

Symmetrical “T”-Shaped Hyperbranched Structural-Repeating-Unit (SRU) Polymers: Converting Unregistrable SRUs to SRUs Registrable by Chemical Abstracts Service’s Registry System

John L. Schultz[†] and Edward S. Wilks*

E. I. Du Pont de Nemours and Company, Wilmington, Delaware 19880

Received April 30, 1996[⊗]

SCION is a DuPont proprietary database that operates by use of Chemical Abstracts Service’s Registry System (CASRS) for substance registration and Messenger software for searching. The CASRS cannot register structural repeating unit (SRU) (i.e., structure-based) polymers with odd numbers of crossing bonds (bonds that cross limiting parentheses or brackets). This paper describes the intellectual conversion of SRUs with an odd number of crossing bonds into hyperbranched, “T”-shaped SRUs with an even number of crossing bonds, so that they can be registered by the CASRS. A new nomenclature system is described for these new SRUs. This paper also includes conversion of other SRUs with even or odd numbers of crossing bonds but incorrect atom ratios, e.g., silsesquioxanes and poly-1,1,2,2-ethanediylidenetetraoxy.

1. BACKGROUND AND GENERAL DESCRIPTION OF THE PROBLEM

SCION is a DuPont proprietary online database that uses the Chemical Abstracts Service Registry System (CASRS) for polymer registration.¹ Prior to adoption of the CASRS for polymer registration, structures were stored in a topology-based Chemical Structure Storage and Search System (CS4),^{2–6} which was an adaptation of the Registry System developed by CAS^{7,8} from work done initially by DuPont.⁹ The Chemical Information System (CIS)—the successor to CS4—incorporated several changes, especially in the area of polymers.⁶

The CIS permitted storage of polymers of the structural repeating unit (SRU) type with any number of crossing bonds (see Point 1) because the concept of a crossing bond as such was not used.

Point 1: A crossing bond is an “open” bond that crosses the limiting brackets of the SRU. Thus, $(-O-CH_2-CH_2-)_n-$ has two crossing bonds, indicated by “ $(-)$ ” and “ $(-)_n-$ ”.

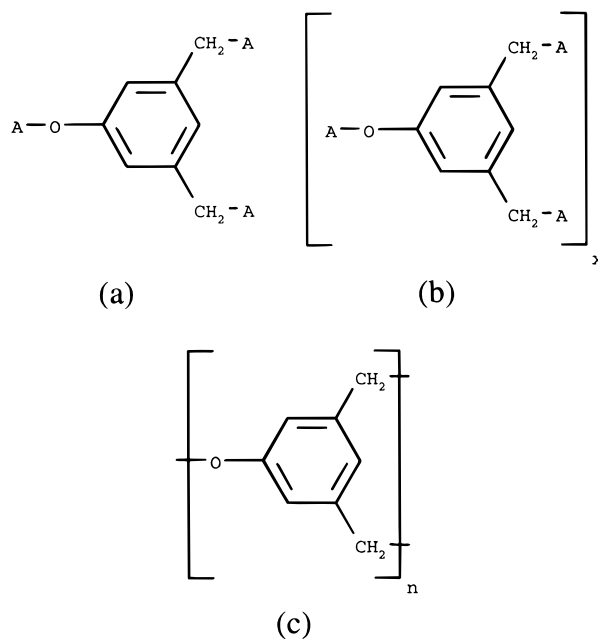
This was achieved by creating a dummy univalent atom “A”, which was used as a terminal moiety in a dummy monomer corresponding to a single occurrence of the SRU. Thus, for poly-oxyethylene (see Point 2), the dummy monomer for the SRU $(-O-CH_2-CH_2-)_n-$ was represented as $A-O-CH_2-CH_2-A$. The polymer was represented as $(A-O-CH_2-CH_2-A)_x$, i.e., it was represented as source-based, not structure-based. The drawback, of course, to use of a source-based representation such as $(A-O-CH_2-CH_2-A)_x$ for an SRU is that the critical head-to-tail orientation information is not contained in the structure.

Point 2: Polymer names in SCION begin “poly-...”, not “poly(...)”.

