

Nomenclature & Intermolecular Forces in Polymer

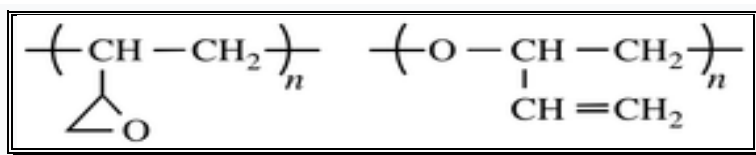
Polymer nomenclature usually applies to idealized representations meaning minor structural irregularities are ignored. A polymer can be named in one of two ways. Source-based nomenclature can be used when the monomer can be identified. Alternatively, more explicit structure-based nomenclature can be used when the polymer structure is proven. Where there is no confusion, some traditional names are also acceptable.

Whatever method is used, all polymer names have the prefix *poly*, followed by enclosing marks around the rest of the name. The marks are used in the order $\{[()]\}$. Locants indicate the position of structural features, e.g., poly (4-chlorostyrene). If the name is one word and has no locants, then the enclosing marks are not essential, but they should be used when there might be confusion, e.g., poly (chlorostyrene) is a polymer whereas polychlorostyrene might be a small, multi-substituted molecule. End-groups are described with α - and ω -, e.g., α -chloro- ω -hydroxy-polystyrene

❖ Source-Based Nomenclature:

Homopolymers

Homopolymers are named using the name of the real or assumed monomer (the 'source') from which it is derived, e.g., poly(methyl methacrylate). Monomers can be named using IUPAC recommendations, or well-established traditional names. Should ambiguity arise, class names can be added.



polyalkylene:vinylloxirane polyether:vinylloxirane

For example, the source-based name poly(vinylloxirane) could correspond to either of the structures shown. To clarify, the polymer is named using the polymer class name followed by a colon and the name of the monomer, i.e., class name:monomer name. Thus on the left and right, respectively, are polyalkylene:vinylloxirane and polyether:vinylloxirane.

Copolymers

The structure of a copolymer can be described using the most appropriate of the connectives shown in Table 1. These are written in italic font.

Table1. Qualifiers for copolymers		
Copolymer	Qualifier	Example
unspecified	<i>co</i> (C)	poly(styrene- <i>co</i> -isoprene)
statistical	<i>stat</i> (C)	poly[isoprene- <i>stat</i> -(methyl methacrylate)]
random	<i>ran</i> (C)	poly[(methyl methacrylate)- <i>ran</i> -(butyl acrylate)]
alternating	<i>alt</i> (C)	poly[styrene- <i>alt</i> -(maleic anhydride)]
periodic	<i>per</i> (C)	poly[styrene- <i>per</i> -isoprene- <i>per</i> -(4-vinylpyridine)]
block	<i>block</i> (C)	poly(buta-1,3-diene)- <i>block</i> -poly(ethene- <i>co</i> -propene)
graft	<i>graft</i> (C)	polystyrene- <i>graft</i> -poly(ethylene oxide)

^a The first name is that of the main chain.

Non-linear polymers

Non-linear polymers and copolymers, and polymer assemblies are named using the italicized qualifiers in Table 2. The qualifier, such as *branch*, is used as a prefix (P) when naming a (co) polymer, or as a connective (C), e.g., *comb*, between two polymer names.

Table 2. Qualifiers for non-linear (co)polymers and polymer assemblies		
(Co)polymer	Qualifier	Example
blend	<i>blend</i> (C)	poly(3-hexylthiophene)- <i>blend</i> -polystyrene

comb	<i>comb</i> (C)	polystyrene- <i>comb</i> -polyisoprene
complex	<i>compl</i> (C)	poly(2,3-dihydrothieno[3,4- <i>b</i>][1,4]dioxine)- <i>compl</i> - poly(vinylbenzenesulfonic acid) ^a
cyclic	<i>cyclo</i> (P)	<i>cyclo</i> -polystyrene- <i>graft</i> -polyethylene
branch	<i>branch</i> (P)	<i>branch</i> -poly[(1,4-divinylbenzene)- <i>stat</i> -styrene]
network	<i>net</i> (C or P)	(<i>net</i> -polystyrene)- <i>ipn</i> -[<i>net</i> -poly(methyl acrylate)]
interpenetrating network	<i>ipn</i> (C)	(<i>net</i> -polystyrene)- <i>ipn</i> -[<i>net</i> -poly(methyl acrylate)]
semi-interpenetrating polymer network	<i>sipn</i> (C)	(<i>net</i> -polystyrene)- <i>sipn</i> -polyisoprene
star	<i>star</i> (P)	<i>star</i> -polyisoprene

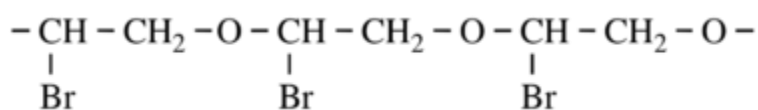
^a In accordance with IUPAC organic nomenclature, square brackets indicate the nature of the locant sites in fused ring systems.

❖ Structure-Based Nomenclature

Regular single-strand organic polymers

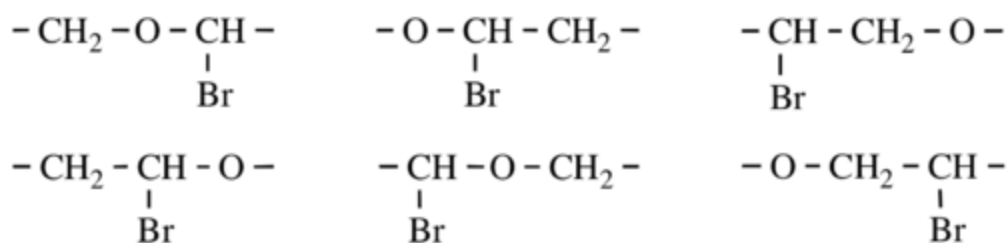
In place of the monomer name used in source-based nomenclature, structurebased nomenclature uses that of the preferred constitutional repeating unit (CRU). It can be determined as follows:

1. a large enough part of the polymer chain is drawn to show the structural repetition, e.g.,



2. The smallest repeating portion is a CRU, so all such possibilities are identified (including multiple directional possibilities for the chain).

For the preceding polymer, they are:



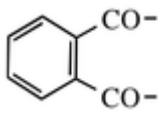


- The next step is to identify the subunits that make up each of these structures, i.e., the largest divalent groups that can be named using IUPAC nomenclature of organic compounds such as the examples that are listed in **Table 3**.
- Using the shortest path from the most senior subunit to the next senior, the correct order of the subunits is determined using **Figure 1**
- The preferred CRU is chosen as that with the lowest possible locant(s) for substituents.

In the above example, the oxy subunits in the CRUs are heteroatom chains. From Figure 1, oxy subunits are senior to the acyclic carbon chain subunits, the largest of which are bromo-substituted $-\text{CH}_2-\text{CH}_2-$ subunits. 1-Bromoethane-1,2-diyl is chosen in preference to 2-bromoethane-1,2-diyl as the former has a lower locant for the bromo-substituent. The preferred CRU is therefore oxy(1-bromoethane-1,2-diyl) and the polymer is thus named poly[oxy(1-bromoethane-1,2-diyl)]. Please note the enclosing marks around the subunit carrying the substituent.

Polymers that are not made up of regular repetitions of a single CRU are called irregular polymers. For these, each constitutional unit (CU) is separated by a slash, e.g., poly(but-1-ene-1,4-diyl/1-vinylethane-1,2-diyl).

Table 3. Representations of divalent groups in polymers

Name	Group ^a	Name	Group ^a
oxy		propylimino	$ \begin{array}{c} -\text{N}- \\ \\ \text{CH}_2\text{CH}_2\text{CH}_3 \end{array} $
sulfanediyl		hydrazine-1,2-diyl	

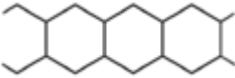
sulfonyl		phthaloyl	
diazenediyl		1,4-phenylene	
imino		cyclohexane-1,2-diyl	
carbonyl		butane-1,4-diyl	
oxalyl		1-bromoethane-1,2-diyl	$\begin{array}{c} 1 \quad 2 \\ -\text{CH} - \text{CH}_2 - \\ \\ \text{Br} \end{array}$
silanediyl		1-oxopropane-1,3-diyl	
ethane-1,2-diyl		ethene-1,2-diyl	
methylene		methylmethylene	$\begin{array}{c} -\text{CH} - \\ \\ \text{CH}_3 \end{array}$

^a To avoid ambiguity, wavy lines drawn perpendicular to the free bond, which are conventionally used to indicate free valences,^[11] are usually omitted from graphical representations in a polymer context.

Regular double-strand organic polymers

Double-strand polymers consist of uninterrupted chains of rings. In a spiro polymer, each ring has one atom in common with adjacent rings. In a ladder polymer, adjacent rings have two or more atoms in common. To identify the preferred CRU, the

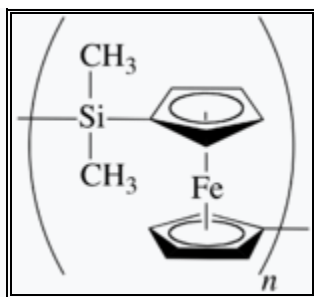
chain is broken so that the senior ring is retained with the maximum number of heteroatoms and the minimum number of free valences.

An example is  The preferred CRU is an acyclic subunit of 4 carbon atoms with 4 free valences, one at each atom, as shown.



It is oriented so that the lower left atom has the lowest number. The free-valence locants are written before the suffix, and they are cited clockwise from the lower left position as: lower-left, upper-left:upper-right, lower-right. This example is thus named poly(butane-1,4:3,2-tetrayl). For more complex structures, the order of seniority again follows **Figure 1**.

❖ Nomenclature of Inorganic and Inorganic-Organic Polymers



Poly[(dimethylsilanediy)ferrocene-1,1'-diyl]

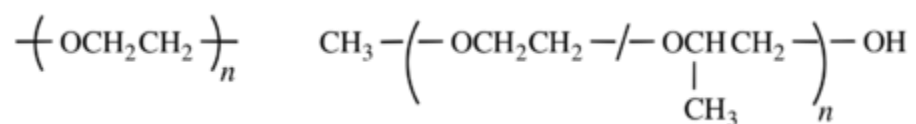
Some regular single-strand inorganic polymers can be named like organic polymers using the rules given above, e.g., $-\text{[O-Si(CH}_3\text{)}_2\text{]}_n-$ and $-\text{[Sn(CH}_3\text{)}_2\text{]}_n-$ are named poly[oxy(dimethylsilanediy)] and poly(dimethylstannanediy), respectively.^[13] Inorganic polymers can also be named in accordance with inorganic nomenclature, but the seniority of the elements is different from that in organic nomenclature. However, certain inorganic and inorganic-organic polymers, for example those containing metallocene derivatives, are at present best named using organic nomenclature, e.g., the polymer shown can be named poly[(dimethylsilanediy)ferrocene-1,1'-diyl].

❖ Traditional Names:

When they fit into the general pattern of systematic nomenclature, some traditional and trivial names for polymers in common usage, such as polyethylene, polypropylene, and polystyrene are retained.

❖ Graphical Representations

The bonds between atoms can be omitted, but dashes should be drawn for chain-ends. The seniority of the subunits does not need to be followed. For single-strand (co)polymers, a dash is drawn through the enclosing marks, e.g., poly[oxy(ethane-1,2-diyl)] shown below left. For irregular polymers, the CUs are separated by slashes, and the dashes are drawn inside the enclosing marks. End-groups are connected using additional dashes outside of the enclosing marks, e.g., α -methyl- ω -hydroxy-poly[oxirane-co-(methyloxirane)], shown below right.



Intermolecular Forces

The intermolecular forces for polymers are the same as for small molecules. Because polymer molecules are so large, though, the magnitude of their intermolecular forces can vastly exceed those between small molecules. The presence of strong intermolecular forces is one of the main factors leading to the unique physical properties of polymers.

Dispersion Forces

Dispersion forces are due to instantaneous dipoles that form as the charge clouds in the molecules fluctuate. Dispersion forces, the weakest of the intermolecular forces, are present in all polymers. They are the only forces possible for nonpolar polymers such as polyethylene.

Dispersion forces depend on the polarizability of a molecule. Larger molecules generally are more polarizable, so large polymers with high molecular weights can have significant dispersion forces. Ultra high molecular weight polyethylene (UHMWPE), which has a molecular weight in excess of 3,000,000 g/mole, is used to make bulletproof vests.

Dipole-Dipole Forces

Dipole-dipole forces result from the attraction between polar groups, such as those in polyesters and vinyl polymers with chlorine pendant groups.

Hydrogen Bonding

Hydrogen bonding can take place when the polymer molecule contains -OH or -NH groups. Hydrogen bonding is the strongest of the intermolecular forces. Polymers such as poly (vinyl alcohol) and polyamides are hydrogen bonded.