Macromolecules

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A Structure-Based Nomenclature for Linear Polymers[1]

Introduction

Linear polymers traditionally have been named on the basis of source, a method of naming that suffers from a number of serious defects and limitations. As the number of new and complex polymers increases, effective communication and retrieval of information require a systematic means for describing these substances. This need was recognized nearly 20 years ago by the Subcommittee on Nomenclature, National Research Council Committee on Macromolecules. Its efforts, requiring several years of study by a large number of polymer and organic chemists on both a national and an international scale, in 1952 became part of a report[2] of the Subcommission on Nomenclature, International Union of Pure and Applied Chemistry Commission on Macromolecules. Of the many nomenclature proposals in the polymer field that have appeared over the years, the 1952 report was by far the most comprehensive. At the time it was adequate for most needs. In the intervening years, the explosive growth of polymer science and the continually changing language of chemistry have necessitated modification and updating of the original IUPAC proposals.

Since most polymer chemistry is organic chemistry, the typical user of polymer nomenclature will expect the names to be not only compatible with organic nomenclature but to require little or no translation from well-developed systematic organic nomenclature. This report presents structure-based polymer nomenclature that adheres as much as possible to the currently accepted principles of organic nomenclature; these principles are now well defined.[3,4] The notion of a repeating structural unit dictates the use of additive nomenclature in naming this unit. In other respects, nomenclatural familiarity has been emphasized.

The rules are designed for linear polymers whose structures can be specifically written using ordinary chemical principles; the rules cannot be used for materials whose chemical structures are unknown. Rules involving stereoregularity have not been given, since the present IUPAC rules,[5] can be readily accommodated by the proposal following.

Rule 1. The Generic Name

A polymer of unspecified chain length is named with the prefix "poly" followed by, in parentheses or brackets, as appropriate, the name of the smallest repeating unit. The generic name for a single-stranded linear polymer is thus *poly(bivalent radical)*. To specify chain length, the appropriate Greek prefix is used in place of "poly"; for example, a linear chain of ten units, a "decamer," is named *deca(bivalent radical)*.

Comment. In the very few instances where short linear polymers receive names similar to those of certain cyclic compounds, the two are readily differentiated by the type of name as well as by the appearance of both parentheses and locants in the polymer name. For example, tri- and tetraphenylene are cyclic compounds of three and four 1,2-phenylene radicals. The linear analogs, under IUPAC Organic Rule A-54.3[3] and by *Chemical Abstracts* practice,[6] are named *o*-ter- and *o*-quaterphenyl. Under the present rule, these are named tri(1,2-phenylene) and tetra(1,2-phenylene), with the hydrogen end groups understood or delineated as in rule 2. The polymer of unspecified length is poly(1,2-phenylene).

Rule 2. End Groups

In high polymers, end groups are usually not specified. Where end groups are a known part of the structure and it is desired to emphasize them, as in telomers, such end groups are named as radicals prefixed by the Greek letters α and ω appearing before the name of the polymer. The α end group is that attached to the

$$Cl\text{-}(CH_2)_n\text{-}CCl_3$$

α-chloro-ω-(trichloromethyl)poly(methylene)

(1) The following rules for the nomenclature of linear organic polymers were prepared by the Committee on Nomenclature, American Chemical Society Division of Polymer Chemistry, the members of which were Robert B. Fox, Chairman (to whom correspondence should be addressed: Code 6120, Naval Research Laboratory, Washington, D. C. 20390), Ralph Beaman, Norbert M. Bikales, B. Peter Block, Waldo E. Cohn, Herbert K. Livingston, Kurt L. Loening, Andrew Mercurio, and Arthur M. Schiller. This nomenclature was approved by the American Chemical Society Council on April 2, 1968 and will have tentative standing for 1 year before becoming official nomenclature of the American Chemical Society. Particular note should be taken of the Appendix following the rules. Here it is recognized that many names of common polymers are well sanctioned by usage. Such names are preferred over those generated by the rules.

(2) "Report on Nomenclature in the Field of Macromolecules, International Union of Pure and Applied Chemistry," *J. Polym. Sci.*, **8**, 257 (1952).

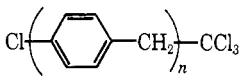
(3) "Definitive Rules for the Nomenclature of Organic Chemistry (IUPAC 1957 Rules), Sections A and B," *J. Amer. Chem. Soc.*, **82**, 5545 (1960).

