Polymer Nomenclature and Structure: A Comparison of Systems Used by CAS, IUPAC, MDL, and DuPont. 3. Comb/Graft, Cross-Linked, and Dendritic/Hyperconnected/Star Polymers

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Polymer nomenclature styles and structure representation systems described, recommended, or used by Chemical Abstracts Service (CAS), the International Union of Pure and Applied Chemistry (IUPAC), MDL Information Systems, Inc. (MDL), and DuPont are compared and contrasted. Structure-based versus source-based nomenclature and structural representations are discussed. Irregular single-strand organic polymers comprise a very large group that includes aftertreated (post-treated); alternating and other periodic; block; comb and graft; cross-linked; and dendritic, hyperconnected, and star polymers. The types covered in this paper (part 3 of 4) are comb and graft; cross-linked; and dendritic, hyperconnected (i.e., hyperbranched and/or hypercross-linked), and star polymers.

6.4. Comb and Graft Polymers. Comb and graft polymers are discussed together because there is overlapping technology, and it is not always possible to distinguish between them. For example, when poly(*p*-aminobenzoyl chloride) is endcapped at the amino end with acetyl chloride and at the chlorocarbonyl end with 2-hydroxyethyl acrylate (HEA), and the resulting PPABA macromonomer is then copolymerized with butyl acrylate (BA), the final product may be perceived as a comb polymer.
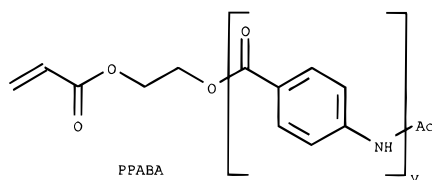
However, when a poly(BA/HEA) copolymer (random or statistical) is aftertreated with *p*-aminobenzoyl chloride, and the resulting side chains are endcapped with acetyl chloride, the final polymer may be perceived as a graft polymer.
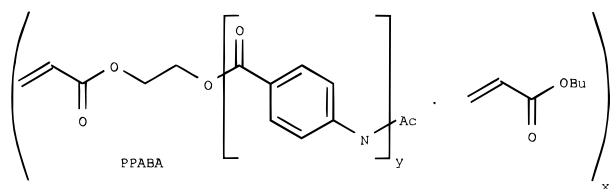
In terms of source-based representation, the two polymers have the same structure, although the two polymer backbones may have different sequential distributions of the monomers that arise from copolymerization of BA and HEA versus BA and PPABA.

6.4.1. CAS Nomenclature and Structure Representation. CAS does not recognize comb polymers as a type. Many (but not all) comb polymers are classified as graft polymers; one type of comb polymer that is *not* registered as a graft polymer is the homopolymer of a macromonomer.[1]

Registration of graft copolymers with the term "graft" as an integral part of the Registry record began with the 12CI (1987). Earlier records are incomplete in their recognition of graft polymers as such; some have the word "graft" somewhere in the text but are not classified as graft polymers, while others have no recognition at all.

6.4.1.1. Structure-Based Method. As with the situation of two or more unterminated SRUs in a copolymer (discussed earlier), CAS reverts to source-based representation for "all-SRU" graft polymers, i.e., polymers with an SRU backbone and an SRU side chain. Thus, for the comb polymer represented by example 6.4.1.1.1, CAS uses the registration style shown as example 6.4.1.1.2.

Example 6.4.1.1.1. An "all-SRU" comb or graft polymer shown in SRU format
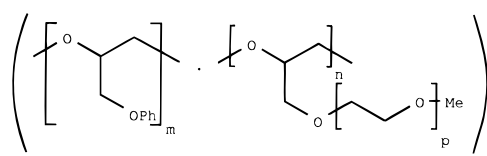
Example 6.4.1.1.2. CAS representation of an all-SRU comb (or graft) polymer

REGISTRY COPYRIGHT 1996 ACS
RN 154353-60-3 REGISTRY
CN Oxirane, (phenoxymethyl)-, polymer with α-methyl-ω-(oxiranylmethoxy)poly(oxy-1,2-ethanediyl), graft (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Poly(oxy-1,2-ethanediyl), α-methyl-ω-(oxiranylmethoxy)-, polymer with (phenoxymethyl)oxirane, graft (9CI)
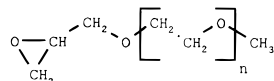MF (C9 H10 O2 . (C2 H4 O)n C4 H8 O2)x
CI PMS
PCT Polyether, Polyether formed
SR CA

LC STN Files: CA, CAPLUS
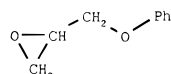DES 8:PM,GRAFT

   CM 1

   CRN 40349-67-5
   CMF (C2 H4 O)n C4 H8 O2
   CCI PMS

   CM 2

   CRN 122−60−1
   CMF C9 H10 O2

:

6.4.1.2. Source-Based Method. When CAS began to register polymers in 1967, no distinction was made between graft copolymers and other copolymers. The information might have been part of the descriptive "index modification", but it was not part of the Registry record (see opening remarks in section 6.4.1).

Differentiation between the polymeric substrate and the applied monomer is not made; e.g., whether 1-hexene is grafted onto 1-heptene homopolymer or vice versa, the preferred index entry is "1-heptene, polymer with 1-hexene, graft" with an additional entry at "1-hexene, polymer with 1-heptene, graft".[2] Thus, CAS makes no distinction between polyA-graft-B and polyB-graft-A.

Application of the text descriptor 8:PM,GRAFT to graft polymers began with the 12CI (1987). Although earlier records do not have it, this is probably of minor importance, because this descriptor is currently displayable but not searchable. Examples 6.4.1.2.1 through 6.4.1.2.2 show typical graft polymers.

Example 6.4.1.2.1. Typical current graft polymer; ", graft" appears in name, and text descriptor 8:PM,GRAFT is part of the Registry record

REGISTRY COPYRIGHT 1995 ACS
RN 155015-73-9 REGISTRY
CN 2-Propenoic acid, 2-methyl-, methyl ester, polymer with ethene and 2-propenoic acid, graft (9CI) (CA INDEX NAME)
:
MF (C5 H8 O2 . C3 H4 O2 . C2 H4)x
CI PMS
PCT Polyacrylic, Polyolefin
SR CA
LC STN Files: CA, CAPLUS
DES 8:PM,GRAFT
:

Example 6.4.1.2.2. Graft polymer containing macromonomer as one component; ", graft" appears in name, and text descriptor 8:PM,GRAFT is part of the Registry record
REGISTRY COPYRIGHT 1995 ACS
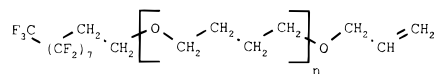RN 144307-94-8 REGISTRY

CN 2,5-Furandione, polymer with α-(3,3,4,4,5,5,6,6,7,7,8,8,-9,9,10,10,10-heptadecafluorodecyl)-ω-(2-propenyloxy)poly-(oxy-1,4-butanediyl), graft (9CI) (CA INDEX NAME)
:
MF ((C4 H8 O)n C13 H9 F17 O . C4 H2 O3)x
CI PMS
PCT Polyether, Polyvinyl
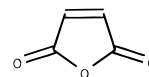SR CA
LC STN Files: CA, CAPLUS
DES 8:PM,GRAFT

   CM 1

   CRN 130425-41-1
   CMF (C4 H8 O)n C13 H9 F17 O
   CCI PMS

   CM 2

   CRN 108−31−6
   CMF C4 H2 O3

As stated above, comb polymers are *classified* as graft polymers, but they are not always so indexed. Example 6.4.1.2.3 is a comb polymer containing the macromonomer α-(2-methyl-1-oxo-2-propenyl)-ω-hydroxypoly(oxy-1,2-ethanediyl), $CH_2=C(Me)-CO-[-O-CH_2-CH_2-]_n-OH$. This polymer *is* classified as a graft polymer.

Example 6.4.1.2.3. Comb polymer indexed by CAS as a graft polymer

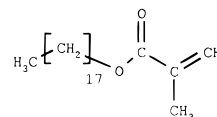REGISTRY COPYRIGHT 1995 ACS
RN 106826-93-1 REGISTRY
CN 2-Propenoic acid, 2-methyl-, methyl ester, polymer with α-(2-methyl-1-oxo-2-propenyl)-ω-hydroxypoly(oxy-1,2-ethanediyl), octadecyl 2-methyl-2-propenoate and 2-propenoic acid, graft (9CI) (CA INDEX NAME)
:
MF (C22 H42 O2 . C5 H8 O2 . C3 H4 O2 . (C2 H4 O)n C4 H6 O2)x
CI PMS
PCT Polyacrylic, Polyether
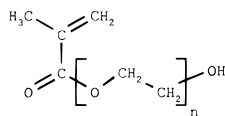SR CA
LC STN Files: CA, CAPLUS
DES 8:PM,GRAFT
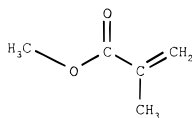
   CM 1

   CRN 32360-05-7
   CMF C22 H42 O2
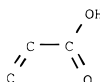

   CM 2

   CRN 25736-86-1
   CMF (C2 H4 O)n C4 H6 O2

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CCI PMS

CM 3

CRN 80-62-6
CMF C5 H8 O2

CM 4

CRN 79-10-7
CMF C3 H4 O2

Use of "comb", "comblike", comb-branched", etc. is stated[1] to be based on the author providing such information for a polymer; these terms will appear in the CA File at the polymer registry number when they appear in a given document. Although it contains the macromonomer F−[−CF$_2$−]$_n$−O−CO−C(Me)=CH$_2$, α-fluoro-ω-[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene), the comb polymer of example 6.4.1.2.4 is *not* indexed as a graft polymer, perhaps through oversight or failure to recognize it as one. Therefore, the point is made that GRAFT as a textual search term in File Registry is currently unreliable because it is not applied consistently.

