Nomenclature and Structural Representation for Linear, Single-Strand Polymers Aftertreated to Hyperconnected Networks

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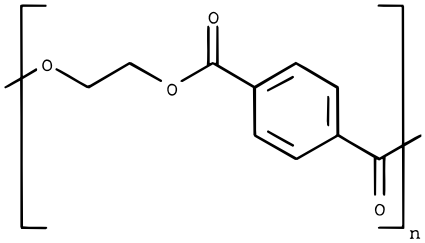
Source-based versus structure-based representations are discussed for linear, single-strand structural-repeating unit (SRU) type polymers that are aftertreated (post-reacted) with bifunctional cross-linking agents to give completely cross-linked, three-dimensional networks. The problems of their structure registration by use of the Chemical Abstracts Service Registry System are discussed, and a structure-based nomenclature and representation system for them is presented.

1. INTRODUCTION AND BACKGROUND

Nomenclature and structural representation of linear, single-strand, structure-based polymers are well documented.[1−5] Representation by structural repeating unit (SRU) is conventional, with the senior atom placed on the left, as illustrated by examples 1−3.

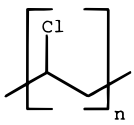
Example 1:



CAS 9CI* Name:
poly(oxy-1,2-ethanediyloxycarbonyl-1,4-phenylenecarbonyl)

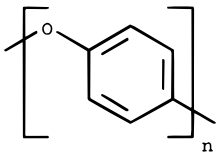
Synonyms: poly(ethylene terephthalate); PET
(* Chemical Abstracts Service Ninth Collective Index)

Example 2:



IUPAC* Name: poly(1-chloroethylene)
Synonyms: poly(vinyl chloride), SRU representation; PVC, SRU representation
(* International Union of Pure and Applied Chemistry)

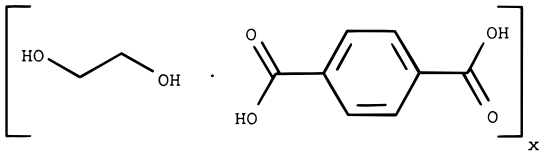
Example 3:



CAS 9CI name: poly(oxy-1,4-phenylene)
Synonyms: poly(oxy-p-phenylene); poly(p-phenylene oxide); PPO

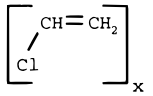
Representation of the polymers in examples 1 and 2 can be source-based instead of structure-based, as shown in examples 4 and 5.

Example 4:



CAS 9CI Name: 1,4-benzenedicarboxylic acid, polymer with 1,2-ethanediol

Example 5:



CAS 9CI name: ethene, 1-chloro-, homopolymer
Synonyms: ethylene, chloro-, polymers; PVC

However, source-based representation of polymers such as the one shown in example 3 is usually avoided because citation of the source monomers gives little or no indication of the polymer structure.

In SCION, a proprietary online database that uses Chemical Abstracts Service (CAS) Eighth Collective Index nomenclature and the Chemical Abstracts Service Registry System (CASRS) for polymer registration,[1] structured polymers are divided into three categories.[1a]

Category 1: Prescribed-Monomer Condensation—condensation polymers of the classes polyamide, polyester, polyimide, polyurethane, and combinations of these, e.g., polyamide-ester (see example 4 above). Regardless of the actual reactants polymerized, monomers in this category are "stylized" to their parents; thus, if terephthaloyl chloride is a reactant, terephthalic acid is the stylized monomer stored as a polymer component.

Category 2: Actual Starting Monomer—carbon-carbon multiple bond monomers (acetylenic, acrylic, ethylenic, and vinyl—see example 5 above) and polymers with incompletely identified structures (e.g., polymers from formaldehyde, melamine, phenol, urea).

Category 3: structural repeating unit (SRU)—all polymers that are not in categories 1 or 2.

† Retired.

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Source-based representation is used for polymers in categories 1 and 2; structure-based representation is used for polymers in category 3. Thus, structure-based representation is used for polymers such as poly(oxyethylene), poly(oxy-*p*-phenylene), poly(iminoethylene), poly(thiopropylene), poly-[(diphenylsilylene)oxy] (see Point 1), etc. Structural representation of these linear SRUs is handled conventionally by the CASRS.

Point 1: By SCION atom priority rules,[6a] Si is senior to O (because it has a higher atomic number); therefore, the SRU for this siloxane is $-(-SiPh_2-O-)_n-$. The CAS structure[3] is $-(-O-SiPh_2-)_n-$ because O is senior to Si; the International Union of Pure and Applied Chemistry (IUPAC) shows it drawn both ways.[7]

In SCION, branching or cross-linking (of any kind and to any degree) in source-based polymers is indicated only by use of the controlled-term textual descriptor POLY-HYPERCONNECTABLE (see Point 2); the name of the polymer, per se, contains no information about branching or cross-linking, although it is usually clear from the names and structures of the comonomers when this has occurred.

Point 2: The term POLY-HYPERCONNECTABLE was chosen in preference to a term such as POLY-HYPERCONNECTED because, although the term is a descriptor to a polymer, it refers to the ability of one or more monomers in a polymer to become hyperconnected during polymerization, whether or not such hyperconnection has actually occurred. Strictly speaking, for an SRU or structure-based polymer that shows hyperconnectivity, the term POLY-HYPERCONNECTED would be more accurate, but it was decided that use of two separate terms would be confusing. The controlled term chosen was POLY-HYPERCONNECTABLE for both source-based and structure-based polymers.

Examples 6, 7, and 8 illustrate types of hyperconnectivity in source-based polymers (see Point 3).

Example 6: POLYAMIDE-BENZOIC, 3,5-DIAMINO- (hyperbranched)

Example 7: POLYESTER-1,3,5-BENZENETRICARBOXYLIC/PENTAERYTHRITOL (hyperbranched and/or hypercross-linked)

Example 8: POLY-ACRYLAMIDE, *N*,*N*′-ETHYLENEBIS-(hyperbranched and/or hypercross-linked)

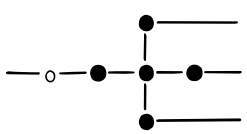
Point 3: Except for the nomenclature and structures shown in examples 1−5, all SRUs and polymers in this paper are theoretical and may or may not have been reduced to practice. Unless otherwise noted, SCION nomenclature[1] is used for all SRU and polymer representations except examples 1−5.

Hyperconnectivity in registration of source-based polymers by use of the CASRS typically does not arise because the few SRUs that are encountered as components of source-based polymers are usually linear e.g., polyoxyethylene or polyoxytetramethylene. Therefore, there are no concerns about even numbers of crossing bonds (see glossary).

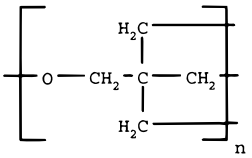
Source-based representation, the usual dodge to avoid facing the issue of naming SRUs, has the disadvantage, as always, that polymer structure is not shown explicitly and therefore has to be inferred.