In contrast, the CASRS stores SRU-type polymers only in polymer format, e.g., $(-O-CH_2-CH_2-)_n-$, for which there is no corresponding theoretical monomer $A-O-CH_2-CH_2-A$; such a monomer cannot be registered.

The dummy-atom concept worked well for most SRUs with an odd number of crossing bonds, even when an SRU was asymmetrical—see example 1. In contrast, the real SRU polymer from 1(a), shown as example 1(c), cannot be registered on a structure basis by the CASRS, which currently requires an SRU to have an even number of crossing bonds.

Examples 1(a) through 1(c). (a) is the dummy monomer, (b) is the corresponding source-based polymer registration, and (c) is the desired SRU-format representation



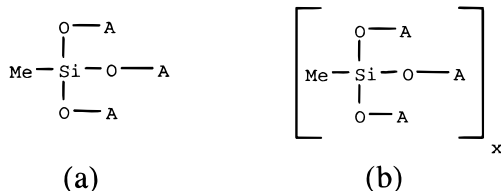
The dummy-atom concept worked less well for polymers such as silsesquioxanes, where the ratio of oxygen to silicon is 1.5:1, because the O:Si ratio in the dummy monomer was incorrect. The imperfect solution used in the CIS was to attach three oxygen atoms to the silicon atom. Thus, the dummy monomer for $(CH_3O_{1.5}Si)_n$ was as shown in example 2(a), and the corresponding polymer was represented as

[†] Retired.

[⊗] Abstract published in *Advance ACS Abstracts*, August 15, 1996.

shown in example 2(b); the latter, taken literally, implied peroxy linkages, which, of course, are not present in silsesquioxanes.

Examples 2(a) and 2(b).

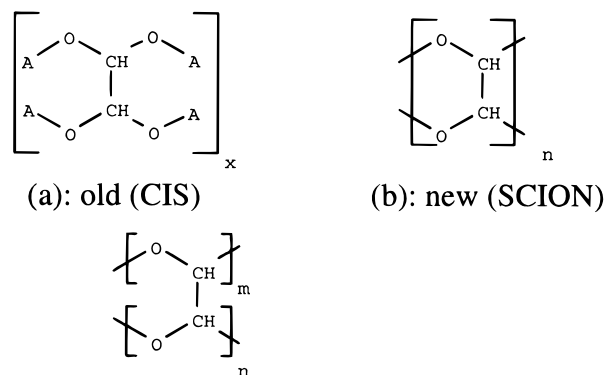


Registration of polymers is currently executed manually for DuPont by CAS keyboarding personnel. This paper describes nomenclature rules to accompany manual encoding of polymers, but the principles behind it might be used for an automated polymer registration system.

Transfer of SCION polymer structure records from the CIS to the CASRS included discontinuance of the dummy-atom concept, which would have created structure-conversion problems for SRU polymers with odd numbers of crossing bonds. This paper presents solutions to most of the problems encountered with SRUs with odd numbers of crossing bonds, such as the silsesquioxane problem shown in example 2.

The dummy-monomer concept worked also for most SRUs with an even number of crossing bonds, although some dummy monomers had incorrect atom ratios. Simultaneously with the conversion of silsesquioxanes, therefore, SRU structures with even numbers of crossing bonds previously structured with too many atoms were revised to give SRUs with correct atomic ratios; e.g., poly-ethanediylidene-1,2-dioxy, previously incorrectly structured as "poly-ethanediylidenetetraoxy", was restructured—see examples 3(a) and 3(b). The true form of poly-ethanediylidene-1,2-dioxy is a hyperbranched polymer, as shown in example 3(c), but this is currently unregistrable because of CASRS limitations.

Examples 3(a) through 3(c). Old (CIS), new (SCION), and idealized (hyperbranched) representations of poly-ethanediylidene-1,2-dioxy



(c): idealized (hyperbranched)

One problem still unresolved is SRU representation of a few asymmetrical polymers with an odd number of crossing bonds, such as the polymers shown above as example 1(c).

2. CONVERSION OF SRUS

A logical system is described for conversion of "odd" SRUs (SRUs with odd numbers of crossing bonds) to

symmetrical "I"-shaped or "even" SRUs (SRUs with even numbers of crossing bonds).

