Statistical, random, and unspecified copolymers are treated as irregular polymers.

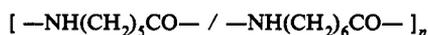
Examples^{a)}

4.2-E1: poly(styrene-*stat*-buta-1,3-diene)

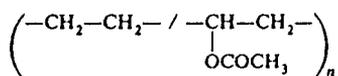


Note: The buta-1,3-diene is exclusively incorporated by 1,4-addition which cannot be reflected in the source-based name.

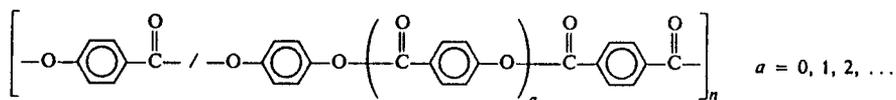
4.2-E2: poly[(6-aminohexanoic acid)-*stat*-(7-aminoheptanoic acid)]



4.2-E3: poly[ethylene-*ran*-(vinyl acetate)]

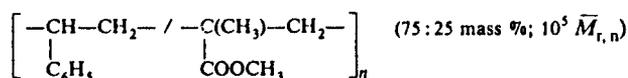


4.2-E4: poly[(4-hydroxybenzoic acid)-*co*-hydroquinone-*co*-(terephthalic acid)]

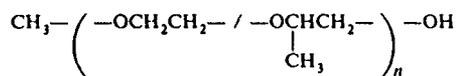


Note: In this graphical representation only esterification reactions have been assumed to occur.

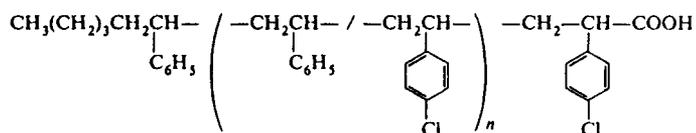
4.2-E5: poly[styrene-*co*-(methyl methacrylate)] (75:25 mass %; $10^5 \bar{M}_{r,n}$)



^{a)} Source-based copolymer names (Refs. 1, 7) are given, followed by proposed formula. (See "A Guide to IUPAC Nomenclature of Organic Compounds (Recommendations 1993)" for changes since publication of Ref. 8).

4.2-E6: α -methyl- ω -hydroxy-poly[(ethylene oxide)-*co*-(propylene oxide)]^{a)}

Note: The dashes for the bonds to the end groups are not drawn through the enclosing marks of the polymer formula, because this formula does not specify which end group is attached to which monomeric unit.

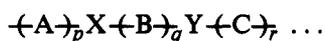
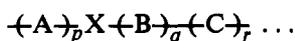
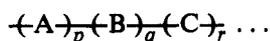
4.2-E7: α -butyl- ω -carboxy-poly[styrene-*co*-(4-chlorostyrene)]
 α -(1-phenylhexyl)- ω -[2-carboxy-2-(4-chlorophenyl)ethyl]-poly[styrene-*co*-(4-chlorostyrene)]
 (Ref. 7)

See note to 4.2-E6.

Note: The formula is more specific than the first of the two given names in that it specifies that the butyl end group is linked to the 2-position of a 1-phenylethyl group and the carboxy group is attached to the 2-position of a 2-(4-chlorophenyl)ethyl group.

4.3 Block Copolymers

Rule 4.3.1: The formulae of **block copolymers** (Ref. 2, Definition 3.35) consisting of a sequence of **regular blocks** (Ref. 2, Definition 3.15) and, if known, **junction units** (Ref. 7, Definition Rule 5.5) in *known* sequential arrangement are written as, e.g.:

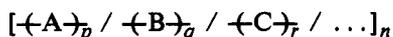


where A, B, C, etc., are the constitutional repeating units of the regular blocks -(A)-_p , -(B)-_q , -(C)-_r , etc., and X, Y, etc., are junction units which are not considered to be parts of the blocks.

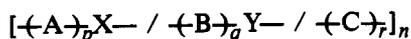
Note 4.3.1: The sequence of dots denotes the presence of further constitutional units or blocks or both.

^{a)} According to "A Guide to IUPAC Nomenclature of Organic Compounds (Recommendations 1993)" the name "propylene oxide" should be replaced by "2-methyloxirane".

Rule 4.3.2: The formulae of block copolymers consisting of sequences of regular blocks and, if known, junction units in an *unknown* sequential arrangement are written with the formulae of blocks and junction units separated by oblique strokes. Thus,



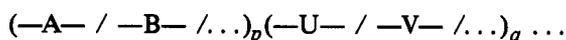
represents a block copolymer consisting of an unknown sequence of regular blocks $\leftarrow A \rightarrow_p$, $\leftarrow B \rightarrow_q$, $\leftarrow C \rightarrow_r$, etc., and



represents a block copolymer consisting of an unknown sequence of regular blocks $\leftarrow A \rightarrow_p$, $\leftarrow B \rightarrow_q$, and $\leftarrow C \rightarrow_r$, with junction units X and Y, attached to $\leftarrow A \rightarrow_p$ and $\leftarrow B \rightarrow_q$, respectively.

