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MACROMOLECULAR DIVISION
COMMISSION OF MACROMOLECULAR NOMENCLATURE*

NOMENCLATURE OF REGULAR DOUBLE-STRAND (LADDER AND SPIRO) ORGANIC POLYMERS

(IUPAC Recommendations 1993)

Prepared by a Working Group Consisting of

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Nomenclature of regular double-strand (ladder and spiro) organic polymers (IUPAC Recommendations 1993)

Abstract

Structure-based and source-based nomenclature rules are extended to regular double-strand (ladder and spiro) organic polymers. A double-strand polymer is defined as a polymer the molecules of which are formed by an uninterrupted sequence of rings with adjacent rings having one atom in common (spiro polymer) or two or more atoms in common (ladder polymer). The structure-based nomenclature rests upon the selection of a preferred constitutional repeating unit (CRU) of which the polymer is a multiple. Rules are also provided for denoting substituents and end groups. The source-based nomenclature identifies the starting monomer(s) from which the double-strand polymer is prepared with addition of an appropriate prefix *"ladder-"* or *"spiro-"*.

CONTENTS

1. INTRODUCTION

In 1976, the IUPAC Commission on Macromolecular Nomenclature published rules on the nomenclature of regular single-strand organic polymers (Ref. 1). A regular single-strand polymer is one the molecules of which can be described by constitutional repeating units with only two terminals composed of one atom each.

In 1985, the Commission jointly with the IUPAC Commission on Nomenclature of Inorganic Chemistry published rules on the nomenclature for regular single-strand and quasi-single-strand inorganic and coordination polymers (Ref. 2). A quasi-single-strand polymer is one the molecules of which can be described by constitutional repeating units connected to the other identical constitutional repeating unit (or to an end group) through a single atom at one terminal and through two atoms at the other terminal.

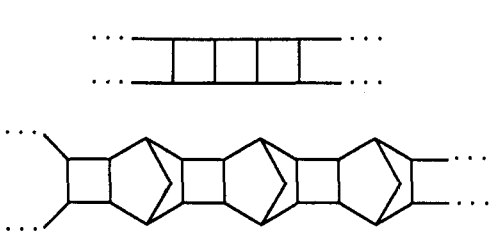
In 1985, the Commission also published rules on source-based nomenclature for copolymers (Ref. 3) which by definition are polymers derived from more than one species of monomer (Ref. 4).

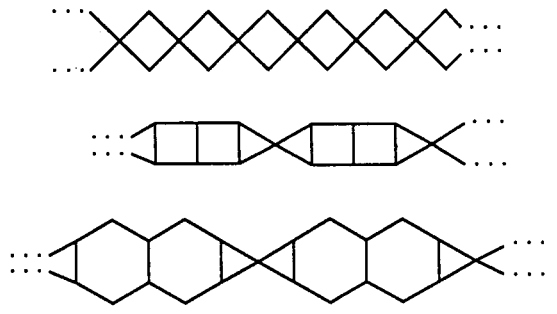
In this report, both the structure-based and source-based nomenclature rules are extended to regular double-strand (ladder and spiro) organic polymers. Double-strand biopolymers, however, such as DNA are not considered here. Rules for quasi-single-strand coordination polymers, resembling spiro polymers yet not covalently bonded, are *not* included.

2. DEFINITIONS

2.1	Regular polymer	A polymer the molecules of which can be described by only one species of constitutional unit in a single sequential arrangement (Ref. 4).
2.2	Constitutional unit	A species of atom or group of atoms present in a chain of a polymer or oligomer molecule (Ref. 4).
2.3	Constitutional repeating unit	The smallest constitutional unit whose repetition describes a regular polymer (Ref. 4).
2.4	Ring	An arrangement of atoms bound to each other in a cyclic manner (a closed chain).
2.5	Ring system	A single ring or a combination of rings linked one to another by atoms common to both.
2.6	Double-strand polymer	A polymer the molecules of which consist of an uninterrupted sequence of rings with adjacent rings having one atom in common (spiro polymer) or two or more atoms in common (ladder polymer).

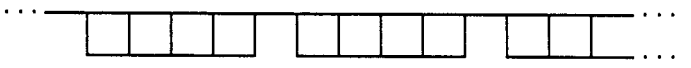
Examples:





NOTE: Partial ladder (imperfect ladder, block ladder) polymers (Ref. 5), in which the sequence of rings is interrupted and a bivalent constitutional repeating unit can be identified, are *not* double-strand polymers. They are named as single-strand polymers.

Example:

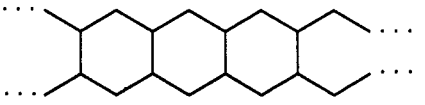


On the other hand, occasional irregular deviations from ideality can be ignored in constructing graphical representations for double-strand polymers and in assigning corresponding names.