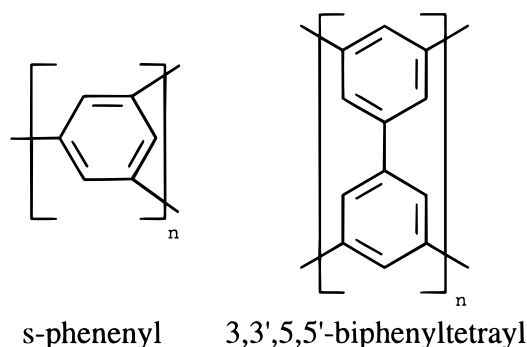
A structure-based nomenclature and representation system for the newly created symmetrical "I"-shaped SRUs is presented. The examples shown are theoretical and may or may not have been reduced to practice.

2.1. Creation of Symmetrical "I"-Shaped SRU Structures from "Odd" SRU Structures. The two-step method for conversion of an "odd" SRU is to

- (1) double the SRU by joining two "odd" SRUs together
- (2) eliminate intellectually superfluous atoms or groups

Symmetrical "odd" SRUs such as s-phenenyl¹³ are doubled to 3,3',5,5'-biphenyltetrayl with no moieties subtracted, as shown in example 4.

Example 4. Conversion of s-phenenyl to 3,3',5,5'-biphenyltetrayl



For asymmetrical "odd" SRUs, which comprised most of the SRUs needing conversion, rules were needed to resolve which of the several "even" SRUs that could be created by doubling the "odd" SRU is chosen to represent the new structure. For example, doubling the "odd" SRU shown in example 5(a) gives three possibilities—5(b) (center-to-center), 5(c) (end-to-end), and 5(d) (center-to-end). Note that the carbon:oxygen ratio in example 5(a) should be 3:1.5, not 3:3 as shown.

Elimination of spurious peroxy linkages formed and removal of additional oxygen atoms to prevent peroxy linkages being formed when successive SRUs are joined creates several possible structures. Thus, 5(b) gives rise to 5(e), 5(f), and 5(g); 5(c) gives rise to 5(h), 5(i), and 5(j); and 5(d) gives rise to 5(k), 5(l), and 5(m).

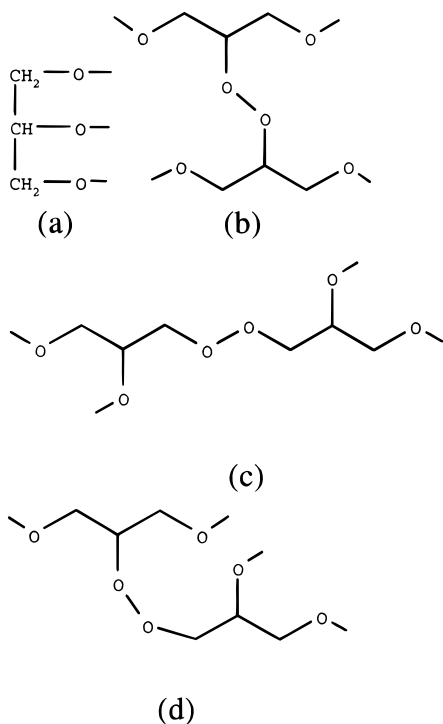
Although all of these "new" structures have the correct carbon:oxygen ratio of 6:3, rules are clearly needed to determine which of the nine possible structures, 5(e)–5(m), created by this two-step process is the preferred one. These rules are presented in section 2.2, and application of them specifically to example 5 is discussed in section 2.3.

Orientation of other hyperbranched SRUs is discussed in section 2.4. Nomenclature rules for these types of hyperbranched SRUs are presented in section 3.

2.2. Rules for Orienting Symmetrical "I"-Shaped Structures Created from "Odd" Structures. The following rules are applied in *descending* order of precedence:

- Rule 2.2.1.** The bridge formed by doubling the SRU must be *vertical*.
- Rule 2.2.2.** The bridge must be as *short* as possible.

