Nomenclature of Organic Polymers*

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Linear organic polymers with regular structures can be named by a systematic nomenclature recently approved tentatively by the American Chemical Society. This nomenclature utilizes the prefix poly-, followed by the name of the bivalent radical comprising the structural repeating unit. Rules to define the beginning and the end of this unit and the direction followed in building the name form the basis of the system, which relies heavily on existing organic nomenclature. The names thus formed have their greatest value for polymers whose structures are not readily derived from a knowledge of the compounds from which the polymers were made.

The structural representation—atoms and bonds—of organic compounds provides a system of communication that is understood by all professional chemists. Often word descriptions are preferred to structures, since they usually conserve space in writing and can be spoken more readily. The words used to name organic compounds are developed according to the principles of organic chemical nomenclature.[1]

These principles make use of hydrocarbon root names, with the addition of prefixes and suffixes to the hydrocarbon roots. The various parent names can be modified to form simple radicals, bivalent radicals, or multivalent radicals. Formal nomenclature tends to be directional, so that one reads from left to right, according to a preestablished hierarchy, in compounds such as 3-hydroxypropionic acid, $HOCH_2—CH_2—COOH$. Emphasis is placed on functional groups, and a certain group, high in the hierarchy, fixes the nature of the final name.

Organic polymers present a particular difficulty when approached by the methods traditionally used. There is no problem with the root names and the usual prefixes and suffixes. It is in detailed application that one encounters difficulty in the search for the functional group highest in the hierarchy, which can then be counted on to give direction to the name. In a sense, the fact that a compound is a polymer represents a functionality having higher significance. A polymer of regular structure invites application of an important and familiar principle of nomenclature: like treatment of like things.

A linear organic polymer with known regular structure—such as the polymer formed by the ring-opening polymerization of β-propiolactone—has a very large number of identical repeating units and only two end groups. It is necessary to restrain the tendency to give one's attention to the carboxylic acid end group and instead to name the polymer with a root derived from the like thing, the

$$—O\overset{\overset{O}{\|}}{C}CH_2CH_2—$$

repeating unit, as oxycarbonylethylene.

Thus, organic polymer nomenclature uses the same principles that are used in naming organic compounds of low molecular weight, and also uses the same prefixes and suffixes. It differs only in the significance attached to the various principles. It recognizes the repeating nature of the chemical structures that make up polymer molecules and gives the greatest weight to like treatment of like things.

A previous article by one of the authors[2] reviewed the methods that have been used in naming polymers. The early nomenclature was essentially "product-by-process," reflecting the interest in patenting the products and the inability to provide a proof of chemical structure other than by inference from the known structure of the starting materials. No further elaboration of the disadvantages of product-based nomenclature is necessary at this time.

The first formal effort to replace "product-by-process" nomenclature is embodied in the 1952 report of the International Union of Pure and Applied Chemistry Subcommission on Nomenclature, Commission on Macro-

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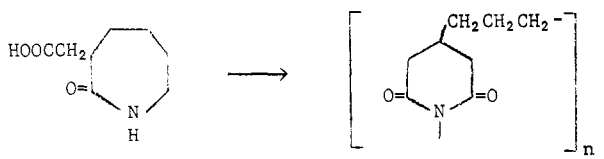
molecules.[3] This proposal defined many of the key terms in polymer chemistry, including the repeat unit. It further suggested that polymers be given names based on their chemical structures; this was to be done by a compound word giving the chemical structure of the repeat unit and an indication that the repeat unit was a part of a polymer.

The 1952 proposal, while sound in concept, encountered some difficulties in detailed application. It was suggested that the repeat unit be named by the appropriate hydrocarbon prefix (meth-, eth-, prop-, etc.) or similar root word. The suffix -amer would indicate the polymeric nature. The direction of organic chemical nomenclature has developed along lines diverging from those indicated in the macromolecular nomenclature approved by 1952. A large number of names for bivalent radicals are now available, using, for example, trimethylene in the way prop- was suggested in 1952. These bivalent-radical names also permit the naming in straightforward—though lengthy—fashion of many radicals that could not have been named without extensive elaboration of the 1952 proposal. Finally, poly- seems well accepted in polymer nomenclature and consistent with general organic nomenclature, whereas the -amer suffix has no previous usage nor any similarity with present practice.

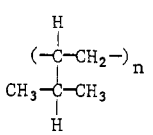
It was for these reasons that some new proposals[4] for naming organic polymers have been developed by the Division of Polymer Chemistry, American Chemical Society, and submitted through the Council Committee on Nomenclature for approval by the American Chemical Society. Recently these proposals were adopted by the Council of the Society for use for one year, after which permanent adoption will be considered. The proposals accept the fundamental IUPAC concepts of macromolecular nomenclature,[3] but modify the application to be consistent with the most recently developed IUPAC-approved organic chemical nomenclature.[1] Numerous examples of the applications of the new nomenclature appear in the literature, as well as in the summaries[2,4] mentioned above.

Some examples from the literature illustrate the use of the new nomenclature. Reimschuessel *et al.*[5] observed an unusual condensation polymerization, the product of which must be described by systematic nomenclature; hexahydro-2-oxo-1*H*-azepine-3-acetic acid yields poly[2,6-dioxo-1,4-piperidinediyl)trimethylene].