Specific examples of double-strand polymers:

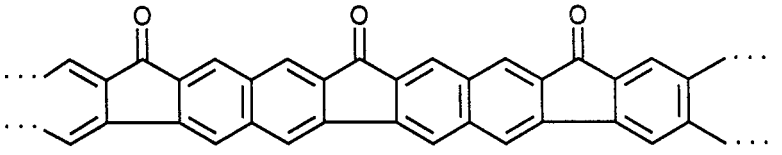
a. constituted of repeatedly fused carbocycles

(i)

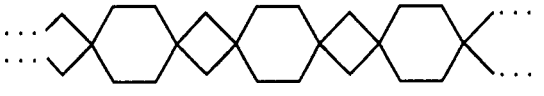


b. constituted of repeatedly fused or spiro carbocyclic systems

(ii)

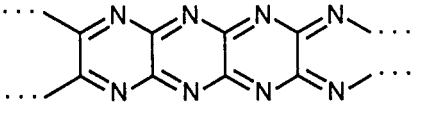


(iii)



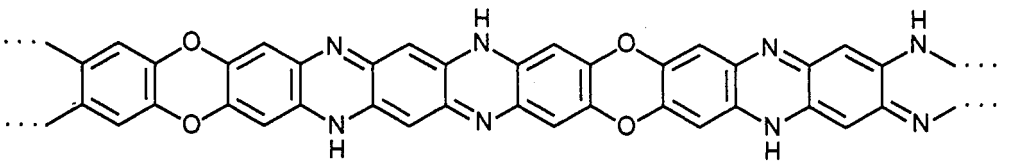
c. constituted of repeatedly fused heterocycles

(iv)

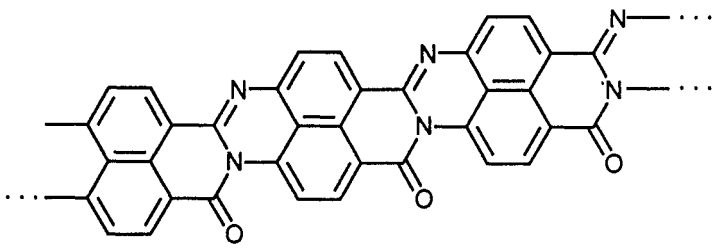


d. constituted of repeatedly fused or spiro heterocyclic systems

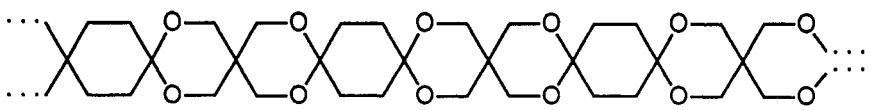
(v)



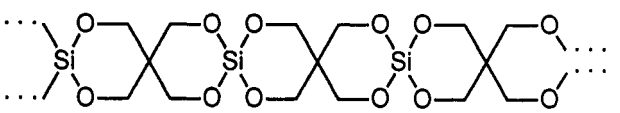
(vi)



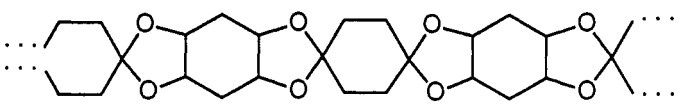
(vii)



(viii)



(ix)



Reviews on double-strand, ladder, and spiro polymers published in the literature (Refs. 5-7) have not addressed their nomenclature in any detailed fashion.

3. STRUCTURE-BASED NOMENCLATURE

3.1 Fundamental principles

This nomenclature rests upon the selection of a preferred *constitutional repeating unit* (CRU) (Refs. 1 and 4) of which the polymer is a multiple; the name of the polymer is the name of this repeating unit prefixed by "poly". The unit itself is named wherever possible according to the established principles of organic nomenclature (Ref. 8). For double-strand polymers, this unit usually is a tetravalent group denoting attachment to four atoms. Since some of these attachments may be double bonds, the unit may be hexavalent or octavalent.

In using this nomenclature, the steps to be followed in sequence are the same as those for regular single-strand polymers:

(1) *identify* the preferred constitutional repeating unit,

(2) *orient* the constitutional repeating unit,

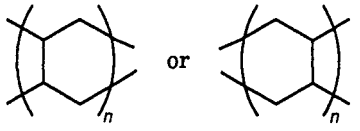
(3) *name* the constitutional repeating unit, and

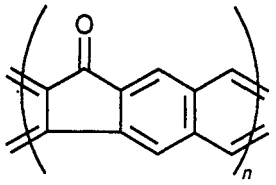
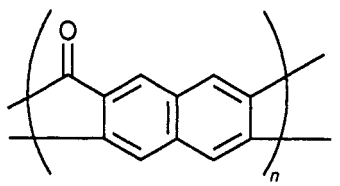
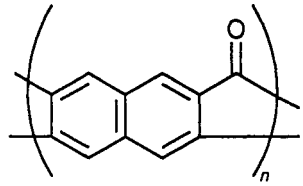
(4) *name* the polymer.

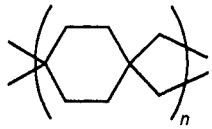
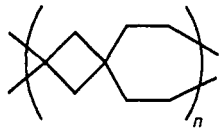
Identification and orientation must precede naming of the polymer.

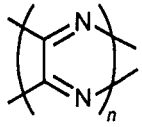
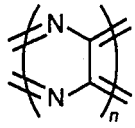
3.2 Identification of the preferred constitutional repeating unit

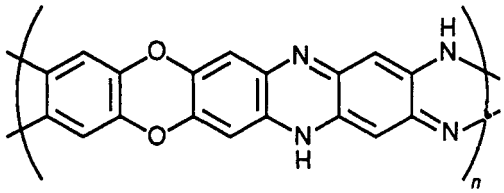
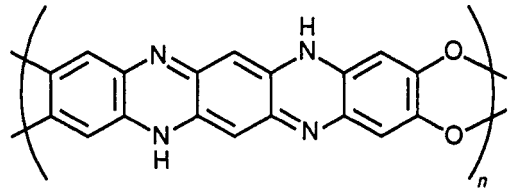
Examples given in Section 2 above have illustrated the repeating nature of the constitutional units within each polymer structure. Some of the ways to break the same structures into constitutional repeating units are illustrated below.