Examples 5(a) through 5(d). Doubling of "odd" 1,2,3-propanetriyltrioxy 5(a) to a symmetrical "I"-shaped SRU - Step 1



•**Rule 2.2.3.** If Rule 2.2.2 leaves a choice, the bridge must be placed as *early* (i.e., as far to the left) as possible with respect to both the upper and lower horizontal atom sequences.

•**Rule 2.2.4.** The total size of the bridge must be as *small* as possible; thus, an unsubstituted bridge is senior to a substituted bridge of equal length.

•**Rule 2.2.5.** Each horizontal atom sequence is drawn with its head atom on the *left*.

Notes on rule 2.2.5: (1) This may move the bridge to the right after its initial position, with respect to the horizontal sequences, has been determined according to rule 2.2.3. Rules for determining the head atom are given elsewhere.^{10a} (2) The "individual bond" rule states that

- Two individual single bonds are senior to a double bond.
- Three individual single bonds are senior to a double bond plus a single bond.
- A double bond plus a single bond is senior to a triple bond.
- Four single bonds are senior to any combination of single and multiple bonds.

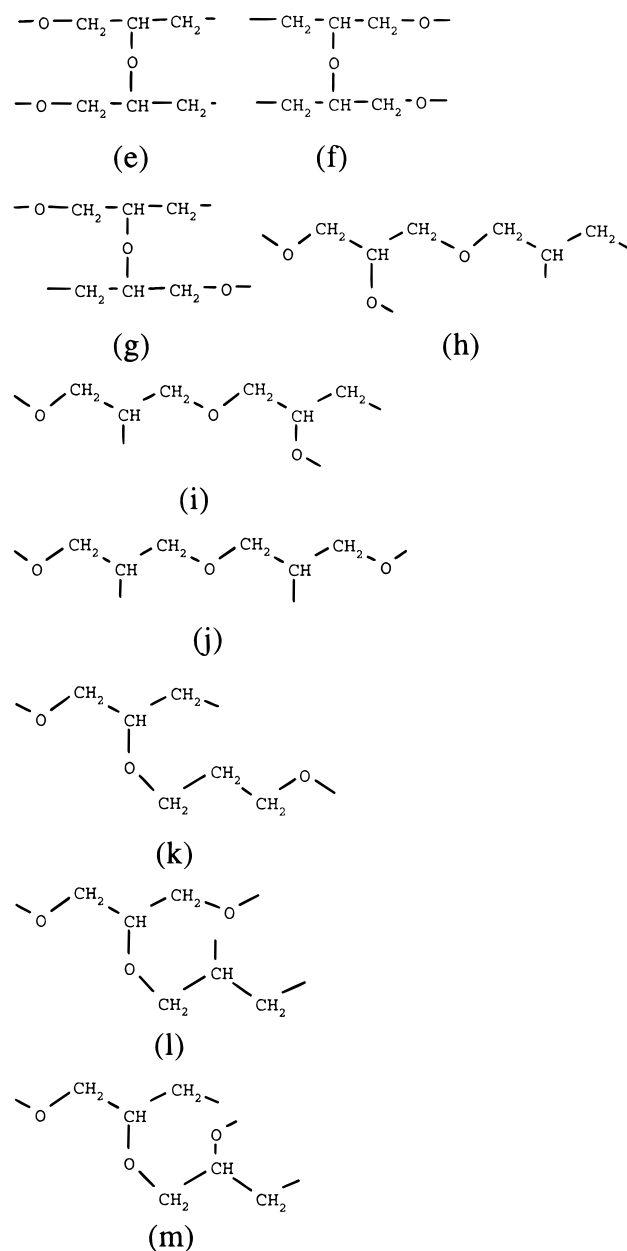
Thus, true methylidyne (branch-point) is senior to "pseudo"-methylidyne in an aromatic ring.

•**Rule 2.2.6.** Substitution in a horizontal atom sequence must be as far to the *left* as possible.

2.3. Application of Rules to Structures of Examples 5(e)–5(m) in Section 2.1. Application of rule 2.2.1 means that examples 5(h)–5(m) must be redrawn with vertical bridges. The redrawn structures, which also show simultaneous application of rules 2.2.3 and 2.2.5, are shown as examples 5(n)–5(s).