(4) "Nomenclature of Organic Chemistry, Section C," Butterworth & Co. (Publishers) Ltd., London, 1965; *Pure Appl. Chem.*, **11**, No. 1–2 (1965).

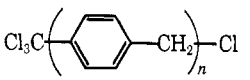
(5) M. L. Huggins, G. Natta, V. Desreux, and H. Mark, *ibid.*, **12**, 645 (1966) ("Report on Nomenclature Dealing with Steric Regularity in High Polymers").

(6) "The Naming and Indexing of Chemical Compounds from *Chemical Abstracts*," *Chem. Abstr.*, **56**, Introduction to the Subject Index (1962).

left side of the senior radical in the repeating unit as defined in the rules below.



α-chloro-ω-(trichloromethyl)poly(1,4-phenylenemethylene)



α-(trichloromethyl)-ω-chloropoly(1,4-phenylenemethylene)

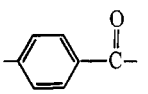
Rule 3. The Bivalent Radical

The smallest repeating structural unit of a linear polymer is a bivalent radical. As far as possible, the IUPAC organic nomenclature rules[3,4] are followed in naming these radicals. Simple structural units contain only one kind of acyclic or cyclic bivalent radical. Complex structural units consist of a series of bivalent radicals, the names of which, cited in the order specified in the rules following, add up to the name of the complete repeating unit. The general principle is that the largest possible bivalent radical within the smallest repeating structural unit will be named.

Comment. Because of numbering difficulties, chain–ring combinations that may undergo substitution in either chain or ring are treated as two entities: 1,4-phenyleneethylene, not 1,4-xylylene; however, common names such as terephthaloyl, where only the ring may be substituted, are used. Many unsymmetrical bivalent radicals, again because of problems with numbering, are *not* used in naming complex structural units: aspartoyl, citraconoyl, glutamoyl, maloyl, and mesaconoyl are examples.

Hexamethylene, ethylene, 1-butenylene, benzylidene, 1,3-phenylene, 3,8-quinolinediyl, and adipoyl are examples of simple radicals. Examples of combinations of simple bivalent radicals are

iminohexamethylene

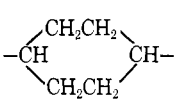


1, 4-phenylenecarbonyl

Note that these and later names always imply a reading of the structure from left to right.

Some of the simple bivalent radicals most commonly encountered are

carbonyl



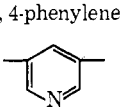
1, 4-cyclohexylene

imino

methylene

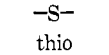
oxy

1, 4-phenylene



3,5-pyridinediyl

thio

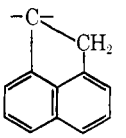


vinylene

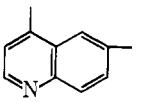
Additional examples of bivalent radicals involving rings are

4-cyclohexen-1,3-ylene

2*H*-pyran-2-ylidene



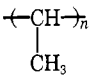
1-acenaphthenylidene



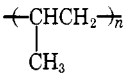
4,6-quinolinediyl

3a. Simple Repeating Units. Naming the Polymer. A polymer whose repeating unit is a simple bivalent radical, such as one of the radicals given in the preceding rule, is named by prefixing "poly" to the name of the radical: poly(methylene), poly(3,5-pyridinediyl), poly-(4-cyclohexen-1,3-xylene).

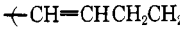
Further examples of polymers with unsubstitutde simple repeating units are



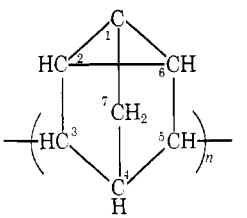
poly(ethylidene) (not poly(methylmethylene), since ethylidene is larger than methylene)



poly(propylene) (not poly(methylethylene); under the IUPAC rules, "propylene" has been retained as an exception when unsubstituted)

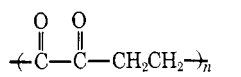


poly(1-butenylene) (not poly(3-butenylene) or poly(vinylene-ethylene); 1-butenylene is the largest identifiable unit with the lowest locant for the double bond. The "all-*cis*" form of this structure is named poly(*cis*-1-butenylene))

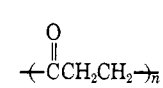


poly(tricyclo[2.2.1.0^{2,6}]hept-3,5-ylene)

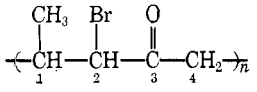
Substituents must be taken into account in writing the structure of the repeating unit. A chain of methylene radicals, one or more of which are substituted, comprises a simple substituted bivalent radical.