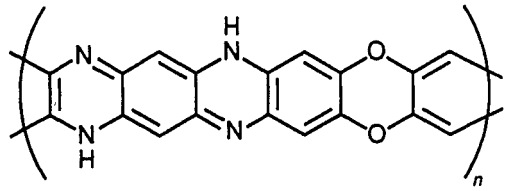
(i)  or

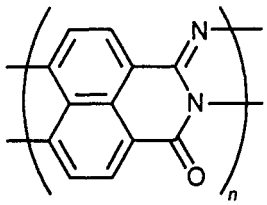
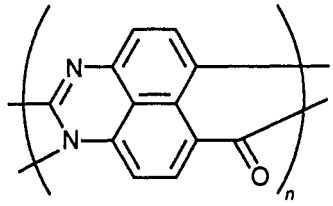
(ii)  or  or 

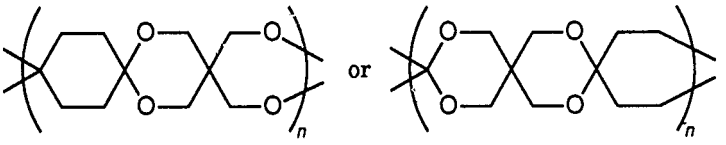
(iii)  or 

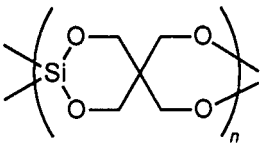
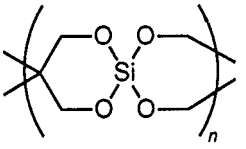
(iv)  or 

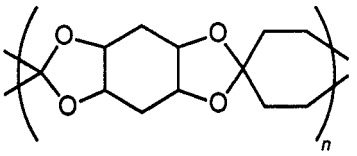
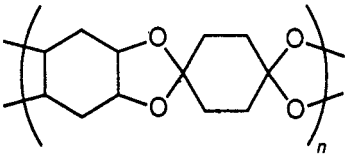
(v)  or 

or 

(vi)  or 

(vii)  or

(viii)  or 

(ix)  or 

To allow construction of a unique name, a single *preferred* constitutional repeating unit must be selected.

RULE 1. The polymer chain is interrupted by breaking a non-aromatic ring (aromatic rings, i.e., those having a chemistry typified by benzene (Ref. 9) are broken only when no other rings are present) by observing the following criteria in decreasing order of priority:

(1) *minimize* the number of free valences of the constitutional repeating unit,

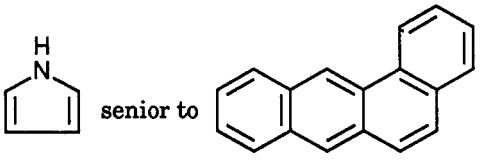
(2) *maximize* the number of most preferred hetero atoms in the ring system,

(3) *retain* the most preferred ring system,

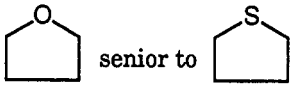
(4) *choose* the longest chain for acyclic constitutional repeating unit.

Seniority of ring systems (Ref. 8, Rule C-14.1) is decided by applying the following criteria, successively, until a decision is reached:

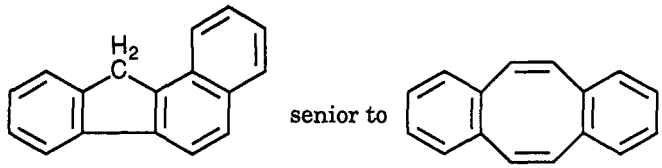
(1) A heterocycle is senior to any carbocycle, regardless of the number of rings



(2) For heterocycles, the criteria are based on the nature and position of the hetero atom (Ref. 8, Rule B-3.1)

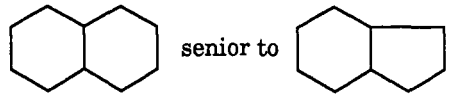


(3) Larger number of rings

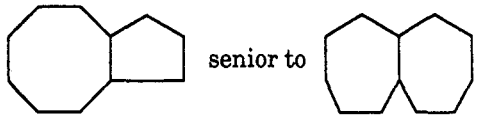


(four rings) (three rings)

(4) Larger individual ring at first point of difference

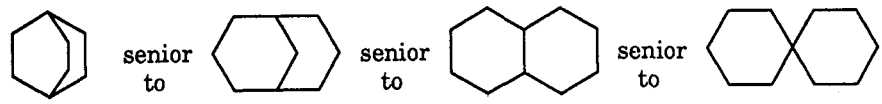


(6,6) (6,5)



(8,5) (7,7)

(5) Larger number of atoms in common among rings



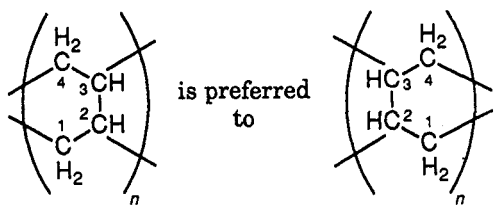
(4) (bridged) (3) (bridged) (2) (*ortho*-fused) (1) (spiro)

For further rules and additional details, Ref. 8 (chapter C-0.14) needs to be consulted.