With all the bridges drawn vertically, structures 5(e), 5(f), and 5(g) may now be compared with structures 5(n)–5(s).

Examples 5(e) through 5(m). Doubling of "odd" 1,2,3-propanetriyltrioxy 5(a) to a symmetrical "I"-shaped SRU - Step 2

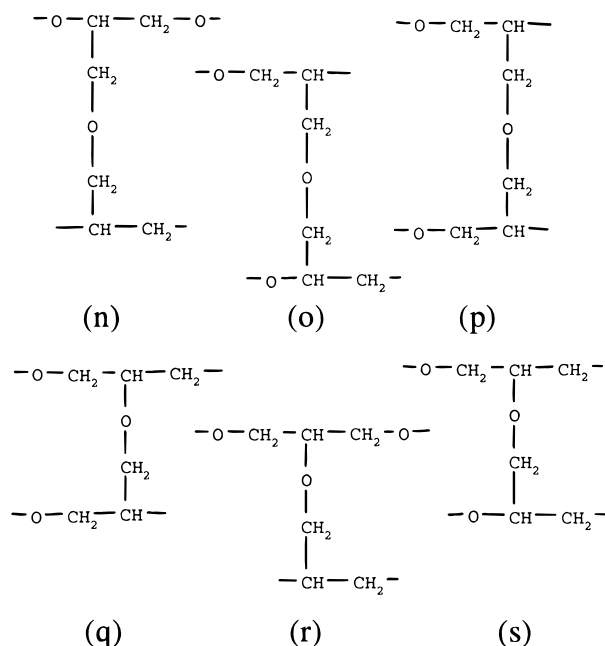


Structures 5(n)–5(s) have longer bridges than structures 5(e), 5(f), and 5(g) and are thus eliminated by rule 2.2.2. Structures 5(f) and 5(g) are incorrectly drawn per rule 2.2.5; when this rule is applied, 5(f) and 5(g) become identical with 5(e). Structure 5(e) is therefore correct for the new SRU.

Note that the structure of example 5(f) is not the "final correct answer". Although 5(f) is correct per application of rule 2.2.3, subsequent application of rule 2.2.5, which is applied *after* rule 2.2.3, places the oxygen atoms on the left in the two horizontal sequences; this results in the vertical bridge moving so that it is one atom further away from the leftmost atom in each horizontal sequence. The bridge is, of course, still connected to the central atoms of the two trimethylene moieties in the horizontal sequences.

Theoretically, the polymer corresponding to structure 5(e) should be represented as shown in example 6(a). Owing to current CASRS limitations, the structure is stored as shown

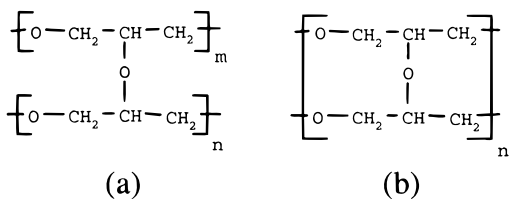
Examples 5(n) through 5(s). Examples 5(h) through 5(m) redrawn to create vertical bridges per Rule 2.2.1



in example 6(b). Structures of this type in the CAS Registry File represent ladder polymers. In SCION, this type of structure is used to represent not ladder but **hyperbranched** polymers, i.e., the $-(\text{O}-\text{C}-\text{C}-\text{C})_m-$ and $-(\text{O}-\text{C}-\text{C}-\text{C})_n-$ linear strings must be perceived intellectually as being in different planes with a vertical $-\text{O}-$ moiety cross-link. Ladder polymers in SCION are discussed elsewhere.¹⁰

Examples 6(a) and 6(b).