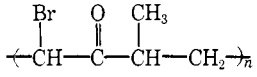
poly(1,2-dioxotetramethylene)



poly(1-oxotrimethylene)

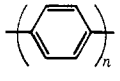


poly(2-bromo-1-methyl-3-oxotetramethylene)

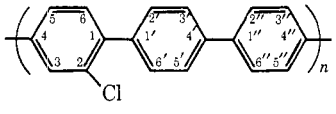


poly(1-bromo-3-methyl-2-oxotetramethylene)

The same reasoning applies to chains of rings



poly(1,4-phenylene)



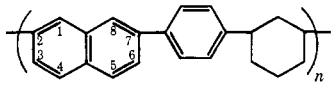
poly(2-chloro-*p*-terphenyl-4,4′′-ylene)

Rule 4. Complex Repeating Units. Beginning and Direction of Citation

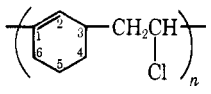
Polymers whose repeating units contain more than one simple bivalent radical can be drawn in several ways. The choice of the beginning and direction of citation of the unit is dictated by both usage and ease of handling indexes. The order of citation in the unit determines the name of the polymer itself. For naming purposes, the order of seniority among the types of bivalent radicals is (1) *heterocyclic rings*, followed by (2) *chains containing hetero atoms*, (3) *carbocyclic rings*, and (4) *chains containing only carbon*, in that order; this order is not affected by substituents. A unit containing both heterocyclic and carbocyclic rings, for example, is written and named so that the heterocyclic ring appears first; the unit should be written with the most senior component at the left end of the unit, and citation should always be from left to right.

4a. Complex Repeating Units Containing Carbocyclic Rings Alone and in Combination with Acyclic Carbon Chains. When a carbocyclic ring system is part of a main polymer chain not containing a hetero atom, the unit is depicted and named with the lowest free valence of the most preferred ring system placed at the left end of the unit. The component bivalent radicals are cited in the direction of the shortest path to the next most favored ring, or, if no other rings are present, to the acyclic bivalent radical earliest in the alphabet. Where two of the same acyclic radicals are present, further choice for direction of citation will favor (a) the radical with the greatest number of substituents, (b) the substituents with the lowest locants, and (c) the substituents occurring earliest in the alphabet. Ring-system preference is based on complexity, with the most senior ring system being that containing the largest number of rings. Further order of seniority[7] is based on the (a) largest individual ring at the first point of difference, (b) largest number of atoms common to the rings, (c) lowest numbers at the first point of difference in the expression for ring junctions, (d) least hydrogenated ring, (e) lowest locants for the free valences of the bivalent radical, and (f) substituents, as given for the acyclic radicals.

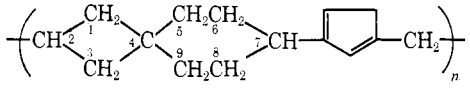
(7) A more complete analysis of these criteria may be found in the IUPAC rules[3] for organic compounds.



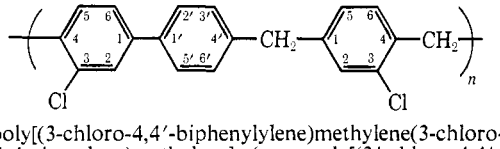
poly(2,7-naphthylene-1,4-phenylene-1,3-cyclohexylene)



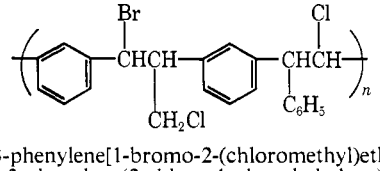
poly[1-cyclohexen-1,3-ylene(2-chloroethylene)]
(substituents are named with prefixes placed within parentheses with the name of the unit to which they are attached)



poly(spiro[3.5]non-2,7-xylene-2,5-cyclopentadien-1,3-ylene-methylene)

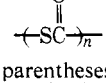


poly[(3-chloro-4,4′-biphenylylene)methylene(3-chloro-1,4-phenylene)methylene] (not poly[(3′-chloro-4,4′-biphenylylene)methylene(2-chloro-1,4-phenylene)methylene]; the substituent in the senior ring system, biphenyl, determines the direction)