Example 6.4.1.2.4. Post-12CI comb polymer *not* indexed by CAS as a graft polymer

REGISTRY COPYRIGHT 1995 ACS
RN 163440-88-8 REGISTRY
CN 2-Propenoic acid, 2-ethylhexyl ester, polymer with 1,1-dichloroethene and α-fluoro-ω-[2-[(2-methyl-1-oxo-2-propenyl)oxy]ethyl]poly(difluoromethylene) (9CI) (CA INDEX NAME)
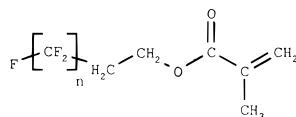:
MF (C11 H20 O2 . C2 H2 Cl2 . (C F2)n C6 H9 F O2)x
CI PMS
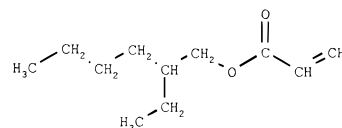PCT Chloropolymer, Polyacrylic, Polyvinyl
SR CAS Registry Services

CM 1

CRN 65530-66-7
CMF (C F2)n C6 H9 F O2
CCI PMS

CM 2

CRN 103-11-7
CMF C11 H20 O2

CM 3

CRN 75-35-4
CMF C2 H2 Cl2

Notes on example 6.4.1.2.4: (1) Tetrafluoroethylene polymers with end groups are represented by the structure-based unit (CF$_2$)$_n$ + end groups, *not* by the source-based unit (C$_2$F$_4$)$_x$; see component 1. (2) This is a Registry Number not generated from CAS indexing, and there are no references in the CA File.[1] Nevertheless, it appears to be a comb polymer and should probably be classified as a graft polymer.

Consistent application by CAS of the modifier ", graft" and the textual descriptor 8:PM,GRAFT to all pertinent polymers in File Registry would be welcome.

6.4.2. IUPAC Nomenclature and Structure Representation. 6.4.2.1. Structure-Based Method. Irregular polymers in which polymer chains are attached to the main chain, as in graft polymers, are named as follows. The attached polymer chains are considered to be substituents to the main chain and named in the same way as regular polymers,[3] or irregular polymers[4a,4b] but without the suffix -yl. The atom in the attached chains nearest to the point of attachment to the main chain is given the locant 1.

A graft polymer with poly(A) blocks grafted to the main chain of a regular polymer consisting of constitutional units Z is named

poly[Z/poly(A)Z]

where poly(A) is the substituent on constitutional unit Z.

A graft polymer having several kinds of of grafts attached to the main chain of a regular polymer consisting of constitutional units Z is named

poly[Z/poly(A)Z/poly(B)Z/poly(C)Z...]

where poly(A), poly(B), poly(C), ... are substituents on the constitutional unit Z.[4c]

Example 6.4.2.1.1. Poly(styrene)(ht) chains are grafted by their tails to poly(ethylene)

Structure

The constitutional units are —CH$_2$— and
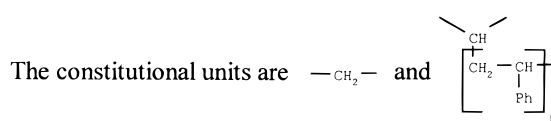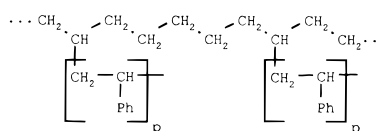
Polymer name: poly[methylene/poly(2-phenylethylene)-methylene]

Other examples of graft polymers of this type are given.[4c]

Irregular polymers in which polymer chains are attached to the main chain through a constitutional unit (linking unit)

different from the constitutional unit of the side chain are named as follows. The polymer side chains are considered to be substituents to the linking unit and named as described in the first paragraph in this section. The side chain together with the linking unit, taken as a whole, is considered to be a substituent to the main chain. In forming the name, the atom in the linking unit nearest to the point of attachment to the main chain is given the locant 1.
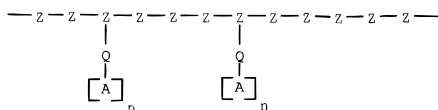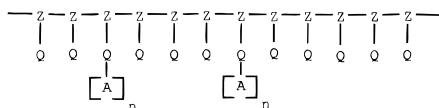
A graft polymer having the structure

i.e., with poly(A) blocks attached through linking unit Q to a regular polymer consisting of constitutional units −Z−, is named
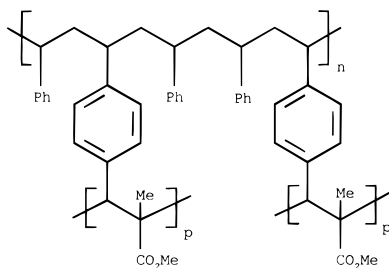
poly{Z/[poly(A)Q]Z}.

A graft polymer having the structure

i.e., with poly(A) blocks attached to substituent Q in a regular polymer consisting of constitutional units −(Q)Z−, is named

poly{(Q)Z/[poly(A)Q]Z}.[4d]

Example 6.4.2.1.2. Poly(methyl methacrylate)(ht) chains are grafted by their tails to some phenyl rings (in the para position) of poly(styrene)

Structure

The linking unit is *p*-phenylene and the graft unit is 2-(methoxycarbonyl)-2-methylethylene.

Polymer name: poly(1-phenylethylene/1-{4-poly[2-(methoxycarbonyl)-2-methylethylene]phenyl}ethylene)

Other examples of graft polymers of this type are given.[4d] IUPAC has also published graphic representations of graft polymers[5a] and an example of a graft polymer with end groups.[4e]

A recent IUPAC paper[6] describes a comb polymer as a macromolecule comprising a main chain with trifunctional points from which linear side chains emanate. If the subchains between the branch points of the main chain and the terminal subchains of the main chain are identical with respect to constitution and degree of polymerization, and the side chains are identical with respect to constitution and degree of polymerization, the macromolecule is termed a regular comb macromolecule. If at least some of the branch

Table 1. IUPAC Source-Based Copolymer Classification

no	type	connective	example
(1)	unspecified	*-co-*	poly(A-*co*-B)
(2)	statistical	*-stat-*	poly(A-*stat*-B)
(3)	random	*-ran-*	poly(A-*ran*-B)
(4)	alternating	*-alt-*	poly(A-*alt*-B)
(5)	periodic	*-per-*	poly(A-*per*-B-*per*-C)
(6)	block	*-block-*	polyA-*block*-polyB
(7)	graft	*-graft-*	polyA-*graft*-polyB

points are of functionalities greater than three, the macromolecule may be termed a brush macromolecule.

Nonlinear copolymer examples given are

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

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

•polystyrene-*comb*-polyacrylonitrile

(Equivalent to polystyrene-*graft*-polyacrylonitrile; *-graft-* is recommended for these cases. However, "comb" cannot be replaced by "graft" if the former is a prefix.

•polystyrene-*comb*-(polyacrylonitrile; poly(methyl methacrylate))
(A comb macromolecule with polyacrylonitrile and poly(methyl methacrylate) side chains.)

6.4.2.2. Source-Based Method. A comb polymer is defined as a main chain, with trifunctional branch points from which linear side chains emanate. If the subchains between the branch points of the main chain and the terminal subchains of the main chain are identical with respect to constitution and degree of polymerization, the macromolecule is termed a regular comb macromolecule. If at least some of the branch points are of functionalities greater than three, the macromolecule may be termed a brush macromolecule.[6]

Example 6.4.2.2.1. A polymer in which both the main chain and side chains are statistical copolymer chains of styrene and acrylonitrile

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

A graft polymer is defined as a polymer comprising molecules with one or more species of block connected to the main chain as side chains; the side chains have constitutional or configurational features that differ from those in the main chain. In a graft polymer the distinguishing feature of the side chains is constitutional, i.e., the side chains comprise units derived from at least one species of monomer different from those which supply the units of the main chain.[7]

As shown in Table 1, for graft polymers the connective is *-graft-*. The simplest graft polymer:
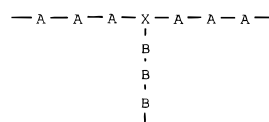
is called polyA-*graft*-polyB where the monomer named first (A in this case) is that which supplied the backbone (main chain) units, while that named second (B) is in the side chain(s).