3.3 Orientation of the constitutional repeating unit

RULE 2. The acyclic constitutional repeating unit that results from breaking the ring is oriented in such a way that the lowest free valence locant is at the lower left.

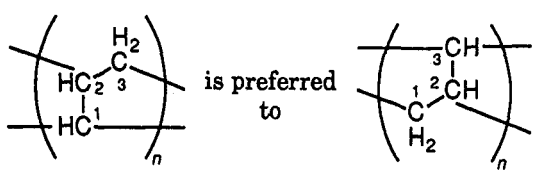
Example:



1,4:3,2- 2,3:4,1-

If there is a further choice, the acyclic unit is oriented to give the lower locant number on the occasion of the first difference.

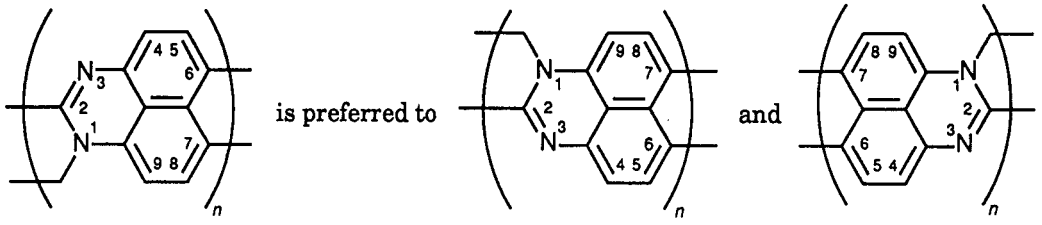
Example:



1,2:3,1- 1,3:3,2-

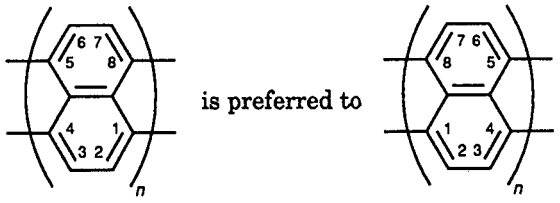
RULE 3. If the preferred constitutional repeating unit contains a ring system with a fixed numbering of locants (Ref. 8), it is oriented (e.g., by rotation) in such a way that the lowest free valence locant is at the lower left and next locants in the ascending order proceed in a clockwise direction.

Example:



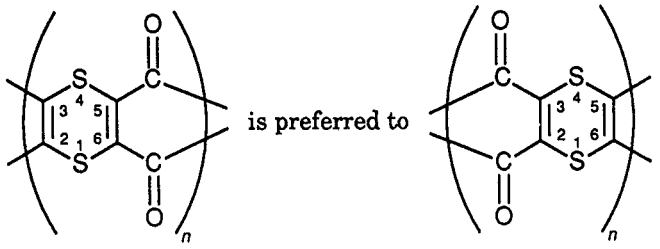
Whenever orienting the ring with the lowest free valence locant at the lower left results in an anticlockwise direction of locants, the orientation is changed to the next lowest free valence locant at the lower left to preserve the ascending order of locants in the clockwise direction.

Example:



RULE 4. If the preferred constitutional repeating unit consists of a ring system and acyclic subunits, it is oriented in such a way that the ring system is on the left side and the acyclic subunits are on the right of the ring system. The ring system is oriented according to RULE 3.

Example:



3.4 Naming of the preferred constitutional repeating unit

RULE 5. The preferred constitutional repeating unit is named as drawn, i.e., from left to right. The name of an acyclic constitutional repeating unit is based on the longest chain with the lowest free valence locant at the lower left with respect to the left parenthesis. The name of a ring system is formed according to the principles of naming carbocyclic and

heterocyclic ring systems. The names are followed by an appropriate suffix, e.g., "2,3:5,6-tetrayl", "2,3:9-triyl-10-ylidene", "2,3-diyl:6,7-diylidene". The free valence locants are always placed just in front of the corresponding ending and are cited in the order:

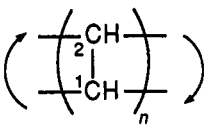
lower left,upper left:upper right,lower right

(i.e., in a clockwise direction), the left locants being separated from the right locants by a colon. Then the names of acyclic subunits (broken ring fragments) are cited in the order: upper right,lower right, preceded by the corresponding locants (the locants refer to the ring system positions where the acyclic subunits are attached).

NOTE: Locants are placed immediately before that part of the name to which they relate, e.g., ethane-1,2:2,1-tetrayl (not 1,2:2,1-ethanetetrayl) or buta-1,3-diene-1,4:3,2-tetrayl (not 1,3-butadiene-1,4:3,2-tetrayl) (Ref. 10).

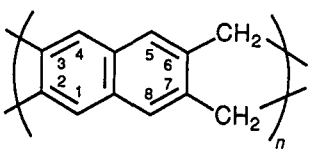
Examples:

1.



poly(ethane-1,2:2,1-tetrayl)
(not ethane-1,2:1,2-diylidene)

2.



poly(naphthalene-2,3:6,7-tetrayl-6,7-dimethylene)

3.5 Naming of the polymer

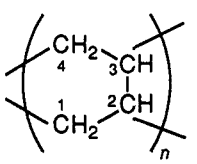
RULE 6. The polymer is named with the prefix "poly" followed by the name of the preferred constitutional repeating unit in parentheses or brackets.