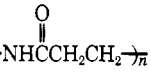


poly[1,3-phenylene[1-bromo-2-(chloromethyl)ethylene]-1,3-phenylene(2-chloro-1-phenylethylene)]

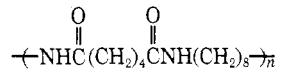
4b. Complex Repeating Units Containing Acyclic Hetero Atoms Alone or in Combination with Carbocyclic Rings and/or Acyclic Carbon Chains. When hetero atoms are part of an acyclic chain in the repeating unit, the unit is depicted and named with the most senior hetero atom placed at the left end of the unit. The most senior atom is O, followed in order by S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, and Hg. Citation of the component bivalent radicals proceeds by the shortest path (number of atoms) to (a) another hetero atom of the *same* kind or (b) the next senior hetero atom. In the absence of a second hetero atom, citation is toward the senior carbocyclic ring or acyclic chain in the unit, as indicated by rule 4a.



poly[thio(carbonyl)] (the parentheses are required to differentiate this structure from $-(-C-)_n-$, poly(thiocarbonyl))

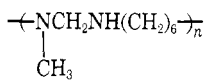


poly(iminocarbonylethylene) (not poly[imino(1-oxotrimethylene)]; carbonyl groups directly attached to hetero atoms are expressed as acyl radicals)

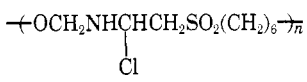


poly(iminoadipoyliminooctamethylene)

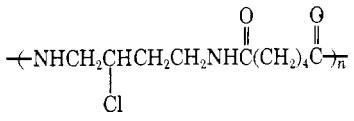
poly(thioiminoethylene)



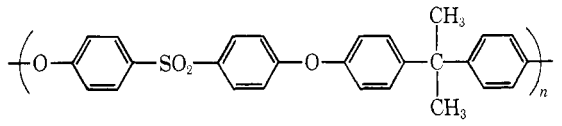
poly[(methylimino)methyleneiminohexamethylene] (not poly[iminomethylene(methylimino)hexamethylene] or poly[(methylimino)hexamethyleneiminomethylene]; the substituted imino group is the senior radical and the single carbon atom is the shortest path to the next hetero atom)



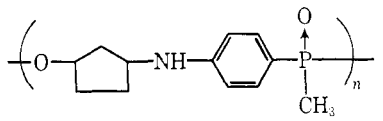
poly[oxymethyleneimino(1-chloroethylene)sulfonylhexamethylene] (not poly[oxyhexamethylenesulfonyl(2-chloroethylene)iminomethylene]; the shortest path from O to S is through the N)



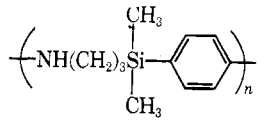
poly[imino(2-chlorotetramethylene)iminoadipoyl]



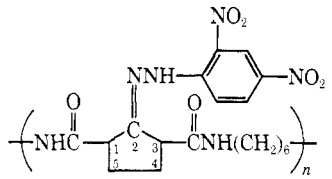
poly(oxy-1,4-phenylenesulfonyl-1,4-phenyleneoxy-1,4-phenyleneisopropylidene-1,4-phenylene) (with equal paths between the oxygen atoms, the path involving the hetero sulfur atom is senior)



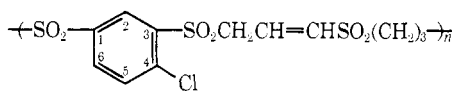
poly[oxy-1,3-cyclopentyleneimino-1,4-phenylene(methylphosphinylidene)]



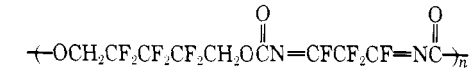
poly[iminotrimethylene(dimethylsilylene)-1,4-phenylene]



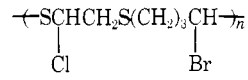
poly[iminocarbonyl-2-[(2,4-dinitrophenyl)hydrazono]-1,3-cyclopentylene]carbonyliminohexamethylene] (derivative-type substituents are expressed by prefixes)



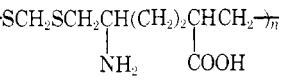
poly[sulfonyl(4-chloro-1,3-phenylene)sulfonyl-2-propenylenesulfonyltrimethylene]



poly[oxy(2,2,3,3,4,4-hexafluoropentamethylene)oxycarbonylnitrilo(tetrafluoropropanediylidene)nitrilocarbonyl]