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Example 6.4.2.2.2. Polystyrene grafted to polybutadiene

polybutadiene-*graft*-polystyrene

Example 6.4.2.2.3. Polyacrylonitrile grafted to a polybutadiene−polystyrene block copolymer at unspecified sites

(polybutadiene-*block*-polystyrene)-*graft*-polyacrylonitrile

If more than one type of graft chain is attached to the backbone, semicolons are used to separate the names of the grafts or their symbolic representations.

Example 6.4.2.2.4. Polystyrene and poly(methyl methacrylate) chains are grafted to a polybutadiene backbone

polybutadiene-*graft*-[polystyrene;poly(methyl methacrylate)]

Graft polymers with known numbers of graft chains are named using numeric prefixes (mono, bis, tris, etc.).

Example 6.4.2.2.5. Three polystyrene grafts per polybutadiene molecule
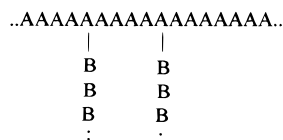
polybutadiene-tris(-*graft*-polystyrene)

If the precise site of grafting is known, it can be specified.

Example 6.4.2.2.6. Decabutadiene-*block*-(methylsilanetriyl-*graft*-polystyrene)-*block*-pentadecabutadiene
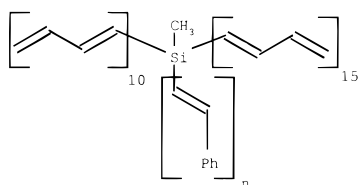

The system of naming graft copolymers is also applicable, in principle, to star copolymers; these are discussed under star polymers in section 6.6.2.

6.4.3. MDL Graphic Representation. 6.4.3.1. Structure-Based Method. As of November 1996 MDL has published no information on the structure-based representation of comb polymers. For structural representation of graft polymers, the starting Sgroup is paired with its grafted, SRU (n) form as an unspecified copolymer (co).[8]

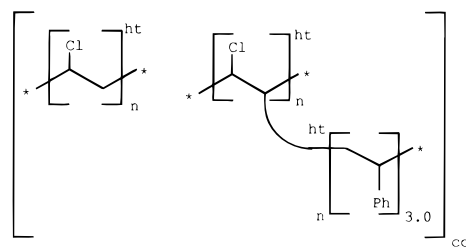For a single graft, the structural representation of

..AAAAAAAAAAAAAAAAA..

is
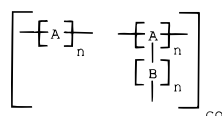
Example 6.4.3.1.1. Poly(1-chloroethylene)(ht)-tris(graft-polystyrene)

Note on example 6.4.3.1.1: Without the accompanying graphic representation, the "tris(graft-polystyrene)" segment of the MDL name above is ambiguous; it could mean "three separate grafts of a polystyrene chain (of unspecified length) onto a poly(1-chloroethylene) backbone (main chain)" or "an unstated number of styrene trimers grafted onto a poly(1-chloroethylene) backbone".

Mixed grafts are represented graphically by an extension of the previous example. Thus, poly(1-chloroethylene)-graft-[polystyrene;poly-(methyl methacrylate)] (MDL name) has the graphic representation:
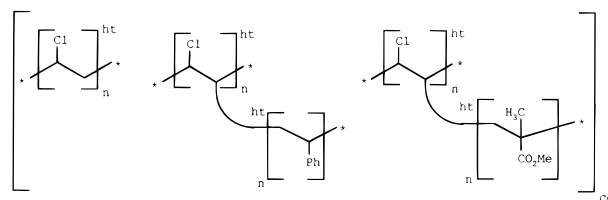
6.4.3.2. Source-Based Method. As of November 1996 MDL has published no information on the source-based representation of comb polymers.

For a process representation of graft polymers, the starting Sgroup is paired with its grafted subscripted (grf) form as an unspecified copolymer (co).

Thus, in the polymer ..AAAAAAAAA..

side chains, represented as polyB, are grafted onto a backbone, represented as polyA
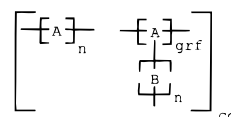
Example 6.4.3.2.1. Polystyrene is grafted onto polybutadiene (the thick bond is used to indicate mixed cis/trans)
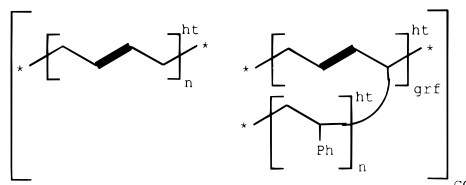
6.4.4. SCION Nomenclature and Structure Representation. In SCION, a comb polymer is any branched polymer with precisely tailored architecture that comprises a backbone to which are attached two or more linear, single-strand

polymeric side chains. The side chains are attached by one end only; if macromonomers with two reactive ends are incorporated into a polymer, it is not considered to be a comb polymer.

Comb polymers are prepared by any of the following methods: (a) copolymerization of a macromonomer (having one or more polymerizable end groups at the same end of the macromonomer) with other monomers; (b) growing side chains onto precise locations on a previously prepared polymer (which becomes the backbone in the final polymer); (c) grafting previously prepared active-end-group polymer chains or macromonomers (which become side chains) at precise locations onto a previously prepared polymer (which becomes the backbone in the final polymer)

In SCION, comb polymers prepared by method c are classified as aftertreated polymers because one polymer is aftertreated with another. This type of polymer is discussed in section 6.1.4. In contrast to SCION rules, polymers prepared by methods a, b, and c are usually called "graft" by DuPont practicing chemists.

In SCION, a graft polymer is defined as branched polymer prepared by the grafting of one or more type of monomer onto a previously prepared polymer (which becomes the backbone in the final polymer); there is usually no control of where grafting occurs. The monomers comprising the side chains may be the same as, or different from, the main-chain monomers. This definition is markedly different from the IUPAC definition given in section 6.4.2.

The general structure of a comb polymer in SCION is

$$A - X - B$$
$$|$$
$$C$$

where A−X−B is the backbone, A, B, and C are polymer chains, and X is a junction unit with a connectivity of three. C must not be connected to another polymer chain. If there is a single occurrence of X, the polymer is classified as a star polymer; if X occurs more than once, the polymer is classified as a comb polymer.

6.4.4.1. Structure-Based Method. Polymers formed by further polymerization of a macromonomer with a polymerizable end group are recognized intellectually as comb polymers. Comb polymers formed by homopolymerization of a macromonomer are named in the style POLY-(POLY-SRU, END GROUP X), where X is a "triradical" that serves as the trifunctional branch point at which the side chain is attached.

Example 6.4.4.1.1. "Poly-oxyethylene, end group 2-(dichloromethylsilyl)ethoxy, end group methoxy" is polymerized under hydrolytic conditions to give a comb polymer

Intellectual structure:

Stored structure:
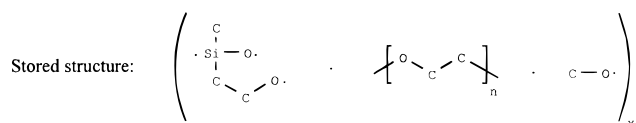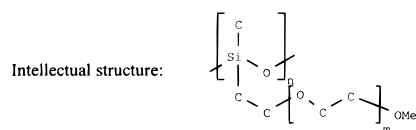
Polymer name: POLY-(POLY-OXYETHYLENE, END GROUP METHOXY, END GROUP (METHYLSILYLI-

DYNE)(ETHYLENEOXY)OXY), COMB (see points 6.4.4.1.1 and 6.4.4.1.2)

Point 6.4.4.1.1: Because of CAS Registry System limitations, use of square brackets in substance names in SCION is not possible; multiple parentheses are therefore used.

Point 6.4.4.1.2: The word COMB is added to names of all comb polymers in SCION so that, when searching, polymers that are graft, comb, or both graft and comb can easily be separated from each other by use of appropriate combinations of the controlled-term textual descriptor POLY-COMB-OR-GRAFT and the free-text words COMB and GRAFT.

The concept of the (METHYLSILYLIDYNE)(ETHYL-ENEOXY)OXY "triradical"
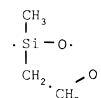
is an imperfect solution to the problem of how to represent an SRU branching from an SRU, but it is considered to be preferable to a representation such as
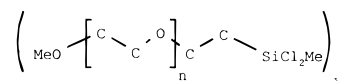
which does not indicate the structure of the final comb polymer. A logical nomenclature system is presented elsewhere[9] for multiradical fragments such as (METHYL-SILYLIDYNE)(ETHYLENEOXY)OXY.

Such comb polymers carry the controlled-term textual descriptor POLY-COMB-OR-GRAFT. Comb polymers are discussed in more detail elsewhere.[10]

Graft polymers formed by the reaction of an existing polymer with monomers such that side chains grow onto an existing backbone (main chain) at unknown reaction sites are named in the style POLY-BACKBONE_SRU, GRAFT SIDECHAIN_SRU; the textual descriptor POLY-COMB-OR-GRAFT is added.