3.6 Polymers constituted of repeatedly fused or spiro carbocycles

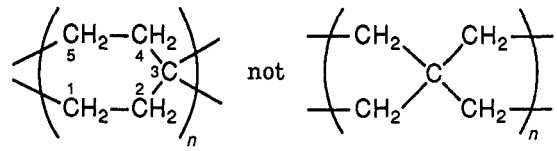
The constitutional repeating unit resulting from a ladder or spiro polymer consisting of a repeating *carbocycle* is a tetravalent acyclic group.

Examples:

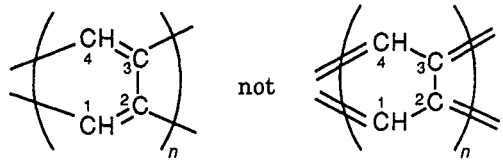
1.



poly(butane-1,4:3,2-tetrayl)

2.  not

poly(pentane-1,5:3,3-tetrayl)
(the longest straight chain is preferred)

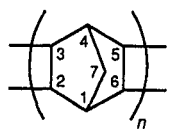
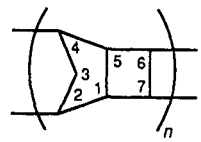
3.  not

poly(buta-1,3-diene-1,4:3,2-tetrayl)
(when an aromatic ring is broken, double bonds are fixed and free valences in the total constitutional repeating unit are minimized)

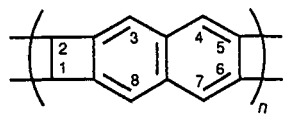
3.7 Polymers constituted of repeatedly fused or spiro carbocyclic systems

The constitutional repeating unit resulting from a ladder or spiro polymer consisting of a repeating *polycarbocyclic* (multi-ring) system is a tetravalent group or a combination of a tetravalent (multivalent) cyclic group with one or two bivalent (multivalent) acyclic groups.

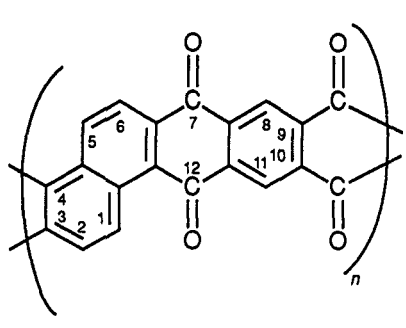
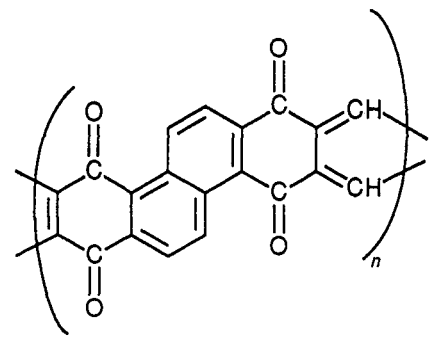
Examples:

1.  not 

poly(bicyclo[2.2.1]heptane-2,3:5,6-tetrayl)
(the preferred two-ring system is 5,5 not 4,5)

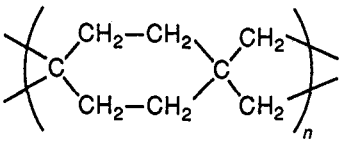
2. 

poly(1,2-dihydrocyclobuta[*b*]naphthalene-1,2:5,6-tetrayl)

3.  not 

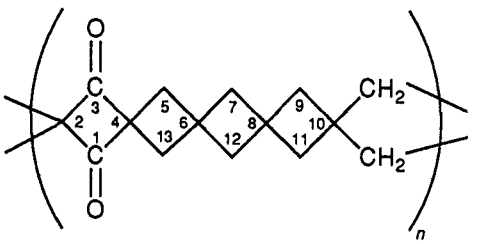
poly[(7,12-dihydro-7,12-dioxobenz[*a*]anthracene-3,4:9,10-tetrayl)-9,10-dicarbonyl]
(unless there is no choice, the aromatic ring is not broken)

4.



poly(cyclohexane-1,1:4,4-tetrayl-4,4-dimethylene)

5.



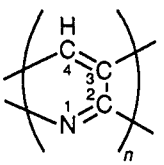
poly[(1,3-dioxotrispiro[3.1.1.3.1.1]tridecane-2,2:10,10-tetrayl)-10,10-dimethylene]

3.8 Polymers constituted of repeatedly fused or spiro heterocycles

The constitutional repeating unit resulting from a ladder or spiro polymer consisting of a repeating *heterocycle* is viewed as a tetravalent (multivalent) acyclic carbon group in which some carbon atoms are replaced by hetero atoms. The constitutional repeating unit is oriented in such a way that hetero atoms have lowest locants and that the hetero atom of highest seniority (Ref. 8, Rule B.1) has lower locant than that of next seniority. The constitutional repeating unit is then named by replacement nomenclature.

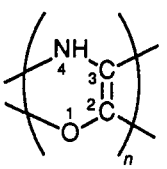
Examples:

1.



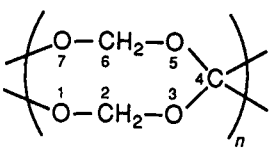
poly(1-azabuta-1,3-diene-1,4:3,2-tetrayl)

2.



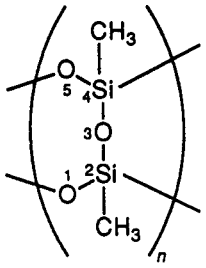
poly(1-oxa-4-azabut-2-ene-1,4:3,2-tetrayl)

3.



