Polymer Nomenclature and Structure: A Comparison of Systems Used by CAS, IUPAC, MDL, and DuPont. 2. Aftertreated (Post-treated), Alternating/Periodic, and Block 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 (i.e. hyperbranched, hypercross-linked), and star polymers. The types covered in this paper (part 2 of 4) include aftertreated (post-treated), alternating and other periodic, and block polymers.

6. NOMENCLATURE AND GRAPHIC REPRESENTATION OF "NONREGULAR", SINGLE-STRAND ORGANIC POLYMERS

This section discusses structure-based and source-based representations of "nonregular" copolymers; the term "nonregular" is used by the author to indicate aftertreated/modified/postreacted, alternating and other periodic copolymers and block (ordered, segmented, and unordered), comb/graft, cross-linked, dendritic, hyperbranched, hypercross-linked, periodic, star, and star block polymers. Tacticity is discussed in section 7 (in part 4 of 4).

6.1. Aftertreated, Modified, or Postreacted Polymers. Different systems used different words to describe a chemical treatment of a polymer that modifies its structure. At the general level, CAS uses "post-treated", MDL uses "modified", and SCION uses "aftertreated"; IUPAC makes no recommendations for a preferred word or phrase. At the specific level, CAS and IUPAC sometimes use a word to describe the treatment, e.g., "chlorinated", "hydrolyzed", etc. MDL uses words such as "brominated" or "chlorinated" in their examples,[1] but these are not nomenclature recommendations.

6.1.1. CAS Nomenclature and Structure Representation. CAS describes post-treated polymers as those polymers that are modified, either partially or completely, after the basic polymer backbone or skeleton has been formed. These modifications may result from a reaction or a series of reactions of the main chain and/or pendent functional groups of the polymer.[4] Post-treatment is indicated by modification terms after the polymer name that describe the nature of the post-treatment.[3]

CAS divides post-treated polymers into three types: structurable and registrable; nameable but not structurable; and nonregistrable.[4]

Three types of general indexing situations may be encountered with post-treated polymers: type 1, post-treated polymers that can be structured and registered with a molecular formula; type 2, post-treated polymers that are not structurable but can be named systematically and are therefore registered with an "Unspecified" molecular formula; type 3, post-treated polymers that cannot be registered.

These three types are discussed below in more detail.

Type 1: Post-treated Polymers, Structured and Registered. These usually include salts of polymers, polymeric charge-transfer complexes, polymer−polymer addition compounds, and polymer addition compounds. These substances may be found by using dictionary terms such as names and formulas or by using structures. In all the examples shown, a colon is used to indicate removal from the complete record of material irrelevant to the discussion.

This type is registered almost as if it were not a post-treated polymer at all. The format for the name of this type of post-treated polymer *implies*, rather than states, that post-treatment has occurred; the message is subtle because, as shown in example 6.1.1.1, the word "homopolymer" occurs *after* the SRU(s) or monomer(s) and *before* the result of the post-treatment. Had sodium acrylate been polymerized, the name would be "2-Propenoic acid, sodium salt, homopolymer". There is no word in the name such as "post-treated", "neutralized", etc. to indicate that post-treatment has occurred. The structural part of the record also takes a form somewhat different from that of an unmodified polymer; component 2, the result of the post-treatment (sodium acrylate in this example), is indented with respect to component 1. This implies that sodium acrylate is a component of poly(acrylic acid), which−strictly speaking−it is not.

Example 6.1.1.1. Sodium salt of poly(acrylic acid) (points of interest indicated by "<=")

RN 9003-04-7 LREGISTRY
CN 2-Propenoic acid, homopolymer, sodium salt (9CI) (CA INDEX NAME)
:
MF (C3 H4 O2)x . x Na
CI COM
PCT Polyacrylic
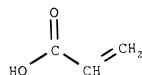:

CM 1
CRN 9003-01-4 <= RN for poly(acrylic acid)
CMF (C3 H4 O2)x
CCI PMS
  CM 2
  CRN 79-10-7 <= RN for acrylic acid
  CMF C3 H4 O2

Well-defined polymers formed by post-treatment may be indexed at their own headings, but this is rare. For example, poly(vinyl alcohol) prepared by complete hydrolysis of poly-(vinyl acetate) is indexed as poly(vinyl alcohol) even though vinyl alcohol is not the monomer from which it is prepared.

Type 2: Post-treated Polymers, Registered but Not Structured. Until 1995, this group comprised post-treated polymers containing ester groups that were named as functional derivatives of reactive chemical groups present in the monomers. All post-treated polymers containing other functional groups (such as indefinite amides, imides, hydrazides, hydrazones, etc.) were indexed as nonregistered post-treated polymers (see type 3 below). This policy was changed in 1995,[5] and CAS is currently in the process of converting type 2 records (post-treated polymers, structured but not registered) into type 1 records (post-treated polymers, structured and registered), but (as of November 1996) the task is incomplete. Compare example 6.1.1.2 (unconverted ester) with example 4.7.1.2.1 (converted ester).

Example 6.1.1.2. Methyl ester of ethylene-maleic anhydride copolymer

REGISTRY COPYRIGHT 1996 ACS
RN 61673-04-9 REGISTRY
CN 2,5-Furandione, polymer with ethene, methyl ester (9CI) (CA INDEX NAME)
:
MF Unspecified
CI PMS, COM, MAN
PCT Manual registration
:
STRUCTURE DIAGRAM IS NOT AVAILABLE
:

Type 3: Post-treated Polymers, neither Structured nor Registered. Post-treated polymers of this type are indexed at the parent substance with the appropriate text. Usually these are derivatives prepared by substitution reactions or by reaction of a functional group. This type also includes nonspecific derivatives; thus, an RN (with an appended "D") may be found with any number of textual terms describing the derivative.

Example 6.1.1.3. CA File entry for nonspecific alkyl esters of poly(acrylic acid)

9003-01-4D, alkyl esters

To search for this type of polymer, the RN for the parent polymer appended with a "D" is linked to textual information describing the modification in the CA File. There is no structure record in the Registry File for an RN such as 9003-53-6D; the "suffix D" concept exists only in bibliographic files such as the CA File.

This search method is also described elsewhere;[6] thus, to retrieve chlorinated derivatives of poly(styrene), the following is suggested as a search strategy:

9003-53-6D (S) ?CHLORIN?

Similarly, to retrieve sulfonated derivatives of poly(styrene), the search strategy suggested is

9003-53-6D (S) ?SULFON?

Examples 6.1.1.4 and 6.1.1.5 illustrate typical index term (IT) field entries retrieved from these searches.

Example 6.1.1.4. Chlorinated poly(styrene) (CA File entry)

9003-53-6D, Polystyrene, chlorinated derivs.

Example 6.1.1.5. Sulfonated poly(styrene) (CA File entry)

9003-53-6D, Polystyrene, sulfonated

Records with registry numbers marked with an asterisk such as that shown in example 6.1.1.6 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.[7] Such registry numbers usually have few or no postings in bibliographic files such as the CA File.

Example 6.1.1.6. Example of CAS RN with asterisk

REGISTRY COPYRIGHT 1995 ACS
RN 123805-10-7 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-tridecyl-ω-hydroxy-, branched, chlorinated (CA INDEX NAME)
MF Unspecified
CI PMS, MAN, GRS
PCT Manual registration
:

6.1.2. IUPAC Nomenclature and Structure Representation. 6.1.2.1. Structure-Based Method. IUPAC[8] gives three examples of aftertreated polymers. The first is chlorinated poly(methylene) (IUPAC name), which contains $-CH_2-$, $-CHCl-$, and $-CCl_2-$ moieties; this is named poly(chloromethylene/dichloromethylene/methylene). This is confusing for two reasons: (1) there is no indication in the polymer name that this is a polymer that has been chlorinated by aftertreatment; (2) if poly(ethylene) is to be called by the SRU name poly(methylene), then, by invocation of inverse logic, the SRU name poly(chloromethylene) could be interpreted as representing poly(1,2-dichloroethylene). Similarly, the SRU name poly(dichloromethylene) could be interpreted as representing poly(tetrachloroethylene). Thus, it might be inferred that the name poly(chloromethylene/dichloromethylene/methylene) is the SRU representation of the terpolymer formed from ethylene, 1,2-dichloroethylene, and tetrachloroethylene. Conceptually, this terpolymer is identical with neither chlorinated poly(ethylene) nor chlorinated poly(methylene).

IUPAC's second example,[8a] chlorinated poly(1-chloroethylene), is called poly(1-chloroethylene/1,1-dichloroethylene/1,2-dichloroethylene/tetrachloroethylene/1,1,2-trichloroethylene/1,2,2-trichloroethylene). It is not clear why two-carbon moieties are considered in this polymer, yet one-carbon

moieties are considered in the first example, before all possible chlorinated moieties are named. This nomenclature is inconsistent with a later IUPAC paper[9a] in which the same polymer, now referred to by its source-based name "chlorinated poly(vinyl chloride)", is called "poly(chloromethylene/dichloromethylene/methylene)". This same name is used in the earlier paper[8a] to indicate "chlorinated poly(methylene)" (IUPAC name), i.e., chlorinated polyethylene.

IUPAC's third example[8a] is the partially hydrolyzed head-to-tail poly(1-acetoxyethylene). This is called poly(1-acetoxyethylene/1-hydroxyethylene). This name gives no indication that the polymer has been aftertreated, and it is potentially ambiguous because partially esterified poly(1-hydroxyethylene) would be presumably be called by the same name.

For situations where process information is not required, the name poly(1-acetoxyethylene/1-hydroxyethylene) may be sufficient. For identification purposes, distinction by name might be desirable when the polymer is derived by different processes, but IUPAC does not address this point. Where process information is desired as part of the name, the following more comprehensive structure-based names are suggested by the author:

poly(1-acetoxyethylene),

aftertreated to poly(1-hydroxyethylene)

The name indicates hydrolysis; other words such as "hydrolyzed", "modified", or "postreacted" could replace "aftertreated".

poly(1-hydroxyethylene),

aftertreated to poly(1-acetoxyethylene)

The name indicates esterification; other words such as "esterified", "modified", or "postreacted", could replace "aftertreated".