Example 6.4.4.1.2. Acetoxy-ended poly-oxytetramethylene is reacted with formaldehyde

Structure:
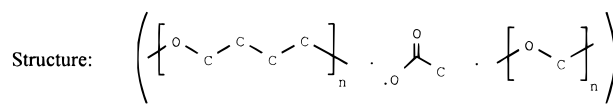
Polymer name: POLY-(OXYTETRAMETHYLENE, END GROUP ACETOXY), GRAFT OXYMETHYLENE
Textual descriptor: POLY-COMB-OR-GRAFT

6.4.4.2. Source-Based Method. The following are considered to be source-based comb polymers:

•a polymer prepared from one type of macromonomer that is capable of reacting at one end only

Example: "homopolymer" from $CH_2=CH-CO-O-CH_2-CH_2-O-[-CO-p-C_6H_4-O-]_n-Me$

•a copolymer prepared from two or more types of macromonomers, each of which is capable of reacting at one end only

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Example: copolymer of $CH_2\!\!=\!\!CH\!-\!CO\!-\!O\!-\!CH_2\!-\!CH_2\!-$ $O\!-\![-CO\!-p\!-C_6H_4\!-O\!-]_n\!-Me$ and $CH_2\!\!=\!\!C(Me)\!-\!CO\!-$ $O\!-\!CH_2\!-\!CH_2\!-\!O\!-\![-CO\!-m\!-C_6H_4\!-\!O\!-]_n\!-Et$

•a copolymer prepared from several species of comonomers, one or more of which may be macromonomers; each macromonomer type is capable of reacting at one end only

Example: copolymer of $CH_2\!\!=\!\!CH\!-\!CO\!-\!O\!-\!CH_2\!-\!CH_2\!-$ $O\!-\![CO\!-p\!-C_6H_4\!-O]_n\!-Me$ and styrene

Example 6.4.4.2.1. Comb polymer
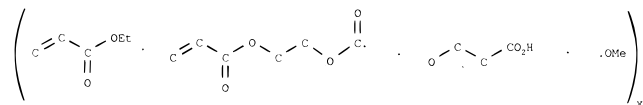Intellectual structure
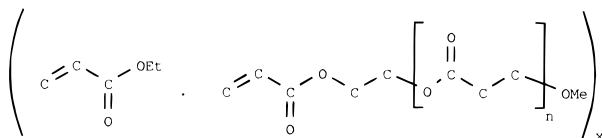
Whether this polymer is classified as an aftertreated polymer, a comb polymer, or a graft polymer depends on how it is prepared. If it is prepared by copolymerizing ethyl acrylate (EA) and the macromonomer shown, it is considered to be a *comb* polymer. If it is prepared by (1) copolymerizing EA and 2-hydroxyethyl acrylate (HEA), then (2) grafting hydracrylic acid to create polyester side chains, and (3) endcapping, it is considered to be an *aftertreated*, *graft* and *comb* polymer. If it is made by reacting poly(EA/HEA) with $Cl\!-\![-CO\!-\!CH_2\!-\!CH_2\!-\!O\!-]_n\!-OMe$, it is also considered to be an *aftertreated*, *graft*, and *comb* polymer.

It is for this reason that the textual descriptor chosen for comb and graft polymers is POLY-COMB-OR-GRAFT. This "combination" controlled-term textual descriptor was chosen as a compromise to span differences in philosophy between DuPont practicing polymer chemists and SCION polymer information management personnel.

There are differences in the stored structures and names of the three polymers—see [A], [B], and [C] below:

[A] Polymer structure, name, and textual descriptors for copolymerized EA/macromonomer:

Stored structure

Polymer name: POLY-ACRYLIC ACID, ETHYL ESTER/ (POLYESTER-HYDRACRYLIC ACID, END GROUP (2-(ACRYLOYLOXY)ETHOXY)CARBONYL, END GROUP METHOXY), COMB
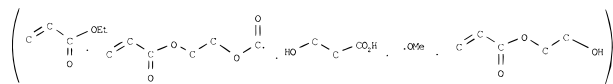Textual descriptors: END GROUP POLYMERIZABLE CC; POLY-COMB-OR-GRAFT; POLYESTER

Note: Until recently the author did not know that the CAS Registry System (CASRS) can store a source-based polymer within a source-based polymer; SCION macromonomers were therefore represented in a *single-level* expression by their component pieces—in this specific example, hydracrylic acid, a methoxy* fragment, and a (2-(acryloyloxy)ethoxy)-carbonyl* fragment. [*The reason for the additional oxygen atom on the methoxy fragment and the additional carbonyl group on the (2-(acryloyloxy)ethoxy)carbonyl fragment is explained elsewhere.[10]] All SCION comb polymer records

will be updated to take advantage of this little-known *multilevel* capability of the CASRS.[11]

[B] Polymer structure, name, and textual descriptors for EA/HEA copolymer grafted with hydracrylic acid and endcapped:
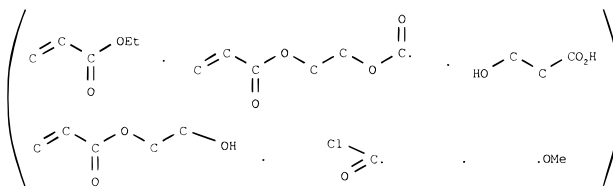
Stored structure

Polymer name: POLY-ACRYLIC ACID, ETHYL ESTER/ ACRYLIC ACID, 2-HYDROXYETHYL ESTER, AFTER-TREATED TO (POLYESTER-HYDRACRYLIC ACID, END GROUP (2-(ACRYLOYLOXY)ETHOXY)CARBO-NYL, END GROUP METHOXY), COMB
Textual descriptors: END GROUP POLYMERIZABLE CC; POLY-AFTERTREATED; POLY-COMB-OR-GRAFT; POLYESTER

[C] Polymer structure, name, and textual descriptors for EA/HEA copolymer reacted with $Cl\!-\![-CO\!-\!CH_2\!-\!CH_2\!-$ $O\!-\!]_n\!-OMe$

Stored structure

Polymer name: POLY-ACRYLIC ACID, ETHYL ESTER/ ACRYLIC ACID, 2-HYDROXYETHYL ESTER, AFTER-TREATED WITH (POLYESTER-HYDRACRYLIC ACID, END GROUP CHLOROCARBONYL, END GROUP METHOXY) TO (POLYESTER-HYDRACRYLIC ACID, END GROUP (2-(ACRYLOYLOXY)ETHOXY)CARBO-NYL, END GROUP METHOXY), COMB
Textual descriptors: END GROUP POLYMERIZABLE CC; POLY-AFTERTREATED; POLYAFT-WT; POLY-COMB-OR-GRAFT; POLYESTER

Although all three polymers have ostensibly the same intellectual structure, the differences in names and stored structures reflect the differences in synthetic methods.

As mentioned in the introduction to section 6.4.4, the SCION definition of a graft polymer differs considerably from the IUPAC definition. The SCION nomenclature style is also different; "poly" is stated once only as the prefix POLY-.

Thus, in SCION, ethylene grafted to polyethylene is named:

POLY-ETHYLENE, GRAFT ETHYLENE

and classified as a graft polymer, whereas it fails to meet the IUPAC definition of a graft polymer.

In contrast to CAS policy (see section 6.4.1.2), where differentiation between the polymeric substrate and the applied monomer is not made, POLY-1-HEPTENE, GRAFT 1-HEXENE and POLY-1 HEPTENE, GRAFT 1-HEXENE are considered to be separate polymers in SCION.

Comb and graft polymers are discussed elsewhere in more detail.[10]

6.5. Cross-Linked Polymers. As the name indicates, two or more separate polymeric chains are connected by a cross-link; it is implied that the cross-link is generally (a) relatively short (and not itself polymeric) and (b) at irregular intervals along the chains, but there seem to be no firm rules on this point. Ladder polymers comprising two linear strands cross-linked at regular intervals are discussed in section 9 (in part 4 of 4).

6.5.1. CAS Nomenclature and Structure Representation. CAS does not discuss in the Index Guide how cross-linked polymers are indexed.[2] The File Registry search:

→ S (PMS/CI AND CROSSLINK?)
NOT CROSSLINKING AGENT

(wherein PMS means polymers, /CI means class identifier, and the ? truncation means that any number of extra letters may follow the term entered) retrieves both structure-based and source-based cross-linked polymers. A text modification such as "crosslinked", "radiation-crosslinked", or "sulfur-crosslinked" is added (see note under example 6.5.1.1.1 on spelling of "crosslinked" without a hyphen). One example of each is given below in the appropriate section.

6.5.1.1. Structure-Based Method. Example 6.5.1.1.1. Radiation-cross-linked structure-based polymer

REGISTRY COPYRIGHT 1995 ACS
RN 68584-45-2 REGISTRY *
Use of this CAS Registry Number alone as a search term in other STN files may result in incomplete search results. For additional information, enter HELP RN at an online arrow prompt (→).
CN Poly(oxy-1,2-ethanediyl), α-hydro-ω-hydroxy-, radiation-crosslinked (CA INDEX NAME)
MF Unspecified
CI PMS, MAN, GRS
PCT Manual registration
:

Notes on example 6.5.1.1.1: (1) In CAS online records, words such as "Radiation-crosslinked" and "Sulfur-crosslinked" are spelled *without* a hyphen in "crosslinked"; editors of this journal prefer the spelling "cross-linked". (2) Records with registry numbers marked with an asterisk such as those shown in these two examples do *not* represent CAS indexing and naming policies. These numbers and names are created by CAS for regulatory agencies to meet their need in identifying articles of commerce.[12] Such registry numbers usually have few or no postings in bibliographic files such as the CA File. These remarks apply also to example 6.5.1.2.1.