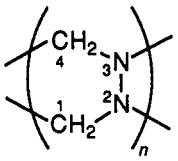
poly(1,3,5,7-tetraoxaheptane-1,7:4,4-tetrayl)

4.



poly(2,4-dimethyl-1,3,5-trioxa-2,4-disilapentane-1,5:4,2-tetrayl)

5.

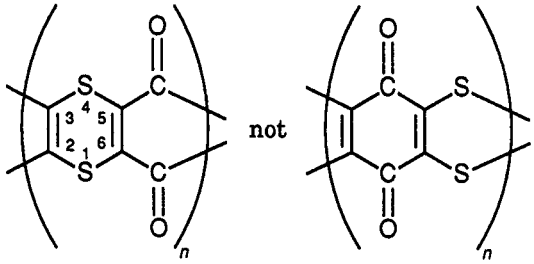


poly(2,3-diazabutane-1,4:3,2-tetrayl)

3.9 Polymers constituted of repeatedly fused or spiro heterocyclic systems

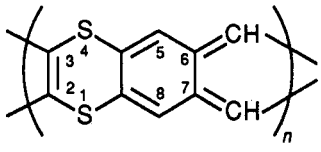
The constitutional repeating unit resulting from a ladder or spiro polymer consisting of a repeating *heterocyclic* ring system is a combination of a tetravalent (multivalent) ring system group with one or two bivalent (multivalent) acyclic groups. If there is a choice, the constitutional repeating unit is oriented in such a way that the acyclic subunit with the terminal atom of higher seniority is at the upper right.

1.

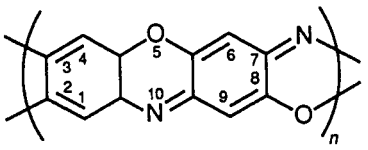


poly(1,4-dithiin-2,3:5,6-tetrayl-5,6-dicarbonyl)
(the carbocyclic ring is broken in preference to the heterocyclic ring to keep the hetero atoms in the ring system)

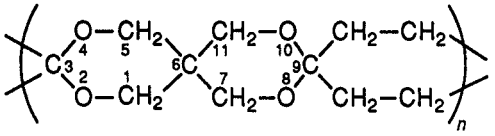
2.



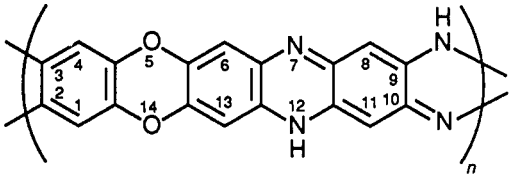
poly(1,4-benzodithiin-2,3-diyl:6,7-diylidene-6,7-dimethylidyne)

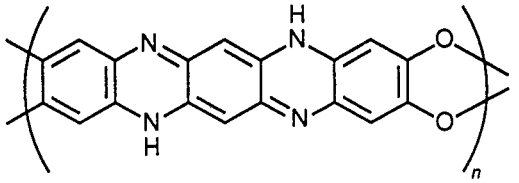
3. 

poly(7*H*-phenoxazine-2,3-diyl:7-ylidene-8-yl-7-nitrilo-8-oxy)
(the heterocyclic ring is broken in preference to the carbocyclic aromatic ring to minimize the number of free valences; the citation of bivalent groups preserves the order "upper right, lower right" in preference to the seniority of hetero atoms)

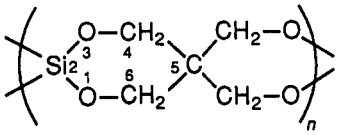
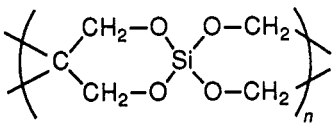
4. 

poly(2,4,8,10-tetraoxaspiro[5.5]undecane-3,3:9,9-tetrayl-9,9-diethylene)
(all hetero atoms are in the ring system)

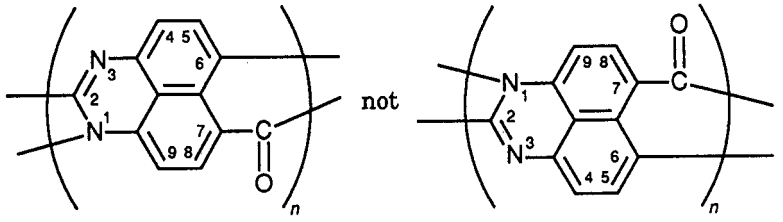
5. 

not 

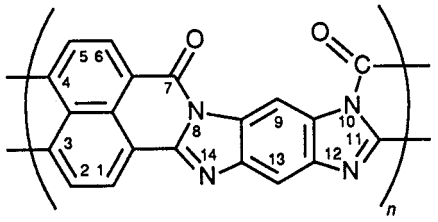
poly([1,4]benzodioxino[2,3-*b*]phenazine-2,3:9-triyl-10(12*H*)-ylidene-9-imino-10-nitrilo)
(the number of preferred hetero atoms is maximized in the ring system; the locants "2,3:9-triyl-10(12*H*)-ylidene" are preferred to "2,3:10-triyl-9(7*H*)-ylidene" (lower locant for indicated hydrogen) to preserve the clockwise order of locant citation)

6.  not 

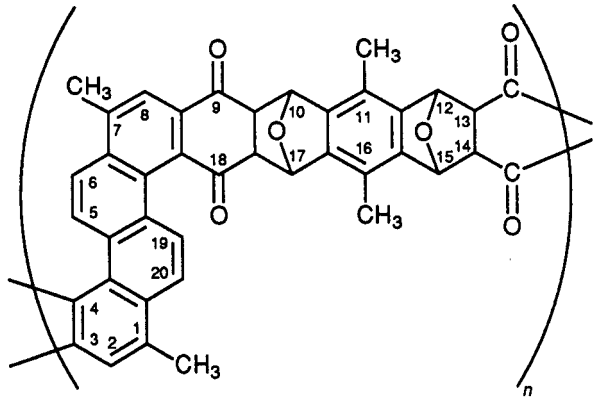
poly[1,3-dioxa-2-silacyclohexane-2,2:5,5-tetrayl-5,5-bis(methyleneoxy)]
(fixed ring numbering decides the orientation)

7. 