Note: ostensibly, this particular example makes little sense because poly(vinyl alcohol) (PVAL) is usually prepared from poly(vinyl acetate) (PVA), and therefore presumably no one would wish to re-esterify hydrolyzed PVAL to obtain poly-PVA/PVAL; however, the examples shown illustrate the nomenclature method.

6.1.2.2. Source-Based Method. As of November 1996, IUPAC has made no recommendations regarding nomenclature or structural representation for aftertreated, modified, or post-treated source-based polymers.

6.1.3. MDL Graphic Representation. 6.1.3.1. Structure-based Method. Aftertreated polymers may be represented in two ways.[1] The traditional method describes a polymer according to the process used to produce it. The problem with this method is that polymers with theoretically identical structures can frequently be prepared by quite different procedures. Thus, partly esterified poly(acrylic acid) can be prepared by partial hydrolysis of poly(methyl acrylate) (a modification), copolymerization of methyl acrylate and acrylic acid, or partial esterification of poly(acrylic acid) (a modification).

Representing such theoretically identical structures as different polymer types is potentially confusing, for both database registration and searching. MDL states that the preferred way to represent chemically altered polymers is to rely solely upon structure for registration and searching.

Process information may then be either attached as Sgroup data or saved in a relational database. In this way, all processes that result in a similar structure are recovered by structure and distinguished by specific associated data.
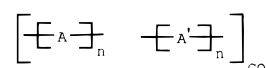
For a single-step modification in which SRU A is modified to SRU A′, the process representation is
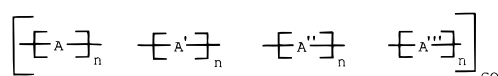
$$\left[\; \left(\!A\!\right)_n \quad \left(\!A'\!\right)_{mod} \right]_n$$
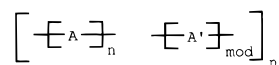
For a two-step modification in which SRU A is modified to SRU A″, while A′ is modified to A‴, the process representation is

$$\left[\; \left[\left(\!A\!\right)_n \quad \left(\!A'\!\right)_{mod}\right]_n \left[\left(\!A''\!\right)_n \quad \left(\!A'''\!\right)_{mod}\right]_{mod} \right]_n$$
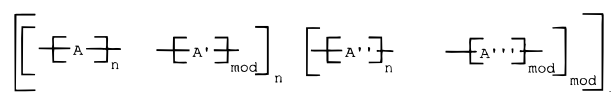
For a purely structural representation, the graphic formats for showing the original and all modified SRU Sgroups are

$$\left[\; \left(\!A\!\right)_n \quad \left(\!A'\!\right)_n \right]_{co}$$

for the first modification and

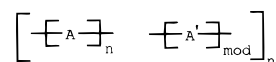$$\left[\; \left(\!A\!\right)_n \quad \left(\!A'\!\right)_n \quad \left(\!A''\!\right)_n \quad \left(\!A'''\!\right)_n \right]_{co}$$
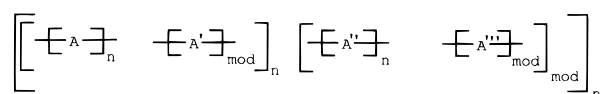
for the second.

6.1.3.2. Source-Based Method. For a process representation, the starting Sgroup is paired with its altered, subscripted (mod) form. For a further modification, ALL of the first modification SRU, not just the modified part, is changed. Thus, the original SRU $-[-A-]_n-$ becomes

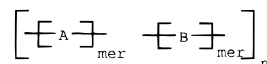$$\left[\; \left(\!A\!\right)_n \quad \left(\!A'\!\right)_{mod} \right]_n$$

for the first modification, and

$$\left[\; \left[\left(\!A\!\right)_n \quad \left(\!A'\!\right)_{mod}\right]_n \left[\left(\!A''\!\right)_n \quad \left(\!A'''\!\right)_{mod}\right]_{mod} \right]_n$$
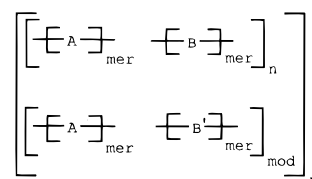
for the second.

MDL illustrates process representations for chlorinated polyethylene and brominated (chlorinated polyethylene).[1]

Another process example is the modification of an alternating bipolymer that has only one component modified. The original polymer
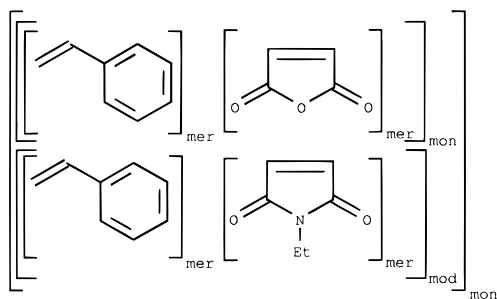
$$\left[\; \left(\!A\!\right)_{mer} \quad \left(\!B\!\right)_{mer} \right]_n$$

becomes

$$\left[\; \left[\left(\!A\!\right)_{mer} \quad \left(\!B\!\right)_{mer}\right]_n \; \left[\left(\!A\!\right)_{mer} \quad \left(\!B'\!\right)_{mer}\right]_{mod} \right]_n$$

The specific example given[1] is the modification of maleic anhydride in poly[styrene-*alt*-(maleic anhydride)] to *N*-

ethylmaleimide; the modified polymer is represented as shown in example 6.1.3.2.1.

Example 6.1.3.2.1.

6.1.4. SCION Nomenclature and Structure Representation. 6.1.4.1. Structure-Based Method.

Aftertreatment in SRU polymers is represented in several different ways. An aftertreatment that produces a "definite" result—i.e., the structure of the new SRU can be completely defined—results in a polymer name of the general format POLY-A, AFTERTREATED TO B, where A and B are the names of the SRUs before and after treatment.[10] The final polymer may still be single-strand (i.e., linear) or it may be cross-linked.

Example 6.1.4.1.1 shows an aftertreated polymer that is still single-strand.

Example 6.1.4.1.1. POLY-OXY(2-(BROMOMETHYL)-TETRAMETHYLENE) reacts with dimethylamine
Structure
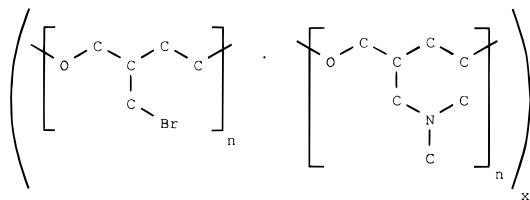
Polymer name: POLY-OXY(2-(BROMOMETHYL)TETRAMETHYLENE), AFTERTREATED TO OXY(2-((DIMETHYLAMINO)METHYL)TETRAMETHYLENE) (see point 6.1.4.1.1)

Point 6.1.4.1.1: Because of current CAS Registry System limitations for the SCION database, brackets "[" and "]" are not used in chemical names; instead multiple parentheses are used.

More specific aftertreatment is not indicated in the name; thus, polymer names such as "Poly-A, chlorinated to B" or "Poly-X, reduced to Y" are not used.

When post-polymerization cross-linking occurs to give a known structure, e.g., formation of a "theoretical" new SRU, its name is integrated into the polymer name and its structure is included as part of the polymer structural record. The name and structure of the new SRU are sufficient to indicate that cross-linking has occurred. The name format for the final polymer is POLY-A, AFTERTREATED TO B, where A is the original SRU and B is the name of the "theoretical" new SRU.

Example 6.1.4.1.2. POLY-OXY(2-BROMOTRIMETHYLENE) is cross-linked by reaction with ethylenediamine
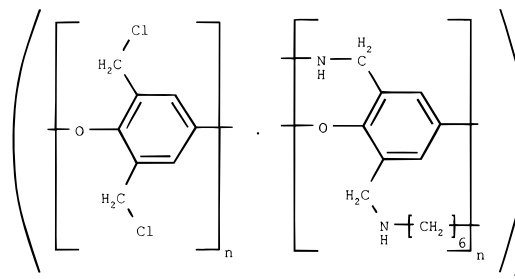
Structure
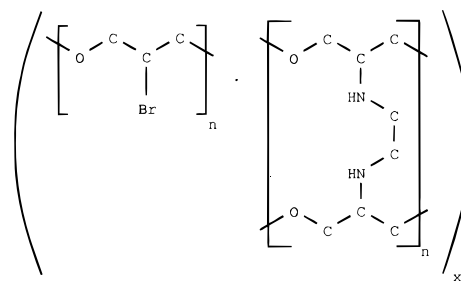
Polymer name: POLY-OXY(2-BROMOTRIMETHYLENE), AFTERTREATED TO ETHYLENEBIS(IMINO-2,1,3-PROPANETRIYL-1-OXY) (see point 6.1.4.1.2)

Point 6.1.4.1.2: A nomenclature system for polymers of this type is described elsewhere.[10,11]

For situations where aftertreatment of a polymer results in a three-dimensional network of known structure, the new SRU is oriented and named. Examples 6.1.4.1.3 and 6.1.4.1.4 illustrate the method.