The CASRS can accommodate branched or cross-linked SRU-based polymers, but the image display is conventional, with brackets or parentheses, only if there are an even number of crossing bonds through the left- and right-limiting parentheses or brackets (hereinafter called limiting brackets - see glossary) that define the SRU. The CASRS cannot currently register an SRU with an odd number of crossing bonds. An SRU with an even number of crossing bonds but with a structure such that the numbers of bonds through the left- and right-limiting brackets are unequal is registrable, but the graphics image of the structure in SCION is nonstandard (see Point 4).

Point 4: POLY-OXYNEOPENTANETETRAYL, the essential SRU of a dendritic Starburst (Reg. trademark, Dow Chemical Company) polyether[9] published in 1989, is registrable by the CASRS. The image appears as shown in structure (a); structure (b) is the desired format.



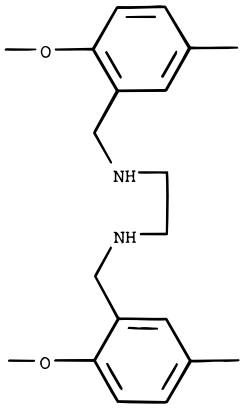
(a)



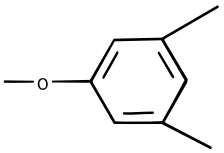
(b)

Thus, the SRU of example 9 can be registered, whereas the SRU of example 10 cannot.

Example 9.



Example 10.



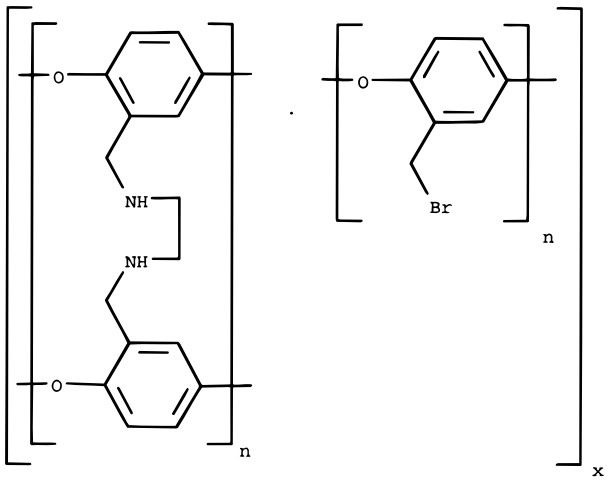
Poly-oxy(2-(bromomethyl)-*p*-phenylene) cross-linked by aftertreatment (see Point 5) with ethylenediamine is represented as the copolymer shown in example 11 (at registration, the components of a multicomponent polymer may be drawn in any order).

Point 5: Multiple parentheses are used in SCION substance names because the CASRS will not accept brackets; the word "aftertreated" is used to describe a post-reacted or post-treated polymer.

Point 6: SCION polymer names of this type begin POLY-..., not POLY(... SCION polymer nomenclature uses CAS 8CI nomenclature, except where this leads to ambiguity. The 8CI moiety name "*as*-phenenyl", used prior to introduction of "1,2,4-benzenetriyl" terminology, is inadequate here because it fails to indicate the precise ring entry and exit points.

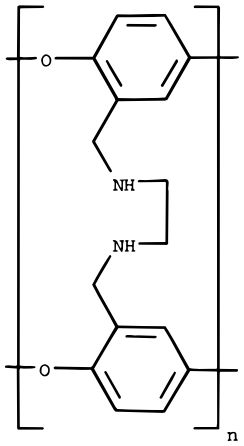
For structure-based polymers in SCION, a hyperbranched homopolymer is defined as one in which the SRU has a "connectivity" of more than two. Thus, the homopolymer of the SRU shown as example 9 is hyperbranched, and it may also be hypercross-linked, i.e., there may be macrocycles present. The homopolymer is shown as example 12.

Example 11:



Name: POLY-OXY(2-(BROMOMETHYL)-P-PHENYLENE), AFTERTREATED TO ETHYLENEBIS(IMINOMETHYLENE-2,1,4-BENZENETRIYL-1-OXY) (see Point 6)
Textual descriptor: POLY-HYPERCONNECTABLE (see Point 2)

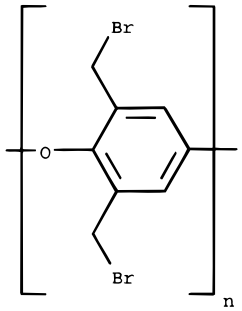
Example 12:



Name: POLY-ETHYLENEBIS(IMINOMETHYLENE-2,1,4-BENZENETRIYL-1-OXY)
Textual descriptor: POLY-HYPERCONNECTABLE

As a logical extension of example 11, if the linear polymer of example 13 is fully cross-linked by aftertreatment with ethylenediamine, a three-dimensional hypercross-linked structure results.

Example 13:



This type of completely cross-linked, three-dimensional network has been given neither nomenclature nor structural representation by CAS[3] or the International Union of Pure and Applied Chemistry (IUPAC).

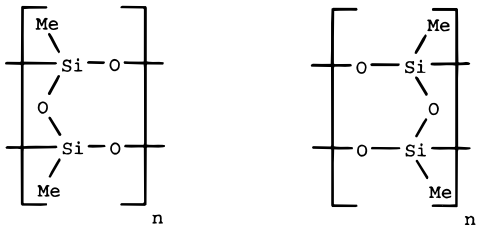
While source-based representations of these hyperconnected polymers are possible, greater precision of structural information can be conveyed by creation, wherever possible, of structure-based representations. This paper discusses the problems with this approach, and solutions to some of them.

Registration of polymers is currently executed manually for DuPont by CAS keyboarding personnel. This paper describes nomenclature rules to accompany manual encoding of polymers, but the principles behind it might be used for an automated polymer registration system.

2. DIFFERENCES IN CONVENTION BETWEEN CAS, IUPAC, AND SCION

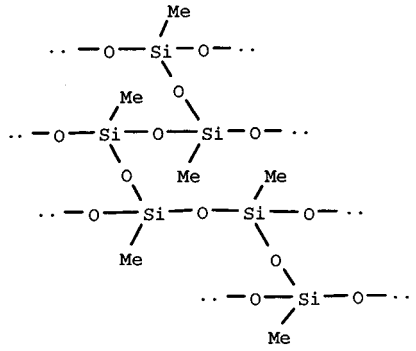
Before the representation of hyperconnected polymers is discussed, it is important to point out that structures such as that shown in example 14a do ***not*** represent a ladder polymer in SCION.

Example 14a. Example 14b.

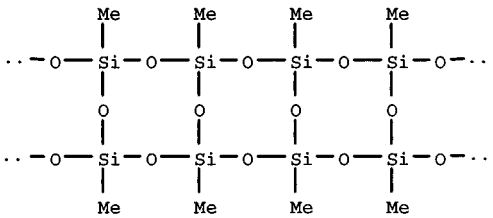


Example 14a represents a ***hyperconnected*** polymer, and it is to be understood that such a structure represents the three-dimensional network shown below as example 15. In contrast, both CAS[2] and IUPAC[8] use the structure shown in example 14b to represent the ladder polymer shown in structure 16.

Example 15.

