

Enhanced Polymer Structure, Searching, and Retrieval in an Interactive Database

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A fully interactive, online, proprietary database that uses Chemical Abstracts Services (CAS) STN MESSENGER software is described. Recent enhancements offered by MESSENGER software for structure records for polymers make this a powerful, flexible tool for polymer registration, searching, and retrieval. Categorization, classification, and naming of polymers are explained. Polymer types include the following: (1) source-based condensation (polyamides, polyesters, polyimides, polyurethanes, and combinations of these, e.g., polyamide-esters); (2) other source-based [carbon-carbon multiple-bond (acetylenic, acrylic, ethylenic, vinyl); other (e.g., formaldehyde, melamine, phenol, urea)]; (3) structural repeating unit (constitutional repeating unit). Source-based versus structure-based representation is discussed. Nomenclature for polymer end groups is presented, together with their database registration. Aftertreated, alternating, block, comb, graft, ladder, and star-shaped polymers are also covered.

1. BACKGROUND

DuPont's original proprietary technical information system—established in 1964—and a later, enhanced version were described in earlier papers.^{1–5} The system comprised two computer-searchable files—a company technical and marketing reports index, based on a controlled-term vocabulary, and a topology-based Chemical Structure Storage and Search System (CS4). CS4 was an adaption of the Registry system developed by Chemical Abstracts Services (CAS)^{6,7} from work done initially by DuPont.⁸ A later version of CS4, renamed the Chemical Information System (CIS), incorporated several changes to the original, especially in the area of polymers.⁵ The original system was operated offline in batch mode and was—by today's standards—very difficult to search. In response to demand from the DuPont technical community for online access to this wealth of information, during the period 1988–1990 the system was converted to a private online database, named SCION, in the CAS Scientific and Technical Information Network (STN International).⁹

Concurrently with migration to STN International, several enhancements were added to the DuPont polymer nomenclature, classification, and retrieval system. These changes permitted much more detail in polymer registration and subsequent searching. The broad principles of DuPont polymer storage and retrieval methods, with emphasis on these enhancements, are described in this paper; examples of polymer syntheses are theoretical and may or may not have been reduced to practice.

2. POLYMER CLASSIFICATION

2.1. Polymer Categories. Polymers are classified into three broad categories, as shown in Table 1.

For category 1 polymers, the term preferred in SCION is “prescribed-monomer condensation” (PMC) or “condensation”. The closest equivalent in CAS and International Union of Pure and Applied Chemistry (IUPAC) polymer nomen-

Table 1. Polymer Categories

- | |
|--|
| 1. PRESCRIBED-MONOMER CONDENSATION (PMC) |
| 2. ACTUAL STARTING MONOMER (ASM) |
| 3. STRUCTURAL REPEATING UNIT (SRU) |

clature is “source-based” polymer, but there are key differences; these are explained in section 2.1.1 below.

For category 2 polymers, the term preferred for SCION is “actual starting material”; this is deliberately chosen to emphasize the contrast with category 1, in which the actual starting materials used for polymerization may or may not be part of the polymer structure or name (see section 2.1.1 for details). The closest CAS or IUPAC equivalent is source-based polymer.

For category 3 polymers, the term preferred for SCION is “structural repeating unit” (SRU), and this term is also used by CAS. IUPAC prefers the term “constitutional repeating unit” (CRU). The two are virtually synonymous.

Each of these is now described in more detail.

2.1.1. PMC Polymers. Based on their chemical constitution, all PMC polymers are assigned to one of fifteen polymer classes. In order to prevent duplicate registration, PMC polymers contain “stylized” component monomer names and molecular formulae, which may or may not be the actual substances used to prepare the polymers. For example, poly(ethylene terephthalate) can be prepared from

ETHYLENE GLYCOL and TEREPHTHALIC ACID

ETHYLENE GLYCOL and
TEREPHTHALOYL CHLORIDE

ETHYLENE GLYCOL and
TEREPHTHALIC ACID, DIMETHYL ESTER

TEREPHTHALIC ACID,
BIS(2-HYDROXYETHYL ESTER)

Regardless of the actual preparative route, this polymer is represented as if it had been prepared from the “stylized” monomers ethylene glycol and terephthalic acid, and is thus named

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POLYESTER-ETHYLENE GLYCOL/
TEREPHTHALIC

The stylized components of the simplest classes of PMC polymers are given in Table 2.

Replacement of oxygen in a functional group by other chalcogens to give polythioamides, polythioesters, etc. does not affect classification (i.e., a polythioamide is assigned to the polyamide class).

More complex PMC polymer classes are built up from combinations of these simple classes; e.g., a polymer prepared from a dicarboxylic acid, a diamine, and a diol is classified as a polyamide-ester. Polycarbonates are classed as polyesters; polyureas are classed as polyamides. Carbonic acid is omitted as a theoretical component of polyurethanes.

2.1.2. ASM Polymers. ASM polymers, for the purposes of registration, contain the names and molecular formulae of the actual substances used to prepare the polymers. Included in this group are acetylenic, acrylic, allyl, ethylenic, and vinyl polymers (substances that polymerize by the opening of a carbon-carbon multiple bond) as well as polyaldehydes, amines, phenols, ureas, etc.

2.1.3. SRU Polymers. An SRU polymer is characterized by having a structure such that the polymer is neither a PMC type nor an ASM type. The SRU is a sequence of atoms which, when repeated, makes up all or part of the polymer backbone.

3. POLYMER NOMENCLATURE

3.1. General Principles. A broad outline of how polymers are named is presented here. The many refinements and variations discussed in the sections following this one frequently affect the names of polymers, and these will become apparent later.

When naming a polymer, names of the actual or stylized monomeric components, or of the SRUs, are arranged alphabetically, with slashes between the components. Each polymer has only one name entry, and cross-referencing is unnecessary.

3.1.1. PMC Polymers. The name begins with the polymer class identifier, e.g., POLYESTER, and continues with the names of the stylized monomers in alphabetical order. A hyphen is used after the polymer class identifier and before the first monomer; monomers are separated by slashes.

Example 1: POLYESTER-ETHYLENE GLYCOL/
TEREPHTHALIC

Note that the word "ACID" is omitted after the word TEREPHTHALIC. Carboxylic acid moieties in PMC polymers are always stylized to the parent acid; therefore, it becomes unnecessary to write the word ACID after the name of the acid. Thus, in a PMC polymer, adipic acid becomes ADIPIC, terephthalic acid becomes TEREPHTHALIC, etc. In PMC polymers, maleic acid and fumaric acid appear as MALEIC and FUMARIC; in ASM polymers, where they polymerize ethylenically, they appear as MALEIC ACID and FUMARIC ACID.

For PMC polymers, key differences between SCION, CAS, and IUPAC representations are:

Table 2. Typical PMC Polymers

polymer class	min no. of components	stylized component(s)
POLYAMIDE	1	AMINO ACID
POLYAMIDE	2	MULTICARBOXYLIC ^a ACID/ MULTIAMINE ^a
POLYESTER	1	HYDROXY ACID
POLYESTER	2	MULTICARBOXYLIC ACID/ MULTIHYDROXY-CPD
POLYIMIDE	1	AMINOMULTICARBOXYLIC ACID
POLYIMIDE	2	MULTICARBOXYLIC ACID/ MULTIAMINE
POLYURETHANE	1	HYDROXYAMINE
POLYURETHANE	2	MULTIAMINE/ MULTIHYDROXY-CPD

^a The prefix MULTI is used within this table to denote a number higher than one; MULTI is used in preference to POLY in order not to convey a polymeric concept.

* PMC polymers are structured with stylized monomers, which may or may not be the actual monomers used in condensation polymerizations

* Only one systematic polymer name is used

* The PMC polymer class is incorporated into the polymer name

* In SCION, condensation-polymer nomenclature is consistent for polymers with any number of monomers. In contrast, CAS and IUPAC nomenclature rules vary according to the number of monomers; polymers with one or two monomers are likely to be named according to structure-representation rules, whereas polymers with three or more monomers are likely to be named according to source-monomer-representation rules.

3.1.2. ASM Polymers. The name begins with POLY- followed by the names of the monomers in alphabetical order. A hyphen is used after the initial POLY and before the first monomer; monomer names are separated by slashes.

Example 2: POLY-ETHYLENE/METHACRYLIC
ACID/STYRENE

Example 3: POLY-FORMALDEHYDE/MELAMINE

3.1.3. SRU Polymers. The name begins with POLY- followed by the names of the SRU components in alphabetical order. A hyphen is used after the initial POLY and before the first SRU component; components are separated by slashes.

Example 4: POLY-OXYMETHYLENE

Of course, no monomer corresponds to the name of the component in an SRU polymer; thus, there is no monomeric, polymerizable substance called oxymethylene. Although poly(oxymethylene) is typically made from formaldehyde, the polymer is not called poly(formaldehyde) (except as a trivial name or synonym); the repeating unit is $-OCH_2-$, and this is the basis for the SRU polymer name.

3.2. Polymer Category Preference. When polymers are named, category preference is

* PMC preferred to ASM

* ASM preferred to SRU

Thus, a PMC polymer is NEVER named as an SRU type.

Table 3. Examples of Mixed-Category Polymers

POLYAMIDE-ADIPIC/1,6-HEXANEDIAMINE WITH POLY-ETHYLENE	[categories 1 & 2]
POLYESTER-ETHYLENE GLYCOL/TEREPHTHALIC WITH POLY-OXYETHYLENE	[categories 1 & 3]
POLY-METHACRYLIC ACID, METHYL ESTER WITH POLY-OXYMETHYLENE	[categories 2 & 3]
POLYAMIDE-HEXANOIC, 6-AMINO- WITH POLY-ETHYLENE WITH POLY-OXYETHYLENE	[categories 1, 2, & 3]

This is in strong contrast to CAS and IUPAC practice, where the main entry for a one- or two-component PMC polymer is frequently in the SRU format, especially for common polymers such as poly(ethylene terephthalate) and nylon 66.

3.3. Mixed-Category Polymers. Polymers containing monomers in more than one category are named with the categories in order of priority, viz., PMC before ASM, ASM before SRU. The word WITH separates the categories IN THE POLYMER NAMES. After the word WITH the prefix POLY is repeated at the beginning of the new category. Some examples are shown in Table 3.

4. POLYMER REGISTRATION

4.1. General Principles. Registration is the process by which each chemical in the database is uniquely identified. Each chemical in the SCION database is assigned a serial number called a C-Number (CNUM). CNUMs are the DuPont equivalent of CAS registry numbers. The CNUM has up to six digits plus a computer-generated check letter added to minimize human error in CNUM handling, e.g., 174306W (for security reasons, all CNUMs in this paper are disguised). Registration is based mainly on chemical structure which is represented by a connection table, unique for each chemical in the system.

The record for a polymer is in two sections: textual and structure. For PMC and ASM polymers, the structure is stored in terms of its real or stylized component monomers. Thus, ETHYLENE is the component monomer for POLY-ETHYLENE homopolymer. For an SRU homopolymer, there is no component monomer, and the stored record takes a modified format. For SRU copolymers, the structure is stored in terms of the SRU homopolymers that together comprise the copolymer. End groups and/or other polymer radical fragments are included as if they were component monomers.

For each component of a polymer (other than an SRU homopolymer), the structural record contains the C-Number, the molecular formula, textual information indicating any special features of the component such as a 2:Z or 2:E designation, and a structure record. 2: indicates a CAS "type 2" substance, i.e., one having geometrical isomerism; an E or a Z indicates a trans or a cis isomer, respectively.

For an SRU homopolymer, the structural record contains the molecular formula enclosed within parentheses with a sub-n outside the closing parenthesis, textual information on any special features of the SRU such as a 2:Z or 2:E designation, and a structure record. Thus, poly(oxyethylene) has the molecular formula $(C_2H_4O)_n$.

4.2. PMC and ASM Polymer Registration. For PMC and ASM polymers, CNUMs of component monomers are used as part of the polymer record; CNUMs used in this way are called descriptors. Thus 172309E and 184920F, CNUMs for ethylene glycol and terephthalic acid, respectively, are descriptors for poly(ethylene terephthalate).

4.3. SRU Polymer Registration. A complex set of rules, based on a "priority" system for choosing a "head" atom

Table 4. Polymer Textual Descriptors

(a) PMC-Category Polymer Class Textual Descriptors	
POLYAMIDE	
POLYAMIDE-ESTER	
POLYAMIDE-ESTER-IMIDE-URETHANE	
POLYAMIDE-ESTER-IMIDE	
POLYAMIDE-ESTER-URETHANE	
POLYAMIDE-IMIDE	
POLYAMIDE-IMIDE-URETHANE	
POLYAMIDE-URETHANE	
POLYESTER	
POLYESTER-IMIDE	
POLYESTER-IMIDE-URETHANE	
POLYESTER-URETHANE	
POLYIMIDE	
POLYIMIDE-URETHANE	
POLYURETHANE	
(b) Other Textual Descriptors	
END GROUP POLYMERIZABLE CC	
END GROUP POLYMERIZABLE NON-CC	
END GROUP, MULTICHAIN	
POLY-AFTERTREATED	
POLY-ALTERNATING	
POLY-BLOCK	
POLY-COMB-OR-GRAFT	
POLY-HOMO	
POLY-LADDER	
POLY-MULTICATEGORY	
POLY-STAR	
POLY-THERMOSET	
POLYAFT-W	
POLYAFT-WT	

and determining which bond connected to it is broken, is used to register SRU polymers. The full set of these rules is beyond the scope of this paper. SRU homopolymers have a CNUM, but no monomer CNUM descriptors. SRU copolymers have CNUM descriptors; however, these are for SRU components and not real chemicals.

4.4. Textual Descriptors. Textual descriptors provide additional information for many polymers. These data are stored in a searchable field in SCION chemical records called the Controlled Term (CT) field and can be very useful in searching. PMC polymer classes, e.g., POLYAMIDE, POLYAMIDE-ESTER, etc. are examples of these descriptors. The textual descriptors currently in use are shown in Table 4. The textual descriptor field is "open ended", i.e., new textual descriptors can be added as required by changes in technology.

The PMC-category textual descriptors, instituted in the early 1960s, have been especially valuable in searches for these types of polymers. For example, a search for pure polyester quaterpolymers with search terms POLYESTER/CT and 4/NC [the /NC field qualifier in MESSENGER software can be used to specify how many components are required in a search statement in searches for multicomponent substances] retrieves polyester quaterpolymers quantitatively, while other polymer classes—polyamide-esters, polyester-imides, etc.—are automatically excluded.

The descriptors listed in part (b) of Table 4 are discussed in subsequent sections. Another type of descriptor, the

sequence descriptor, is discussed in section 10.

5. POLYMER BACKBONE TYPES

5.1. Homopolymers versus Nonhomopolymers. The concept of being able to identify any homopolymer easily was an important feature of the old DuPont private database before the ability to search polymers interactively by use of the /NC (number of components) field qualifier was made available by CAS. It is still a useful feature, and homopolymers are searchable by use of the controlled term POLY-HOMO as an alternative to use of the /NC field qualifier. This feature is especially valuable for retrieving homopolymers independently of whether end group fragments are part of the structure. Addition of end group fragments to a polymer's structure changes the number of components (/NC field qualifier), whereas the homopolymer concept is unchanged.

5.1.1. Definition of a Homopolymer. A polymer is classified as a homopolymer if it fulfills at least one of the following conditions:

1. The polymer is formed from one monomer.

Example 5: POLYAMIDE-BENZOIC,
P-AMINO- (example of PMC homopolymer)

Example 6: POLY-ETHYLENE
(example of ASM homopolymer)

2. The polymer is formed from two monomers, neither of which can polymerize by itself to form a PMC polymer.

Example 7: POLYAMIDE-1,6-HEXANEDIAMINE/
ISOPHTHALIC

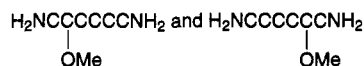
Example 8: POLYURETHANE-
ETHYLENEDIAMINE/POLY-OXYETHYLENE

3. The polymer name cites only one structural repeating unit (SRU).

Example 9: POLY-OXYETHYLENE
(example of SRU homopolymer)

Two-component PMC polymers containing asymmetrical component monomers that may polymerize randomly in "left-hand" or "right-hand" versions in the polymer chain are still classified as homopolymers; "handedness" is ignored in terms of classifying the polymer.

For example, POLYAMIDE-ADIPIC/1,6-HEXANEDIAMINE, 2-METHOXY- is classified as a HOMOPOLYMER, regardless of which way the 2-methoxy-1,6-hexanediamine units are aligned. Thus



are "the same" from the point of view of polymer registration.

In contrast, the following are *NOT* classified as homopolymers: 1. PMC polymers containing two component monomers (A and B) when A and B are not required to alternate to form the polymer and

Example 10: POLYAMIDE-BENZOIC,
P-AMINO-/BENZOIC, 4-AMINO-3-CHLORO-

(2) mixed category polymers that contain the word WITH

in the polymer name.

Example 11: POLYAMIDE-ADIPIC/
1,6-HEXANEDIAMINE WITH POLY-ETHYLENE

5.2. Random versus Nonrandom Polymers. A polymer is assumed to be random and is registered without special textual descriptor(s), when the source document either explicitly states that the polymer is random, or omits any discussion that it has special features, such as alternating, block, comb, star, etc. When a polymer has one or more special features, appropriate key words are built into the polymer name and/or textual descriptor field. Examples are ALTERNATING, BLOCK, COMB, GRAFT, and STAR.

5.3. Alternating Polymers. The word ALTERNATING in the polymer name and the textual descriptor POLY-ALTERNATING are used for copolymers and only when necessary.

Example 12: POLYAMIDE-1,4-BUTANEDIAMINE/
CARBONIC/P-PHENYLENEDIAMINE,
ALTERNATING

TEXTUAL DESCRIPTORS:
POLY-ALTERNATING; POLYAMIDE

The word ALTERNATING in the name indicates that the polymer has some kind of repeat pattern, as opposed to a completely random distribution of the two amines. Possibilities are ABCB, ABABCBCB (where A = 1,4-butanediamine; B = carbonic; C = *p*-phenylenediamine), etc. (and the name would be the same). The name indicates that the polymer is not random, but the precise nature of the alternation is not included in the polymer name.

Two-component PMC homopolymers such as POLYESTER-ETHYLENE GLYCOL/TEREPHTHALIC (PET) are not classified as alternating polymers. Although PET is alternating in the sense that the ethylene glycol and terephthalic moieties alternate, the term ALTERNATING would be superfluous because neither ethylene glycol nor terephthalic acid can itself produce a PMC polymer. PET is a homopolymer that can be neither an alternating polymer nor a block polymer.

Another case of an apparently alternating polymer that is not so named is POLY-CHLOROPRENE that is polymerized in the 1,4 mode and then hydrogenated. The final product looks identical with POLY-ETHYLENE/ETHYLENE, CHLORO-, ALTERNATING. However, it is named POLY-CHLOROPRENE, AFTERTREATED TO HYDRO. (Polymeric fragments such as HYDRO are discussed in section 9.)

5.4. Block Polymers. Polymers are registered as block polymers when they are so identified in source documents. Soft-segment elastomers (see below) are usually an exception. The word BLOCK appears in the polymer name, and the textual descriptor POLY-BLOCK is part of the polymer structural record.

Example 13: POLYAMIDE-BENZOIC,
M-AMINO-/BENZOIC, P-AMINO-, BLOCK

TEXTUAL DESCRIPTORS: POLYAMIDE;
POLY-BLOCK

No distinction is currently made between polymers that have the same component monomer combinations but different block arrangements.

Elastomers containing soft segments such as POLY-OXYPROPYLENE (example 14) are not classified as block polymers because they are blocky by nature, in the sense that the poly(oxypropylene) soft segment is a separate block. Therefore, soft-segment elastomers do not need to be identified by the word BLOCK. The poly(oxypropylene) is understood in this context to have hydroxy end groups; thus, it is a macrodiol.

Example 14: POLYESTER-ETHYLENE GLYCOL/
POLY-OXYPROPYLENE/TEREPHTHALIC

TEXTUAL DESCRIPTOR: POLYESTER

However, for a polymer that can be either blocky or random, further information is indicated in the name. Wherever possible, the precise section that is blocky is so noted and enclosed within parentheses for added clarity. Examples 15, 16, and 17 illustrate this.

Example 15: POLYESTER-ETHYLENE GLYCOL/
POLY-OXYETHYLENE/POLY-OXYPROPYLENE/
TEREPHTHALIC

TEXTUAL DESCRIPTOR: POLYESTER

Example 16: POLYESTER-ETHYLENE GLYCOL/
POLY-OXYETHYLENE/POLY-OXYPROPYLENE/
TEREPHTHALIC, BLOCK

TEXTUAL DESCRIPTORS: POLYESTER;
POLY-BLOCK

Example 17: POLYESTER-ETHYLENE GLYCOL/
(POLY-OXYETHYLENE/OXYPROPYLENE,
BLOCK)/TEREPHTHALIC

TEXTUAL DESCRIPTORS: POLYESTER;
POLY-BLOCK

The elastomer of example 15 contains two separate soft segments; poly(oxyethylene) and poly(oxypropylene). The name in example 16 is ambiguous because the position of the word BLOCK fails to specify in what way the polymer is blocky; therefore, the name is unacceptable unless the source document states only that it is a block polymer without specifying more precisely how the polymer is "assembled". Example 17 contains a soft segment that is a "preassembled" block polymer of poly(oxyethylene) and poly(oxypropylene).

5.5. Macromonomers. The term macromonomer, or macromer, is used somewhat loosely in polymer chemistry; it generally means "a macromolecule (i.e., a polymer) that functions as a giant monomer by virtue of one or more end groups that can enter into a further polymerization reaction". Macroamines or macrodiols are often used as monomers in PMC polymers, e.g., soft-segment elastomers. Macromonomers with reactive ethylenic or (meth)acrylic end groups at one end and inert groups at the other are often ASM or SRU types.

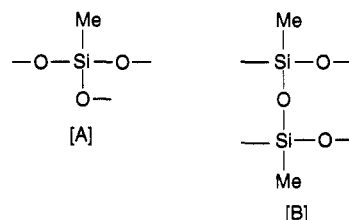
Macromonomers are registered with an appropriate textual descriptor such as END GROUP POLYMERIZABLE CC or END GROUP POLYMERIZABLE NON-CC. CC is a symbol for carbon-carbon multiple bond. The main poly-

meric components are registered, together with fragments representing polymerizable end groups. Nonreactive fragments, such as inert end groups, are named as part of the macromonomer and registered when identified by the source document. The derivation and nomenclature of end group names is discussed in section 6.

Example 18: POLY-ETHYLENE, TETRAFLUORO-, END GROUP HYDRO, END GROUP 3-(METHACRYLOYLOXY)PROPYL is registered with the CNUM for monomeric tetrafluoroethylene, the CNUM for the hydro end group fragment (.H), and the CNUM for the 3-(methacryloyloxy)propyl end group fragment (.CH₂-CH₂-CH₂-O-C(=O)-C(Me)=CH₂). Here, the CNUMs are in the Component Registry Number (CRN) field and are searchable by use of the /CRN field qualifier.

5.6. Branched SRU Polymers. The old DuPont database had a number of branched polymers represented by "trivalent" SRUs such as (METHYLSILYLIDYNE)TRIOXY. However, the CAS Registry system cannot accommodate structures having an odd number of open ends. In the SCION database, the problem was resolved by restructuring these SRU units to have an even number of "open ends". In most cases the SRU was "doubled", and three linking atoms were eliminated. This also brought the SRU closer to the ideal representation.