Example 6.1.4.1.3. Poly-oxy(2,6-bis(chloromethyl)-*p*-phenylene) is cross-linked with 1,6-hexanediamine
Structure

Polymer name: POLY-OXY(2,6-BIS(CHLOROMETHYL)-P-PHENYLENE), AFTERTREATED TO (<-L)(OXY-2,1,3,5-BENZENETETRAYL)(5R;1U;3D)-(5R->)-(1U)-(METHYLENEIMINO)(L<-)-(3D)(METHYLENEIMINO-HEXAMETHYLENE)(R->)

Note on example 6.1.4.1.3: Rules governing the novel nomenclature and structure representations devised for this polymer and the next one are presented elsewhere.[11]

Example 6.1.4.1.4. Poly-(diaminophosphorylidyne)nitrilo is cross-linked with Cl−CH₂−CH₂−S−CH₂−CH₂−Cl
Structure
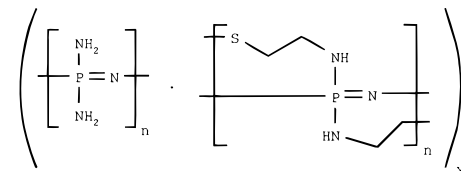
Polymer name: POLY-(DIAMINOPHOSPHORYLIDYNE)-NITRILO, AFTERTREATED TO (<-L)(THIOETHYL-ENEIMINO)(D)-PHOSPHORANEPENTAYL(L;D;R)-(L<-)-(D)(IMINOETHYLENE)(R->)-(R)NITRILO(R->)

Note on example 6.1.4.1.4: The head atom has changed from P in the original, linear SRU to S in the new SRU; this change affects both structure and nomenclature.

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An aftertreatment that produces an "indefinite" result—i.e., the structure of the new SRU cannot be completely defined—results in a polymer name of the general format POLY-A, AFTERTREATED TO B, where A is the name of the original SRU and B is the name of a fragment attached at an unknown site to the SRU by the aftertreatment. Thus, if poly(oxyethylene) is chlorinated, the resulting polymer has chloro groups attached at irregular intervals on unidentified backbone (main chain) carbon atoms.

Example 6.1.4.1.5. Chlorination of poly-oxyethylene
Structure
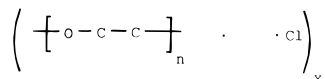
Polymer name: POLY-OXYETHYLENE, AFTERTREATED TO CHLORO
Text descriptors: POLY-AFTERTREATED; POLYAFT-CHLORO

Note on example 6.1.4.1.5: For "indefinite-aftertreatment" polymers, names of fragments, preceded by POLY-, are added as descriptors (in the /CT field) to permit retrieval by name as an alternative approach to retrieval by MF. A search for the text-controlled term POLYAFT-CHLORO/CT is a fast route to retrieval of all post-chlorinated polymers in the SCION chemical file.

Another type of aftertreatment, in which one SRU polymer reacts with another, results in the name format POLY-A, AFTERTREATED WITH POLY-B TO C, where A and B are the original SRUs and C is the "theoretical" new SRU. SRUs A and B are alphabetized, regardless of whether, intellectually, one is perceived as the treated polymer and the other as the agent of treatment. Salt formation, the formation of comb polymers, and cross-linking are common types of interpolymer reaction. For cross-linked polymers, the cross-link itself may be either nonpolymeric or polymeric. One example of each kind is given.

Example 6.1.4.1.6. POLY-OXY(1-AMINOETHYLENE) and POLY-OXY(1-CARBOXYETHYLENE) react to form a salt
Reaction
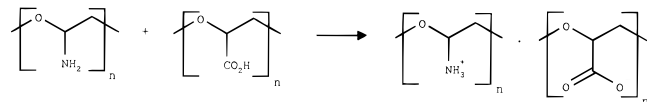
Stored structure
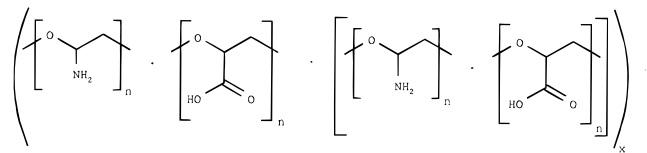
Polymer name: POLY-OXY(1-AMINOETHYLENE), AFTERTREATED WITH POLY-OXY(1-CARBOXYETHYLENE) TO OXY(1-CARBOXYETHYLENE), OXY(1-AMINOETHYLENE) SALT

When a comb polymer is formed, the "theoretical" new SRU is usually named as a polymer with a multiple-radical fragment at one end—see example 6.1.4.1.7.

Example 6.1.4.1.7. POLY-OXYETHYLENE with one allyloxy* and one methoxy* end group reacts with POLY-(METHYLSILYLENE)OXY to form a comb polymer (*the concept in SCION of dealing with end groups without splitting functional groups is discussed in detail elsewhere[10])
Reaction
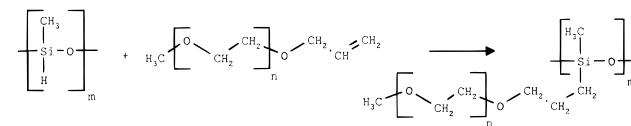
Stored structure
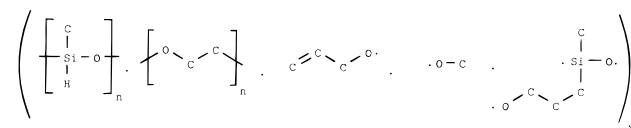
Polymer name: POLY-(METHYLSILYLENE)OXY, AFTERTREATED WITH (POLY-OXYETHYLENE, END GROUP ALLYLOXY, END GROUP METHOXY) TO (POLY-OXYETHYLENE, END GROUP METHOXY, END GROUP (METHYLSILYLIDYNE)OXY(TRIMETHYLENEOXY)), COMB
Text descriptors: END GROUP POLYMERIZABLE NON-CC; POLY-AFTERTREATED; POLY-COMB-OR-GRAFT; POLYAFT-WT

Notes on example 6.1.4.1.7: Nomenclature of multiradical fragments is discussed elsewhere;[12] the text descriptor POLYAFT-WT is used when one polymer is aftertreated with another and the structure of the theoretical new monomer is known. The "polymerizable end group" of this polymer is a type that does not involve a carbon—carbon double bond.

Note that the word COMB appears in names of comb polymers. This is discussed in more detail in section 6.4.4.

In the previous example, the aftertreatment results in grafting at specific sites. Even if the precise grafting sites are not known, the overall concept of one polymer reacting with another is considered in SCION to be an *aftertreatment*, not a graft.
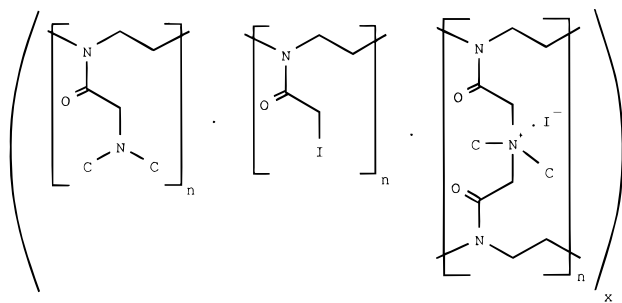
An aftertreatment that results in a nonpolymeric cross-link is shown as example 6.1.4.1.8.

Example 6.1.4.1.8. POLY-(((DIMETHYLAMINO)ACETYL)-IMINO)ETHYLENE and POLY-((IODOACETYL)IMINO)-ETHYLENE cross-link

Intellectually, the polymer structure is
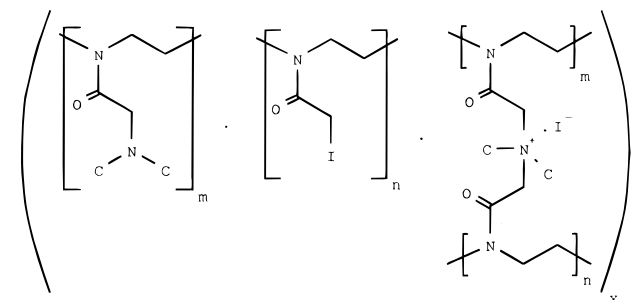
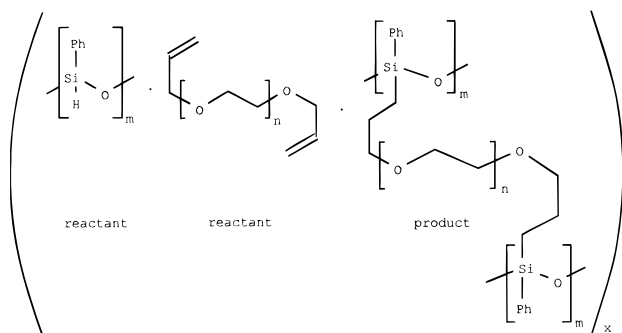However, because of current CAS Registry System limitations, the stored structure is

Polymer name: POLY-(((DIMETHYLAMINO)ACETYL)-IMINO)ETHYLENE, AFTERTREATED WITH POLY-((IODOACETYL)IMINO)ETHYLENE TO DIMETHYL-IMINIOBIS(METHYLENECARBONYLNI-TRILOETHYLENE), IODIDE

The next example in this section shows an aftertreatment that results in a polymeric cross-link. The name format is POLY-A, AFTERTREATED WITH POLY-B TO C. The two SRUs A and B are alphabetized regardless of which is the original backbone and which is the polymeric cross-linking agent; C is the name of the "theoretical" new monomer, which in this case is represented as a macromonomer with multiple radical ends.

Example 6.1.4.1.10. Poly-(phenylsilylene)oxy is cross-linked by reaction with "Bis(allyloxy)poly-oxyethylene"

Intellectually, the polymer structure is

However, because of current CAS Registry System limitations, the stored structure is
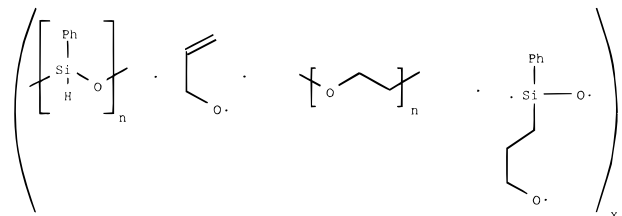
It is therefore necessary to see the polymer name as well as the stored structure to comprehend the chemistry.

Polymer name: POLY-(OXYETHYLENE, END GROUP ALLYLOXY), AFTERTREATED WITH POLY-(PHENYL-SILYLIDENE)OXY TO (POLY-OXYETHYLENE, END GROUP (PHENYLSILYLIDYNE)OXY(TRIMETHYL-ENEOXY)) (see Point 6.1.4.1.3)

Point 6.1.4.1.3: When end groups are associated with a specific polymer in a final name of this kind that cites more than one polymer, each polymer name with its end groups is parenthesized to avoid confusion about which end groups

belong to which polymer. In these cases, in the final polymer name the first polymer to be cited begins poly-(..., whereas other polymer names begin (poly-... .