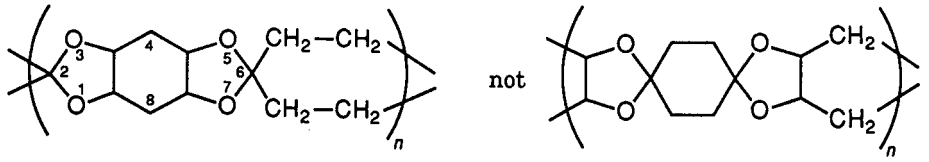
poly(1*H*-perimidine-1,2:6,7-tetrayl-7-carbonyl)
(lower free valence locant is at the lower left)

8. 

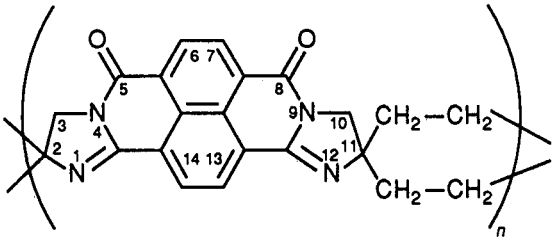
poly[(7-oxo-7*H*,10*H*-benz[*de*]imidazo[4′,5′:5,6]benzimidazo[2,1-*a*]-isoquinoline-3,4:10,11-tetrayl)-10-carbonyl]

9. 

poly[(9,9a,10,12,13,14,15,17,17a,18-decahydro-1,7,11,16-tetramethyl-9,18-dioxo-10,17:12,15-diepoxyphenanthro[1,2-*a*]pentacene-3,4:13,14-tetrayl)-13,14-dicarbonyl]

10. 

poly[(hexahydrobenzo[1,2-*d*:4,5-*d*′]bis[1,3]dioxole-2,2:6,6-tetrayl)-6,6-diethylene]
(fused ring system is preferred to spiro ring system, because of larger number of atoms in common among rings)

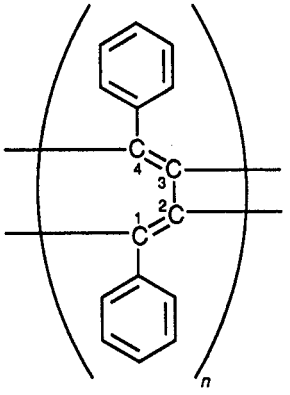
11. 

poly[(2,3,5,8,10,11-hexahydro-5,8-dioxobenzo[*lmn*]diimidazo-[2,1-*b*:1′,2′-*j*][3,8]phenanthroline-2,2:11,11-tetrayl)-11,11-diethylene]
(fused ring system is retained intact and spiro ring broken)

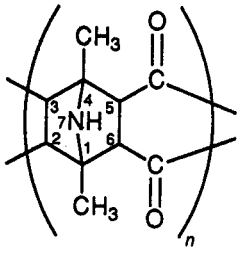
3.10 Substituents

Substituents that are clearly part of the constitutional repeating unit are denoted by means of prefixes affixed to the name of the subunit to which they are bound.

Examples:

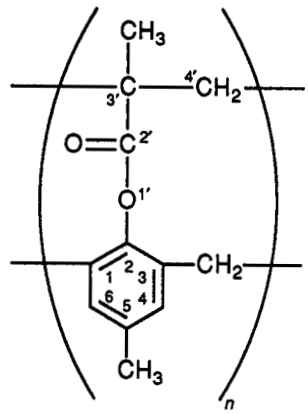
1. 

poly(1,4-diphenylbuta-1,3-diene-1,4:3,2-tetrayl)

2. 

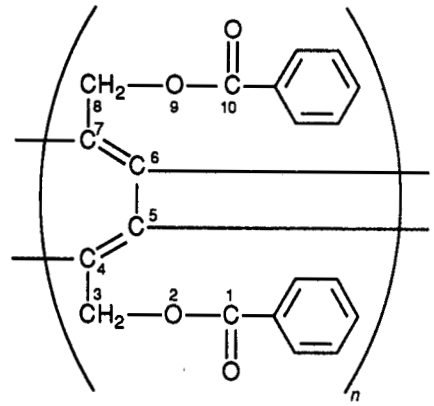
poly[(1,4-dimethyl-7-azabicyclo[2.2.1]heptane-2,3:5,6-tetrayl)-5,6-dicarbonyl]

3.