6.5.1.2. Source-Based Method. Example 6.5.1.2.1. Sulfur-cross-linked source-based polymer

REGISTRY COPYRIGHT 1995 ACS
RN 141686-52-4 REGISTRY *
Use of this CAS Registry Number alone as a search term in other STN files may result in incomplete search results. For additional information, enter HELP RN at an online arrow prompt (→).

CN 1,3-Butadiene, 2-methyl-, polymer with 2-methyl-1-propene, chlorinated, sulfur-crosslinked (CA INDEX NAME)
MF Unspecified
CI PMS, MAN, GRS
PCT Manual registration
:

Notes on example 6.5.1.2.1: See notes beneath example 6.5.1.1.1.

Since 1987, cross-linking agents are consistently included in the registration for cross-linked polymers. These agents, however, are not tagged as such except where they appear as a trade name and need to be distinguished from other material with the same trade name, such as in example 6.5.1.2.2.[1]

Example 6.5.1.2.2. Citation of cross-linking agent in polymer

RN 160917-22-6 REGISTRY
CN Phenol, 4,4′-(1-methylethylidene)bis-, polymer with (chloromethyl)oxirane and T 31 (crosslinking agent) (9CI) (CA INDEX NAME)
:
MF (C15 H16 O2 . C3 H5 Cl O . Unspecified)x
CI PMS
PCT Epoxy resin, Manual component, Polyother
SR CA
LC STN Files: CA, CAPLUS
:

A more typical case of a cross-linked polymer is shown as example 6.5.1.2.3.[1]

Example 6.5.1.2.3. Typical cross-linked polymer; cross-linking agent not identified by name

RN 143410-57-5 REGISTRY
CN Phenol, 4,4′-(1-methylethylidene)bis-, polymer with benzenamine and (chloromethyl)oxirane (9CI) (CA INDEX NAME)
:
MF (C15 H16 O2 . C6 H7 N . C3 H5 Cl O)x
CI PMS
PCT Epoxy resin, Polyother
SR CA
LC STN Files: CA, CAPLUS
:

This policy of including the cross-linking agent in the polymer is described in Chapter VII entitled "Summary of 12CI Changes Affecting Polymer Registration" in the Polymer Searching Handbook.[13]

6.5.2. IUPAC Nomenclature and Structure Representation. 6.5.2.1. Structure-Based Method. IUPAC has published no specific recommendations on nomenclature or structural representations for cross-linked structure-based polymers.

6.5.2.2. Source-Based Method. IUPAC defines a cross-link as a small region in a macromolecule from which at least four chains emanate, which is formed by reactions involving pairs of sites or groups on existing macromolecules or by interactions between existing macromolecules.[6] The small region can be an atom, a group of atoms, or a number of branch points connected by bonds, groups of atoms, or oligomeric chains. In the vast majority of cases a cross-

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link is a covalent structure but the term is also used to describe sites of weaker chemical interactions, portions of crystallites, and even physical entanglements.

Cross-links, the branch units of star macromolecules and other junction units, are optionally specified by their source-based names after the name of the macromolecule with the Greek connective ν (.nu.), separated by hyphens. When the content of the cross-linking monomer is high, the macro-molecule is treated as a copolymer molecule.

Example 6.5.2.2.1. Polybutadiene vulcanized with sulfur

net-polybutadiene-ν-sulfur

Example 6.5.2.2.2. Polystyrene cross-linked with a small quantity of divinylbenzene

net-polystyrene-ν-divinylbenzene

Example 6.5.2.2.3. Polystyrene cross-linked with a small quantity of divinylbenzene insufficient to form a network

branch-polystyrene-ν-divinylbenzene

Taken together, examples 6.5.2.2.2 and 6.5.2.2.3 contravene the concept of consistency in polymer information management; since neither name states quantitatively the amount of divinylbenzene present, and no information is given on the absolute content of divinylbenzene necessary to change from the "branch-" category to the "net-" category, it is clear that a copolymer of styrene and divinylbenzene could be classified as "net-" by one person and "branch-" by another. The author opines that it is hazardous to assign two different names of this type to polymers with different concentrations of the same comonomers, because retrieval problems may result. Therefore, the soundness of the nomenclature is questionable.

Example 6.5.2.2.4. Poly(ethyl acrylate) cross-linked with ethylene dimethacrylate

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

(*l-branch* means long-chain-branched)

By the definition given above, IUPAC appears to exclude cross-linking that occurs during polymerization. However, the examples given above imply that the cross-linking comonomer can be added during polymerization.

6.5.3. MDL Graphic Representation. 6.5.3.1. Structure-Based Method. Use of the MDL definition of a homopolymer circumvents the need to use the "xl" Sgroup subtype in graphic representation of cross-linked polymers.[8]
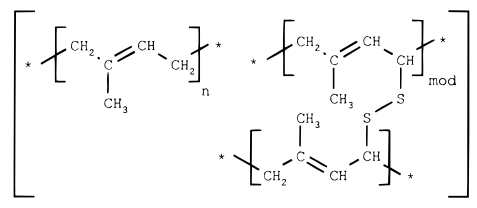
A polymer that is cross-linked after polymerization is represented as a modified homopolymer. Thus, the cross-linked polymer
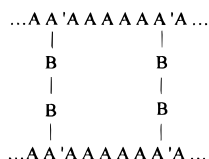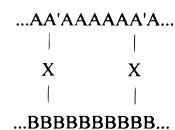

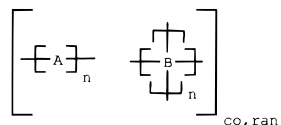is named polyA-graft-polyB and has the graphic representation:
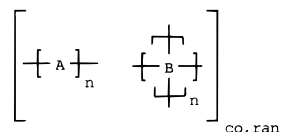
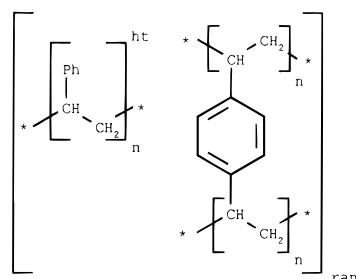**Example 6.5.3.1.1.** Vulcanized rubber (cross-linked after polymerization)

A polymer that is cross-linked during polymerization is represented as unspecified (co) or random (ran). Thus, the cross-linked polymer:

is named polyA-co-polyB and has the graphic representation

Example 6.5.3.1.2. Poly[styrene-ran-(divinylbenzene)] (cross-linked during polymerization)

6.5.3.2. Source-Based Method. MDL gives no specific examples of how to structure source-based cross-linked polymers.

6.5.4. SCION Nomenclature and Structure Representation. 6.5.4.1. Structure-Based Method. Postpolymerization cross-linking that gives a known structure is discussed under aftertreated polymers in section 6.1.4.1.

When post polymerization cross-linking results in an unknown structure, the registration number of the polymer that was cross-linked is indexed in the reactant role, and the controlled term CROSSLINKING is indexed in the same index link in the SCION bibliographic file that corresponds to CAS file CA (see point 6.5.4.1.1).

Point 6.5.4.1.1: SCION controlled terms correspond approximately to CAS Index Terms, although the latter are not selected from a thesaurus or authority list. SCION controlled terms closely related to a single concept are indexed in the same link; controlled terms associated with different concepts are indexed in different links. For two

controlled terms A and B, for example, the command "search A and B" retrieves documents with A and B in different links or the same link; in contrast, "search A (L) B" (where (L) is the "link" operator) retrieves only documents containing A and B in the same link.

For postpolymerization cross-linking there is no indication at the polymer level that cross-linking *per se* has occurred. Neither textual descriptors such as POLY-CROSSLINKED or CROSSLINKED POLYMER nor addition of a phrase such as "crosslinked" after the polymer name is used.

Cross-linking during polymerization sometimes gives hypercross-linked structures; these are discussed in section 6.6.4. Apart from this type, cross-linking *per se* during polymerization is not indicated at the polymer level. The combination of polymer name and structure is usually sufficient to convey the concept of whether cross-linking occurred during polymerization. For example, the hydrolytic copolymerization of a dichlorodimethylsilane/*p*-phenylenebis(dichloromethylsilane) mixture clearly leads to cross-linking. The final polymer is: POLY-(DIMETHYLSILYLENE)-OXY/P-PHENYLENEBIS((METHYLSILYLIDYNE)-OXY). In cases of doubt, the controlled term CROSSLINKING is added to the same indexing link in the bibliographic file as the polymer registration number.

6.5.4.2. Source-Based Method. Postpolymerization cross-linking that gives a known structure is discussed under aftertreated polymers in section 6.1.4.2.