When more than one aftertreatment is applied to a polymer, the "products" (i.e., theoretical new SRUs) of *all* the aftertreatments appear in the polymer name, even if some of them are no longer present. Examples 6.1.4.1.11 and 6.1.4.1.12 show the method; note that structures and names of intermediate SRUs or fragments, e.g., poly-oxy(2-((di-methylamino)methyl)tetramethylene) in example 6.1.4.1.11 and chlorosulfonyl in example 6.1.4.1.12, are retained in the final name, even if reaction to the next step is complete.

Example 6.1.4.1.11. Multiple aftertreatment of poly-oxy-(2-(bromomethyl)tetramethylene) with (a) dimethylamine, and (b) methyl iodide

Structure
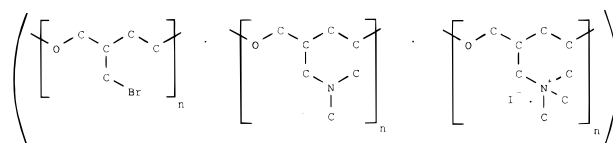
Polymer name: POLY-OXY(2-(BROMOMETHYL)TET-RAMETHYLENE), AFTERTREATED TO OXY(2-((DI-METHYLAMINO)METHYL)TETRAMETHYLENE)/OXY-(2-((TRIMETHYLAMMONIO)METHYL)TETRA-METHYLENE), IODIDE

Example 6.1.4.1.12. Multiple aftertreatment of poly-oxy-ethylene; chlorination/chlorosulfonation with SO_2Cl_2 and subsequent amination
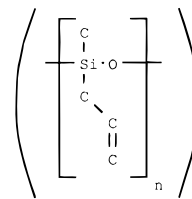
Structure

Polymer name: POLY-OXYETHYLENE, AFTERTREAT-ED TO CHLORO/CHLOROSULFONYL/SULFAMOYL

In multiple-aftertreatment names, the SRUs generated by the various aftertreatments are always alphabetized in the final polymer name, *regardless of the chemical sequence.*

If aftertreatment of an SRU results in further polymeri-zation, the SRU is regarded, for naming purposes, as if it were a monomer; it is parenthesized and preceded with POLY-; see example 6.1.4.1.13.

Example 6.1.4.1.13. Further (ethylenic) polymerization of poly-(allylmethylsilylene)oxy

Structure

Polymer name: POLY-(POLY-(ALLYLMETHYLSILYL-ENE)OXY)

6.1.4.2 Source-Based Method. Aftertreatment in source-based polymers is represented in one of two ways: (A) the

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structure of the "theoretical" new monomer (produced by the aftertreatment) is known; (B) the resulting polymer has an incompletely defined structure.

A: An aftertreatment that produces a "definite" result—i.e., the structure of the "theoretical" new monomer is known—results in a polymer name of the general format POLY-A, AFTERTREATED TO B, where A and B are the names of the monomers before and after treatment. The final polymer may still be single-strand (i.e., linear) or it may be cross-linked.

Examples 6.1.4.2.1 and 6.1.4.2.2 show aftertreated polymers that are still single-strand.

Example 6.1.4.2.1. (Compare with MDL representation—see example 6.1.3.2.1.)

Structure
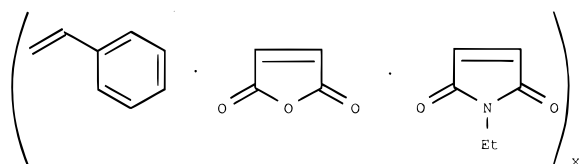
Polymer name: POLY-MALEIC ANHYDRIDE/STYRENE, ALTERNATING, AFTERTREATED TO MALEIMIDE, N-ETHYL-
Text descriptors: POLY-ALTERNATING; POLY-AFTER-TREATED

Example 6.1.4.2.2. Reduction of nitro-groups in a polyester

Structure
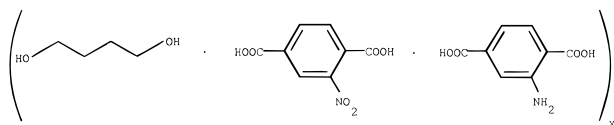
Polymer name: POLYESTER-1,4-BUTANEDIOL/TEREPH-THALIC ACID, NITRO-, AFTERTREATED TO TEREPH-THALIC ACID, AMINO-
Text descriptors: POLYESTER; POLY-AFTERTREATED

In multiple aftertreatments, *all* theoretical new monomers formed are cited, even if they are subsequently completely reacted. Thus, if the polymer of example 6.1.4.2.2 is subsequently reacted with 1,2-dibromoethane, the resulting cross-linked polymer has the structure, name, and descriptors given in example 6.1.4.2.3; even if all the aminoterephthalic acid is reacted, it still appears as a component of the final polymer.

Example 6.1.4.2.3. The polyester from 1,4-butanediol and nitroterephthalic acid is reduced, and the resulting polymer is cross-linked with 1,2-dibromoethane

Structure
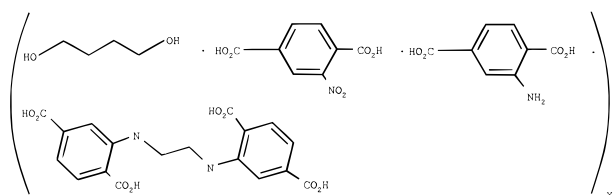
Polymer name: POLYESTER-1,4-BUTANEDIOL/TEREPH-

THALIC ACID, NITRO-, AFTERTREATED TO TEREPH-THALIC ACID, AMINO-/TEREPHTHALIC ACID, (ETH-YLENEDIAMINO)DI-
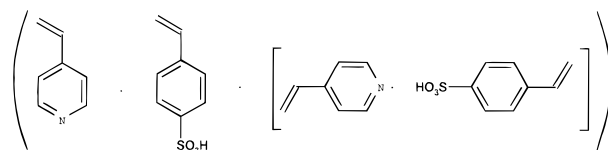Text descriptors: POLYESTER; POLY-AFTERTREATED; POLY-HYPERCONNECTABLE (see Point 6.1.4.2.1)

Point 6.1.4.2.1: Addition of the text descriptor POLY-HYPERCONNECTABLE—see section 6.6.4—is used to indicate that a polymer *may* be hyperbranched or hypercross-linked.

Another type of aftertreatment, in which one polymer reacts with another, results in the name format POLY-A, AFTERTREATED WITH POLY-B TO C, where A and B are the original monomers and C is the "theoretical" new monomer. Monomers A and B are alphabetized, regardless of whether, intellectually, one is perceived as the treated polymer and the other as the agent of treatment. Salt formation, the formation of comb polymers, and cross-linking are common types of interpolymer reaction. For cross-linked polymers, the cross-link itself may be either nonpolymeric or polymeric. One example of each kind is given.

Example 6.1.4.2.4. Poly-*p*-vinylbenzenesulfonic acid and poly-*p*-vinylpyridine react to form a salt (example of nonpolymeric, ionic cross-link)
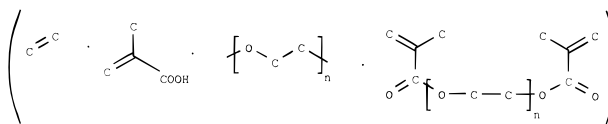
Structure

Polymer name: POLY-BENZENESULFONIC ACID, P-VINYL-, AFTERTREATED WITH POLY-PYRIDINE, P-VINYL- TO BENZENESULFONIC ACID, P-VINYL-, P-VINYLPYRIDINE SALT
Text descriptors: POLY-AFTERTREATED; POLY-HY-PERCONNECTABLE; POLYAFT-WT
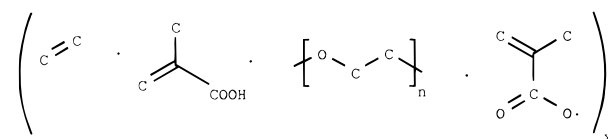
Note on example 6.1.4.2.4: See note on example 6.1.4.1.7 for an explanation of the text descriptor POLYAFT-WT.

Example 6.1.4.2.5. An ethylene/methacrylic acid copolymer is esterified with poly-ethylene glycol (example of polymeric cross-link)
Intellectual structure

Stored structure

Polymer name: POLY-ETHYLENE/METHACRYLIC ACID, AFTERTREATED WITH POLY-OXYETHYLENE TO (POLY-OXYETHYLENE, END GROUP METHACRYL-OYLOXY)

Text descriptors: POLY-AFTERTREATED; POLY-HY-PERCONNECTABLE; POLYAFT-WT

The reason for representing the newly formed cross-link as "$CH_2\!=\!C(Me)\!-\!CO\!-\!O\!-\![poly\text{-}oxyethylene]\!-\!O\!-\!CO\!-\!C(Me)\!=\!CH_2$" instead of the conventional $CH_2\!=\!C(Me)\!-\!CO\!-\![-O\!-\!CH_2\!-\!CH_2\!-]_n\!-\!O\!-\!CO\!-\!C(Me)\!=\!CH_2$ is discussed in detail elsewhere.[10]

If an aftertreatment results in further polymerization, the name of the polymer is treated as if it were a monomer. It is parenthesized and preceded with POLY-; see example 6.1.4.2.6.

Example 6.1.4.2.6. Further (ethylenic) copolymerization with ethylene of the polyester from maleic acid and poly-oxyethylene
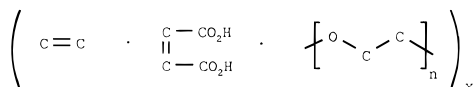
Structure

Polymer name: POLY-ETHYLENE/POLY-(POLYESTER-MALEIC ACID/POLY-OXYETHYLENE)

B: For aftertreatments that produce an "indefinite" result—i.e., structures of new monomers cannot be completely defined—the name format is the same: POLY-A, AFTERTREATED TO B. However, in these cases B is a fragment that represents the group attached or produced at an unknown site by the aftertreatment.