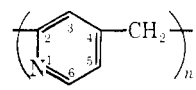


poly[thio(1-chloroethylene)thio(4-bromotetramethylene)] (direction is determined by the lower locant in the first cited radical)

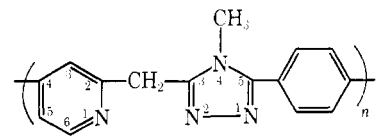


poly[thiomethylenethio(2-amino-5-carboxyhexamethylene)] (direction is determined by the alphabetically earliest substituent)

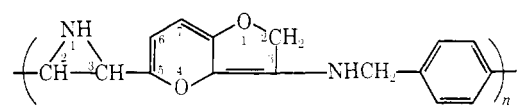
4c. Complex Repeating Units Containing Heterocyclic Ring Systems. Polymers containing a heterocyclic ring are named by citing first the senior heterocyclic ring bivalent radical and proceeding by the shortest path (number of atoms) in descending order of preference (a) to another of the same heterocyclic ring; (b) to the next senior heterocyclic ring; (c) to the senior acyclic bivalent radical containing a hetero atom (see rule 4b); (d) to the senior carbocyclic ring system (see rule 4a); and (e) to the senior acyclic radical (see rule 4a). The order of seniority in heterocyclic ring systems, in descending order of preference, is[8] (a) the largest ring system containing any number of nitrogen atoms; (b) the system containing the most nitrogen among ring systems of the same size; (c) the ring (not having nitrogen) containing the most hetero atoms most senior in the list given in rule 4b; and (d) the component containing the greatest number of rings, etc., following the order of complexity for carbocycles given in rule 4a. Since heterocyclic rings have fixed numbering, the senior heterocyclic ring is placed at the left end of the repeating unit and oriented so that the lowest free valence locant is at the left of the ring.



poly(2,4-pyridinediylmethylene)

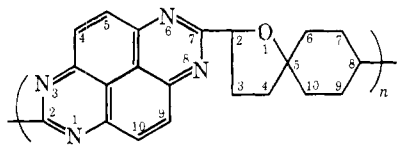


poly[4,2-pyridinediylmethylene(4-methyl-4*H*-1,2,4-triazole-3,5-diyl)-1,4-phenylene]

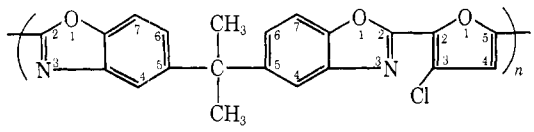


poly(2,3-aziridinediyl-2*H*-furo[3,2-*b*]pyran-5,3-diylimino-methylene-1,4-phenylene)

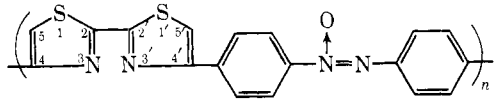
(8) For a more detailed listing, see ref 3, Rule B3.



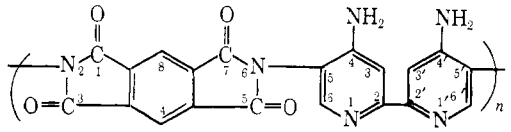
poly(quinazolino[6,5,4-*def*']quinazoline-2,7-diyl-1-oxaspiro[4.5]dec-2,8-ylene)



poly[2,5-benzoxazolediylisopropylidene-5,2-benzoxazolediyl(3-chloro-2,5-furandiyl)]



poly([2,2'-bithiazole]-4,4'-diyl-1,4-phenylene-*ONN*-azoxy-1,4-phenylene)

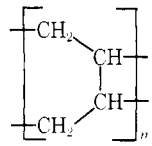


poly[(5,7-dihydro-1,3,5,7-tetraoxobenzo[1,2-*c*:4,5-*c*']-dipyrrole-2,6(1*H*,3*H*)-diyl)-(4,4'-diamino[2,2'-bipyridine]-5,5'-diyl)]

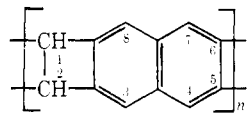
Rule 5

5a. "Ladder" or Double-Stranded Polymers. Linear Double-Stranded Polymers Having Tetravalent Repeating Units. The repeating units of ladder polymers are named in a manner analogous to that for naming bivalent units. The relation of the four free valences is denoted by pairs of locants separated by a colon; *pairs* of locants imply a linear double-stranded polymer.