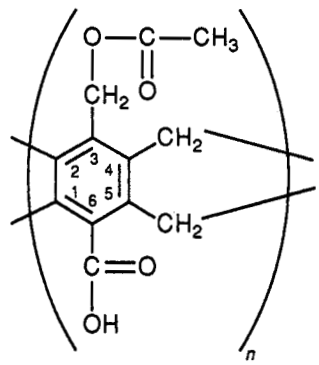
poly[[[3′,5-dimethyl-2-(2′-oxo-1′-oxabutyl)benzene]-1,3′:4′,3-tetrayl]-3-methylene]
(for a quasi-acyclic constitutional repeating unit which includes path along a ring, the acyclic part with primed locants is treated as a substituent on the ring)

4.



poly(1,10-dioxo-1,10-diphenyl-2,9-dioxadeca-4,6-diene-4,7:6,5-tetrayl)

5.



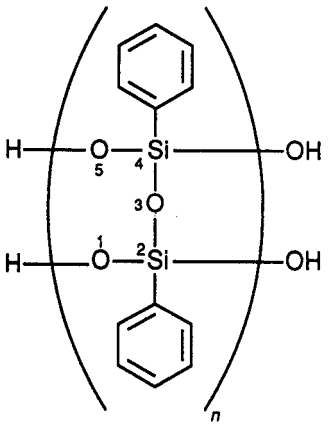
poly[[3-(acetoxymethyl)-6-carboxybenzene-1,2:4,5-tetrayl]-4,5-dimethylene]
(for substituted structures, free valences have preference over substituents when competing for low locants)

3.11 End groups

RULE 7. End groups are specified by prefixes cited in front of the name of the polymer. The ends designated by α and α′ are those attached to the left side of the constitutional repeating unit as drawn and named by the preceding rules; the end groups attached to the right side are designated by ω and ω′. The designations and names of the end groups proceed in a clockwise direction starting from the lower left: α,α′,ω,ω′.

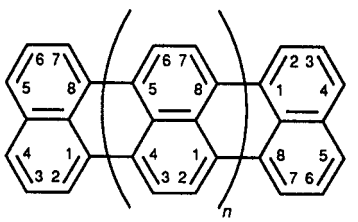
Examples:

1.



α,α′-dihydro-ω,ω′-dihydroxypoly(2,4-diphenyl-1,3,5-trioxa-2,4-disilapentane-1,5:4,2-tetrayl)

2.



α,α′:ω,ω′-bis(naphthalene-1,8-diyl)poly(naphthalene-4,5:8,1-tetrayl) (in order to preserve the ascending order of locants in the clockwise direction, the lowest possible free valence locant of the constitutional repeating unit placed at the lower left is 4 rather than 1)

4. SOURCE-BASED NOMENCLATURE

For many polymers, the structural identity of all the constitutional repeating units and of their sequential arrangement is not known, yet some indication is available as to their general characterization such as ladder or spiro polymers.

At times, it is also useful to identify the starting monomers especially for such complex polymers as double-strand polymers, the synthesis of which is often a multi-step reaction involving condensation, cyclization, and crosslinking.

It may also be useful at times to provide both source- and structure-based names for the same polymer. For a couple of examples below (6 and 11), references within this document are given to the corresponding constitutional repeating units and their names.

The source-based nomenclature identifies the starting material(s) from which the ladder or spiro polymer is prepared. It is derived from the nomenclature system for copolymers (Ref. 3). The system is based on the following principles:

(1) A homopolymer is described by the prefix "poly" followed by citation of the name of the monomer used. For monomer names consisting of two or more words, and for names containing substituents, parentheses or brackets are used.

(2) A copolymer, including a polymer obtained from two complementary monomers, is described by the prefix "poly" followed by citation in parentheses or brackets of the names of the monomers used. For monomer names consisting of two or more words, and for names containing substituents, additional parentheses or brackets are used. The monomer names are linked through a connective (infix) "*-alt-*", "*-per-*", or "*-co-*".

NOTE: "*-co-*" is used for cases where it is not possible to establish alternating or periodic structure.

(3) The specification of the type of structure in a polymer is shown by an italicized prefix "*ladder-*" or "*spiro-*" preceding "poly".

(4) No seniority rule is provided for the order of citation of the monomer names.

(5) Semisystematic or trivial names for monomers, which are well established by usage, are allowed.

Examples:

1. *ladder*-poly(methyl vinyl ketone)

2. *ladder*-poly(1,4-diphenyldiacetylene)

3. *ladder*-poly(2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone)

4. *spiro*-poly[dispiro[3.1.3.1]decane-2,8-bis(carbonyl chloride)]

5. *ladder*-poly[(pyromellitic dianhydride)-*alt*-(1,2,5,6-tetraamino-anthraquinone)]

6. *ladder*-poly[(1,4,5,8-naphthalenetetracarboxylic acid)-*alt*-(1,2,4,5-tetraaminobenzene)]

   NOTE: For the corresponding structure-based representation, see example 8 in Section 3.9.

7. *ladder*-poly[pyromellitonitrile-*alt*-[9,9-bis(4-aminophenyl)fluorene]]

8. *ladder*-poly[(1,2,4,5-tetramethylenecyclohexane)-*alt*-*p*-benzoquinone]

9. *ladder*-poly[(2,5-diaminoterephthalic acid)-*alt*-(2,5-dicyano-terephthaloyl chloride)]

10. *ladder*-poly[(2-vinylbutadiene)-*co*-(tetramethylene fumarate cyclic dimer)]

11. *spiro*-poly(1,4-cyclohexanedione-*co*-pentaerythritol)

NOTE: For the corresponding structure-based representation, see example 4 in Section 3.9.

5. ACKNOWLEDGMENT

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