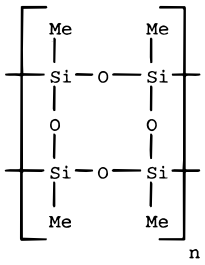


Example 16.



The ladder polymer of example 16 is represented in SCION by the structure given in example 17.[6]

Example 17:

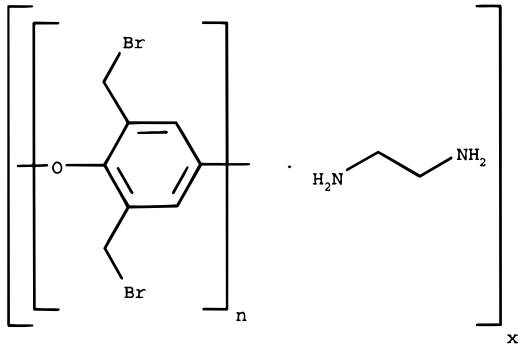


CAS and IUPAC both use structure 14b (not 14a) as the ladder structure because of a difference in atom priorities (see Point 1 above).

3. SOURCE-BASED VERSUS STRUCTURE-BASED REGISTRATION FOR HYPERCONNECTED POLYMERS

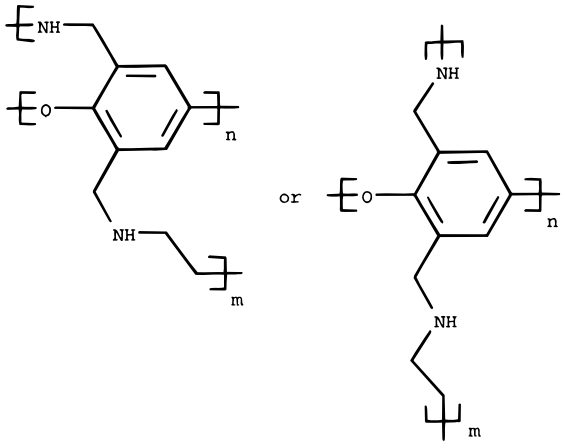
A source-based representation of a hyperconnected structure like the one obtained by cross-linking the linear polymer of example 13 with ethylenediamine is possible—see example 18—but it is inadequate because it fails to show the structure of the final SRU, which is completely known—see example 19.

Example 18.



Name for example 18: POLY-ETHYLENEDIAMINE/POLY-OXY(2,6-BIS(BROMOMETHYL)-P-PHENYLENEDIAMINE)

Example 19.

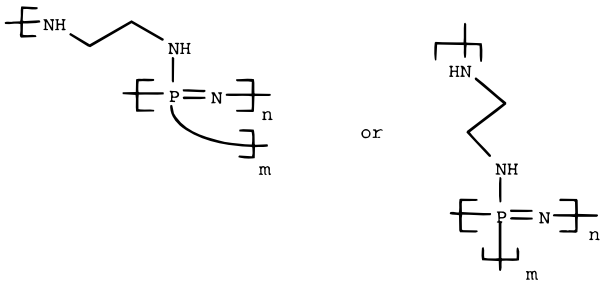


On the assumption that the software used for polymer registration can accommodate it, as a registration principle the known structure of a hyperconnected SRU should be registered. However, for situations where the software used for polymer registration cannot accommodate the structure-based representation of a hyperconnected polymer, a source-based representation is the "next-best" solution.

4. STRUCTURE-BASED REPRESENTATIONS OF HYPERCONNECTED POLYMERS: DISCUSSION OF THE PROBLEM

The theoretical structure-based representation for the hyperconnected polymer prepared by aftertreatment of poly-oxy(2,6-bis(bromomethyl)-*p*-phenylene) with ethylene-diamine is shown as example 19 above. Example 20 shows a hyperconnected polymer obtained by the aftertreatment of poly (diaminophosphoranylidyne)nitrilo with 1,2-dichloro-ethane or by the aftertreatment of poly-(dichlorophos-phoranylidyne)nitrilo with ethylenediamine.

Example 20.



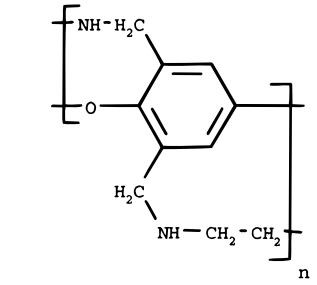
For examples 19 and 20 and other similar polymers hyperconnected by an aftertreatment, the problem is not with structural representation on paper but with computer image storage in the chemical file of SCION. Although the CASRS will accept more than one pair of crossing bonds, it permits only one set of limiting brackets, and these are applied in the horizontal plane or *x*-axis; it will not currently accept the SRUs shown in examples 19 and 20. In order to register such structures, a "force-fit" is necessary. Thus, the polymer of example 19 can be redrawn as shown in example 21a. Several other structures are also possible—see examples 21b−f.

Structures 21a and 21b are perceived intellectually as two different polymers, but the CASRS would "perceive" them as being the same.[10] Structures 21c and 21d are intellectually the same (because 21c can be rotated about the *x*-axis to give 21d), and the CASRS would also "perceive" them as the same.[10] Structures 21e and 21f are perceived intellectu-ally as two different polymers, but the CASRS would "perceive" them as being the same.[10]

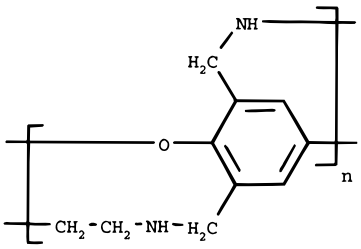
Similarly, the polymer of example 20 can be drawn in a number of ways, as shown in examples 22a−f, but these would be "perceived" by the CASRS as only three separate structures; the CASRS would equate 22a with 22b, 22c with 22d, and 22e with 22f.[10]

Clearly, it is unacceptable to have more than one structure for the same SRU. Therefore, if the polymers of structures shown as examples 19 and 20 are to be registered, new rules are needed to ensure that the same polymer is not registered more than once because it was drawn differently. Section 5 of this paper is devoted to developing a set of rules for the nomenclature and structural representation of these linear, single-strand, structure-based polymers that become hyper-connected by aftertreatment with bifunctional cross-linking

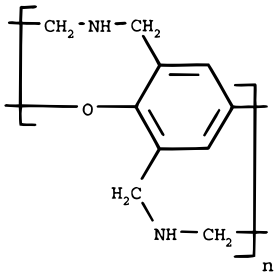
Examples 21a-21f.