poly(1,2:1,2-ethanediylidene)

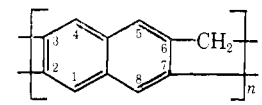


poly(1,4:2,3-butanetetrayl)

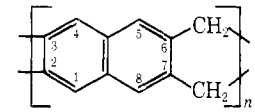


poly(1,2-dihydrocyclobuta[*b*]naphthalene-1,2:5,6-tetrayl)

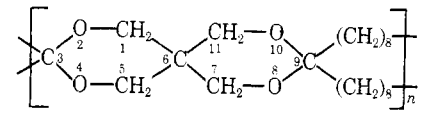
5b. Linear Double-Stranded Polymers Having Repeating Units with Both Bivalent and Tetravalent Radicals. In those cases where the ring structure of a polymer is such that the unit is a combination of bivalent and tetravalent radicals, the unit is depicted with the tetravalent radical component at the left end of the unit. If hetero atoms are present, the ring should be broken at points that (a) minimize the number of free valences and (b) place the maximum number of most senior hetero atoms at the earliest possible positions in the repeating unit, reading from left to right; these positions will not necessarily correspond to the lowest locants in the final numbering of the ring.



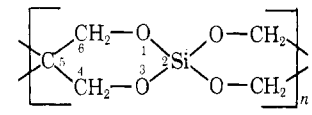
poly(2,3:6,7-naphthalenetetrayl-6-methylene)



poly(2,3:6,7-naphthalenetetrayl-6,7-dimethylene)

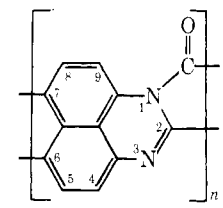


poly[2,4,8,10-tetraoxaspiro[5.5]undecane-3,9-diylidene-9,9-bis(octamethylene)]



A B

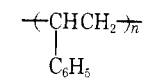
poly[1,3-dioxa-2-silacyclohexane-5,2-diylidene-2,2-bis(oxymethylene)] (placement of the hetero atoms in ring A is determined by the shortest path from these to the hetero atoms in segment B)



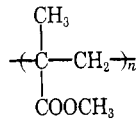
poly(perimidine-6,7:1,2-tetrayl-1-carbonyl)

Appendix: Structure and Common Names for Some Simple Polymers

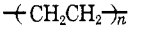
It is not intended that the names generated by application of the foregoing rules should supplant the accepted trivial names used for common polymers (compare the accepted trivial name acetic acid in preference to the systematic name ethanoic acid). To indicate how readily structure-based names can be formed, the following list of frequently encountered polymers gives, first, the preferred trivial name and, second, the structure-based name. The last two examples are of strictly delineated structures; random copolymers are not covered by the structure-based system.



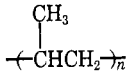
polystyrene
poly(phenylethylene)



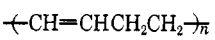
poly(methyl methacrylate)
poly[1-(methoxycarbonyl)-1-methylethylene]



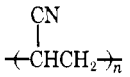
polyethylene (no corresponding structure-based name)



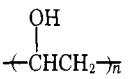
polypropylene
poly(propylene)



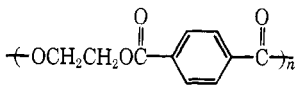
polybutadiene
poly(1-butenylene)



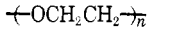
polyacrylonitrile
poly(cyanoethylene)



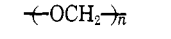
poly(vinyl alcohol)
poly(hydroxyethylene)



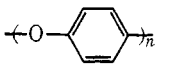
poly(ethylene terephthalate)
poly(oxyethyleneoxyterephthaloyl)



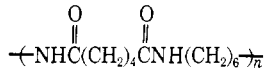
poly(ethylene oxide)
poly(oxyethylene)



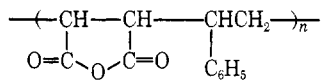
polyformaldehyde
poly(oxymethylene)



poly(phenylene oxide)
poly(oxy-1,4-phenylene)



poly(hexamethylenediamine-*co*-adipic acid)
poly(iminoadipoyliminohexamethylene)



poly(maleic anhydride-*co*-styrene)
poly[(tetrahydro-2,5-dioxo-3,4-furandiyl)(1-phenylethylene)]