When postpolymerization cross-linking results in an unknown structure, the polymer that was cross-linked is indexed as a reactant and the controlled term CROSSLINKING is indexed in the same index link as the polymer registration number—see point 6.5.4.1.1 in section 6.5.4.1.

For postpolymerization cross-linking there is no indication at the polymer level that cross-linking *per se* has occurred. Neither textual descriptors such as POLY-CROSSLINKED or CROSSLINKED POLYMER nor addition of a phrase such as "crosslinked" after the polymer name is used.

Cross-linking during polymerization that gives hypercross-linked structures is discussed in section 6.6.4. Apart from this type, cross-linking *per se* during polymerization is not indicated at the polymer level. The combination of polymer name and structure is usually sufficient to convey the concept of whether cross-linking occurred during polymerization. For example, depending upon reactant concentrations and reaction conditions, the terpolymerization of ethylene glycol, glycerol, and adipic acid may give branching, cross-linking, or residual unreacted hydroxy groups (on the glycerol). As may be seen in example 6.5.4.2.1, the polymer name and textual descriptor give no indication of whether branching or cross-linking has occurred.

Example 6.5.4.2.1. Terpolymer from adipic acid, ethylene glycol, and glycerol

Polymer name: POLYESTER-ADIPIC ACID/ETHYLENE GLYCOL/GLYCEROL
Textual descriptors: POLYESTER; POLY-HYPERCONNECTABLE

If the source document states that the polymer is cross-linked, the controlled term CROSSLINKING is added to the same indexing link as the polymer registration number.

6.6. Dendritic, Hyperbranched, Hypercross-Linked, Star, and Star-Block Polymers. These groups of polymers

are discussed together because there is overlapping technology that makes it difficult to discuss them separately. In the last decade there has been a sharp rise in the interest of these types of polymers; for example, at the 210th ACS meeting (August, 1995), out of a total of 302 presentations in the Division of Polymeric Materials: Science and Engineering (PMSE), 44 (32 papers and 12 posters; total, 15%) discussed dendritic and hyperbranched polymers.

According to Tomalia et al,[14a] dendrimers have three distinguishing architectural features: an initiator core, interior layers (generations) composed of repeating units radially attached to the initiator core, and an exterior or surface of terminal functionality attached to the outermost generation.

These dendrimers differ from classical monomers or oligomers by their extraordinary symmetry, high branching, and maximized (telechelic) terminal functionality. Dendrimer synthesis is accomplished by a variety of strategies involving time-sequenced propagation techniques. The resulting dendrimers grow in a geometrically progressive fashion. Chemical bridging of these dendrimers leads to "Starburst"* polymers.[14b]

*Note: "Starburst" is a registered trademark of the Dow Chemical Company.[15]

However, the term dendrimer is interpreted by other scientists as having a much broader meaning than the one described by Tomalia. For example, Cloutet et al.[16] describe the polymer shown as example 6.6.1 as a dendritic block polymer, although it might be more appropriate to call it a branched star polymer.

Example 6.6.1. Dendritic block polymer (Cloutet at al.)
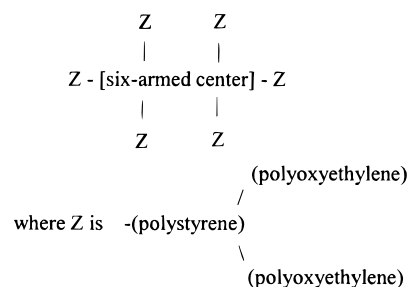
According to Turner,[17] hyperbranched polymers are highly branched, non-cross-linked polymers prepared by the step-growth polymerization of AxB (or ABx) polymers. Thus, A2B means that for every two type A reactive groups there is one type B reactive group, while AB2 means that for every one type A reactive group there are two type B reactive groups. AB2 and AB3 (or A2B and A3B) are the commonest; ABx (or AxB) types where $x > 3$ tend to be so sterically crowded that polymerization is difficult unless the reactive groups are well separated. Typical AB2 (or A2B) monomers are shown as examples 6.6.2 and 6.6.3.
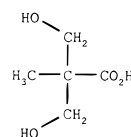
Example 6.6.2   Example 6.6.3
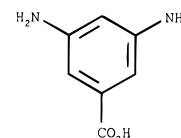
Voit[18] describes the essential differences between dendrimers and hyperbranched polymers rather differently:

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•Dendrimers are prepared by a stepwise approach; they are structurally perfect or nearly perfect (i.e., the branching ideality approaches 100%), their size is limited (i.e., they cannot grow forever), and their molecular weight is dependent upon the number of generations.

•Hyperbranched polymers may be prepared by a one-step synthesis under conventional polycondensation conditions; their molecular weight is dependent upon the condensation reaction, not upon the number of generations, and the branching ideality is typically between 50% and 75%.

It is not necessary for *every* monomer to have a connectivity of more than two; example 6.6.4 shows a hyperbranched polymer in which every other monomer has this feature. The structure-based representation of this polymer necessitates at least two SRUs, both with three crossing bonds.

Example 6.6.4. Polyester from glycerol and adipic acid

Source-based representation
(HO-CH$_2$-CH(OH)-CH$_2$-OH . HO$_2$C-(CH$_2$)$_4$-CO$_2$H)$_x$

Possible structure-based representation
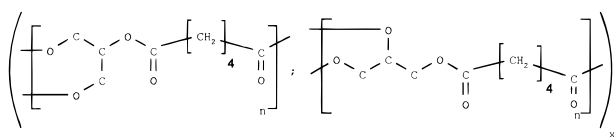
The terms "star polymer" and "star-shaped polymer" are used somewhat imprecisely. The same term is used to describe at least two physically different polymeric "clusters". A star polymer may be a polymer comprising a precise center of known structure from which a known number of arms radiate; the arms may contain one or more SRUs, and the SRUs may be random, statistical, or blocky; the latter are usually star-block polymers.

A star polymer may also comprise an unknown number of arms connected to the center of the cluster by addition to the reaction mass of a second, multifunctional monomer or SRU that ties all the linear growing polymer chains together into a cross-linked (microgel) core. These are sometimes called star-branch polymers.[19]

A third type of star polymer comprises a dendritic core from which emanate a known number of arms.[20]

In any of these types of star polymers, the arms may be all the same, or different arms may have different compositions; the latter are called hetero-star copolymers[21] or miktoarm star polymers.[22] IUPAC calls these variegated star polymers.[6]

6.6.1. CAS Nomenclature and Structure Representation. Sections 6.6.1.1 through 6.6.1.4 were provided by CAS editorial staff.[1]

6.6.1.1. General Indexing Guidelines. Dendrimers, like oligomers, are handled as regular organic compounds or as polymers, depending on the degree of polymerization. The number of non-hydrogen atoms is also a factor in handling dendrimers.

•Low-generation dendrimers having 10 or fewer repeating units and a non-hydrogen atom count less than 253 are structured and named as specific nonpolymeric compounds.

Example 6.6.1.1.1

RN 153358-94-2 REGISTRY

IN 1,3-Propanediamine, N,N″,N″″-(nitrilotri-2,1-ethanediyl)-tris[N-(3-aminopropyl)-

Example 6.6.1.1.2.

RN 153358-95-3 REGISTRY

IN 4,8,11,14,18-Pentaazaheneicosanedinitrile, 11-[2-[bis[3-[bis(2-cyanoethyl)amino]propyl]amino]ethyl]-8,14-bis[3-[bis-(2-cyanoethyl)amino]propyl]-4,18-bis(2-cyanoethyl)-

•Higher-generation dendrimers having more than 10 repeating units *or* a non-hydrogen atom count greater than 253 (thus forcing a manual registration at a lower degree of polymerization) are structured and named as polymers.

The information given below focuses on dendrimers handled as polymers.

6.6.1.2. Dendritic Polymers. Polymers having dendritic or starburst structure are indexed at the controlled term DENDRITIC POLYMERS, which was added as a new index heading starting with the 13th Collective Index Period in 1992. Additional index entries are made for the specific dendrimers as illustrated in the examples below. The approach (divergent or convergent) for preparing dendrimers is usually indicated in the text modification when so specified by the author of the source document. Currently CAS has no specific nomenclature for dendrimers; they are named according to regular polymer nomenclature rules. The polyfunctional core used in either the divergent or convergent approach is not included in the polymer registration.

Example 6.6.1.2.1. Divergent approach: a Starburst* polyamide-polyamine prepared by Michael addition reaction from an ammonia core, Me acrylate, and ethylenediamine. (*Starburst is a registered trademark of the Dow Chemical Company.[15])

26937-01-9 Ethylenediamine-Me acrylate copolymer
      (dendritic, from divergent approach, ...)

Dendritic polymers
      (polyamide-polyamines, from divergent approach, ...)

Polyamides
      (polyamine-, dendritic, from divergent approach, ...)

Example 6.6.1.2.2. Convergent approach: a polyether wedge having peripheral benzyl and cyano groups is prepared using 3,5-dihydroxybenzyl alcohol and is linked through tris-(4-hydroxy-phenyl)ethane as a polyfunctional core to give a dendrimer.