Thus, if poly-ethylene is chlorinated, the resulting polymer has chloro groups attached at irregular intervals on unidentified backbone (main chain) carbon atoms.

Example 6.1.4.2.7. Chlorination of poly-ethylene

Stored structure
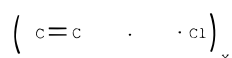
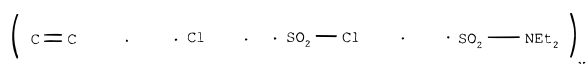Polymer name: POLY-ETHYLENE, AFTERTREATED TO CHLORO
Text descriptors: POLY-AFTERTREATED; POLYAFT-CHLORO

Note on example 6.1.4.2.7: See note under example 6.1.4.1.5 for an explanation of the descriptor POLYAFT-CHLORO.

For "indefinite-aftertreatment" polymers that undergo multiple aftertreatments, each "theoretical" fragment produced by the aftertreatment is added as a component and named in the complete polymer name, *even if it is no longer present*—see example 6.1.4.2.8.

Example 6.1.4.2.8. Polyethylene chlorinated/chlorosulfonated with sulfonyl chloride and subsequently treated with diethylamine

Structure

Polymer name: POLY-ETHYLENE, AFTERTREATED TO CHLORO/CHLOROSULFONYL/(DIETHYLAMINO)SULFONYL

Text descriptors: POLY-AFTERTREATED; POLYAFT-CHLORO; POLYAFT-CHLOROSULFONYL; POLYAFT-(DIETHYLAMINO)SULFONYL

Partial hydrogenation of poly-1,3-butadiene gives a polymer in which the exact locations of the added hydrogen atoms are unknown; this structure is represented as shown in example 6.1.4.2.9.

Example 6.1.4.2.9. Partially reduced poly-1,3-butadiene

Stored structure
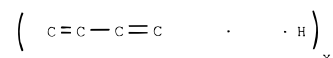
Polymer name: POLY-1,3-BUTADIENE, AFTERTREATED TO HYDRO
Text descriptors: POLY-AFTERTREATED; POLYAFT-HYDRO

Aftertreatment of polymers in SCION is described more fully elsewhere.[10]

6.2. Alternating and Other Periodic Copolymers. An alternating copolymer is one in which two SRUs or monomers alternate. Other periodic copolymers also contain SRUs or monomers in an ordered sequence.

6.2.1. CAS Nomenclature and Structure Representation. 6.2.1.1. Structure-Based Method. CAS makes no reference to alternating or periodic structure-based polymers in the Index Guide.[3] In contrast to IUPAC policy (see section 6.2.2.1), examples 6.2.1.1.1 and 6.2.1.1.2 show that neither "alternating" nor "periodic" is used as a modifier by CAS in SRU polymers. The text descriptors "alternating" and "periodic" are not used with SRUs because any alternation or periodicity would be obvious in the structure and would not need to be differentiated from another similar structure by means of a text descriptor.[13]

Example 6.2.1.1.1. Poly(oxymethylene-oxyethylene) "alternating" polymer

REGISTRY COPYRIGHT 1995 ACS
RN 28726-47-8 REGISTRY
CN Poly(oxymethyleneoxy-1,2-ethanediyl) (9CI) (CA INDEX NAME)
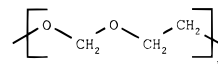OTHER NAMES:
CN 1,3-Dioxolane polymer, sru
CN Poly(oxymethyleneoxyethylene)
MF (C3 H6 O2)n
CI PMS
PCT Polyether
LC STN Files: CA, CAPLUS, CJACS, USPATFULL

Example 6.2.1.1.2. Poly(oxymethylene-oxyethylene-oxyethylene) "periodic" polymer

REGISTRY COPYRIGHT 1995 ACS
RN 80411-09-2 REGISTRY
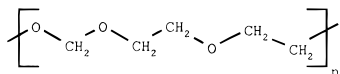CN Poly(oxymethyleneoxy-1,2-ethanediyloxy-1,2-ethanediyl) (9CI) (CA INDEX NAME)
MF (C5 H10 O3)n
CI PMS
PCT Polyether
LC STN Files: CA, CAPLUS

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6.2.1.2. Source-Based Method. Registration of alternating copolymers with the term "alternating" as an integral part of the Registry record began with the 12CI (1987). Alternating polymers are distinguished from random polymers by indexing as copolymers at the monomer names. The term "alternating" is cited in a special modification after all other structural information but before descriptive phrases relating to properties, uses, etc.[3a]

Example 6.2.1.2.1. Alternating (butoxymethyl)oxirane/carbon dioxide polymer

REGISTRY COPYRIGHT 1995 ACS
RN 108080-86-0 REGISTRY
CN Oxirane, (butoxymethyl)-, polymer with carbon dioxide, alternating (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Carbon dioxide, polymer with (butoxymethyl)oxirane, alternating (9CI)
MF (C7 H14 O2 . C O2)x
CI PMS
PCT Polycarbonate, Polycarbonate formed, Polyether, Polyether formed
SR CA
LC STN Files: CA, CAPLUS
DES 8:PM,ALTERNATING
:

The text descriptor 8:PM,ALTERNATING, applied to alternating polymers, is displayable but not currently searchable.

CAS does not index polymers with the term "periodic".

6.2.2. IUPAC Nomenclature and Structure Representation. 6.2.2.1. Structure-Based Method. IUPAC defines an alternating polymer as a copolymer comprising two species of monomeric units (hereinafter called monomers) distributed in alternating sequence.[14] As far as possible, alternating and periodic polymers are treated as regular polymers.[9b] Thus, (AB)$_n$ represents an alternating copolymer. Alternating sequence arrangements can form constitutionally regular structures and may, in those cases, be named utilizing the structure-based nomenclature for regular single-strand organic polymers. For example, the alternating copolymer of maleic anhydride (MANH) and styrene (STY) is named poly[(2,5-dioxotetrahydrofuran-3,4-diyl)(1-phenylethylene)]; the structure is as shown in example 6.2.2.1.1.

Example 6.2.2.1.1. IUPAC structure-based representation of the MANH/STY alternating copolymer
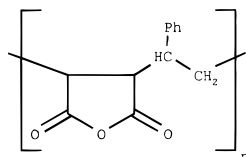
Other examples of periodic copolymers are
(A-*per*-B-*per*-C)
(A-*per*-B-*per*-B)
(A-*per*-A-*per*-B-*per*-C)
(A-*per*-B-*per*-A-*per*-C)

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

If these polymers are regular, they can also be named according to the structure-based nomenclature for regular single-strand organic polymers. Thus, copolymerization of formaldehyde and oxirane might yield the periodically sequenced copolymer shown as example 6.2.2.1.2.

Example 6.2.2.1.2. Formaldehyde/oxirane "poly-OCOC-COCC" periodic polymer (compare example 6.2.2.2.3)

Structure
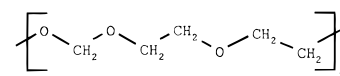
Polymer name: poly(oxymethyleneoxyethyleneoxyethylene)

From the two examples above, it can be seen that the structure-based nomenclature system indicates very clearly the precise nature of the polymer, i.e., whether it is alternating or periodic, and the structures confirm this.

6.2.2.2. Source-Based Method. IUPAC defines an alternating copolymer as a copolymer comprising two species of monomers distributed in alternating sequence.[14] The arrangement −ABABAB− or (AB)$_n$ thus represents an alternating copolymer. An alternating sequence arrangement of monomers is represented by (A-*alt*-B), and the corresponding polymer is named poly(A-*alt*-B) (see Table 1).

Example 6.2.2.2.1. IUPAC source-based representation of the MANH/STY alternating copolymer

Polymer name: poly[styrene-*alt*-(maleic anhydride)]

If an alternating sequence arrangement forms a constitutionally regular structure, it may also be named by structure-based nomenclature.

For simple alternating polymers, an alternative, more concise nomenclature is offered: for example, the polymer of example 6.2.2.2.1 may also be named alt-copoly(styrene/maleic anhydride).

In addition to alternating polymers, other structures are known in which the monomers appear in an ordered sequence, e.g.

−ABCABCABC− or (ABC)$_n$
−ABBABBABB− or (ABB)$_n$
−AABBAABB− or (AABB)$_n$
−ABACABAC− or (ABAC)$_n$

For these copolymers, the periodic sequence arrangement of monomers is represented by

(A-*per*-B-*per*-C)
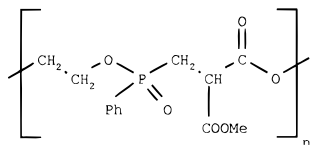(A-*per*-B-*per*-B)
(A-*per*-A-*per*-B-*per*-B)
(A-*per*-B-*per*-A-*per*-C)

and the corresponding periodic copolymers are named

poly(A-*per*-B-*per*-C)
poly(A-*per*-B-per-B)
poly(A-*per*-A-*per*-B-*per*-B)
poly(A-*per*-B-*per*-A-*per*-C)

If these polymers are regular, they may also be named by structure-based nomenclature.

Example 6.2.2.2.2. Terpolymer from ethylene phenylphosphonite, methyl acrylate, and carbon dioxide

Polymer name: poly[(ethylene phenylphosphonite)-*per*-(methyl acrylate)-*per*-(carbon dioxide)]

Example 6.2.2.2.3. The periodic polymer "poly-OCOC-COCC" from formaldehyde and oxirane (compare example 6.2.2.1.2)
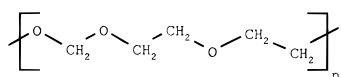
Polymer name: poly[formaldehyde-*per*-(ethylene oxide)-*per*-(ethylene oxide)]

Note that in the last two examples IUPAC combines source-based nomenclature with structure-based representations.

