NAMING ORGANIC POLYMERS

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Organic polymers have been traditionally named on the basis of the monomer used, a hypothetical monomer, or a semisystematic structure. Alternatively, they may be named in the same way as organic compounds, i.e., on the basis of a structure as written. While the former methods, often called "source-based nomenclature", frequently result in ambiguity and multiple names for a single material, the latter method, termed "structure-based nomenclature", generates a sometimes cumbersome unique name for a given polymer, independent of its source. Within their limitations, both types of names are acceptable and well-documented.[1] The use of stereochemical descriptors with both types of polymer nomenclature has been published.[1]

TRADITIONAL POLYMER NAMES

Monomer-Based Names

"Polystyrene" is the name of a polymer made from the monomer styrene. Generally, the name of the monomer should be enclosed in parentheses, as in "poly(methyl methacrylate)" or "poly(4-bromostyrene)" to more clearly identify the monomer. Many names are often possible for a given polymer with this method: "poly(ethylene glycol)", "poly(ethylene oxide)", and "poly(oxirane)" describe the same polymer. Sometimes, the name of a hypothetical monomer is used, as in "poly(vinyl alcohol)". Even though a name like "polyethylene" covers a multitude of materials, the system does provide understandable names when a single monomer is involved in the synthesis of a single polymer. When one monomer can yield more than one polymer, as with 1,3-butadiene, some sort of structural notation must be used to identify the product, and one is not far from a formal structure-based name.

Copolymers, Block Polymers, and Graft Polymers. Monomer-based names are more complex when more than one monomer is involved. Some common polymers have been given names based on an apparent structure, as with "poly(ethylene terephthalate)". A better system has been approved by the IUPAC.[1] With this method, the arrangement of the monomeric units is introduced through use of an italicized connective placed between the names of the monomers. For monomer names represented by A, B, and C, the various types of arrangements are

Type	Connective	Example
unspecified	*-co-*	poly(A-*co*-B)
statistical	*-stat-*	poly(A-*stat*-B)
random	*-ran-*	poly(A-*ran*-B)
alternating	*-alt-*	poly(A-*alt*-B)
periodic	*-per-*	poly(A-*per*-B-*per*-C)
block	*-block-*	polyA-*block*-polyB
graft	*-graft-*	polyA-*graft*-polyB

A long dash may be used in place of the word "block". These connectives can be used in combination and with small joining units. Names such as "poly[ethylene-*ran*-(vinyl chloride)]" and "polystyrene-*block*-dimethylsilylene-*block*-polybutadiene" result.

STRUCTURE-BASED POLYMER NOMENCLATURE

Regular Single-Strand Polymers

Structure-based nomenclature has been approved by the IUPAC[4] and is currently being updated; it is used by *Chemical Abstracts*.[5] Monomer names are not involved. To the extent that a polymer chain can be described by a repeating segment of the chain, it can be named "poly(repeating unit)", where "repeating unit" is, in most cases, a bivalent group.

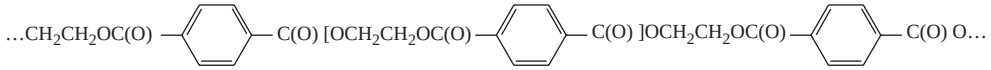
Since there are usually many possible repeating units in a given chain, it is necessary to select systematically one, called the "constitutional repeating unit" (CRU), to provide a unique and unambiguous name, "poly(CRU)", where "CRU" is a recitation of the names of successive units as one proceeds through the CRU. For this purpose, a portion of the main chain structure that includes at least two repeating sequences is written out. These sequences will be composed of bivalent subunits such as $-CH_2-$, -O-, and groups from ring systems, each of which can be named by the usual rules of nomenclature.[6,7]

Where a chain is simply one long sequence of a single subunit, that subunit is itself the CRU, as in "poly(methylene)" or "poly(1,4-phenylene)". In chains having more than one kind of subunit, a seniority system is used to determine the beginning of the CRU and the direction to move along the main chain atoms (following the shortest path in rings) to complete the CRU. For citation of the first, most senior, subunit, the descending order of seniority is (1) heterocyclic rings, (2) hetero atoms, (3) carbocyclic rings, and, lowest, (4) acyclic groups containing only carbon atoms.