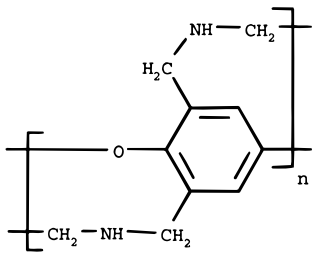
21a



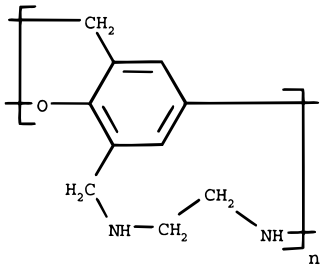
21b



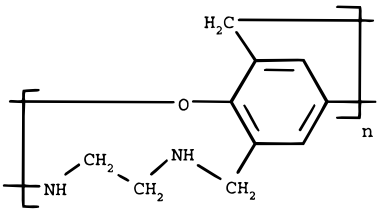
21c



21d

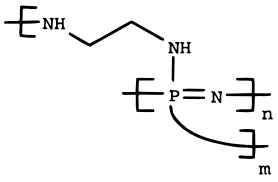


21e

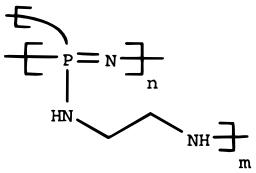


21f

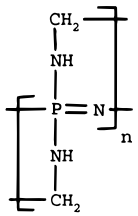
Examples 22a-f.



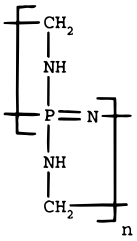
22a



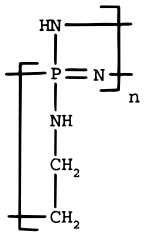
22b



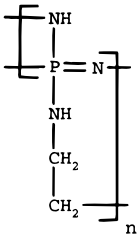
22c



22d



22e



22f

agents; structure-based polymers that become hyperconnected during polymerization are excluded.

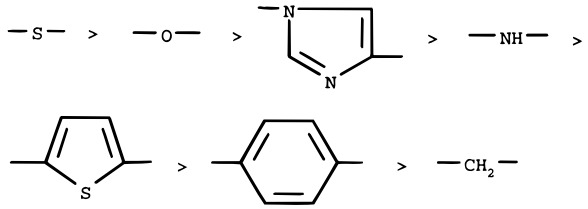
5. LINEAR, SINGLE-STRAND, STRUCTURE-BASED POLYMERS HYPERCONNECTED WITH BIFUNCTIONAL CROSS-LINKING AGENTS

5.1. Identifying the SRU. At least two complete sequences of the SRU are drawn. An exhaustive set of rules,[6a] the presentation of which is outside the scope of this paper, is used to determine SRU subunit seniority. Briefly, because (a) ring bonds cannot be broken in order to draw the SRU and (b) seniority is determined by the atomic numbers and environment of individual atoms, seniority usually works out as follows: (1) heterocyclic rings in which the heteroatom is also connected to at least one other backbone atom by an open-chain (nonring) bond; (2) heteroatoms in chains; (3) heterocyclic rings in which the heteroatom is not also connected to at least one other backbone atom by an open-chain (nonring) bond; (4) carbocyclic rings; (5) carbon chains (see Point 7). For SRUs with two or more dissimilar heterocyclic rings, there are further rules for choosing the senior heterocyclic ring. For situations where a heteroatom in the chain is the SRU head atom, the heteroatom with the highest atomic number is chosen. Thus, the most senior atom is Bi, followed in order by Pb, Hg, Te, Sb, Sn, Se, As, Ge, S, P, Si, O, N, B, etc.

5.2. Orienting the SRU. As a logical extension of the rules used to orient SRUs in linear, single-strand, structure-based polymers, by which the senior atom is placed on the left, for hyperconnected polymers the rules given below are applied in decreasing order of precedence.

•**Rule 5.2.1.** Draw the original linear backbone in the horizontal plane with the senior atom on the left.

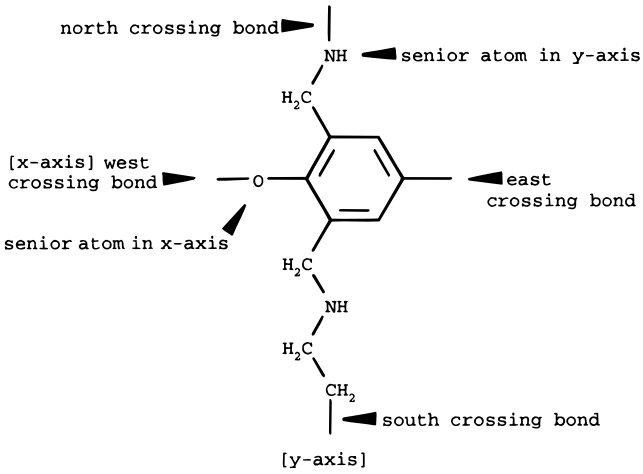
Point 7: SCION seniority examples (> means "is senior to").



•**Rule 5.2.2.** Draw the newly formed hyperconnection atom sequence in the vertical plane with the senior atom at the top.

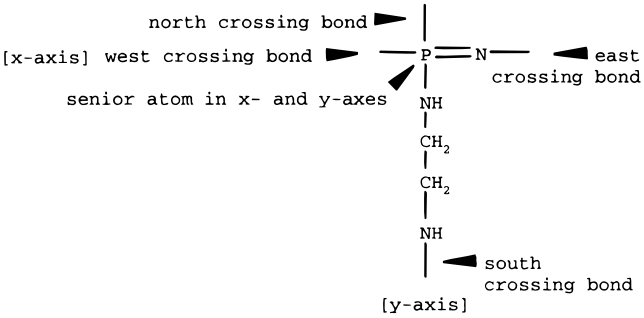
•**Rule 5.2.3.** Identify the four crossing bonds of the SRU. The west crossing bond is the bond to the left of the senior atom in the *x*-axis. The east crossing bond is the bond to the right of the last atom in the *x*-axis. The north crossing bond is the bond above the senior atom in the *y*-axis. The south crossing bond is the bond below the last atom in the *y*-axis—see examples 23 and 24.

Example 23.



- x-axis (original linear SRU): senior atom (oxygen) is placed on the left
- y-axis (newly formed hyperconnection): senior atom (nitrogen) is placed at the top

Example 24.



- x-axis (original linear SRU): senior atom (phosphorus) is placed on the left
- y-axis (newly formed hyperconnection): senior atom (phosphorus) is placed at the top

•**Rule 5.2.4.** Determine whether the north crossing bond and west crossing bond emanate from the same atom. If they do, follow rules 5.2.4.1 and 5.2.4.2; if they do not, follow rules 5.2.4.3 and 5.2.4.4. Then proceed to rule 5.2.5.

•**Rule 5.2.4.1.** Move the north crossing bond to the east side of the atom from which it emanates and extend it to the east.

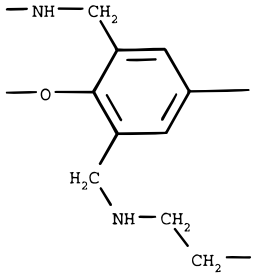
•**Rule 5.2.4.2.** Move the south crossing bond to the west side of the atom from which it emanates and extend it to the west.

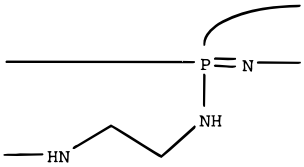
•**Rule 5.2.4.3.** Move the north crossing bond to the west side of the atom from which it emanates and extend it to the west.

•**Rule 5.2.4.4.** Move the south crossing bond to the east side of the atom from which it emanates and extend it to the east.