129371-31-9D, 3,5-Dihydroxybenzyl alcohol homopolymer,
      benzyl-terminated, cyano group-contg.
      (dendritic, from convergent approach ...)

Dendritic polymers
      (polyethers, from convergent approach ...)

Polyethers
      (dendritic, from convergent approach ...)

6.6.1.3. Dendritic Macromers and Graft Copolymers. Dendritic macromers are handled as other macromers and their copolymers are indexed as graft copolymers unless cross-linking is involved.

Example 6.6.1.3.1. A polyether dendrimer is prepared from 3,5-dihydroxybenzyl alcohol by a convergent-growth approach, modified to give a styryl functional group, and then copolymerized with styrene.

The copolymer is indexed at

141577-20-0D, 3,5-Dihydroxybenzyl alcohol-styrene graft copolymer, benzyl-terminated
(dendritic, from convergent-growth approach, ...)

Dendritic polymers
(polyether-polystyrene, graft, from convergent-growth approach, ...)

Polyethers
(polystyrene-, graft, from convergent-growth approach, ...)

6.6.1.4. Dendritic Block Copolymers. Dendritic block copolymers have been encountered that were prepared by reacting polyethylene glycol with a fourth-generation dendrimer.

The polymer is indexed at

143104-76-1D, Ethylene oxide-3,5-dihydroxybenzyl alcohol block copolymer,
benzyl-terminated
(triblock, dendritic, ...)

Dendritic polymers
(polyether-polyoxyalkylene, block, triblock, ...)

Polyethers
(polyoxyalkylene-, dendritic, block, triblock, ...)

6.6.2. IUPAC Nomenclature and Structure Representation. IUPAC has recently addressed star and star-block polymer representations.[5b,6] As of November 1996, no specific recommendations on nomenclature or structure representation for dendrimers or hyperbranched polymers have been published.

6.6.2.1. Structure-Based Method. Although it is described in the section on block polymers, IUPAC describes a star copolymer[5b] comprising a silicon atom surrounded by two poly(buta-1,3-diene) chains and two polystyrene chains—see example 6.6.2.1.1.

Example 6.6.2.1.1

Structure
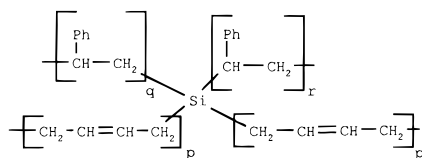
This polymer is given the structure-based name

bis[poly(but-2-ene-1,4-diyl)][poly(1-phenylethylene)][poly-(2-phenylethylene)]silane

Two source-based names are also given

polystyrene-*block*-{silanetetrayl-bis[-*graft*-poly(buta-1,3-diene)]}-*block*-polystyrene

poly(buta-1,3-diene)-*block*-[silanetetrayl-bis-(*graft*-polystyrene)]-*block*-poly(buta-1,3-diene)

The reference states that the buta-1,3-diene is incorporated by 1,4-addition, which cannot be reflected in the source-based name.

6.6.2.2. Source-Based Method. A recent IUPAC paper on source-based nomenclature[6] describes a star polymer as a macromolecule containing a single branch point from which linear chains (arms) emanate. In a regular star polymer all arms are identical with respect to constitution and degree of polymerization. A variegated star has different arms composed of different monomers.

Examples of nonlinear homopolymers are

•4-*star*-polystyrene

•*star*-polystyrene-*ν*-methyltrichlorosilane

(Polystyrene cross-linked with methyltrichlorosilane; the Greek letter *ν* (.nu.) is used to indicate that cross-linking is present.)

Examples of nonlinear copolymers are

•*star*-[polystyrene-*block*-poly(methyl methacrylate)]

(Each arm of the star molecule is a block polymer chain.)
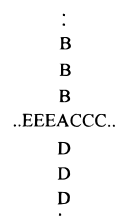
•*star*-(polyA-*block*-polyB-*block*-polyC)

(A star copolymer molecule, each arm of which consists of the same block-copolymer chain.)

•*star*-(polyA; polyB; polyC)

(A variegated star copolymer molecule consisting of arm(s) of polyA, arm(s) of polyB, and arm(s) of polyC.)

6.6.3. MDL Graphic Representation. 6.6.3.1. Structure-Based Method. MDL has not indicated how dendrimer or hyperbranched structures are to be represented.

The indexing of star polymers (which MDL calls star-block polymers) is described for the generic polymer[8]

```
              :
              B
              B
              B
         ..EEEACCC..
              D
              D
              D
              :
```

The illustration given is for polyE-block[A-graft(polyB-;polyD)]-block-polyC], which may depicted structurally as shown in example 6.6.3.1.1

Example 6.6.3.1.1. MDL structural representation of a star-block polymer
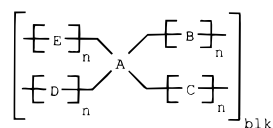
Example 6.6.3.1.2[8] shows a star-block polymer of 1,3-butadiene, isoprene, methyl methacrylate, and styrene with a silanetetrayl center (the thick bond is used to indicate mixed cis/trans).

Example 6.6.3.1.2
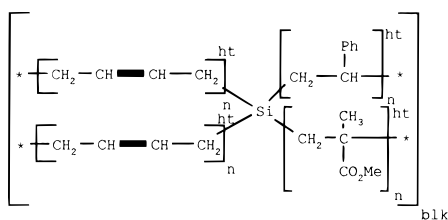
MDL names this polymer polystyrene-block-[silanetetrayl-graft-(poly butadiene;polyisoprene)]-block-poly(methyl methacrylate). Depending upon which blocks are perceived as the "main chain" and which the "graft", it is clear that this polymer could have at least 11 other names. Also, although the graphical representation is structure-based, the name given is source-based.

6.6.3.2. Source-Based Method. MDL has not indicated how dendrimers, hyperbranched polymers, star polymers, or star-block polymers are to be represented by source-based methods.

6.6.4. SCION Nomenclature and Structure Representation. Dendritic, hyperbranched, and star polymers are named and structured in SCION by extension of the procedures described in sections 4 and 5 but with the addition of the POLY-HYPERCONNECTABLE textual descriptor when appropriate (see point 6.6.4.1).

Point 6.6.4.1: The textual descriptor POLY-HYPERCONNECTABLE is used for all dendritic, hyperbranched, and star polymers except those with discrete, nonpolymeric cores. Because there is sometimes uncertainty about whether a polymer designed to be hyperbranched is also cross-linked, one single textual term is used for both types of polymer. From a polymer registration point of view, this "combined term" circumvents the need to know whether a hyperbranched polymer is also cross-linked. The term implies that hyperbranching and/or cross-linking *can* or *may* occur, rather than that it *has* occurred, because it refers to the SRU or monomer, although the descriptor is applied to the polymer containing that SRU or monomer.

When cited by source documents, discrete-core structures and peripheral end groups are stored as fragments of the complete polymer structure, and they are both identified in the polymer name as "end group ...", regardless of which is the core and which is the peripheral end group. Monomers or SRUs present in dendritic- or microgel-type cores are indexed as components of the complete polymer.

According to SCION rules, structures of dendritic, hyperbranched, and star polymers may be registered as source-based, structure-based, or a combination of these.

Examples are given in sections 6.6.4.1 through 6.6.4.3. Dendritic and star polymers are discussed in greater detail elsewhere.[23]

6.6.4.1. Structure-Based Method. Dendritic and hyperbranched polymers indexed as structure-based polymers contain, as components of the registered polymer structure, the SRU(s) that constitute the arms, plus the core and peripheral end groups (as fragments) when they are cited in the source document. No distinction is made between dendritic and hyperbranched polymers, either structurally or

in terms of the accompanying textual descriptors. However, dendrimers are more likely than hyperbranched polymers to have a core fragment indexed. Example 6.6.4.1.1 illustrates the method.

Example 6.6.4.1.1. "Poly-s-phenenyl" (poly-1,3,5-benzenetriyl)
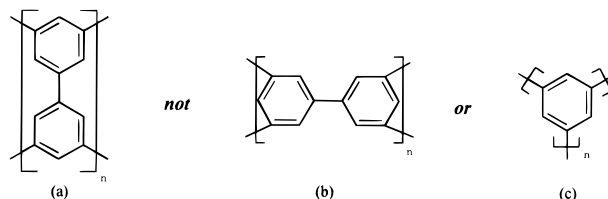
Polymer name: POLY-3,3′,5,5′-BIPHENYLTETRAYL
Textual descriptors: POLY-HOMO; POLY-HYPERCONNECTABLE

Notes on example 6.6.4.1.1: (1) Both dendritic[24] and hyperbranched[25] versions of this polymer have been reported. (2) SCION rules[26] state that the bridge must be *vertical*, as in structure a, not horizontal, as in structure b. (3) Because of the inability of the CAS Registry System to store SRUs with an odd number of crossing bonds, this polymer is registered in SCION as structure a; structure c is unregistrable.

Star polymers indexed as structure-based polymers contain, as components of the registered polymer structure, the SRU(s) that constitute the arms, plus the core and peripheral end groups (as fragments) when they are cited in the source document. The method is illustrated in example 6.6.4.1.2.