Example 19: (METHYLSILYLIDYNE)TRIOXY, structure A, was changed to (1,3-DIMETHYLDISILOXANE-DIYLIDENE)-1,3-DIOXY, structure B. Neither structure matches the ideal "(METHYLSILYLIDYNE)SESQUIOXY" (CH₃O_{1.5}Si), but B (C₂H₆O₃Si₂) is closer than A (CH₃O₃Si). Additionally, A implied a peroxy linkage, which was incorrect. B must be interpreted in the sense that when two SRUs are joined, Si may bond only to O, but this is true of most SRUs; for example, in poly(oxyethylene), -(OCH₂-CH₂)_n-, O may bond only to C. Structure B does NOT represent a ladder polymer.



5.7. Ladder Polymers. Ladder polymers are a special class of SRU polymers; they are composed of two or more linear polymer backbones connected by cross-links repeated regularly along the multiple-strand backbone. All backbone atoms are thus in fused or spiro rings. A complete set of rules for identifying, orienting, and naming ladder SRUs was developed by J. L. Schultz in the 1970s.¹⁰

5.8. Star-Shaped Polymers. Star-shaped—or, simply, "star"—polymers are characterized by having "arms" and a central core; the latter is frequently cross-linked.

Theoretically, the smallest number of arms radiating from a central, multiply substituted core in a star polymer is three. Thus, glycerol reacted with ethylene oxide could be called a star polymer. In practice, star polymers are registered as such only when the source document explicitly discusses either star polymers or star polymer technology. The word STAR appears in the polymer name, and the polymer carries the textual descriptor POLY-STAR.

No distinction is made in the naming of star polymers as to whether they are prepared "arm" first or core first. The "arms" may be block or random. Some examples follow.

Example 20: Methacrylic acid (MAA) and methyl methacrylate (MMA) are copolymerized until the monomers are virtually completely consumed; ethylene dimethacrylate (EDMA) is added to the living polymer to tie the arms together into a cross-linked core:

NAME: POLY-METHACRYLIC ACID/
METHACRYLIC ACID, ETHYLENE ESTER/
METHACRYLIC ACID, METHYL ESTER, STAR

TEXTUAL DESCRIPTOR: POLY-STAR

Example 21: Ethylene dimethacrylate (EDMA) is polymerized to create the core, and then methacrylic acid (MAA) and, subsequently, methyl methacrylate (MMA) are added to the living ends to create "blocky" arms:

NAME: POLY-METHACRYLIC ACID/
METHACRYLIC ACID, ETHYLENE ESTER/
METHACRYLIC ACID, METHYL ESTER,
BLOCK, STAR

TEXTUAL DESCRIPTORS: POLY-BLOCK,
POLY-STAR

5.9. Thermoset Polymers. Polymers that are thermosetting, rather than thermoplastic, have the textual descriptor POLY-THERMOSET.

Example 22: POLY-FORMALDEHYDE/PHENOL

TEXTUAL DESCRIPTOR: POLY-THERMOSET

5.10. Use of the "POLY-MULTICATEGORY" Textual Descriptor. The textual descriptor POLY-MULTICATEGORY is used for all polymers that contain more than one of the three categories PMC, ASM, SRU. However, the special-input-descriptor 8:DP,MUL is used only when it is necessary to distinguish between polymers of intellectually different compositions that have the same component monomer combination; compare examples 23 and 24.

Example 23: POLYESTER-ETHYLENE GLYCOL/
POLY-OXYETHYLENE/TEREPHTHALIC

Special-input-descriptor: none

Example 24: POLYESTER-ETHYLENE GLYCOL/
TEREPHTHALIC WITH POLY-OXYETHYLENE

Special-input-descriptor: 8:DP,MUL [The special-input-descriptor 8:DP was assigned by CAS to DuPont for exclusive use in SCION during substance registration. The "8:DP" segment is fixed, but the rest of the expression is free-text. Generally, in the free-text segment, the first three letters of a key word are used to indicate a substance's key property; thus, MUL indicates a multicategory polymer, FRA indicates a polymer fragment, etc. This special-input-descriptor is used especially to distinguish between different PMC polymer classes which have the same stylized monomers, e.g., polyamides and their corresponding polyimides. Other examples of the 8:DP special-input-descriptor are used elsewhere in this paper.]

Example 23 is a polyester elastomer containing a PEG soft segment. Example 24 is a polymer that contains a PET segment and a PEG segment; the source document does not explicitly state what kind of polymer it is. Some possibilities are the elastomer of example 23; a PET/PEG block polymer; or carboxy-ended PET that is "chain-extended" or "coupled" with PEG. In the absence of more information, a more precise polymer name is impossible unless unwarranted assumptions are made.

6. POLYMER END GROUPS

6.1. Introduction. In the SCION database, an end group is defined as a grouping of atoms that terminates a polymer backbone and is different from the main body of the polymer. An end group can be either literally on the end of a polymer chain or within a polymer. If it occurs within a polymer, it joins two or more identical or different polymer chains. End groups are further defined to include only groups that are different from those normally present on the polymer. By this definition POLY-OXYETHYLENE, which normally is terminated by "naturally occurring" hydro and hydroxy groups, i.e., H-(O-C-C)n-OH, would not qualify as a polymer with end groups cited in the polymer name. This is covered in more detail in section 6.2.3. End groups include as many atoms and/or groups as necessary until the group "touches" a "repeat unit", plus enough more to complete a functional group. A functional group is here defined as a complete group such as -CO₂H, -NH₂, -OH, or nonpolymeric derivatives thereof. For example, PET with acid ends capped by esterification with methanol is named

POLYESTER-ETHYLENE GLYCOL/
TEREPHTHALIC, END GROUP
METHOXYCARBONYL

not

END GROUP METHOXY

This rule is maintained even when carbonic acid is one of the components. Thus, the polyester prepared from phosgene and bisphenol A, and endcapped by esterification with ethanol, is named

POLYESTER-CARBONIC/PHENOL,
4,4'-ISOPROPYLIDENEDI-, END GROUP
ETHOXYCARBONYL

Connecting groups in polymers other than cross-linking moieties are known as multichain end groups. These are discussed in more detail in section 9.

End groups having free valencies are registered as separate entities. This procedure is different from the CAS practice of naming the end groups, totaling up the atoms in all the end groups, and placing them as a suffix in the molecular formula (MF) field after the polymer MF indicated by (...)x or (...)n. This is illustrated in more detail in section 6.2.2.

End groups are registered as if they were free radicals, diradicals, triradicals, etc. However, to distinguish them from genuine free radicals, they carry both the textual descriptor FRAGMENT, which is searchable, and the special-input-field textual descriptor 8:DP,FRA, which is added to circumvent possible rejection by the computer as a duplicate of a free radical with an identical structure. The 8:DP,FRA

descriptor displays as part of the structure record but is not currently searchable.

For example, the ACETOXY free radical and the END GROUP ACETOXY have identical structures, $\cdot\text{O}-\text{C}(=\text{O})-\text{CH}_3$, but the END GROUP ACETOXY carries the searchable textual descriptor FRAGMENT and the special-input-field textual descriptor 8:DP,FRA.

6.2. Nomenclature for Polymers Containing End Groups. **6.2.1. General Principles.** End groups are named from the outside toward the point of attachment, e.g., $\cdot\text{NH}-\text{C}(=\text{O})-\text{p}-\text{C}_6\text{H}_4-\text{Cl}$ is named P-CHLOROBENZAMIDO, and each is stored as a fragment.

Further examples are:

$\text{CH}_3-\text{C}(=\text{O})-\text{NH}\cdot$ ACETAMIDO

$\text{CH}_3-\text{O}-\text{C}(=\text{O})\cdot$ METHOXYCARBONYL

$\text{HO}_2\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{C}(=\text{O})\cdot$

(3-CARBOXYPROPOXY)CARBONYL

$\text{C}_1-\text{CH}_2-\text{CH}_2-\text{O}\cdot$ 2-CHLOROETHOXY

$(\text{CH}_3)_2\text{N}-\text{C}(=\text{O})\cdot$ DIMETHYLCARBAMOYL

In the naming of polymers, END GROUP terms follow the parts of the polymer name that cite the polymer class (if a PMC polymer), the component monomers, and any special attributes, such as BLOCK, STAR, etc.:

Example 25: POLYESTER-1,4-BUTANEDIOL/
ETHYLENE GLYCOL/ISOPHTHALIC,
BLOCK, END GROUP METHOXYCARBONYL

Even if both end groups of a polymer are identical, the end group is cited only once. Example 26 shows the name for the polyamide from adipic acid and 1,4-butanediamine with two acetamido end groups.

Example 26: POLYAMIDE-ADIPIC/
1,4-BUTANEDIAMINE, END GROUP ACETAMIDO

Polymers with two dissimilar end groups have both end groups named:

Example 27: POLYAMIDE-BENZOIC, P-AMINO-,
END GROUP BENZAMIDO, END GROUP
ETHOXYCARBONYL

For polymers with alternative structures for an end group, i.e., more than one structure is known to be present, alternative structures are named with slashes between them:

Example 28: POLY-METHACRYLIC ACID/
METHACRYLIC ACID, ETHYLENE ESTER/
METHACRYLIC ACID, METHYL ESTER,
BLOCK, STAR, END GROUP
1-((2-(ALLYLOXY)ETHOXY)CARBONYL)-
1-METHYLETHYL/2-(2-(ALLYLOXY)-
ETHOXY)CARBONYL)PROPYL

6.2.2. End Groups on SRU Polymers. End groups on SRU polymers are discussed in some detail because they represent a radical departure from current conventions, in contrast to most occurrences of end groups on PMC and ASM polymers.

End group nomenclature for SRU polymers in the standard chemical literature has posed problems for many years. Hydroxy-group-ended polyethylene glycol (PEG), usually represented as $\text{H}(\text{O}-\text{CH}_2-\text{CH}_2)_n\text{-OH}$, is used as an example here.

First, a nomenclature-versus-structure problem is immediately apparent. It is misleading to misrepresent one of the two hydroxy groups in PEG as a hydro group, because, chemically speaking, it is not. Viewed chemically, both ends in PEG are the same and deserve to be treated in the same way.

Secondly, there are the hazards of a nomenclature-driven system: whether to name the polymer $\text{POLY}(\text{OXY}-1,2\text{-ETHANEDIYL})$, $\alpha\text{-HYDRO-}\omega\text{-HYDROXY-}$ or $\text{POLY}(\text{OXY}-1,2\text{-ETHANEDIYL})$, $\alpha\text{-HYDROXY-}\omega\text{-ga-HYDRO-}$. (CAS text representations α and ω are used to indicate the first and last letters of the Greek alphabet.) A rule is needed to decide whether the size of the end group or its name and/or alphabetization determines its position in the polymer name.

Methoxy-PEG poses a similar problem—by the same argument, the methoxy group in methoxy-PEG should be recognized as a methoxy (ether) group, not as a methyl group. Similarly, nomenclature rules are needed to decide whether the end groups should be expressed as $\alpha\text{-HYDRO-}\omega\text{-METHOXY-}$ or $\alpha\text{-METHYL-}\omega\text{-HYDROXY-}$. When polyols like glycerol react with ethylene oxide, the confusion escalates rapidly with names like $\text{POLY}(\text{OXY}-1,2\text{-ETHANEDIYL})$, α , α' , α'' -1,2,3-PROPANETRIYL TRIS($\omega\text{-HYDROXY-}$).

The new method recognizes the chemical nature of each end group and stores a fragment that portrays its chemical structure as accurately as possible. Each end group is named according to its structure. The method introduces an extra atom that is not in the polymer, but the advantages are deemed to outweigh the disadvantages.

ADVANTAGES:

- * the name indicates the true and complete identity of the terminating end group
- * polymer name does not determine how end groups are named
- * each end group is named separately by a set of rules, and end group terms are added after the polymer name
- * Greek symbols such as α/ω , or α , α' , α''/ω , etc., are not needed

DISADVANTAGE:

- * an extra atom is apparently introduced

The examples given below illustrate the method.

Example 29: Polyethylene glycol with hydroxy end groups does not have the end groups cited in the polymer name unless the source document explicitly discusses them. Therefore, there are two entries for PEG—one without end groups, for source documents that cite no end groups, and one with one or two hydroxy end groups. CAS also has two entries—one for PEG with no end groups cited, and one that cites both end groups:

DUPONT NAME: POLY-OXYETHYLENE

TEXTUAL DESCRIPTOR: POLY-HOMO

MF: (C₂H₄O)_nDUPONT NAME: POLY-OXYETHYLENE,
END GROUP HYDROXY

TEXTUAL DESCRIPTOR: POLY-HOMO

MF: ((C₂H₄O)_n.HO)_x

Compare:

CAS NAME: POLY(OXY-1,2-ETHANEDIYL)

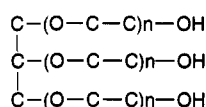
MF: (C₂H₄O)_nCAS NAME: POLY(OXY-1,2-ETHANEDIYL),
.alpha.-HYDRO-.omega.-HYDROXY-MF: (C₂H₄O)_n.H₂O

Note that the DuPont name POLY-OXYETHYLENE, END GROUP HYDROXY does not distinguish between (a) PEG with one hydroxy end group and one unknown end group and (b) PEG with hydroxy groups on both ends. To be 100% accurate would have required three names for PEG:

- (1) POLY-OXYETHYLENE
- (2) POLY-OXYETHYLENE, END GROUP
HYDROXY (one end -OH, other unknown)
- (3) POLY-OXYETHYLENE, END GROUP
HYDROXY, END GROUP HYDROXY or:
POLY-OXYETHYLENE, END GROUPS HYDROXY
(both ends hydroxy)

Distinction between (2) and (3) above is currently judged to be an unnecessary degree of detail.

Example 30: Glycerol is reacted with ethylene oxide; the resulting polymer is:



NAME: POLY-OXYETHYLENE, END GROUP
HYDROXY, END GROUP
1,2,3-PROPANETRIYLTRIOXY

TEXTUAL DESCRIPTORS: END GROUP,
MULTICHAIN; POLY-HOMO

Example 31: *N*-Acetyl-*p*-phenylenediamine is reacted with ethylene oxide; the product is deacetylated and reacted further with propylene oxide:

H(O-CH(CH₃)-CH₂)_x-(O-CH₂-CH₂)_y-NH-*p*-
C₆H₄-NH-(CH(CH₃)-CH₂-O)_zH

NAME: POLY-OXYETHYLENE/OXYPROPYLENE,
BLOCK, END GROUP HYDROXY, END GROUP
P-PHENYLENEDIIMINO

TEXTUAL DESCRIPTORS: END GROUP,
MULTICHAIN; POLY-BLOCK

6.2.3. Multichain End Groups. Polymers having connecting groups other than cross-linking moieties qualify for the textual descriptor END GROUP, MULTICHAIN.

Whether a polymer containing a multiradical fragment qualifies for the textual descriptor END GROUP, MULTICHAIN depends on the polymer, rather than on the fragment.

If the fragment is used as a starting point in the creation of a polymer containing two or more similar or dissimilar polymeric segments, or if it is created by reaction of end groups in such a way that polymer backbones are then "tied together" by the new fragment, it probably qualifies for the textual descriptor END GROUP, MULTICHAIN.

Example 32: A polymer prepared by reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidine (HTMP) with ethylene oxide qualifies for the textual descriptor END GROUP, MULTICHAIN, because ethylene oxide polymerizes from both the 4-OH group and the heterocyclic nitrogen; thus, HTMP becomes a diradical fragment embedded within the final polymer:

POLY-OXYETHYLENE, END GROUP HYDROXY,
END GROUP OXYETHYLENE(2,2,6,6-TETRA-
METHYL-1,4-PIPERIDINEDIYL)OXY

Example 33: A polymer with an isocyanate end group that trimerizes to a s-triazine ring with three polymer chains attached qualifies for the textual descriptor END GROUP, MULTICHAIN.

In contrast, a polymer containing a multiradical fragment that represents cross-linking does not qualify for the textual descriptor END GROUP, MULTICHAIN—see example 34.

Example 34: Polyethylene is treated with sulfuryl chloride to give chloro and chlorosulfonyl groups. The aftertreated (post-treated) polymer is further reacted with 1,4-butanedi-amine:

POLY-ETHYLENE, AFTERTREATED TO
((4-AMINOBTYL)AMINO)SULFONYL/
CHLORO/CHLOROSULFONYL/
TETRAMETHYLENEBIS(IMINOSULFONYL)

6.3. Implicit versus Explicit End Groups. It has already been stated in section 6.1 above that naturally occurring end groups of polymers, e.g., the hydroxy end groups of POLY-OXYETHYLENE are not cited when the polymers are incorporated as macromonomers in other polymers, e.g., a PMC polymer such as POLYESTER-POLY-OXYETHYLENE/TEREPHTHALIC. In these cases, the hydroxy end groups are implicit, both because they are naturally occurring in poly(oxyethylene), and because the -OH end group must be present for the polyester to be formed.

However, there are situations where polymer end groups are not implicit. In these cases, end groups are cited as part of the name, and end-group fragments are included as part of the polymer structure. Examples 35 and 36 illustrate the method.

Example 35: POLY-STYRENE, END GROUP
CARBOXY

Example 36: POLY-ISOPRENE, END GROUP
HYDROXY

It is desirable, although not essential, to know the exact linkage between the polymer chain and the end group, but,

Table 5. Graft Polymers

POLYAMIDE-ADIPIC/1,4-BUTANEDIAMINE,
GRAFT ACRYLAMIDE
POLY-ETHYLENE, GRAFT OXYETHYLENE
POLYAMIDE-ADIPIC/1,6-HEXANEDIAMINE,
GRAFT ESTER-ADIPIC/ETHYLENE GLYCOL
POLY-ACRYLONITRILE, GRAFT ESTER-
HYDRACRYLIC, 2,2-DIMETHYL-

Table 6. Nine Basic Comb Polymer Types

type	backbone type	side-chain
1	PMC	PMC
2	PMC	ASM
3	PMC	SRU
4	ASM	PMC
5	ASM	ASM
6	ASM	SRU
7	SRU	PMC
8	SRU	ASM
9	SRU	SRU

if this is not given in the source document, it is still helpful to indicate the end group(s) when known. Compare examples 37 and 38.

Example 37: POLY-OXYPROPYLENE, END
GROUP 2-AMINOPROPOXY
("Jeffamine" D series; exact end-group structure known)

Example 38: POLY-OXYPROPYLENE, END
GROUP AMINO (exact end-group structure
unknown; only the amino end groups are
known to be present)

This concept is extended to PMC polymers that contain such polymers functioning as macromonomers. Compare examples 39 and 40.

Example 39: POLYESTER-ADIPIC/ETHYLENE
GLYCOL/(POLY-STYRENE, END
GROUP CARBOXY)

Example 40: POLYESTER-ADIPIC/ETHYLENE
GLYCOL/(POLY-STYRENE, END
GROUP HYDROXY)

7. GRAFT AND COMB POLYMERS

7.1. Graft Polymers. The grafting of polymers is a significant field of technology. Grafting, as a distinct step in the manufacture of certain polymers, is given recognition in the names of DuPont polymers. The word GRAFT appears in polymer names, and the textual descriptor POLY-COMB-OR-GRAFT is used. The single textual descriptor POLY-COMB-OR-GRAFT is used both for graft polymers and for comb polymers, in preference to use of separate textual descriptors POLY-COMB and POLY-GRAFT, because comb polymers are sometimes referred to in source documents as graft polymers.

Graft polymers follow the nomenclature rules stated earlier, but with one important additional feature; the word GRAFT, while an integral part of the name, in effect divides the polymer name into two or more parts. Priority rules apply separately to each part. Table 5 gives some examples. NOTE: the prefix POLY is not repeated after the word GRAFT and before the grafted monomers cited in the poly-

mer name; for grafts of PMC monomers to a PMC polymer of a different PMC class or to ASM or SRU polymers, the PMC class is cited after the word GRAFT and before the grafted monomers are cited in the polymer name—see third and fourth examples in Table 5.

For block polymers that are grafted, the name states (in order) the alphabetized component monomers, the word BLOCK, and details of the graft.

Example 41: POLY-ACRYLIC ACID, ETHYL
ESTER/METHACRYLIC ACID, BLOCK,
GRAFT MALEIC ANHYDRIDE

TEXTUAL DESCRIPTORS: POLY-BLOCK;
POLY-COMB-OR-GRAFT

7.2. Comb Polymers. Comb polymer registration is sometimes a skillful combination of information from the source document and the knowledge and experience of the person registering the polymer. This is because, as mentioned above, some comb polymers are referred to in source documents as graft polymers.

As the name implies, comb polymers are in the shape of a comb; they are characterized by having polymeric side-chains, or "teeth", attached to or protruding from a polymeric backbone. Side chains are always "single-ended"—that is, they are attached to backbones by one end only. If they are double-ended, the polymer is not classified as a comb polymer.

All comb polymers are registered with the textual descriptor POLY-COMB-OR-GRAFT, but the word COMB is not a part of the polymer name. Comb polymers also have an additional textual descriptor such as END GROUP POLYMERIZABLE CC or END GROUP POLYMERIZABLE NON-CC. The first is for polymerizable end groups containing carbon-carbon multiple bonds, such as vinyl or (meth)acryloyl; the second is for other polymerizable end groups.

The nine basic types of comb polymer considered are summarized in Table 6. Key points on the nine types are as follows:

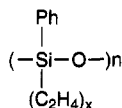
Types 1, 4, and 7: The side-chain is named using the rules for PMC polymers. The complete side-chain name, including the polymer type, stylized comonomers, and end group terms, is then parenthesized; this name is then alphabetized (on the P for POLY...), as if it were just another monomer, together with other comonomer names in the final polymer name. In type 1, the backbone and side-chain can contain the same PMC polymer class or two different ones.

Types 2, 5, and 8: The side-chain is named using the rules for ASM polymers. The complete name for the side-chain, including the end group terms, is then parenthesized; this name is then alphabetized (on the P for POLY...), as if it were just another monomer, together with other comonomer names in the final polymer name.

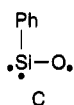
Types 3, 6, and 9: The side-chain is named using the rules for SRU polymers. The complete name for the side-chain, including the end group terms, is then parenthesized; this name is then alphabetized (on the P for POLY...), as if it were just another monomer, together with other comonomer names in the final polymer name.

Types 7, 8, and 9: Comb polymers with SRU backbones present a naming problem: how can an SRU polymer be named when it has another pendent polymer attached? The

current preferred method is to name the pendent polymer, together with its end groups, one of which is expressed as a multiradical; enclose this name in parentheses; and precede it with POLY-. This is preferred to naming the comb polymer without indicating the backbone SRU structure. Thus, when polyethylene with a dichlorophenylsilyl end group is polymerized under hydrolytic conditions, the name POLY-(POLY-ETHYLENE, END GROUP (PHENYLSILYLIDYNE)OXY) is used to represent the comb polymer



Nomenclature rules for multiradical polymer fragments such as (PHENYLSILYLIDYNE)OXY (structure C) are discussed elsewhere.¹¹



8. AFTERTREATED POLYMERS

8.1. Introduction. Aftertreatment processes, as distinct steps in the manufacture of certain polymers, are given recognition in the names of DuPont polymers. The words AFTERTREATED TO or AFTERTREATED WITH appear in polymer names, and the textual descriptor POLY-AFTERTREATED is used.

Aftertreated polymers follow the nomenclature rules stated earlier, but with an important additional feature; the words AFTERTREATED TO or AFTERTREATED WITH, while an integral part of the name, divide the polymer name into two or more parts. Priority rules apply separately to each part.

8.2. "AFTERTREATED TO" Polymers. Example 42 shows a typical aftertreated polymer—the preparation of an ionomer:

Example 42: POLY-ETHYLENE/METHACRYLIC ACID/STYRENE, AFTERTREATED TO METHACRYLIC ACID, ALUMINUM SALT

NOTE: The prefix POLY is not repeated after the words AFTERTREATED TO and before the aftertreated part of the polymer name.

The monomer theoretically created by the aftertreatment is named and added to the polymer name after the words AFTERTREATED TO, although it was never actually a monomer.

When multiple aftertreatments occur, all monomers theoretically created are alphabetized and placed in the polymer name after the words AFTERTREATED TO, regardless of the actual chemical sequence. Thus, a *p*-vinylbenzenesulfonic acid/styrene copolymer is aftertreated to the sulfonyl chloride and then to the sulfonamide; the polymer name is

POLY-BENZENESULFONIC ACID, P-VINYL-/STYRENE, AFTERTREATED TO BENZENESULFONAMIDE, P-VINYL-/BENZENESULFONYL CHLORIDE, P-VINYL-

TEXTUAL DESCRIPTOR: POLY-AFTERTREATED

For polymers that are both aftertreated and grafted, THE GRAFT PART ALWAYS PRECEDES THE AFTERTREATED PART in the polymer name, regardless of actual chemical sequence—see example 43.

Example 43: POLY-ACRYLIC ACID/ETHYLENE, GRAFT AMIDE-ADIPIC/1,5-PENTANEDIAMINE, AFTERTREATED TO ACRYLIC ACID, LITHIUM SALT/ACRYLIC ACID, POTASSIUM SALT

TEXTUAL DESCRIPTORS:

POLY-AFTERTREATED; POLY-COMB-OR-GRAFT

For block polymers that are aftertreated, the name states (in order) the alphabetized component monomers, the word BLOCK, and details of the aftertreatment—see example 44.

Example 44: POLY-ACRYLIC ACID, ETHYL ESTER/METHACRYLIC ACID, BLOCK, AFTERTREATED TO ACRYLIC ACID

TEXTUAL DESCRIPTORS:

POLY-AFTERTREATED; POLY-BLOCK

For block polymers that are both grafted and aftertreated, the name states (in order) the alphabetized component monomers, the word BLOCK, and details of the graft and aftertreatment—see example 45.

Example 45: POLY-ACRYLIC ACID/METHACRYLIC ACID, ETHYL ESTER, BLOCK, GRAFT MALEIC ANHYDRIDE, AFTERTREATED TO MALEIMIDE

TEXTUAL DESCRIPTORS:

POLY-AFTERTREATED; POLY-BLOCK;
POLY-COMB-OR-GRAFT

8.3. "AFTERTREATED WITH" Polymers. The expression AFTERTREATED WITH is used in a polymer name when one polymer is treated with another.

When the end result is known and chemically describable in terms of a new theoretical monomer formed, the format used is

POLY-MONOMER_A/MONOMER_B (etc.)
AFTERTREATED WITH POLY-MONOMER_C/
MONOMER_D (etc.) TO MONOMER_E

Such polymers carry the textual descriptors

POLY-AFTERTREATED and POLYAFT-WT

When the end result is unknown or chemically indescribable in terms of new theoretical monomers formed, the format used is

POLY-MONOMER_A/MONOMER_B (etc.)
AFTERTREATED WITH POLY-MONOMER_C/MONOMER_D (etc.)

Such polymers carry the textual descriptors

POLY-AFTERTREATED and POLYAFT-W

9. POLYMERIC FRAGMENTS OTHER THAN END GROUPS

Polymeric fragments other than end groups are registered as if they were free radicals, diradicals, triradicals, etc. They

also carry the special textual descriptor 8:DP,FRA to distinguish them from genuine free radicals (8:DP,FRA was explained in section 5.10).

These fragments usually arise from treatment of an already-formed polymer in such a way that their sites of attachment are not precisely known. Polymers containing these fragments are called "indefinite-aftertreatment" polymers to convey the concept that the aftertreatment occurred at an indefinite location.

The rules for naming "uniradical" polymeric fragments are the same as for end groups with one point of attachment; fragments are named from the outside toward the point of attachment. Thus, .SO₂-Cl is called CHLOROSULFONYL, and .SO₂-NH-Ph is called PHENYLSULFAMOYL. The rules for naming multiradical fragments are discussed elsewhere.¹¹

The post-chlorination of polyethylene is shown as example 46. During chlorination, chlorine atoms, which may be considered to be chloro groups, are attached at unknown sites to the polyethylene backbone. The product is named as an aftertreated polymer with the fragment as the aftertreated part of the name.

Example 46: POLY-ETHYLENE,
AFTERTREATED TO CHLORO
TEXTUAL DESCRIPTORS: POLY-
AFTERTREATED; POLYAFT-CHLORO

Note that for indefinite-aftertreatment polymers, the fragment name, preceded by POLYAFT-, is added as a searchable textual descriptor; thus, it can be retrieved by name, molecular formula, or CNUM.

If more than one fragment is attached by this indefinite aftertreatment process, the fragments are alphabetized and separated by slashes in the polymer name. Thus, treatment of polyethylene with sulfuryl chloride results in attachment of chloro and chlorosulfonyl groups at unknown sites on the polyethylene backbone. The resulting polymer—see example 47—is called

Example 47: POLY-ETHYLENE, AFTERTREATED
TO CHLORO/CHLOROSULFONYL
TEXTUAL DESCRIPTORS: POLY-
AFTERTREATED; POLYAFT-CHLORO;
POLYAFT-CHLOROSULFONYL

As in the case of aftertreated polymers discussed above when the precise location of the aftertreatment is known, when multiple indefinite aftertreatments occur, the fragments created are alphabetized and placed in the polymer name after the words AFTERTREATED TO, regardless of the actual chemical sequence. If the polymer of example 47 is further treated with 1,6-hexanediamine, some cross-linking occurs; the resulting polymer is named as shown in example 48.

Example 48: POLY-ETHYLENE, AFTERTREATED
TO ((6-AMINO-HEXYL)AMINO)SULFONYL/
CHLORO/CHLOROSULFONYL/
HEXAMETHYLENEBIS(IMINO-SULFONYL)

TEXTUAL DESCRIPTORS:

POLY-AFTERTREATED;
POLYAFT-((6-AMINOHEXYL)AMINO)-
SULFONYL; POLYAFT-CHLORO;
POLYAFT-CHLOROSULFONYL; POLYAFT-
HEXAMETHYLENEBIS(IMINOSULFONYL)

The HEXAMETHYLENEBIS(IMINOSULFONYL) diradical fragment of structure [.SO₂-NH-(CH₂)₆-NH-SO₂.] is created in this polymer as a result of cross-linking between .SO₂-Cl groups on two different polymer chains.

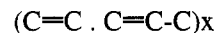
10. SPECIAL INPUT FIELD CODES

10.1. Sequence Descriptors. With the transfer of polymer records to SCION, several polymer registration problems were encountered. These had to be resolved to avoid rejection during registration of some pairs or groups of polymers that are intellectually different but were "perceived" as duplicates by the computer registration process.

Intellectually, the three polymers

1. POLY-ETHYLENE/PROPENE
2. POLY-ETHYLENE, GRAFT PROPENE
3. POLY-PROPENE, GRAFT ETHYLENE

are different, but in SCION the computer-stored chemical descriptors for all three are identical.



The textual descriptor POLY-COMB-OR-GRAFT is part of the record for polymers 2 and 3, and, although it is usable at search, it is not "considered" by the computer to be a distinguishing feature during registration. Thus, once any one of these three is registered, input of the others is rejected as a "duplicate".

Sequence descriptors were invented to overcome this registration problem. They are stored in the special input (STE) field which is considered in the registration process. Polymer 1 above would not be assigned a sequence descriptor, and polymers 2 and 3 would have different descriptors, which assures acceptance of all three as unique polymers.

Sequence descriptors are currently used only for graft and aftertreated polymers. Graft polymer sequence descriptors contain the letter G in the sequence. Aftertreated polymer sequence descriptors contain the letter A in the sequence. "Graft + aftertreated" polymer sequence descriptors contain both the letter G and the letter A in the sequence.

10.1.1. Sequence Descriptors for Graft Polymers. Examples of sequence descriptors for some graft polymers are shown in Table 7. All eight polymers are computer-stored as (C=C . C=C-C)x, because a monomer is not repeated within a polymer storage record unless "bound", e.g., as a salt or complex. Thus, attempted registration of (C=C . C=C . C=C-C)x fails. The sequence descriptor is the only feature that individualizes each polymer.

10.1.2. Sequence Descriptors for Aftertreated Polymers. The same problem that has been described in the preceding section also applies to aftertreated polymers versus copolymers having the same monomer combinations. For example, if polymer 1 in Table 8 is already registered, attempts to register polymers 2 and/or 3 will fail.

Table 7. Sequence Descriptors for Graft Polymers Containing Ethylene and Propene Molecular Formula (C₂H₄.C₃H₆)_x

polymer name	sequence descriptor
1. POLY-ETHYLENE/PROPENE	none
2. POLY-ETHYLENE, GRAFT PROPENE	1G2
3. POLY-PROPENE, GRAFT ETHYLENE	2G1
4. POLY-ETHYLENE/PROPENE, GRAFT ETHYLENE	12G1
5. POLY-ETHYLENE/PROPENE, GRAFT PROPENE	12G2
6. POLY-ETHYLENE, GRAFT ETHYLENE/ PROPENE	1G12
7. POLY-PROPENE, GRAFT ETHYLENE/ PROPENE	2G12
8. POLY-ETHYLENE/PROPENE, GRAFT ETHYLENE/PROPENE	12G12

Table 8. Sequence Descriptors for Aftertreated Polymers Containing Acrylic Acid and Methyl Acrylate

polymer name	sequence descriptor
1. POLY-ACRYLIC ACID/ACRYLIC ACID, METHYL ESTER	none
2. POLY-ACRYLIC ACID, AFTERTREATED TO ACRYLIC ACID, METHYL ESTER	1A2
3. POLY-ACRYLIC ACID, METHYL ESTER, AFTERTREATED TO ACRYLIC ACID	2A1

To circumvent this problem, sequence descriptors are used, both to ensure uniqueness during registration and to provide an additional textual descriptor for searching.

10.1.3. Derivation of Sequence Descriptors. A sequence descriptor is derived as follows:

1. Alphabetize all the monomers in a polymer name (regardless of the actual order in the polymer name).
2. Delete any duplicates.
3. Number the remaining monomers 1, 2, 3, etc.
4. Apply the numbers to the monomers in their correct positions in the polymer name. Use G for the word GRAFT and A for the word AFTERTREATED.
5. The order in which the numbers now read, with the letters A and/or G inserted, becomes the sequence descriptor.

**Example 49: POLY-ETHYLENE/PROPENE,
GRAFT ETHYLENE**

[1] ETHYLENE; ETHYLENE; PROPENE

[2] ETHYLENE; PROPENE

[3] ETHYLENE = 1; PROPENE = 2

[4] POLY-ETHYLENE/PROPENE,
GRAFT ETHYLENE

[5] 12G1

Because the special input field for chemical substances is not searchable by MESSENGER software, the sequence descriptor is also stored as a searchable controlled term. Its use as a search term can give precise retrieval of the desired polymer. Thus, a search for POLY-ETHYLENE/PROPENE, GRAFT ETHYLENE with the following logic:

Search (303492G AND 208569E)/CRN
AND 2/NC AND PMS/CI

where: 303492G = CNUM for ethylene)

208569E = CNUM for propene

CRN = Component Registry Number

NC = number of components

PMS = polymers

CI = class identifier)

retrieves all eight polymers in Table 7. Note that in the above search logic, 2/NC is used, not 3/NC, because the polymer record contains the CNUM for ethylene only once, in spite of the fact that the word ETHYLENE appears twice in the polymer name.

Addition to the search logic of the search term POLY-COMB-OR-GRAFT does not solve the problem. The logic

Search (303492G AND 208569E)/CRN
AND 2/NC AND POLY-COMB-OR-GRAFT/CT

still retrieves seven of the eight (Numbers 2–8) in Table 7.

Addition of the correct sequence descriptor to the search logic pinpoints the required polymer. The logic:

Search (303492G AND 208569E)/CRN AND
2/NC AND POLY-COMB-OR-GRAFT/CT
AND 12G1/CT

retrieves only polymer no. 4 in Table 7.

10.2. Polymer Class Special Input Codes. Polymer class textual descriptors assigned to PMC polymers are likewise not “considered” to be a distinguishing feature during registration. This can result in problems in registration of certain polyamides and polyimides. For example, once a polyimide is registered, an attempt to register the corresponding intermediate polyamic acid (which is registered in SCION as a polyamide) fails because the monomer combination is the same for both polymers; the computer does not “consider” the textual descriptors POLYAMIDE or POLYIMIDE during registration. To circumvent this problem, a polymer class symbol is used in the special input field. These are tabled in Table 9.

11. SUMMARY

The combination of a fully interactive, online database, and recent enhancements in structure records has created a powerful, flexible tool for polymer registration, searching, and retrieval. Key structure enhancements discussed are

- * Implementation of a comprehensive system for registering and naming comb polymers
- * Implementation of registration of alternating, block, and star polymers
- * Implementation of registration of molecular structures for fragments of aftertreated (posttreated) polymers as separate, searchable entities, and development of a nomenclature system for them
- * Inclusion in polymer names of end groups in a novel way that circumvents use of Greek letters (.alpha., .omega., etc.) and development of a nomenclature system for them
- * Structuring and registration of polymer end groups as separate entities, which permits them to be searched by molecular formula and/or name

Table 9. Special Input Field Codes for PMC Polymers To Ensure Uniqueness at Registration

PMC polymer class	polymer class symbol
POLYAMIDE	PA
POLYAMIDE-ESTER	PAE
POLYAMIDE-ESTER-IMIDE	PAEI
POLYAMIDE-ESTER-IMIDE-URETHANE	PAEIU
POLYAMIDE-ESTER-URETHANE	PAEU
POLYAMIDE-IMIDE	PAI
POLYAMIDE-IMIDE-URETHANE	PAIU
POLYAMIDE-URETHANE	PAU
POLYESTER	PE
POLYESTER-IMIDE	PEI
POLYESTER-IMIDE-URETHANE	PEIU
POLYESTER-URETHANE	PEU
POLYIMIDE	PI
POLYIMIDE-URETHANE	PIU
POLYURETHANE	PU

* Implementation of sequence descriptors to circumvent computer rejection (during registration) of intellectually different polymers perceived by the computer to be "duplicates" and to enhance retrieval accuracy with some types of search queries

* Resolution of the classic "(methylsilylidyne)sesquioxo" structure dilemma to provide an SRU with correct Si/O atom ratio and structure indexable with MESSENGER software.

* Implementation of special-input-field codes, to ensure uniqueness at registration, for (1) PMC polymers of different classes with the same monomer combinations (e.g., polyamides vs polyimides); (2) polymers with special features

(e.g., alternating, block, comb, graft, ladder, star) vs homopolymers or random copolymers with the same combination of monomers. Special textual descriptors were also developed as an aid to searching.

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