Theoretical and actual representations of the polymer from the symmetrical "I"-shaped SRU shown as example 5(e)



2.4. Orientation of Other Hyperbranched SRUs.

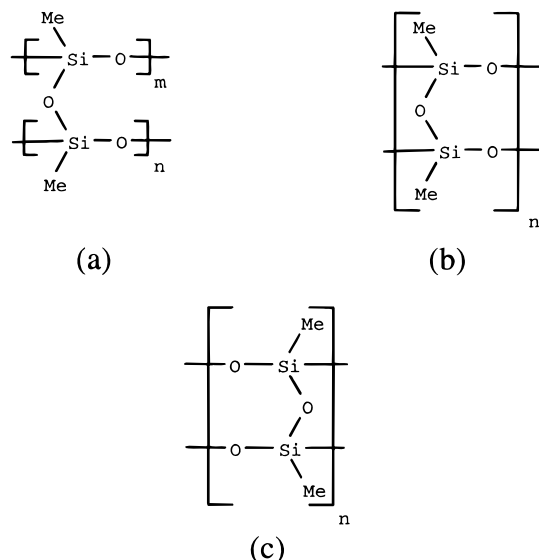
Structures such as ethanediylidenetetraoxy are restructured to ethanediylidene-1,2-dioxy (see example 3 above).

The silsesquioxane problem shown above as example 2 was resolved by creation (on paper) of the SCION hyperbranched SRU shown as example 7(a); the silicon atoms are on the left because by SCION atom priority rules^{10a} silicon is senior to oxygen. Unfortunately, because of CASRS limitations, the polymer of example 7(a) has to be registered in a modified format—see example 7(b); as in example 6(b), the latter does **not** represent a ladder polymer in SCION (see Point 3). CAS and one of us (E.S.W.) discovered the silsesquioxane resolution independently at about the same time. However, the CAS structure, shown as example 7(c), represents a ladder polymer, and the oxygen atoms are on

the left because CAS priority rules dictate that oxygen is senior to silicon.¹²

Example 7.

Resolution of the silsesquioxane problem



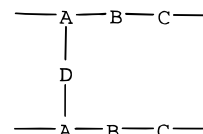
Point 3: Ladder and spiro polymers in SCION are registered by a unique system.¹⁰

Other SRUs such as neopentetetrayltetraoxy were restructured to neopentetetrayldioxy. This structure and other examples are shown in Table 1; names of the SRUs in Table 1 are given in Table 2.

3. NOMENCLATURE RULES FOR SYMMETRICAL "I"-SHAPED SRUS

Two sets of rules are given below for the new "I"-shaped SRUs.

Rules 3.1–3.2 were created to cover "I"-shaped SRUs of the general structure



where A, B, and C, are unitary moieties and D is a vertical bridge containing one or more unitary moieties. In this case the vertical bridge is attached to the leftmost moiety in both the upper and lower horizontal sequences, and the upper and lower horizontal sequences are identical.

•Rule 3.1. If the vertical linear sequence (VLS)—the bridge itself, plus one additional "junction-unit" atom on each end of the bridge—has a unitary name according to the CAS 8th Collective Index nomenclature, it is used (see Points 4, 5, and 6).

Point 4: A "junction-unit" atom is one at which branching occurs; e.g.,



Point 5: If an unsubstituted multiradical is named by not combining more than one radical name,¹¹ then it is unitary.

Table 1. Examples of SRUs, Previously Represented with Incorrect Molecular Formulas, Restructured with Four Crossing Bonds (Limiting Brackets or Parentheses Are Omitted for Clarity)

STR. No.	ORIGINAL STRUCTURE	REVISED STRUCTURE
1.		
2.		
3.		
4.		
5.		
6.		
7.		
8.		
9.		

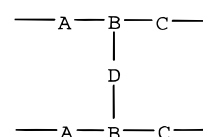
If it is named by combining two or more radical names, then it is not unitary. Substitution with groups is allowed. Thus, DISILOXANEDIYLLIDENE, (METHYLIMINO), OXALYL, OXY, TRIMETHYLENE, and UREYLENE are typical unitary names. IMINO is unitary; therefore, although (METHYLIMINO) is compound, it is still unitary. Similarly, although UREYLENE comprises three diradicals, because it is named without combining names of diradicals, it is considered to be unitary. In contrast, (CARBONYLOXY), (ETHYLENESULFONYL), and (METHYLENE-*p*-PHENYLENE), are not unitary because each name is built from two radical names. CAS lists unitary and nonunitary names¹¹ but does not define “unitary”.