If copolymer structures comprise several types of periodic sites, only some of which are always occupied by particular species of monomers (A, B...), and sites of the other types are occupied by two or more types of monomer (U, V...) in irregular arrangement, the names of the monomers in the latter sites are embraced by parentheses and are separated by semicolon(s). Thus, the polymer with the sequence arrangement −AUAVAVAUAVAUAU− is named poly[A-*alt*-(U;V)].

Example 6.2.2.2.4. The random terpolymer of ethylene glycol, isophthalic acid, and terephthalic acid[9c] is named

poly[(ethylene glycol)-*per*-(isophthalic acid;terephthalic acid)]

For simple periodic polymers, an alternative nomenclature is offered; *per*-copoly(A/B/B) may be written as either *per*-copoly(A/bisB) or *alt*-copoly(A/bisB).

Thus, the name of the polymer of example 6.2.2.2.3 may also be written as poly[formaldehyde-*per*-bis(ethylene oxide)].
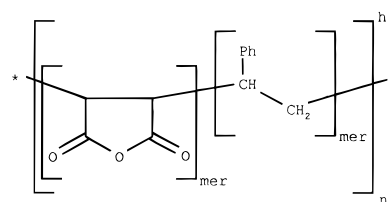
6.2.3. MDL Graphic Representation. 6.2.3.1. Structure-Based Method. MDL represents the alternating copolymer ...ABABAB... as poly(A-*alt*-B) with the graphical representation
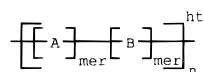

The example given[1] is

poly-[(2,5-dioxotetrahydrofuran-3,4-diyl)(1-phenylethylene)]

which is given the graphical representation

Other periodic copolymers depicted are summarized in Table 2.

6.2.3.2. Source-Based Method. Alternating copolymers are represented as homopolymers by use of mer Sgroups in source materials unit (SMU) Sgroups. Thus, the alternating copolymer ...ABABAB... , or poly(A-*alt*-B), is represented by
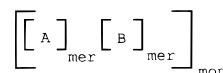

Example 6.2.3.2.1. Poly[styrene-*alt*-maleic anhydride)]
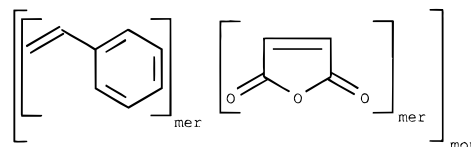
Periodic copolymers such as ...ABCABCABC... , or poly-(A-*per*-B-*per*-C), are represented by
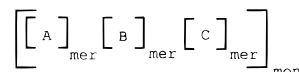
Other periodic copolymers are structured analogously; for example, the polymer from terephthalic acid and tetraethylene glycol is represented as poly(A-*per*-B-*per*-B-*per*-B-*per*-B) and structured as shown in example 6.2.3.2.2.

Example 6.2.3.2.2. Periodic polymer from terephthalic acid and tetraethylene glycol
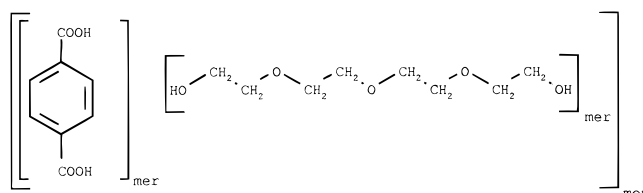
**6.2.4. SCION Nomenclature and Structure Representation. 6.2.4.1. Structure-Based Method.** No SRU polymers in SCION are named as alternating; for example, "poly-oxyethylene/oxytetramethylene, alternating" becomes SRU "poly-oxyethyleneoxytetramethylene" with structure −[−O−CH_2−CH_2−O−CH_2−CH_2−CH_2−CH_2−]$_n$−. Although this can be viewed as an alternating polymer of oxyethylene and oxytetramethylene SRUs, SCION nomenclature rules specify that such polymers are named according to the complete SRU.

Periodic polymers are given no special recognition or treatment. For example, the periodically sequenced copolymer

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Table 2. Summary of MDL periodic polymer representations

Generic Polymer Format	Computer Representation and Name Style

..(AAA..)B(CCC..)B..

polyA-B-block-(polyC-B)

..(AAA..)B(CCC..)..

polyA-B-block-polyC

AAA..(BCCBCBB..)
or (BBCCCBC..)..AAA

poly[A-block-poly(B-ran-C)]

AAA..BBB..(BAABABB..)
or (BBAAABA..)..AAA..BBB

poly(A-ran-B)-block-polyA-block-polyB

Poly(styrene-ran-butadiene)-block-polystyrene-block-polybutadiene is represented thus (the thick bond is used to indicate mixed cis/trans).
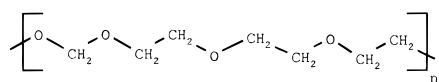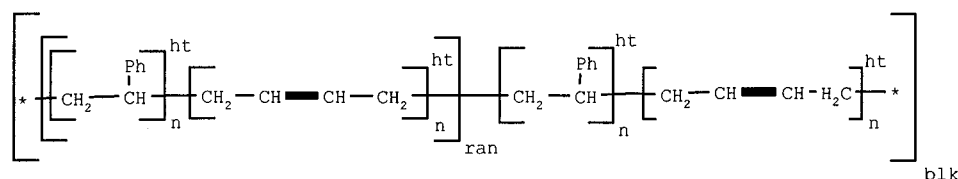
is simply named POLY-OXYMETHYLENEOXYETHYL-ENEOXYETHYLENEOXYETHYLENE.

6.2.4.2. Source-Based Method. The alternating concept is used for polymers of types such as $(ABABAB)_x$ or $(ABACABACABAC)_x$.

The alternating concept is used in SCION only when it is necessary to indicate that comonomers alternate in copolymers where other arrangements are possible, e.g., random or statistical. For example, depending upon the catalyst, carbon monoxide and ethylene can polymerize to give either a random/statistical or a strictly alternating copolymer.

For PMC polymers, the nomenclature style for alternating copolymers is POLY_CLASS-A/B, ALTERNATING or POLY_CLASS-A/B/C, ALTERNATING, where POLY_CLASS is one of the 15 condensation class names listed in Table 3, and A, B, and C are stylized monomers.

For ASM polymers, the nomenclature style for alternating copolymers is POLY-A/B, ALTERNATING, where A and B are actual monomers.

For both of these classes, the text descriptor POLY-ALTERNATING is added. Six examples illustrate the method.

Table 3. SCION PMC-Category Polymer Classes

POLYAMIDE
POLYAMIDE-ESTER
POLYAMIDE-ESTER-IMIDE
POLYAMIDE-ESTER-IMIDE-URETHANE
POLYAMIDE-ESTER-URETHANE
POLYAMIDE-IMIDE
POLYAMIDE-IMIDE-URETHANE
POLYAMIDE-URETHANE
POLYESTER
POLYESTER-IMIDE
POLYESTER-IMIDE-URETHANE
POLYESTER-URETHANE
POLYIMIDE
POLYIMIDE-URETHANE
POLYURETHANE

Example 6.2.4.2.1. Alternating polyamide from m-aminobenzoic acid and p-aminobenzoic acid

Polymer name: POLYAMIDE-BENZOIC ACID, M-AMINO/BENZOIC ACID, P-AMINO-, ALTERNATING
Text descriptors: POLYAMIDE; POLY-ALTERNATING

Example 6.2.4.2.2. Alternating polyester formed from adipic acid, ethylene glycol, and glycolic acid

Polymer name: POLYESTER-ADIPIC ACID/ETHYLENE GLYCOL/GLYCOLIC ACID, ALTERNATING
Text descriptors: POLYESTER; POLY-ALTERNATING

The POLY-ALTERNATING descriptor indicates that the sequence must be ...AD/HO−CH$_2$−COOH/EG/HOOC−CH$_2$−OH..., where AD is adipic, HO−CH$_2$−COOH is glycolic, and EG is ethylene glycol. Thus, an adipic acid unit cannot be connected directly to an ethylene glycol unit, or the polymer would be random or statistical, not alternating.

Example 6.2.4.2.3. Alternating polyamide formed from adipic acid, azelaic acid, and 1,6-hexanediamine

Polymer name: POLYAMIDE-ADIPIC ACID/AZELAIC ACID/1,6-HEXANEDIAMINE, ALTERNATING
Text descriptors: POLYAMIDE; POLY-ALTERNATING

The concept POLY-ALTERNATING also distinguishes between the polyurea prepared from hexamethylene diisocyanate (HMDI) and 1,8-octanediamine (D8), versus the random or statistical polyurea prepared from 1,6-hexanediamine (D6), D8, and phosgene—see examples 6.2.4.2.4 and 6.2.4.2.5. Polyureas in SCION are classified as polyamides with carbonic acid as a stylized monomer.

Example 6.2.4.2.4. Alternating polyurea from HMDI and D8

Structure: (CH$_2$O$_3$.H$_2$N-(CH$_2$)$_6$-NH$_2$.H$_2$N-(CH$_2$)$_8$-NH$_2$)$_x$

Polymer name: POLYAMIDE-CARBONIC ACID/1,6-HEXANEDIAMINE/1,8-OCTANEDIAMINE, ALTERNATING
Text descriptors: POLYAMIDE; POLY-ALTERNATING

Example 6.2.4.2.5. Random/statistical polyurea from phosgene, D6, and D8

Structure: (CH$_2$O$_3$.H$_2$N-(CH$_2$)$_6$-NH$_2$.H$_2$N-(CH$_2$)$_8$-NH$_2$)$_x$

Polymer name: POLYAMIDE-CARBONIC ACID/1,6-HEXANEDIAMINE/1,8-OCTANEDIAMINE
Text descriptor: POLYAMIDE

Note on examples 6.2.4.2.4 and 6.2.4.2.5: A unique input text descriptor must be added as part of the structure of one of these two polymers; failure to comply results in acceptance of the first structure to be keyed and rejection of the second as a "duplicate", because duplicate detection by the CAS Registry System is based on structure alone. Common SCION practice is to add a descriptor such as 8:DP,ALT to the alternating polymer - 8 for CAS Class 8 substance; DP for DuPont; ALT for alternating. These special text descriptors are currently displayable but not searchable.

Example 6.2.4.2.6. Alternating copolymer from styrene and maleic anhydride

Polymer name: POLY-MALEIC ANHYDRIDE/STYRENE, ALTERNATING
Text descriptor: POLY-ALTERNATING

Alternating polymers are also described elsewhere.[10] Periodic copolymers are currently given no special recognition in SCION.

6.3. Block Polymers. This section discusses structure-based and source-based ordered, segmented, and unordered block polymers, and polymers with "nonpolymeric spacer units" or "junction units". Star-block polymers are discussed under star polymers (section 6.6 in part 3 of 4).

6.3.1. CAS Nomenclature and Structure Representation. When CAS began to register polymers in 1967, no distinction was made between block copolymers and other copolymers. The information might have been part of the descriptive "index modification", but it was not part of the Registry record. Registration of block copolymers with the term "block" as an integral part of the Registry record began with the 12CI (1987).

No distinctions are made between ordered, segmented, and unordered block polymers. The text descriptor 8:PM,-BLOCK, applied to block polymers, is currently displayable but not searchable.

6.3.1.1. Structure-Based Method. The block polymer shown as example 6.3.1.1.1 shows the CAS method for indexing block polymers by the structure-based method. Compare this with the source-based representation shown as example 6.3.1.2.1.

Example 6.3.1.1.1. Combined source-/structure-based record for block polymer of poly(oxyethylene) and poly(oxytetramethylene)

REGISTRY COPYRIGHT 1995 ACS
RN 154422-71-6 REGISTRY
CN Poly(oxy-1,4-butanediyl), α-hydro-ω-hydroxy-, polymer with α-hydro-ω-hydroxypoly(oxy-1,2-ethanediyl), block (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Poly(oxy-1,2-ethanediyl), α-hydro-ω-hydroxy-, polymer with α-hydro-ω-hydroxypoly(oxy-1,4-butanediyl), block (9CI)
MF ((C4 H8 O)n H2 O . (C2 H4 O)n H2 O)x
CI PMS
PCT Polyether, Polyether formed
SR CA
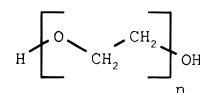LC STN Files: CA, CAPLUS, TOXLIT, USPATFULL
DES 8:PM,BLOCK
:
CM 1
  CRN 25322-68-3
  CMF (C2 H4 O)n H2 O
  CCI PMS
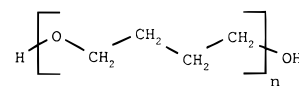

CM 2
CRN 25190−06−1
CMF (C4 H8 O)n H2 O
CCI PMS

6.3.1.2. Source-Based Method. Block polymers are distinguished from random polymers by indexing as copolymers at the monomer names. The term "block" is cited in a special modification after all other structural information;[3a] see examples 6.3.1.2.1 and 6.3.1.2.2, and compare the first of these with example 6.3.1.1.1.

Example 6.3.1.2.1. Source-based record for block copolymer of oxirane and tetrahydrofuran "poly(oxyethylene/oxytetramethylene)"

REGISTRY COPYRIGHT 1996 ACS
RN 112869-03-1 REGISTRY

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CN Furan, tetrahydro-, polymer with oxirane, block (9CI) (CA INDEX NAME)
OTHER CA INDEX NAMES:
CN Oxirane, polymer with tetrahydrofuran, block (9CI)
OTHER NAMES:
CN Ethylene oxide-tetrahydrofuran block copolymer
MF (C4 H8 O . C2 H4 O)x
CI PMS, COM
PCT Polyether, Polyether formed
SR CA
LC STN Files: CA, CAPLUS, CAPREVIEWS, TOXLIT, USPATFULL
DES 8:PM,BLOCK
  CM 1
  CRN 109-99-9
  CMF C4 H8 O

  CM 2
  CRN 75-21-8
  CMF C2 H4 O

The conclusion drawn from examples 6.3.1.1.1 and 6.3.1.2.1 is clear: for every polymer search, structure-based and source-based formats may exist and *should be searched for complete retrieval*.

Example 6.3.1.2.2. Source-based block polyurea/urethane

REGISTRY COPYRIGHT 1995 ACS
RN 9052-55-5 REGISTRY
CN Urea, polymer with 1,3-diisocyanatomethylbenzene, 1,6-hexanediamine and α-hydro-ω-hydroxypoly(oxy-1,2-ethanediyl), block (9CI) (CA INDEX NAME)
:
OTHER NAMES:
CN 1,6-Hexanediamine-polyethylene glycol-tolylene diisocyanate-urea block polymer
MF (C9 H6 N2 O2 . C6 H16 N2 . (C2 H4 O)n H2 O . C H4 N2 O)x
CI PMS
PCT Polyether, Polyurea, Polyurea formed, Polyurethane, Polyurethane formed
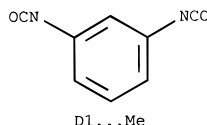LC STN Files: CA, CAPLUS
DES 8:PM,BLOCK
  CM 1
  CRN 26471-62-5
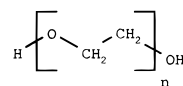 CMF C9 H6 N2 O2
  CCI IDS
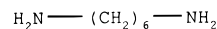 CDES 8:ID

D1...Me

  CM 2
  CRN 25322-68-3
  CMF (C2 H4 O)n H2 O
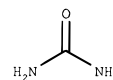
CCI PMS

CM 3
CRN 124-09-4
CMF C6 H16 N2

H_2N—$(CH_2)_6$—NH_2

CM 4
CRN 57-13-6
CMF C H4 N2 O

:

6.3.2. IUPAC Nomenclature and Structure Representation. 6.3.2.1. Structure-Based Method.

A polymer that consists of an irregular sequence of blocks of SRUs A, B, C, and D is named poly(A)/poly(B)/poly(C)/poly(D).[8a]

Block polymers in which the sequential arrangement of regular blocks is known are named by using *dashes* (symbol —) for the bonding of blocks with each other and with junction units:

poly(A)—Xa—poly(B)—Xb—poly(C)—Xc—...

where A, B, C, ... are the names of SRUs and Xa, Xb, Xc, ... are the names of junction units.[8b,8c] The connective *-block-* may be omitted. The order of citation of the block names corresponds to the order of the blocks in the chain as written from left to right. If there are no junction units, or they are not known, the polymer is named:

poly(A)—poly(B)—poly(C)—...

A polymer consisting of repeated specific sequences is named:

poly[poly(A)—Xa—poly(B)—Xb—poly(C)—Xc—...][8a]

Example 6.3.2.1.1. A triblock copolymer of structure (O-p-$C_6H_4)_p$—[CH_2-CH(CN)]$_q$—(CH_2-CH_2-O)$_r$ is named poly-(oxy-1,4-phenylene)—poly(2-cyanoethylene)—poly-(ethyleneoxy). However, if the same polymer is drawn "mirror-image", namely, (O-CH_2-$CH_2)_r$—[CH(CN)-$CH_2]_q$—(C_6H_4-O)$_p$, it is named poly(oxyethylene)—poly(1-cyanoethylene)—poly(1,4-phenyleneoxy). Thus, every linear block polymer can have a least two names, which will depend upon structure orientation. Depending upon end groups and/or placement of parentheses, therefore, even more names may be possible.

Example 6.3.2.1.2. A diblock of structure [(CH_2-CH_2-O)$_m$—(SiMe$_2$)—(CHCl-CH_2)]$_n$ is named poly(ethyleneoxy)—dimethylsilanediyl—poly(1-chloroethylene). Drawing this polymer "mirror-image", namely, [(CH_2-CHCl)$_n$—(SiMe$_2$)—(O-CH_2-CH_2)]$_m$, results in the name

poly(oxyethylene)—dimethylsilanediyl—poly(2-chloroethylene).

Note on example 6.3.2.1.2: IUPAC currently prefers to use silanediyl in names such as these;[8,9] older documents[e.g.14] used silylene.

A segmented polyurethane example is also given.[8c] IUPAC rules for, and graphic representations of, block polymers are also given elsewhere.[9d]

6.3.2.2. Source-Based Method. As shown in Table 1, IUPAC block copolymers contain the connective *-block-*. The block sequence arrangement is represented by

A_k-*block*$_m$-B_k , A-*block*-(A-*stat*-B), etc.

The corresponding polymers are named polyA-*block*-polyB, polyA-*block*-poly(A-*stat*-B), etc., respectively. If no ambiguity arises, a long dash may be used to designate connections, as follows:

polyA—polyB

For complex cases, use of *-block-* rather than the long dash is always encouraged. The order of citation of the block names corresponds to the order of succession of the blocks in the chain as written from left to right. This means that in a systematic polymer name index an AB block polymer needs to be named both polyA-*block*-polyB and polyB-*block*-polyA, for the simple reason that if it is named only as polyB-*block*-polyA a name search for polyA-*block*-polyB will probably fail to locate it. Similarly, an ABC block polymer needs to be named polyA-*block*-polyB-*block*-polyC, polyC-*block*-polyB-*block*-polyA, and so on.

Examples cited[14a] include
·polystyrene-*block*-polybutadiene
·polystyrene-*block*-polybutadiene-*block*-polystyrene
·poly(styrene-*stat*-butadiene)-*block*-polystyrene-*block*-polybutadiene
·polystyrene-*block*-polybutadiene-*block*-poly(methyl methacrylate)

Block polymers containing a known or unknown number of repetitions of the block sequence are named with the appropriate multiplying prefix.

Examples
·tris(polyA-*block*-polyB-*block*-polyC)
·poly(polyA-*block*-polyB-*block*-polyC)

Known or unknown lengths of individual blocks may also be expressed with the appropriate multiplying prefix.

Examples
·oligoA-*block*-octaB
·poly(oligoA-*block*-polyB-*block*-triC)

Block polymers containing blocks separated by junction units or "nonpolymeric spacer units" have the name of the junction unit inserted in the appropriate place; the connective, *-block-*, may be omitted.
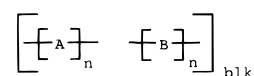
Examples
·polystyrene-*block*-dimethylsilylene-*block*-polybutadiene
or: polystyrene—dimethylsilylene—polybutadiene
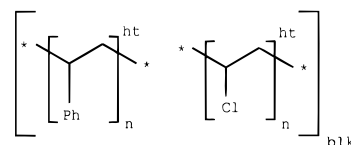·polystyrene-*block*-dimethylsilylene-*block*-polystyrene or: polystyrene—dimethylsilylene—polystyrene

Note on these examples: See note beneath example 6.3.2.1.2 on IUPAC's use of silylene versus silanediyl.

6.3.3. MDL Graphic Representation. 6.3.3.1. Structure-Based Method. The unordered block polymer polyA-*block*-polyB, which represents the polymer AAA...BBB or
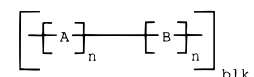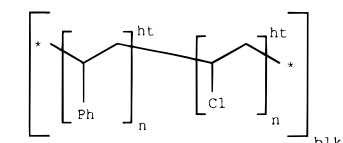
the polymer BBB...AAA, is depicted as[1]

Example 6.3.3.1.1. Poly-styrene-block-chloroethylene

The ordered block polymer polyA-block-polyB, which represents only the polymer AAABBB, is depicted as

Example 6.3.3.1.2. Poly-styrene-block-chloroethylene

Similar depictions are given for unordered and ordered triblock polymers. The unordered polymer is AAA...BBB...CCC, or BBB...AAA...CCC, etc. (six possibilities). The ordered polymer is AAA...BBB...CCC.
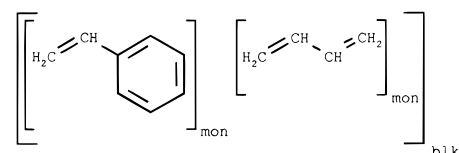
Graphic representations are also given for the segmented block polymer poly[[A-block-B]-C].

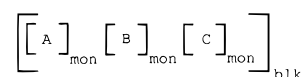**6.3.3.2. Source-Based Method.** Source-based unordered diblock polymers are registered in the format
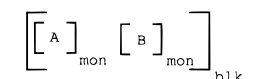
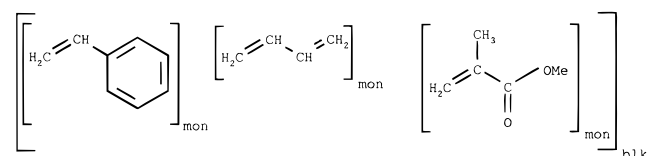This represents either of the two polymers AAA-BBB or BBB-AAA.

Example 6.3.3.2.1. Polystyrene-block-polybutadiene

Similarly, unordered triblock polymers are registered in the format

Example 6.3.3.2.2. Polystyrene-block-polybutadiene-block-poly(methyl methacrylate)

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This represents AAA-BBB-CCC, AAA-CCC-BBB, BBB-AAA-CCC, etc.; the total number of possibilities is six. Ordered block polymers, i.e., those in which the precise block order is specified, are registered by the structure-based method and not by the source-based method.

6.3.4. SCION Nomenclature and Structure Representation. 6.3.4.1. Structure-Based Method. Block polymers are indicated in two ways. The polymer name carries the suffix ", BLOCK", and the text descriptor POLY-BLOCK is added.[10]

Example 6.3.4.1.1. Triblock of poly-oxyethylene, poly-oxypropylene, and poly-oxytetramethylene

Molecular formula: $[(C_4H_8O)n.(C_3H_6O)n.(C_2H_4O)n]x$

Structure
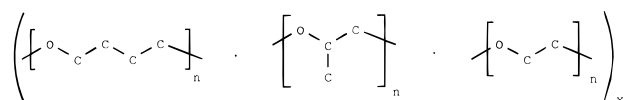
Polymer name: POLY-OXYETHYLENE/OXYPROPYLENE/OXYTETRAMETHYLENE, BLOCK
Text descriptor: POLY-BLOCK

Currently there is no precise indication of block sequence. Thus, it is not possible to distinguish between $(AAA..BBB..CCC)_n$, $(AAA..CCC..BBB)_n$, $(BBB..AAA..CCC)_n$, etc. Neither is it possible to distinguish between all-block polymers and part-block/part-random polymers. A precise text block notation system exists, but it has not yet been applied to block polymer registration.

6.3.4.2. Source-Based Method. Block polymers are named by alphabetizing the monomers, separating them with slashes, prefacing the result with POLY_CLASS- (in the case of PMC polymers) or POLY- (in the case of ASM polymers), and adding ", BLOCK" as a suffix. The text descriptor POLY-BLOCK is also added.

Example 6.3.4.2.1. A block polymer comprising a polyester segment from adipic acid and ethylene glycol, and a polyamide segment from ethylenediamine and oxalic acid

Structure

$(HO_2C\text{-}(CH_2)_4\text{-}CO_2H.H_2NCH_2CH_2NH_2.HOCH_2CH_2OH.$
$HO_2C\text{-}CO_2H)_x$

Polymer name: POLYAMIDE-ESTER-ADIPIC ACID/ETHYLENEDIAMINE/ETHYLENE GLYCOL/OXALIC ACID, BLOCK
Text descriptors: POLYAMIDE-ESTER; POLY-BLOCK

Precise block sequence information is not currently stored; thus, it is not possible to ascertain from either the polymer name or structure which acid is in the polyester segment and which is in the polyamide segment. However, should it be judged necessary (e.g., for business reasons) to store this information, a simple block sequence code in the form of a text descriptor could be added. Such a descriptor would enable distinction between:

POLYAMIDE-ETHYLENEDIAMINE/OXALIC ACID-BLOCK-POLYESTER-ADIPIC/ETHYLENE GLYCOL

and

POLYAMIDE-ADIPIC ACID/ETHYLENEDIAMINE-BLOCK-POLYESTER-ETHYLENE GLYCOL/OXALIC ACID

Example 6.3.4.2.2. A styrene/butadiene/styrene triblock polymer

Structure: $(CH_2{=}CH{-}CH{=}CH_2$. $Ph{-}CH{=}CH_2)_x$

Polymer name: POLY-1,3-BUTADIENE/STYRENE, BLOCK
Text descriptor: POLY-BLOCK

No distinction is currently made in either name or structure between the B/S diblock polymer poly-1,3-butadiene/styrene, the B/S/B triblock polymer poly-1,3-butadiene/styrene/1,3-butadiene, and the S/B/S triblock polymer poly-styrene/1,3-butadiene/styrene. As discussed above, a simple text sequence code could be implemented if necessary.

Notice in example 6.3.4.2.2 that styrene is allowed to appear only once in the structure record, regardless of whether the polymer is "poly-1,3-butadiene/styrene" or "poly-styrene/1,3-butadiene/styrene". Current CAS Registry System limitations prohibit registration of polymers with the same monomer appearing more than once, unless it is "nested" (parenthesized), such as part of a salt. Thus, attempted registration of the polymer of example 6.3.4.2.3 fails.

Example 6.3.4.2.3. Attempted literal registration of "poly-styrene/1,3-butadiene/styrene" by CAS Registry System (registration fails)

Structure (forbidden): $(Ph\text{-}CH{=}CH_2.CH_2{=}CH\text{-}CH{=}CH_2.$
$Ph\text{-}CH{=}CH_2)_x$

For linear block polymers containing a junction unit or "nonpolymeric spacer unit", the junction unit is named as an end group, although it is in the middle of the polymer. The text descriptor END GROUP, MULTICHAIN is added.

Example 6.3.4.2.4. $H_2N\text{-}[\text{polyethylene}]\text{-}CO_2H$ (polyethylene chain with one amino end group and one carboxy end group) and $H_2N\text{-}[\text{polystyrene}]\text{-}CO_2H$ (polystyrene chain with one amino end group and one carboxy end group) are coupled by esterification with 1,4-butanediol; notice that the nonrepeating ester groups become part of the multichain end group

Stored structure
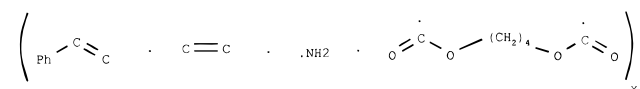
Polymer name: POLY-ETHYLENE/STYRENE, BLOCK, END GROUP AMINO, END GROUP TETRAMETHYLENEBIS(OXYCARBONYL)
Text descriptors: POLY-BLOCK; END GROUP, MULTICHAIN

Branched block polymers of the type
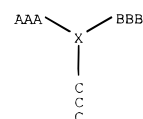
containing a junction unit X with a connectivity of three are discussed under comb polymers in section 6.4.4.

Although elastomers containing hard segments (e.g., polyesters from ethylene glycol and terephthalic acid) and soft segments [e.g., poly(oxyethylene) or poly(oxytetramethylene)] are blocky by nature, in SCION they are not classified or named as block polymers. Block polymers are also discussed elsewhere.[10]

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

REFERENCES AND NOTES

(1) MDL Information Systems, Inc., 14600 Catalina St. San Leandro, CA 94577. "Software for Chemical Research—Polymer Representation" (Second Draft).

(2) IUPAC. Glossary of Basic Terms in Polymer Science (1994 Draft) (Metanomski, W. V., Chemical Abstracts Service, personal communication, 1995).

(3) *Chemical Abstracts Index Guide*; Chemical Abstracts Service: Columbus, OH, 1994; Appendix IV, Section 222.

(4) Searching for Polymer Information in CAS ONLINE; Chemical Abstracts Service, March 1990, pages 110—118 (Publication C1EJ-0390).

(5) Ostrum, G. K.; Teague, S. J. Enhanced Access to Polymer Information from CAS. Presented as paper CINF-031, 210th ACS National Meeting, Chicago, IL, August 20—24, 1995.

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