Note 4.3.2: The sequence of dots denotes the presence of further constitutional units or blocks or both.

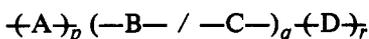
Rule 4.3.3: The formulae of block copolymers consisting of a sequence of irregular blocks are written as:



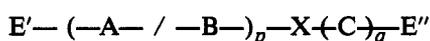
where A, B, etc., and U, V, etc., are the constitutional repeating units of the irregular blocks $(-A- / -B- / \dots)_p$, $(-U- / -V- / \dots)_q$, etc.

Note 4.3.3.1: The sequence of dots denotes the presence of further constitutional units or blocks or both.

Note 4.3.3.2: The bonds emanating from the first and last constitutional or junction unit of an irregular block are written within the enclosing marks when it is not known to which of the units of the irregular block the other blocks or the end groups of the polymer are attached. Thus,



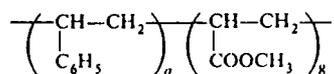
represents a block copolymer consisting of an irregular block $(-B- / -C-)_q$ (see Rules 3.1 and 1.6) between and connected to the regular blocks $\leftarrow A \rightarrow_p$ and $\leftarrow D \rightarrow_r$ and



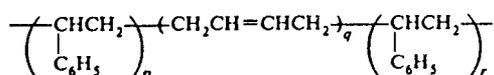
represents a block copolymer consisting of an irregular block $(-A- / -B-)_p$ linked on one end via a junction unit $-X-$ to the regular block $\leftarrow C \rightarrow_q$ with the end group E'' and on the other end to the end group E' .

Examples^{a)}

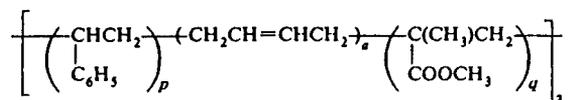
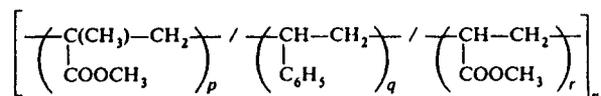
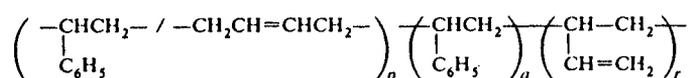
4.3-E1: oligostyrene-*block*-octakis(methyl acrylate)



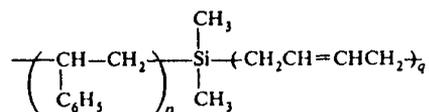
4.3-E2: polystyrene-*block*-1,4-polybutadiene-*block*-polystyrene



^{a)} Source-based copolymer names (Refs. 1, 7) are given, followed by proposed formula. (See "A Guide to IUPAC Nomenclature of Organic Compounds (Recommendations 1993)" for changes since publication of Ref. 8).

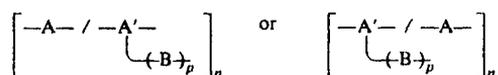
4.3-E3: tris[polystyrene-*block*-1,4-oligobutadiene-*block*-poly(methyl methacrylate)]4.3-E4: poly[poly(methyl methacrylate)-*block*-polystyrene-*block*-poly(methyl acrylate)]4.3-E5: poly(styrene-*stat*-buta-1,3-diene)-*block*-polystyrene-*block*-1,2-polybutadiene

See note to 4.2-E1.

4.3-E6: polystyrene-*block*-dimethylsilanediyl-*block*-1,4-polybutadiene

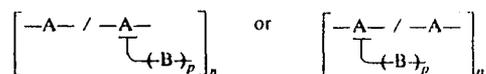
4.4 Graft Copolymers

Rule 4.4.1: The formula of a graft copolymer consisting of a polymeric backbone of monomeric units A to which an unknown number of blocks of monomeric units B (grafts) are linked at **known** sites to some of the monomeric units A, is written as:



where A' denotes the monomeric unit A **modified** by the substitution with the graft.

Rule 4.4.2: The formula of a graft copolymer consisting of a polymeric backbone of monomeric units A to which an unknown number of blocks of monomeric units B (grafts) are linked at **unknown** sites to some of the monomeric units A, is written as:



where the horizontal line under the **unmodified** monomeric unit A denotes that the point of attachment of the graft is not known.

Note: If the backbone of a graft copolymer is itself a copolymer consisting of monomeric units A, B, and it is not known to which of the monomeric units A or B, nor at which site of the individual units A or B, the grafts ---(C---)_p are attached, the formula is written as:

