Name of the Teacher: DR. SUBHANKAR SARDAR Class: Semester-6 Paper: DSE-4 (Polymer Chemistry) Topic: Nomenclature of polymers.

Comments: Read as much as you can.

Reference: Polymer Chemistry book by Carraher

Polymer Nomenclature

As with most areas of science, names associated with reactions, particular chemical and physical tests, etc., were historically derived with few overall guiding principles. Further, the wide diversity of polymer science permitted a wide diversity in naming polymers. Even though the International Union of Pure and Applied Chemistry (IUPAC) has a long-standing commission associated with the nomenclature of polymers [reports include "Report on nomenclature in the field of macromolecules," *Journal of Polymer Science*, *8*, 257 (1952); "Report on nomenclature dealing with steric regularity in high polymers," *Pure and Applied Chemistry*, *12*, 645 (1966); "Basic definitions of terms relating to polymers," *IUPAC Information Bull*. App., *13*, 1 (1971); and "Nomenclature of regular single-strand organic polymers," *Macromolecules*, *6*(2), 149 (1973)], most of these suggestions for naming of simple polymers have not yet been accepted by many in the polymer science community.

Although there is wide diversity in the practice of naming polymers, we will concentrate on the most utilized systems.

COMMON NAMES

Little rhyme or reason is associated with the common names of polymers. Some names are derived from the place of origin of the material, such as *Hevea brasiliensis*—literally "rubber from Brazil"—for natural rubber. Other polymers are named after their discoverer, as is Bakelite, the three-dimensional polymer produced by condensation of phenol and formaldehyde, which was commercialized by Leo Baekeland in 1905.

Portions adapted from C. Carraher, G. Hess, and L. Sperling, *J. Chem. Ed.*, 64(1), 36 (1987) and L. H. Sperling W. V. Metanomski, and C. Carraher, *Appl Polym Science* (C. Craver and C. Carraher, eds.), Elsevier, New York, 2000.

For some important groups of polymers, special names and systems of nomenclature were invented. For example, the nylons were named according to the number of carbons in the diamine and carboxylic acid reactants (monomers) used in their syntheses. The nylon produced by the condensation of 1,6-hexanediamine (6 carbons) and sebacic acid (10 carbons) is called nylon-6,10.



Similarly, the polymer from 1,6-hexanediamine and adipic acid (each with 6 carbons) is called nylon-6,6 or nylon-66, and the nylon from the single reactant caprolactam (6 carbons) is called nylon-6.

SOURCE-BASED NAMES

Most polymer names used by polymer scientists are source-based; i.e., they are based on the common name of the reactant monomer, preceded by the prefix "poly." For example, polystyrene is the most frequently used name for the polymer derived from the monomer 1-phenylethene, which has the common name styrene.



The vast majority of polymers based on the vinyl group $(CH_2 = CHX)$ or the vinylidene group $(CH_2 = CX_2)$ as the repeat unit are known by their source-based names. For example, polyethylene is derived from the monomer ethylene, poly(vinyl chloride) from the monomer vinyl chloride, and poly(methyl methacrylate) from methyl methacrylate:



Many condensation polymers are also named in this manner. In the case of poly(ethylene terephthalate), the glycol portion of the name of the monomer, ethylene glycol, is used in constructing the polymer name, so that the name is actually a hybrid of a sourcebased and a structure-based name.



This polymer is well known by trade names, such as Dacron, or its common grouping, polyester.

Although it is often suggested that parentheses be used in naming polymers of more than one word [like poly(vinylidene chloride)] but not for single-word polymers (like polyethylene), many authors omit entirely the use of parentheses for either case (like polyvinylidene chloride). Thus there exists a variety of practices with respect to even source-based names.

Copolymers are composed of two or more monomer units. Source-based names are conveniently used to describe copolymers by using an appropriate term between the names of the monomers. Any of a half dozen or so connecting terms may be used, depending on what is known about the structure of the copolymer. When no information is specified about the sequence of monomer units in the copolymer, the connective term *co* is used in the general format poly(A-*co*-B), where A and B are the names of the two monomers. An unspecified copolymer of styrene and methyl methacrylate would be called poly[styrene-*co*-(methyl methacrylate)].

Kraton, the yellow rubber-like material on the bottom of many running shoes, is an example of a copolymer about which structural information is available. It is formed from a group of styrene units, i.e., a "block" of polystyrene, attached to a group of butadiene units, or a block of polybutadiene, which is attached to another block of polystyrene forming a triblock copolymer. The general representation of such a block copolymer is —AAAAABBBBBAAAAA—, where each A or B represents an individual monomer unit. The proper source-based name for Kraton is polystyrene-*block*-polybutadiene-*block*-polybutadiene-*block*-polystyrene, with the prefix "poly" being retained for each block.

STRUCTURE-BASED NAMES

Although source-based names are generally employed for simple polymers, the international body responsible for systematic nomenclature of chemicals, IUPAC, has published a number of reports for the naming of polymers, now being accepted for more complex polymers. The IUPAC system names the components of the repeat unit, arranged in a prescribed order. The rules for selecting the order of the components to be used as the repeat unit are found elsewhere [*Macromolecules*, 6(2), 149 (1973); *Pure and Applied Chemistry*, 48, 373 (1976), 57, 149 (1985), and 57, 1427 (1985)]. However, once the order is selected, the naming is straightforward for simple linear molecules, as indicated in the following examples:



A listing of source- and structure-based names for some common polymers is given in Table 1.

LINKAGE-BASED NAMES

Many polymer "families" are referred to by the name of the particular linkage that connects the polymers (Table 2). The family name is "poly" followed by the linkage name. Thus,

 Table 1
 Source- and Structure-Based Names

Source-based names	Structure-based names
Polyacrylonitrile	Poly(1-cyanoethylene)
Poly(ethylene oxide)	Polyoxyethylene
Poly(ethylene terephthalate)	Polyoxyethyleneoxyterephthaloyl
Polyisobutylene	Poly(1,1-dimethylethylene)
Poly(methyl methacrylate)	Poly[(1-methoxycarbonyl)-1-methylethylene]
Polypropylene	Poly(1-methylethylene)
Polystyrene	Poly(1-phenylethylene)
Polytetrafluoroethylene	Polydifluoromethylene
Poly(vinyl acetate)	Poly(1-acetoxyethylene)
Poly(vinyl alcohol)	Poly(1-hydroxyethylene)
Poly(vinyl chloride)	Poly(1-chloroethylene)
Poly(vinyl butyral)	Poly[(2-propyl-1,3-dioxane-4,6-diyl)methylene]

Family name	Linkage	Family name	Linkage
Polyamide	_N−C−	Polyvinyl	-c-c-
Polyester		Polyanhydride	
Polyurethane	_o−_c−_n−	Polyurea	o ∥ −n−C−n−
Polyether	-0-	Polycarbonate	
		Polyphosphate ester	0 -0-P-0-R-
Polysiloxane	-O-Si-		OR
Polysulfide	—S—R—	Polysuifones	

Table 2Linkage-Based Names

those polymers that contain the carbonate linkage are known as polycarbonates; those containing the ether linkage are called polyethers, etc.

CHEMICAL ABSTRACTS-BASED POLYMER NOMENCLATURE

The most complete indexing of any scientific discipline is done in chemistry and is provided by Chemical Abstracts (CA). Almost all of the modern searching tools for chemicals and chemical information depend on CA for at least some of their information base. It is critical for polymer chemists to have some grasp of how CA names chemical compounds. The full description of the guidelines governing the naming of chemical compounds and related properties is given in Appendix IV at the end of the CA *Index Guide*. This description is about 200 pages. While small changes are made with each new edition, the main part has remained largely unchanged since 1972.

CA organizes the naming of materials into twelve major arrangements that tie together about 200 subtopics. These main topic headings are

- A. Nomenclature systems and general principles
- B. Molecular skeletons
- C. Principal chemical groups
- D. Compound classes
- E. Stereochemistry and stereoparents
- F. Specialized substances
- G. Chemical substance names for retrospective searches
- H. Illustrative list of substituent prefixes
- J. Selective bibliography of nomenclature of chemical substances
- K. Chemical prefixes
- L. Chemical structural diagrams from CA Index Names
- M. Index

The section dealing with polymers is subtopic 222: Polymers. The subsection on polymers builds on the foundations given before. Some of the guidelines appear to be confusing and counterproductive to the naming of polymers, but the rules were developed for the naming of small molecules. Following is a description of the guidelines that are most important to polymer chemists. Additional descriptions are found in the CA Appendix IV itself and in articles listed in the readings. Appendix IV concentrates on linear polymers. A discussion of other more complex polymeric materials is also found in articles cited in the readings section.

General Rules

In the chemical literature—in particular, systems based on Chemical Abstracts—searches for particular polymers can be conducted using the Chemical Abstracts Service number, (CAS #) (where known) or the repeat unit. The International Union of Pure and Applied Chemistry (IUPAC) and CAS have agreed on a set of guidelines for the identification, orientation, and naming of polymers based on the structural repeat unit (SRU). IUPAC refers to polymers as "poly(constitutional repeat unit)" while CAS utilizes a "poly(structural repeating unit)." These two approaches typically give similar results.

Here we will practice using the sequence "identification, orientation, and naming," first by giving some general principles and finally by using specific examples.

In the *identification* step, the structure is drawn, usually employing at least two repeat units. Next, in the *orientation* step, the guidelines are applied. Here we concentrate on basic guidelines. Within these guidelines are subsets of guidelines that are beyond our scope.

Structures will generally be drawn in the order, from left to right, in which they are to be named.

Seniority

The starting point for the naming of a polymer unit involves determining seniority among the subunits.

A. This order is

Heterocyclic rings> Greatest number of most preferred acyclic heteroatoms> Carbocyclic rings> Greatest number of multiple bonds> Shortest path or route (or lowest locant) to these substituents Chains containing only carbon atoms.

with the symbol ">" indicating "is senior to." This is illustrated below.



This order is partially derived from guidelines found in other sections such as Section 133, Compound Radicals, where the ordering is given as

Greatest number of acyclic hetero atoms> Greatest number of skeletal atoms> Greatest number of most preferred acyclic hetero atoms> Greatest number of multiple bonds> Lowest locants or shortest distance to nonsaturated carbons.

The lowest locant or shortest distance refers to the number of atoms from one senior subunit to the next most senior subunit when there is only one occurrence of the senior subunit.

This order refers to the backbone and not substitutions. Thus, polystyrene and poly(vinyl chloride) are contained within the "chains containing only carbon atoms" grouping. B. For ring systems the overall seniority is

Heterocyclic> Carbocyclic

but within the rings there is also an ordering (Section 138) that is

Nitrogenous heterocyclic> Heterocyclic> Largest number of rings> Cyclic system occurring earliest in the following list of systems spiro, bridged fused, bridges nonfused, fused> Largest individual ring (applies to fused carbocyclic systems)> Greatest number of ring atoms

For example,



C. For hetero-atomed linear chains or cyclic rings, the order of seniority is O > S >Se > Te > N > P > As > Sb > Bi > Si > Ge > Sn > Pb > B > Hg.

Thus, because $-O - CH_2$ —is senior to $-S - CH_2$ —, it would be named first in a polymer that contained both $-O - CH_2$ — and $-S - CH_2$ —segments. Further, a polymer containing these alternating units would *not* be poly(thiomethyleneoxymethylene) but would be named poly(oxymethylenethiomethylene).

Another example,

is named poly[oxy(1-oxy-1,2-ethanediyl)] or less preferred poly[oxy(1-oxoethylene)] but not poly[(2-oxo-1,2-ethanediyl)oxy] or poly[(2-oxoethylene)oxy].

D. In rings, unsaturation is senior to saturation. The more unsaturated, the more senior with all other items being equal. Thus 1,4-phenylene is senior to 2,5-cyclohexadiene-1,4-diyl, which in turn is senior to 2-cyclohexene-1,4-diyl, which is senior to 1,4-cyclohexaned-

iyl. For linear chains —CH=CH=CH=CH= is senior to —CH=CH=CH_2—CH $_2$ —, which is in turn senior to the totally saturated chain segment.

Route

B. Where path lengths are equal, such as in some nylons, the repeat unit is named so that the heteroatom "N" is first named and then the more highly substituted (carbonyl) unit appears next. Thus, nylon 3,3, with the structure

$$\begin{array}{ccc} & O & O \\ \parallel & \parallel \\ --(--NH-C--CH_2--C--NH--CH_2---CH_2---CH_2--)_n--- \end{array}$$

is named poly[imino(1,3-dioxo-1,3-propanediyl)imino-1,3-propanediyl].

C. In otherwise identical subunits, there are three items to be considered in decreasing order of importance:

- 1. Maximum substitution: thus, 2,3,5-trichloro-*p*-phenylene is senior to 2,5-dichloro-*p*-phenylene which in turn is senior to 2-chloro-*p*-phenylene,
- 2. Lowest locants: thus, 2,3-dichloro-*p*-phenylene is senior to 2,5-dichloro-*p*-phenylene,
- 3. Earliest alphabetical order: thus, 2-bromo-*p*-phenylene is senior to 2-chloro-*p*-phenylene that is senior to 2-iodo-*p*-phenylene.

D. Where there is no conflict with other guidelines, multiple bonds should be assigned the lowest locants; in rings, double bonds are senior to single bonds; in acyclic carbon chains, double bonds are senior to triple bonds, which are in turn senior to single bonds. Thus, the polymer from 1,3-butanediene polymerized in the so-called "1,4—" mode is usually drawn as -(-C-C-C--)- but it is named as drawn as -(-C-C-C--)- and named poly(1-butene-1,4-diyl) with the appropriate "cis-" or "trans-" designation. Polyisoprene, typically drawn as

$$-(-CH_2-C(CH_3)=CH-CH_2-)_n$$

is frequently named poly(2-methyl-1,3-butadiene) but it is named as though its structure is

$$-(C(CH_3) = CH - CH_2 - CH_2 -)_n$$

with the name poly(1-methyl-1-butene-1,4-diyl).

Substituents are named as one of several classes. The most important ones are dealt with here. For monoatomic radicals from borane, methane, silane (and other Group IVA elements) they are named by replacing the "ane" ending with "yl," "ylene," and "ylidyne" to denote the loss of one, two, or three hydrogen atoms, respectively.

 H_2B — boryl H_3C — methyl H_2C = methylene HC= methylidyne

Acyclic hydrocarbon radicals are named from the skeletons by replacing "ane," "ene," and "yne" suffixes by "yl," "enyl," and "ynyl," respectively.

$$\begin{array}{c} CH_3 \longrightarrow CH_2 \longrightarrow ethyl \quad CH_3 \longrightarrow CH_2 \longrightarrow CH_2 \longrightarrow Propyl \quad \label{eq:ch2} \longrightarrow CH_2 \longrightarrow CH_$$

Table 3 contains the names of selected bivalent radicals that may be of use to polymer chemists.

Searching

Polymers from a single monomer are indexed at the monomer name with the term "homopolymer" cited in the modification. Thus, polymers of 1-pentene are listed under the monomer

1-Pentene

homopolymer

Polymers formed from two or more monomers such as condensation polymers and copolymers, and homopolymers are indexed at each inverted monomer name with the modifying term "polymer with" followed by the other monomer names in uninverted alphabetical order. The preferential listing for identical heading parents is in the order: (a) maximum number of substituents, (b) lowest locants for substituents, (c) maximum number of occurrences of index heading parent, and (d) earliest index position of the index heading. Examples are

1-Petene

polymer with 1-hexene 2,5-Furandione polymer with 1,4-butanedisulfonic acid

Silane, dichlorodiethyl-

polymer with dichlorodiphenylsilane

Although the percentage composition of copolymers (i.e., the ratio of comonomers) is not given, copolymers with architecture other than random or statistical are identified as "alternating, block, graft, etc." Random or statistical copolymer are not so identified in the CA index. Oligomers with definite structure are noted as dimer, trimer, tetramer, ...

Often, similar information is found at several sites. For instance, for copolymers of 1-butene and 1-hexene, information will be listed under both 1-butene and 1-hexene, but because the listings are not necessarily complementary both entries should be consulted for completeness.

CA's policy for naming acetylenic, acrylic, methacrylic, ethylenic, and vinyl polymers is to use the source-based method, and source-based representation is used to depict the polymers graphically; thus, a synonym for polyethene is polyethylene and not poly(1,2-

"Common" or "trivial" name	CAS name	Structure
Adipyl, adipoyl	1,6-Dioxo-1,6-hexanediyl	CO(CH ₂) ₄ CO
1,4-Butanediyl	1,4-Butanediyl	—(CH ₂) ₄ —
Carbonyl	Carbonyl	—CO—
Diglycoloyl	Oxybis (1-oxo-2,1-ethanediyl)	
Ethylene	1,2-Ethanediyl	$-CH_2-CH_2-$
Imino	Imino	—NH—
Iminodisulfonyl	Iminobis(sulfonyl)	$-SO_2$ -NH $-SO_2$ -
Methene, methylene	Methylene	—CH2—
Oxybis(methylenecar-	Oxybis[(1-oxo-2,	$-NHCO-CH_2-O-CH_2-$
bonylimino)	1-ethanediyl)imino)]	CO—NH—
Pentamethylene	1,5-Pentanediyl	$-(CH_2)_5$
p-Phenylene	1,4-Phenylene	
Phenylenedimethylene	1,4-Phenylenebis(methylene)	— НСН —
Phenylenedioxy	1,4-Phenylenebis(oxy)	-0
Sebacovl	1 10-Dioxo-1 10-decanedivl	$-CO-(CH_2)_{\circ}CO-$
bebuebyi	1,10 Dioxo 1,10 decuiediyi	-CH-HCH-
Styrenyl	1-Phenyl-1,2-ethanediyl	
Sulfonyl, sulfuryl	Sulfonyl	_SO ₂
Tartaroyl	2,3-Dihydroxy-1,4-dioxo-1, 4-butanediyl	—СО—СН(ОН)—СН(ОН)—СО—
Terephthaloyl	1,4-Phenylenedicarbonyl	-co-
Thio	Thio	—S—
Thionyl	Sulfinyl	—SO—
Ureylene	Carbonyldiimino	—NH—CO—NH—
Vinylene	1,2-Ethenediyl	-CH=CH-

Table 3 Names of Selected Bivalent Radi

In this text we typically employ the more "common" (semisystematic or trivial) names of polymers, but it is important in searching the literature using any CA-driven search engine that you be familiar with CA naming for both monomers and polymers.

ethanediyl); a synonym for poly-1-propylene is polypropylene, and poly(vinyl alcohol) is named ethenol, homopolymer although ethenol does not exist. Thus, these polymers are named and represented structurally by the source-based method, not the structure-based method.

Examples

Following are examples that illustrate CAS guidelines for naming.





Poly(oxy-1,4-phenylene)

Poly(thio-1,4-phenylene)

Poly(oxy1,2-ethanediyloxycarbonyl-1,4phenylenecarbonyl)

Poly(imino-1,4-phenyleneiminocarbonyl-1,4-phenylenecarbonyl)

TRADE NAMES, BRAND NAMES, AND ABBREVIATIONS

Trade (and/or brand) names and abbreviations are often used to describe materials. They may be used to identify the product of a manufacturer, processor or fabricator and may be associated with a particular product or with a material or modified material. Trade names are used to describe specific groups of materials that are produced by a specific company or under licence of that company. Bakelite is the trade name given for the phenol-formaldehyde condensation polymer developed by Baekeland. A sweater whose contents are described as containing Orlon contains polyacrylonitrile fibers that are "protected" under the Orlon trademark and produced or licenced to be produced by the holder of the Orlon trademark. Also, Carina, Cobex, Dacovin, Darvic, Elvic, Geon, Koroseal, Marvinol, Mipolam, Opalon, Plioflex, Rucon, Solvic, Trulon, Velon, Vinoflex, Vygen, and Vyram are all trade names for poly(vinyl chlorides) manufactured by different companies. Some polymers are better known by their trade name than their generic name. For instance, polytetrafluoroethylene is better known as Teflon, the trade name held by DuPont. An extensive listing of trade names is given in Appendix B of this text.

Abbreviations, generally initials in capital letters, are also employed to describe materials. Table 4 contains a listing of some of the more widely employed abbreviations and the polymer associated with the abbreviation.

COPOLYMERS

Generally, copolymers are defined as polymeric materials containing two or more kinds of mers. It is important to distinguish between two kinds of copolymers—those with statistical distributions of mers or at most short sequences of mers (Table 5), and those containing long sequences of mers connected in some fashion (Table 6).

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Abbreviation	Polymer	Abbreviation	Polymer
ABS	Acrylonitrile-butadiene-styrene copolymer	CA	Cellulose acetate
EP	Epoxy	HIPS	High-impact polystyrene
MF	Melamine-formaldehyde polymer	PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile	SBR, PBS	Butadiene-styrene copolymer
PBT	Poly(butylene terephthalate)	PC	Polycarbonate
PE	Polyethylene	PET	Poly(ethylene terephthalate)
PF	Phenol-formaldehyde polymer	PMMA	Poly(methyl methacrylate)
PP	Polypropylene	PPO	Poly(phenylene oxide)
PS	Polystyrene	PTFE	Polytetrafluoroethylene
PU	Polyurethane	PVA, PVAc	Poly(vinyl acetate)
PVA, PVAI	Poly(vinyl alcohol)	PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)	SAN	Styrene-acrylonitrile
UF	Urea-formaldehyde polymer		copolymer

 Table 4
 Abbreviations for Selected Polymeric Materials

 Table 5
 Short Sequence Copolymer Nomenclature

Туре	Connective	Example
Homopolymer	None	PolyA
Unspecified	-co-	Poly(A-co-B)
Statistical	-stat-	Poly(A-stat-B)
Random	-ran-	Poly(A-ran-B)
Periodic	-per-	Poly(A-per-B-per)
Alternating	-alt-	Poly(A-alt-B)
Network	net-	net-PolyA

 Table 6
 Long Sequence Copolymer Nomenclature

Туре	Connective	Example
Block copolymer	-block-	PolyA-block-polyB
Graft copolymer	-graft-	PolyA-graft-polyB
AB-crosslinked	-net-	PolyA-net-polyB
Polymer blend	-blend-	PolyA-blend-polyB
Interpenetrating network polymer Starblock	-ipn- or -inter- star-	net-PolyA-ipn-net-polyB star-(PolyA-block-polyB)