Application of rule 5.2.4 to the structures shown in examples 23 and 24 results in creation of the structures shown as examples 25 and 26, respectively.

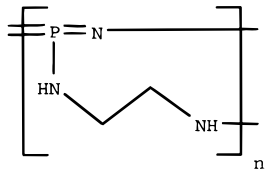
Example 25. Example 26.





Note on Rule 5.2.4: if the north and west crossing bonds emanate from the same atom, moving the north crossing bond to the west side may appear on paper to show two single bonds extending to the west (see example 22b above), but at registration the CASRS will telescope the two single bonds to a double bond. Thus, registration of the polymer of example 22b will result in the incorrectly registered structure of example 27.

Example 27.



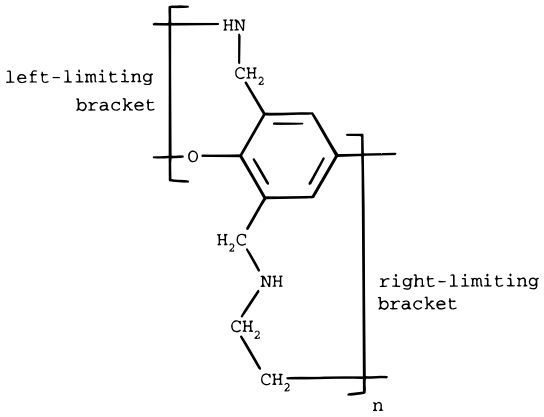
•**Rule 5.2.5.** Add limiting brackets and a sub *n* to convert the SRU into the final polymer. Draw an opening left-limiting bracket to "enclose" the two bonds extending to the west, and a closing right-limiting bracket to "enclose" the two bonds extending to the east. Add a subscript *n* outside and at the bottom of the closing right-limiting bracket.

Thus, the SRUs of examples 25 and 26 become the polymers of examples 28 and 29.

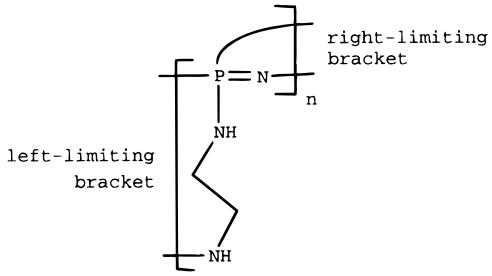
Once the positions of the crossing bonds, relative to the limiting brackets, have been determined by rules 5.2.1—5.2.5, the polymers may be rearranged for neater visual appearance. Thus, the structures of examples 28 and 29 may be redrawn as shown in examples 21a and 30, respectively.

A key point in structures such as those shown in examples 21a and 30 is that the path of the original linear, single-strand SRU is still traceable by following the atom sequence from a to a′ (see example 30), while the path of the newly formed hypercross-link is traceable by following the atom sequence from b to b′. These paths preserve, as far as

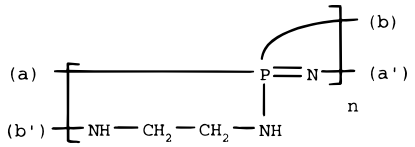
Example 28.



Example 29.



Example 30.

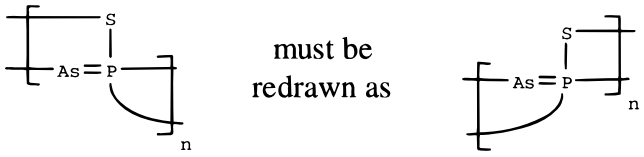


possible, the concept of superimposition of hyperconnection in the *y*-axis upon the original linear, single-strand SRU in the *x*-axis.

In the unlikely event that a hypercross-linked structure has south and east crossing bonds that emanate from the same atom, these two bonds must not pass through the same limiting bracket because the CASRS would telescope them to a double bond during registration. In such a situation, the structure must be redrawn so that the south bond exits through the left crossing bond and the east bond exits through the right crossing bond—see example 31.

Example 31.

Reorientation of structure having south and east bonds emanating from the same atom



Note on example 31: arsenic (As) was the head atom in the original linear SRU and is still the head atom in the new hyperconnected SRU—see section 5.1.

5.3. Naming the SRU. There is an inherent difficulty in creating a nomenclature system for x-shaped SRUs such as those contained in the polymers shown as examples 28 and 29—namely, how to deal with the junction moiety or unit, whether it is a ring (see example 28) or a single atom (see example 29). Whether the complete name of the SRU begins with a linear moiety or atom sequence that connects to the central junction unit, or with the central junction unit itself, merely naming the remaining moieties that emanate from the central junction unit is insufficient to indicate in which direction they go. Therefore nomenclature must include directions.

Nomenclature of these x-shaped SRUs is based upon the following rules. Structural examples are given in section 5.4. A glossary of new symbols, introduced specifically for nomenclature of hyperconnected networks, is appended.

•**Rule 5.3.1.** Select the head atom of the SRU. This may be an atom in the original linear SRU atom sequence, an atom in the newly formed hyperconnection atom sequence, or the junction unit itself, depending on which is senior according to SCION priority rules.[6a]

•**Rule 5.3.2.** If the head atom is not the junction unit, follow rules 5.3.3—5.3.12. If the head atom is the central junction unit, skip rules 5.3.3—5.3.5 and follow rules 5.3.6—5.3.12.

•**Rule 5.3.3.** Start with the head atom and name the entire linear sequence from left to right as far as, but exclusive of, the junction unit. Parenthesize compound sequences as necessary.

Examples: OXY; (OXYMETHYLENE)

•**Rule 5.3.4.** Preface the name generated by rule 5.3.3 with the parenthesized symbol (⟨-L) to indicate that a bond originates from the left-limiting bracket of the SRU and is connected to the left of the first moiety.

Examples: (<-L)OXY; (<-L)(OXYMETHYLENE)

•**Rule 5.3.5.** Determine whether a change of direction is necessary to connect the linear string (named by rule 5.3.3) to the junction unit.

•**Rule 5.3.5.1.** If no change of direction is needed, the name generated by rule 5.3.3 needs no suffix; proceed to rule 5.3.6.

•**Rule 5.3.5.2.** If a change of direction is needed, e.g., go upward or downward, add the appropriate parenthesized suffix, e.g., (U) or (D) respectively.

Note on Rule 5.3.5.2: If a change of direction is needed, it will always be downwards, because the head atom of the SRU is either to the left of, or above, the junction unit (see rules 5.2.1—5.2.2).

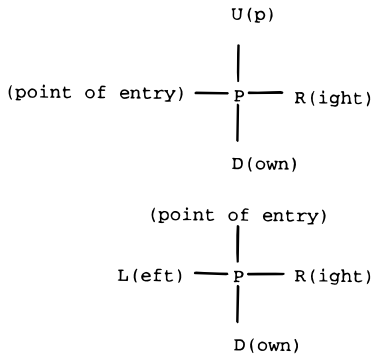
•**Rule 5.3.6.** Name the junction unit.

Examples: 1,2,3,5-BENZENETETRAYL*; 2,1,3,5-BENZENETETRAYL*; PHOSPHORANEPENTAYL

*Note on rule 5.3.6: the first number cited is always the point of entry into a ring or ring system; thus, for 2,1,3,5-BENZENETETRAYL, entry to the ring is at the 2-position.