Point 6: SCION polymer nomenclature uses CAS 8CI nomenclature, except where this leads to ambiguity. CAS 8CI moiety names such as “*s*-phenenyl”, “*as*-phenenyl”, and “*v*-phenenyl”, used prior to introduction of terminology such as “1,3,5-benzenetriyl”, “1,2,4-benzenetriyl”, “2,1,4-benzenetriyl”, etc., may be inadequate in certain names because they fail to indicate precise ring entry and exit points (see, for example, SRU 8 in Table 2).

Note on rule 3.1: carbon chains must not be broken, even when transitioning from vertical bridge moieties to moieties in horizontal sequences.

•Rule 3.2. If there is no unitary name for the VLS, the SRU is named by naming the central unitary moiety of the VLS and following it with DI... or BIS(... Names of moieties in horizontal sequences follow the name of the moiety or moieties in the vertical bridge without pause. The final polymer name is the name of the complete moiety sequence preceded by POLY-. In the final polymer name the only indication of transition from the moieties in the vertical bridge to the moieties in the horizontal sequences is the appearance of a “triradical name” that indicates branching.

Rules 3.3–3.4 were created to cover “I”-shaped SRUs of the general structure



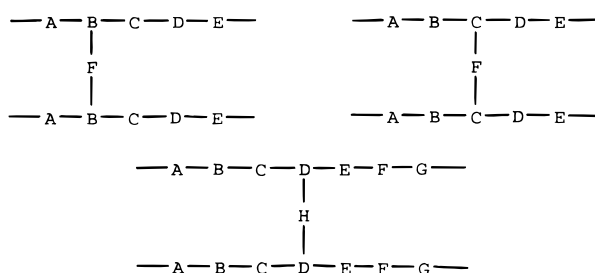
where A, B, and C, are unitary moieties and D is a vertical bridge containing one or more unitary moieties. In this case the vertical bridge is attached to moieties other than the leftmost in both the upper and lower horizontal sequences, and the upper and lower horizontal sequences are identical.

•**Rule 3.3.** Apply Rule 3.1 (see above).

•**Rule 3.4.** If there is no unitary name for the VLS, the SRU is named by naming the central unitary moiety of the VLS and following it with DI... or BIS(... Names of the horizontal-sequence moieties A and C are alphabetized and follow the name of the moiety or moieties in the vertical bridge without pause.

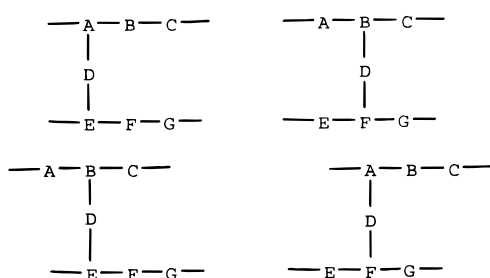
The final polymer name is the name of the complete moiety sequence preceded by POLY-. In the final polymer name the only indication of transition from the moieties in the vertical bridge to the moieties in the horizontal sequences is the appearance of a "triradical name" that indicates branching. Locants, especially on junction units B, are often critical for indicating points of entry and exit. Thus, 2,1,3-PROPANETRIYL indicates entry at the central carbon and exit from carbons 1 and 3.

Other, more complex situations, e.g., structures such as



and so on are covered by a logical extension of the above rules—see, for example, structures 5 and 6 in Table 1.

Asymmetrical structures such as



and so on will be covered in a separate paper.¹⁴

CONCLUSIONS

SRU polymers with odd numbers of crossing bonds that are unregistrable by the CASRS were converted into "I"-shaped SRUs with an even number of crossing bonds to make them registrable. Two other types of SRU polymers—silsesquioxanes, and SRUs with even numbers of crossing bonds but with incorrect atomic ratios—were restructured as