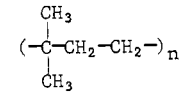


Here, a name based on the starting material could in no way convey the idea that a change in ring size had taken place.

Kennedy and Langer[6] reviewed the evidence that 3-methyl-1-butene with a Ziegler catalyst forms poly(isopropylethylene),

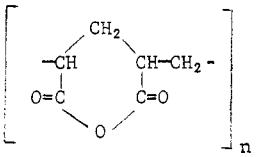


but on cationic polymerization forms poly(1,1-dimethyltrimethylene).



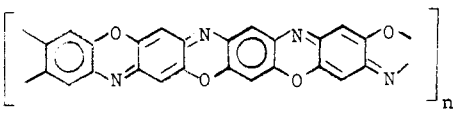
The formation of two distinct polymers from the same source makes structure-based names mandatory.

Acrylic anhydride in solution polymerizes[7] exclusively to a polymer requiring two vinyl groups per repeat unit, the structure of which is poly[(tetrahydro-2,6-dioxo-2*H*-pyran-3,5-diyl)methylene].



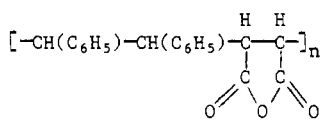
A rather drastic structural change from an open-chain monomer to a ring-containing polymer has occurred; any attempt to describe such a polymer must include this fact, while the nature of the monomer is of relatively little importance to the description.

It has even been possible to name some very complex repeat units, such as the ladder polymers, in which the repeat unit is a tetravalent radical, not a bivalent radical. Stille and Freeburger[8] have done this for poly[(3*H*-[1,4]-benzoxazino[3,2-*b*]triphenodioxazine - 2,11,12 - triyl - 3 - ylidene) - 3 - nitrilo - 2 - oxy].



In some cases, it may be more desirable to "name" the compounds by drawing out the chemical structure. This method may become especially attractive with increasing use of chemical typewriters and structure-based systems for indexing and searching.[9,10]

Concern is sometimes expressed about the need for a nomenclature for high molecular weight substances made by copolymerization. If the product is an alternating copolymer, a structure-based nomenclature is straightforward. For example, stilbene and maleic anhydride copolymerize under the conditions studied by Lewis and Mayo[11] to form poly[(tetrahydro-2,5-dioxo-3,4-furandiyl)(1,2-diphenylethylene)].



If the product is a random copolymer, its chemical structure cannot be specified. Each molecule in the polymerization product will have a unique chemical composition, but the sequence by which the units are combined cannot be specified by any present method of analysis. The product cannot be named by the current procedures that have been developed for chemical nomenclature.

Alternating copolymers such as the Lewis-Mayo product given above are in fact regular polymers, just as are those homopolymers that have the same repeat unit throughout the molecule. In addition to alternating and random copolymers, we recognize block copolymers (...*AAAAABBBBAAAAA*...) and graft copolymers

(...*AAAAXAAAAA*...).
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B
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B
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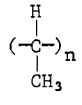
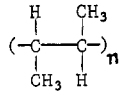
With sufficient analytical information, these could be named (poly *A*)(poly *B*)(poly *A*) or bis(poly *A*)(poly *B*)*X*, but no such nomenclature scheme has been fully developed as yet. Ultimately, it would be desirable to replace poly- by a numerical prefix if, for example, the blocks or grafts had been made by a technique assuring narrow molecular weight distribution.

The fact that almost all organic polymers of regular structure are only isolated as mixtures of molecules of different molecular weight does not limit the proposed nomenclature. The polymer name has the prefix poly-, which does not imply any exact knowledge of the degree of polymerization, nor does it imply that all molecules have the same degree of polymerization. Where such knowledge exists, it can be transmitted by use of the appropriate prefix, such as eicosa- if the degree of polymerization is twenty. "Homoplethemer" has been suggested[12] as the generic term for such polymers in which the degree ("pleth") of polymerization is the same for all molecules.

The subject of a nomenclature for stereospecific polymers has been dealt with by the International Union of Pure and Applied Chemistry Subcommission on Macromolecules,[13] using the words isotactic and syndiotactic. We can also consider an alternate nomenclature that distinguishes the isotactic polymer , poly(ethylidene),



and the syndiotactic polymer, poly(1*R*:2*S*-dimethylethylene).



Extension of present methods of nomenclature of two- and three-dimensional polymers appears possible. For example, a polymer represented by the two-carbon repeating unit

could be given the systematic name poly(ethanehexayl).

"Semiorganic" polymers with metallic or metalloid main chain atoms can be named using multivalent-radical nomenclature where it is available. For example, a dimethyl silicone could be named "poly[oxy(dimethylsilylene)]." Structure-based polymer nomenclature is not likely to advance ahead of the nomenclature of nonpolymeric compounds. Recognition of the problems posed by polymer nomenclature, however, should stimulate much activity in other nomenclature areas.

In summary, we can state that a nomenclature has been developed for organic polymers that is consistent with accepted organic nomenclature and applicable quite generally to polymers of regular structure. Experience with this nomenclature has been favorable to date. Further improvement can be expected with further experience.

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