•**Rule 5.3.7.** By means of a suffix in the form of a parenthesized expression, indicate bonds that emanate from the junction unit. Indicate the direction of each bond that emanates from the junction unit, and, if necessary, preface it with an integer that indicates from which position on the unit each bond emanates.

Single-atom examples.



Name: PHOSPHORANEPENTAYL(X;Y;Z); within the parenthesized expression, X, Y, and Z can each independently be D, L, R, or U, with the following restriction: only three of the four directions (D, L, R, U) are emanation points.

•If the point of entry is from the left, only D, R, and U are possible.

Then:

If X is D, Y and Z may only be R and U, or U and R
If X is R, Y and Z may only be D and U, or U and D
If X is U, Y and Z may only be D and R, or R and D

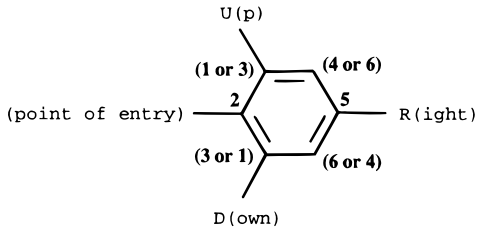
•If the point of entry is from above, only D, L, and R are possible.

Then:

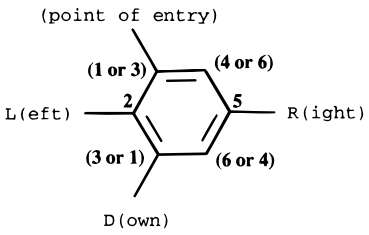
If X is D, Y and Z may only be L and R, or R and L
If X is L, Y and Z may only be D and R, or R and D
If X is R, Y and Z may only be D and L, or L and D

The order in which D, R, and U (for entry from the left) or D, L, and R (for entry from above) are cited depends upon the rest of the name of the SRU. This is explained in rule 5.3.10.1 below.

Ring-system examples (rings are numbered with the lowest-possible set of locants):



Name: 2,1,3,5-BENZENETETRAYL(nX;nY;nZ)



Name: 1,2,3,5-BENZENETETRAYL(nX;nY;nZ)

Within the parenthesized expressions in these two names, *n* is an integer that indicates a ring or ring-system locant, and X, Y, and Z can each independently be D, L, R, or U, with the following restrictions: only three of the four directions are emanation points.

•If the point of entry is from the left, only D, R, and U are possible.

Then:

If X is D, Y and Z may only be R and U, or U and R
If X is R, Y and Z may only be D and U, or U and D
If X is U, Y and Z may only be D and R, or R and D

•If the point of entry is from above, only D, L, and R are possible.

Then:

If X is D, Y and Z may only be L and R, or R and L
If X is L, Y and Z may only be D and R, or R and D
If X is R, Y and Z may only be D and L, or L and D

For entry from the left, determination of the correct integers to be used as prefixes for D, R, and U, and the order in which *n*D, *n*R, and *n*U, are cited depend upon the rest of the name of the SRU. This is explained in rule 5.3.10.2 below.

For entry from above, determination of the correct integers to be used as prefixes for D, L, and R, and the order in which *n*D, *n*L, and *n*R, are cited depend upon the rest of the name of the SRU. This is explained in rule 5.3.10.2 below.

•**Rule 5.3.8.** Determine if there are any bonds that emanate from the junction unit and exit directly as crossing bonds through a limiting bracket without "passing through" a moiety. Within the final SRU name each bond of this type is indicated by one of the following "letter-plus-arrow" symbols.

Symbol	Meaning
(D->)	a bond emanates downwards from the junction unit and terminates as a crossing bond through the right-limiting bracket
(D<-)	a bond emanates downwards from the junction unit and terminates as a crossing bond through the left-limiting bracket
(L<-)	a bond emanates from the left side of the junction unit and terminates as a crossing bond through the left-limiting bracket
(R->)	a bond emanates from the right side of the junction unit and terminates as a crossing bond through the right-limiting bracket
(U->)	a bond emanates upwards from the junction unit and terminates as a crossing bond through the right-limiting bracket
(U<-)	a bond emanates upwards from the junction unit and terminates as a crossing bond through the left-limiting bracket

•**Rule 5.3.9.** Name all the linear sequences that emanate from the junction unit. Name them in the direction of "radiating out from" the junction unit. If one was already named by rule 5.3.3, omit this from the sequences names by this rule. Parenthesize compound sequences as necessary.

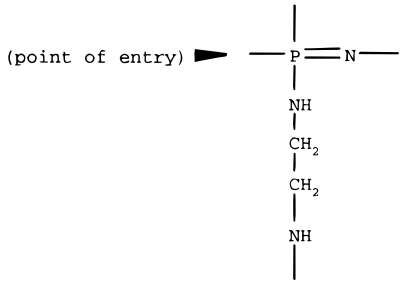
Examples: (IMINOETHYLENEIMINO); NITRILO

•**Rule 5.3.10.** Precede each name generated by rule 5.3.9 with a prefix in the form of a parenthesized symbol. For a single-atom junction unit, follow rule 5.3.10.1; for a ring or ring-system junction unit, follow rule 5.3.10.2.

•**Rule 5.3.10.1.** For a single-atom junction unit, select a letter (D, L, R, or U) that corresponds to one emanation position.

Note on rule 5.3.10.1: in this SRU the (iminoethylene-imino) moiety lies below the junction unit, while the nitrilo moiety lies to the right of it. Thus, the correct prefixes are

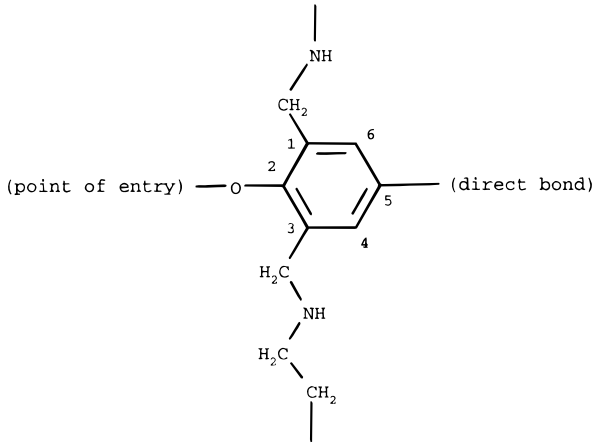
Examples:
(D)(IMINOETHYLENEIMINO); (R)NITRILO



D and R respectively, and therefore the final moiety names are (D)(IMINOETHYLENEIMINO) and (R)NITRILO.

•**Rule 5.3.10.2.** For a ring or ring-system junction unit, select a letter (D, L, R, or U) that corresponds to one emanation position from the ring or ring system. Prefix the letter with an integer that indicates from which ring or ring-system locant the bond emanates. Parenthesize the integer + letter combination.