Table 2. Names of SRUs Depicted in Table 1

1. OXYBIS(1-ETHANYLIDENE-2-YL-1-OXY)
2. 2,4-PENTANEDIYLIDENE-2,4-DIOXY
3. NEOPENTANETETRAYLDIOXY
4. HEXAMETHYLENEBIS(OXY(1,2,3-PROPANETETRIYL-2-OXY)) (see Point 7)
5. OXYBIS(*p*-PHENYLENECARBONYL-1,3,5-BENZENETRIYL-3-(CARBONYL-4,4'-BIPHENYLENE)-5-(CARBONYL-*p*-PHENYLENEOXY)) (see Point 6)
6. OXYBIS(2,1,6-HEXANETRIYL-1-OXY)
7. *m*-PHENYLENEBIS(*s*-TRIAZINE-2,4,6-TRIYL-4-*m*-PHENYLENE)
8. METHANETETRAYLBIS(NITRILO-2,1,4-BENZENETRIYL-4-(NITRILOMETHANETETRAYLNITRILO-*p*-PHENYLENE)-1-OXY) (see Point 6)
9. 4,4'-BIPHENYLYLENEBIS((HYDROXYMETHYLIDYNE)-4,4'-BIPHENYLENE)¹³

symmetrical "I"-shaped SRUs with correct atom ratios. A nomenclature system was devised for the new SRUs.

Point 7: The CASRS will not accept combinations of parentheses and brackets for substance names in SCION; therefore, multiple parentheses are used.

ACKNOWLEDGMENT

The authors thank Mr. Joseph Donahue and Dr. David Stauffer of MDL for acquisition of and tutorials on ISIS/Draw.

REFERENCES AND NOTES

- (1) Patterson, J. A.; Schultz, J. L.; Wilks, E. S. Enhanced Polymer Structure, Searching, And Retrieval in an Interactive Database. *J. Chem. Inf. Comput. Sci.* **1995**, 35, 8–20.
- (2) Montague, B. A.; R. F. Schirmer, R. F. Du Pont Central Report Index: System Design, Operation and Performance. *J. Chem. Doc.* **1968**, 8, 33–41.
- (3) Hoffman, W. S. An Integrated Chemical Structure Storage and Search System Operating at Du Pont. *J. Chem. Doc.* **1968**, 8, 3–13.
- (4) Hoffman, W. S. Du Pont Information Flow System. *J. Chem. Doc.* **1972**, 12, 116–124.
- (5) Schultz, J. L. Handling Chemical Information in the Du Pont Central Report Index. *J. Chem. Doc.* **1974**, 14, 171–179.
- (6) Schultz, J. L. Polymer Nomenclature, Classification, and Retrieval in the Du Pont Central Report Index. *J. Chem. Inf. Comput. Sci.* **1975**, 15, 94–100.
- (7) Morgan, H. L. The Generation of a Unique Machine Description for Chemical Structures - A Technique Developed at Chemical Abstracts Service. *J. Chem. Doc.* **1965**, 5, 107–113.
- (8) Leiter, D. P.; Morgan, H. L.; Stobaugh, R. E. Installation and Operation of a Registry for Chemical Compounds. *J. Chem. Doc.* **1965**, 5, 238–242.
- (9) Gluck, D. J. A Chemical Structure Storage and Search System Developed at Du Pont. *J. Chem. Doc.* **1965**, 5, 43–51.
- (10) Schultz, J. L.; Wilks, E. S. A Nomenclature and Structural Representation System for Ladder and Spiro Polymers; (a) Appendix: SCION Database Chemical File: Atom Priority Rules. *J. Chem. Inf. Comput. Sci.* **1996**, 36, 786–793.
- (11) Naming and Indexing of Chemical Compounds (1969 Edition), Chemical Abstracts Service (Copyright 1969, the American Chemical Society); Appendix IV (pp 3059–3076).
- (12) Chemical Abstracts Service 1994 Index Guide; Appendix IV, Section 222.
- (13) Webster, O. W.; Kim, Y. H.; Gentry, F. P.; Farlee, R. D.; Smart, B. E. *Polym. Prepr.* **1992**, 33(1), 186–7.
- (14) Schultz, J. L.; Wilks, E. S. A Nomenclature and Structural Representation System for Asymmetrical "I"-Shaped Hyperbranched Polymers. (Submitted for publication in *J. Chem. Inf. Comput. Sci.*).

CI9600420