Example 6.6.4.1.2. Six-arm star polymer from 1,2,3,4,5,6-cyclohexanehexol and ethylene oxide
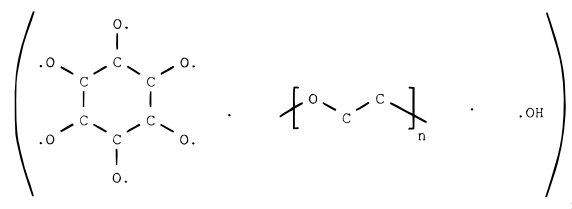
Polymer name: POLY-OXYETHYLENE, STAR, END GROUP 1,2,3,4,5,6-CYCLOHEXANEHEXOXY, END GROUP HYDROXY
Textual descriptors: END GROUP, MULTICHAIN; POLY-HOMO; POLY-STAR

Note on example 6.6.4.1.2: The reason why the core contains six oxygen atoms is explained in section 4.7.4.1 and in more detail elsewhere.[10]

6.6.4.2. Source-Based Method. Dendritic and hyperbranched polymers indexed as source-based polymers contain, as components of the registered polymer structure, the monomers that constitute the arms, plus the core and peripheral end groups when they are cited in the source document. The next two examples illustrate the method.

Example 6.6.4.2.1. Dendrimer from 2,2-bis(hydroxymethyl)propionic acid with a pentaerythritol core and peripheral

hydroxy groups
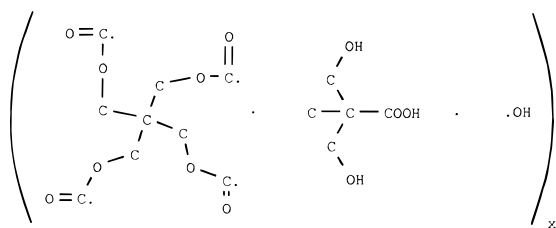
Polymer name: POLYESTER-PROPIONIC ACID, 2,2-BIS-(HYDROXYMETHYL)-, END GROUP HYDROXY, END GROUP NEOPENTANETETRAYLTETRAKIS(OXYCARBONYL)

Textual descriptors: POLY-HOMO; POLY-HYPERCONNECTABLE; END GROUP, MULTICHAIN

Note on example 6.6.4.2.1: The reason why the core fragment contains four carbonyl groups in addition to the (expected) four oxygen atoms is explained in section 4.7.4.1 and in more detail elsewhere.[10]

Example 6.6.4.2.2. Hyperbranched polyamide from 3,5-diaminobenzoic acid (no central core; no peripheral end groups except those naturally occurring, i.e., −COOH and −NH$_2$)
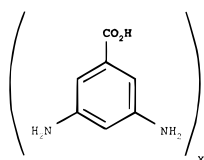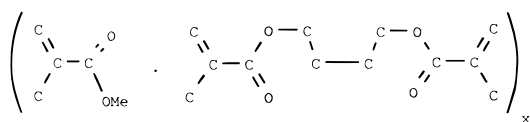
Polymer name: POLYAMIDE-BENZOIC ACID, 3,5-DIAMINO-

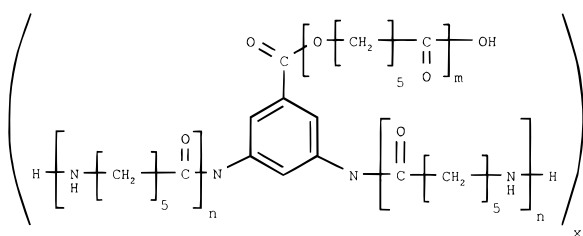Textual descriptors: POLYAMIDE; POLY-HOMO; POLY-HYPERCONNECTABLE

Star polymers indexed as source-based polymers contain, as components of the registered polymer structure, the monomers that constitute the arms. For star polymers with a microgel core, the monomers contained in the core are also registered when known; for star polymers with a discrete (nonpolymeric) core, the core (as a fragment) is also registered when known. Peripheral end groups are also registered when known. The method is illustrated in examples 6.6.4.2.3 and 6.6.4.2.4.

Example 6.6.4.2.3. Star polymer with methyl methacrylate arms and tetramethylene dimethacrylate microgel core
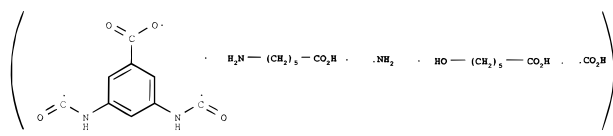
Example 6.6.4.2.4. Three-miktoarm star terpolymer

Intellectual structure

Stored structure

Polymer name: POLYAMIDE-ESTER-HEXANOIC ACID, 6-AMINO-/HEXANOIC ACID, 6-HYDROXY-, STAR, END GROUP AMINO, END GROUP CARBOXY, END GROUP OXYCARBONYL-1,3,5-BENZENETRIYL-3-(IMINOCARBONYL)-5-(IMINOCARBONYL)

Textual descriptors: END GROUP, MULTICHAIN; POLYAMIDE-ESTER; POLY-BLOCK; POLY-STAR; POLY-VARIEGATED

Notes on example 6.6.4.2.4: (1) There is no direct indication in either the polymer name or textual descriptors that one arm is a poly(caprolactone) arm and the other two are poly(caprolactam) arms. The POLY-BLOCK descriptor would also be used if one arm were poly(caprolactone) and the other two were poly(caprolactam)/poly(caprolactone) blocks. A nomenclature system for "triradicals" such as this core is described elsewhere.[9] (2) SCION uses CAS Eighth Collective Nomenclature rules (8CI) except for a few rare situations where 8CI fails to denote locants adequately, e.g., in *as*-phenenyl and *v*-phenenyl radicals. In these cases, points of entry into the ring cannot be described but have to be deduced from the cited locants of the groups beyond the phenenyl radical. Use of "benzenetriyl" here greatly clarifies the entry and exit locants, e.g., 1,2,4-; 2,1,4-; 4,1,2-, etc., because the first locant cited is always the ring entry point. Although this is probably unnecessary for *s*-phenenyl, for the sake of uniformity in nomenclature, SCION uses "benzenetriyl", vice "phenenyl" in all three cases.

**6.6.4.3. Mixed-Class (Source-Based/Structure-Based) Method.** As explained fully elsewhere,[10] multicategory polymers contain the word WITH in the polymer name between the categories, and ASM (see section 4.5.2) names precede SRU names. A multicategory star polymer is shown as example 6.6.4.3.1.

Example 6.6.4.3.1. Multi-category, three-miktoarm star terpolymer

Intellectual structure
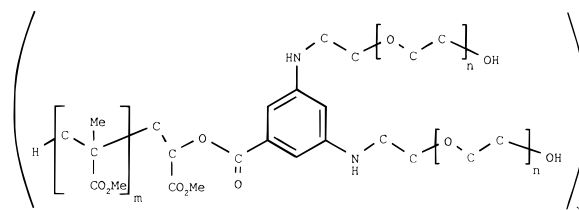
Stored structure
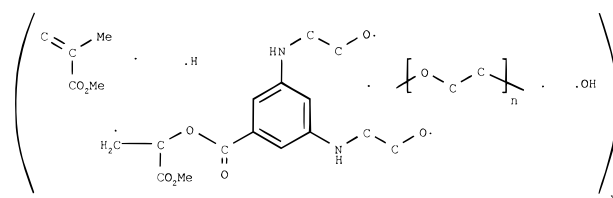
Polymer name: POLY-METHACRYLIC ACID, METHYL ESTER WITH POLY-OXYETHYLENE, STAR, END

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GROUP HYDRO, END GROUP HYDROXY, END GROUP OXY(CARBONYL-1,3,5-BENZENETRIYL-3-(IMINOETHYLENEOXY)-5-(IMINOETHYLENEOXY))(1-(METHOXYCARBONYL)ETHYLENE)

Textual descriptors: POLY-BLOCK; POLY-MULTICATEGORY; POLY-STAR; POLY-VARIEGATED

6.6.4.4. Nomenclature for Variegated Star Polymers. Although variegated star polymers are frequently synthesized by preparing one type of arm, creating a core, and then proceeding with synthesis of other types of arms,[21] SCION currently contains no provisions for naming them in a manner that indicates how, or by what sequence, they are made. Such a procedure is unacceptable in SCION because it would allow the possibility of a polymer (containing the same monomers) made by two different methods being given two different names. For example, suppose that monomer A is polymerized to give type-A arms, a "microgel-core-former" such as divinylbenzene is added, and subsequently type-B arms are grown by addition of a different monomer. Assuming that names for monomers A and B alphabetically precede divinylbenzene, the SCION name would be poly-A/B/benzene, divinyl-. Names such as poly-A/benzene, divinyl-/B for the case cited, and poly-B/benzene, divinyl-/A for the heteroarm star made by the "reverse procedure" are unacceptable.

SUMMARY AND CONCLUSIONS

Until all four parts are published, any attempt to write a comprehensive summary and conclusions would be premature; this section is therefore postponed until the end of part 4.

ACKNOWLEDGMENT

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