Examples:
(1U)(METHYLENEIMINO); (3D)(METHYLENEIMINOETHYLENE)



Note on rule 5.3.10.2: alphabetization is based on the ***name*** of the moiety, not its prefix. Therefore, (U)(METHYLENEIMINO) alphabetically precedes (D)(METHYLENEIMINOETHYLENE). It can now be determined that the full prefix to (METHYLENEIMINO) is (1U) and the full prefix to (D)(METHYLENEIMINOETHYLENE) is (3D), because the lowest possible ring locant is assigned to the sequence that alphabetizes first. Therefore, the final names of these two sequences are (1U)(METHYLENEIMINO) and (3D)-(METHYLENEIMINOETHYLENE).

•**Rule 5.3.11.** Follow each sequence name generated by rule 5.3.10 with a suffix in the form of parenthesized symbol comprising a combination of

(1) a letter L or R to indicate whether the bond that emanates from the sequence goes to the left or right; and
(2) a left or right arrow to indicate that the bond terminates as a crossing bond through a left- or right-limiting bracket.

Examples: (D)(IMINOETHYLENEIMINO)(L<-); (R)NITRILO(R->)

•**Rule 5.3.12.** Assemble the complete name of the SRU in the order given by rules 5.3.12.1−5.3.12.5 below.

•**Rule 5.3.12.1.** Write the name of the head atom (generated by rule 5.3.3), prefixed by the (⟨-L) symbol (generated by rule 5.3.4) and followed by any suffix indicating change of direction (generated by rule 5.3.5) if one is applicable. If there is no head atom generated by rules 5.3.3−5.3.5, proceed to rule 5.3.12.2.

•**Rule 5.3.12.2.** Write the name of the junction unit (generated by rule 5.3.6), followed by its suffix (generated by rule 5.3.7).

•**Rule 5.3.12.3.** Write symbols for any bonds that emanate from the junction unit and exit directly as crossing bonds through a limiting bracket without "passing through" moieties (generated by rule 5.3.8).

•**Rule 5.3.12.4.** Write the names of moieties or linear sequences (generated by rule 5.3.9), alphabetized, and each preceded by its own prefix (generated by rule 5.3.10) and followed by its own suffix (generated by rule 5.3.11).

•**Rule 5.3.12.5.** Insert hyphens between the name segments created by rules 5.3.12.1−5.3.12.4.

•**Rule 5.3.13.** Name the polymer by adding POLY- as a prefix to the entire SRU name (generated by rules 5.3.12.1−5.3.12.5).

5.4. Examples of Names of Hyperconnected Polymers. Some examples are given to illustrate the nomenclature system.

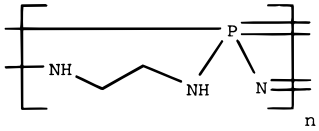
Example 28 (see above for structure): POLY-(<-L)(OXY-2,1,3,5-BENZENETETRAYL)(5R;1U;3D)-(5R->)-(1U)(METHYLENEIMINO)(L< -)-(3D)(METHYLENEIMINOETHYLENE)(R->)

Explanation of name: the name of the junction unit, 2,1,3,5 BENZENETETRAYL, indicates that entry into the ring is via the 2-position. The bond from the 5-position emanates to the right from the junction unit and becomes a crossing bond through the right-limiting bracket. This is cited, as (5R-⟩), before any named sequences that follow the junction unit. (METHYLENEIMINO) alphabetically precedes (METHYLENEIMINOETHYLENE); therefore the (METHYLENEIMINO) linear sequence emanates from the lower of two possible locants, namely the 1-position, as indicated by (1)(METH...). The (METHYLENEIMINOETHYLENE) linear sequence emanates from the 3-position, as indicated by the (3)(METH...).

Example 29 (see above for structure): POLY-(<-L)PHOSPHORANEPENTAYL(U;D;R)-(U->)-(D)(IMINOETHYLENEIMINO)-(L<-)-(R)NITRILO(R->)

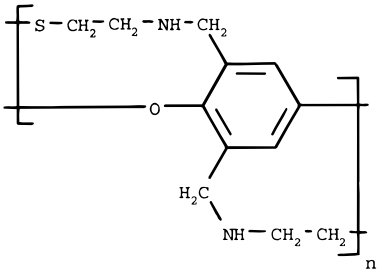
Note on example 29: it is not explicitly stated that there is a double bond between the PHOSPHORANEPENTAYL and NITRILO moieties and that a single bond from the right of the NITRILO moiety becomes a crossing bond through the right-limiting bracket. However, the only other possibility, shown as example 32, is chemically nonsense.

Example 32.



Example 33.

Poly-oxy(2,6-bis(bromomethyl)-p-phenylene), hyperconnected with 2,2'-thiobis(ethylamine)

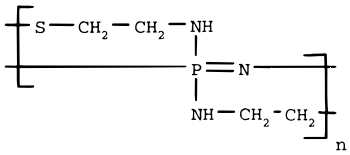


Name: POLY-(<-L)(THIOETHYLENEIMINOMETHYLENE)(D)-1,2,3,5-BENZENETETRAYL (5R;3D;2L)-(5R->)-(3D)(METHYLENEIMINOETHYLENE)(R->)-(2L)OXY(L<-)

Note on example 33: In this example sulfur is the head atom in the newly formed hyperconnection (in SCION, S is senior to O and N—see section 5.1). Therefore naming starts with the (S−C−C−NH−C) linear sequence.

Example 34.

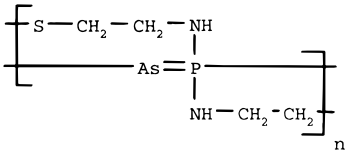
Poly-(dichlorophosphoranylidene)nitrilo, hyperconnected with 2,2'-thiobis(ethylamine)



Name: POLY-(<-L)(THIOETHYLENEIMINO)(D)-PHOSPHORANEPENTAYL(L;D;R)-(L<-)-(D)(IMINOETHYLENE)(R->)-(R)NITRILO(R->)

Example 35.

Poly-arsylidyne(diaminophosphoranylidyne), hyperconnected with bis(2-chloroethyl) sulfide



Name: POLY(<-L)(ARSYLIDYNEPHOSPHORANEPENTAYL)(R;D;U)-(R->)-(D)(IMINOETHYLENE)(R->)-(U)(IMINOETHYLENETHIO)(L<-)

Note on example 35: arsenic (As) was the head atom in the original linear SRU and is still the head atom in the new hyperconnected SRU—see section 5.1. The (R;D;U) can refer only to PHOSPHORANEPENTAYL; had it referred to the As atom, it would have followed ARSYLIDYNE immediately.

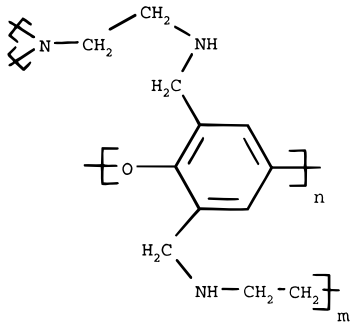
6. LINEAR, SINGLE-STRAND, STRUCTURE-BASED POLYMERS HYPERCONNECTED WITH TRIFUNCTIONAL CROSS-LINKING AGENTS

The use of a trifunctional agent, versus a bifunctional one, for preparation of hyperconnected networks from linear, single-strand, structure-based polymers introduces another difficulty that is insurmountable with the current version of the CASRS; the result of the reaction is an SRU with an odd number of crossing bonds, which makes it unregistrable. The polymer is shown as example 36.