Within each of these classes, there is a further order of seniority that follows the usual rules of nomenclature. Thus, among hetero atoms, the descending order of seniority is O, S, Se, N, P, As, Si, Ge, B, with other atoms fitted in according to their place in the Periodic Table. The descending order of seniority among heterocylic rings is (a) a ring system containing N; (b) a ring system containing a hetero atom (other than N) as high as possible in the order of hetero atoms given above; (c) a ring system having the greatest number of rings; (d) a ring system with the largest individual ring; (e) a ring system with the largest number of hetero atoms. Among equivalent ring systems, preference is given to the one having lowest locants for the free valences in the subunit, and among otherwise identical ring systems, the one having least hydrogenation is senior. Lowest locants in unsaturated chains are also given preference. Lowest locants for substituents, independent of kind except for alphabetical order, are the final determinant of seniority.

Direction within the repeating unit depends upon the shortest path, in main chain atoms, from the most senior subunit to another subunit of the

same kind or to a subunit next lower in seniority. Once identification of the CRU is established, the name of the CRU is formed from the names of largest possible subunits within the CRU. For example, the main chain of the polymer traditionally named "poly(ethylene terephthalate)" has the structure



The CRU is enclosed in brackets and read from left to right. It is selected because -O- is the most senior subunit, and two carbon atoms is the shortest path to the next -O-. The structure-based name of this polymer is then "poly(oxyethyleneoxyterephthaloyl)", not much longer than the traditional name and much more adaptable to the complexities of substitution. As organic nomenclature evolves, more systematic names can be applied to the subunits, such as "ethane-1,2-diyl" instead of "ethylene".

Structure-based nomenclature can also be used when the CRU has no carbon atoms. An example is the polymer traditionally named "poly(dimethylsiloxane)", which on the basis of structure would be named "poly(oxydimethylsilylene)" or "poly(oxydimethylsilanediyl)". This nomenclature method has also been applied to inorganic and coordination polymers[8] and to double-strand (ladder and spiro) organic polymers.[9]

Additional examples of both structure-based and traditional names will be found in the tables of glass transition temperatures (**13**-4 to 11) in this *Handbook* as well as in the *Chemical Abstracts* indexes and in the IUPAC documents.

Irregular Single-Strand Polymers

Polymers that cannot be described by the repetition of a single CRU or comprise units not all connected identically in a directional sense can also be named on a structure basis.[10] These include copolymers, block and graft polymers, star polymers, and chemically modified polymers. They are given names of the type "poly(A/B/C...)", where A, B, C, etc. are the names of the component constitutional units, the number of which are minimized. The constitutional units may include regular or irregular blocks as well as atoms or atomic groupings, and each is named by the method described above or by the rules of organic nomenclature.

The oblique stroke denotes an unspecified arrangement of the units within the main chain. For example, a statistical copolymer derived from styrene and vinyl chloride with the monomeric units joined head-to-tail is named "poly(1-chloroethylene/1-phenylethylene)". A polymer obtained by 1,4 polymerization and both head-to-head and head-to-tail 1,2 polymerization of 1,3-butadiene would be named "poly(but-2-ene-1,4-diyl/1-vinylethylene/2-vinyl-ethylene)". A long dash is used separate components of block polymers, as in "poly(A)—poly(B)—poly(C)" or "poly(A)—X—poly(B)". Graft polymers are named in the same way as a substituted polymer but without the ending "yl" for the grafted chain: "poly[Z/poly(A)Z]" is the name of a regular polymer consisting of Z units in which some have grafts of "poly(A)". Star polymers are treated as a central unit with substituent blocks, as in "tetrakis(polymethylene)silane".

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