This necessitates use of source-based registration to store such polymers, as discussed in section 3 above. The polymer

Example 36.

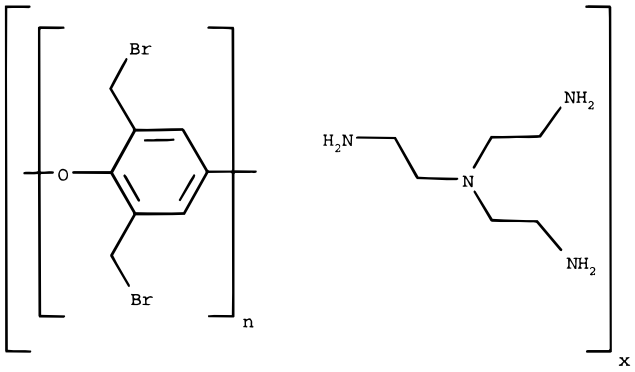
Poly-oxy(2,6-bis(bromomethyl)-p-phenylene), hyperconnected with 2,2',2''-triaminotriethylamine



in example 36 can be registered as given in example 37, but the polymer structure has to be deduced.

Example 37.

Source-based registration of the polymer of example 36



Name: POLY-TRIETHYLAMINE, 2,2',2''-TRIAMINO- WITH POLY-OXY(2,6-BIS(BROMOMETHYL)-P-PHENYLENE) (see Point 8)

Point 8: According to SCION polymer nomenclature rules,[1] this is an example of a mixed-category polymer—see section 1 above.

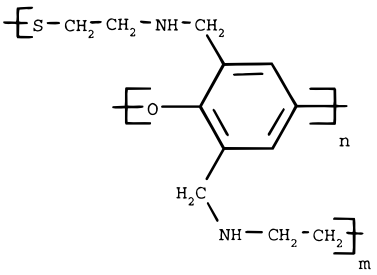
7. CONCLUSIONS

Structure-based representations have been discussed for linear, single strand structural-repeating unit (SRU) type polymers that are aftertreated (post-reacted) with bifunctional cross-linking agents to give completely cross-linked, three-dimensional networks. The problems of their registration by use of the Chemical Abstracts Service Registry System have been discussed, and a structure-based nomenclature and representation system has been devised.

8. RECOMMENDATION

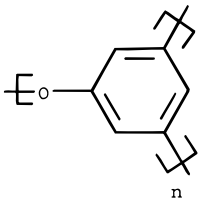
It is recommended that the Chemical Abstracts Service Registry System be improved to permit structure-based registration of structures such as those shown in examples 36 and 38. This entails accommodation of SRUs with any number of crossing bonds (odd or even) and any number of limiting brackets.

Example 38.



Registration of polymers with structures such as that shown as example 39 is also needed; currently, the CASRS cannot accommodate such structures.

Example 39.



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APPENDIX: GLOSSARY OF SYMBOLS AND TERMS FOR NOMENCLATURE OF HYPERCONNECTED NETWORKS

CROSSING BOND: an "open" bond that crosses the limiting brackets of the SRU. Thus, $-(-O-CH_2-)_n-$ has two crossing bonds, indicated by "−(−" and "−)−".

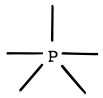
"D", "L", "R", and "U": symbols indicating "down", "left", "right", and "up", respectively. D, L, R, and U are used to indicate

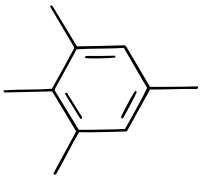
(a) a point of entry into an SRU

(b) a change of direction within an SRU

For example, (⟨-L)OXY(D) indicates that from a left-limiting bracket there is a crossing bond that connects to the left side of an OXY moiety; from the OXY moiety a bond emanates downwards, and the downwards direction is maintained until either a junction unit is reached or another directional letter (L, R, or U) indicates a change in direction. Thus, (⟨-L)-OXY(D) is line notation for

JUNCTION UNIT: any moiety with a connectivity of more than two that functions as a branching point within the SRU. Examples

PHOSPHORANEPENTAYL 

1,2,3,5-BENZENETETRAYL 

PHOSPHINIDYNE 

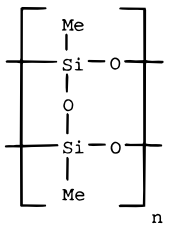
Note: phosphinidyne (−P═) is not a junction unit here.

LEFT-LIMITING BRACKET: the left bracket that identifies the start of the SRU (see also limiting bracket).

LIMITING BRACKET: a bracket that defines the limits of the SRU. Thus, $-(-O-CH_2-)_n-$ has two limiting brackets, indicated by "(" and ")".

LIMITING PARENTHESES: intellectually interchangeable with limiting bracket. For linear, single-strand SRUs, parentheses are usually used; for ladder polymers and other, larger SRUs that cannot be written on one line, brackets (also known as "square brackets") are used. For simplicity, all parentheses or brackets in this paper are called "brackets".

Examples:

-(O-CH_2-)$_n$- ; -[-O-CH_2-]$_n$- ; 

MOIETY: any fragment of the SRU that comprises either a linear single-strand or sequence, e.g., −S−, $-CH_2-$, $-NH-CH_2-CH_2-$, etc., or a junction unit.

RIGHT-LIMITING BRACKET: the right bracket that identifies the end of the SRU (see also limiting bracket).

"⟨-": a symbol indicating a bond that "comes from" or "goes to" the left, i.e., it is a crossing bond that passes through the left-limiting bracket of the SRU.

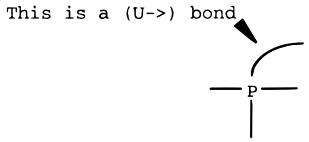
"-⟩": a symbol indicating a bond that "comes from" or "goes to" the right, i.e., it is a crossing bond that passes through the right-limiting bracket of the SRU.

(⟨-L): a double symbol indicating a crossing bond that "comes from" or "goes to" the left-limiting bracket and is connected to the left side of the moiety whose name follows the symbol. Thus, (⟨-L)OXY indicates -[-O... as an entry point through a left-limiting bracket.

(L⟨-): a double symbol indicating a bond that is connected to the left side of the moiety whose name precedes the symbol and becomes a crossing bond through the left-limiting bracket. Thus, THIO(L⟨-) indicates −[−S... as an exit point through the left-limiting bracket.

(R-⟩): a double symbol indicating a bond that is connected to the right side of the moiety whose name precedes the symbol and becomes a crossing bond through the right-limiting bracket. Thus, METHYLENE(R-⟩) indicates ...CH_2-]− as an exit point through the right-limiting bracket.

(U-⟩): a double symbol indicating a bond that is connected to the top of the moiety whose name precedes the symbol and becomes a crossing bond through the right-limiting bracket. The (U-⟩) is shown in the following example:



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