Some Problems in Polymer Nomenclature*

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The historical development of polymer chemistry has led to many systems of naming polymeric substances. Many of these systems are based on a method of preparation or on an assumed or real monomer. Inconsistencies and deficiencies of such nomenclature are discussed, and some of the problems which arise in connection with the dissemination and retrieval of polymer information are pointed out. The alternative to "source" nomenclature is a system based on chemical structure; no such system has yet received universal acceptance. For linear polymers, structure names can be based on the conventional or modified conventional names of the bifunctional radicals comprising the mer, or they can be based on an assumed reaction of hypothetical monomers. The ultimate test of any system is not only that of usefulness but usability by the average chemist, and the pitfalls here are emphasized.

Polymer science, like biochemistry, has undergone an explosive growth in the last 20 years. One aspect of this growth has been in the synthesis of new polymers, the number and variety of which are reaching prodigious proportions. The complexity of the new polymer structures is such that our language is no longer capable of handling communication concerning them. That complexity, however, is of a special type. It is sufficiently ordered that it would appear that the problem of names for such entities is amenable to some sort of systematization. In many types of polymers, there would seem to be little excuse for resort to trivial names or circumlocutions in attempts at description.

We will be mainly concerned here with the naming of substances characterized by long chains of atoms which contain the same structural unit repeated many times. Macromolecules without repeating chemical structures, polymer classification, and the definitions of terms in polymer science will not be discussed.

Organic polymers command the greatest interest. An example of such a polymer would be a chain of methylene groups. If this structure were typical, the nomenclature problem would be the same as that for low molecular weight organic compounds. However, there is a little more to it. Bearing in mind that any polymer chain may have structural imperfections which are generally ignored for nomenclature purposes; remembering that all manner of terminating groups may be found for one kind of chain; and knowing that molecular weight distribution may well be as important as chemical structure in describing a polymer, we still have some of the structural naming problems to contend with which are indicated in Figure 1.

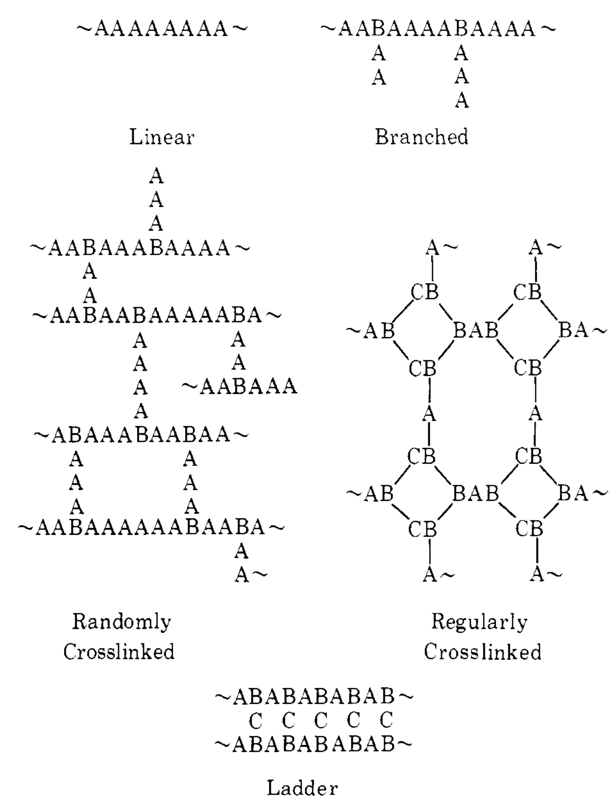

Figure 1. Two-Dimensional Polymer Chains

Here are some two-dimensional arrays of atoms of a type commonly found in polymer systems. Next to the others, the linear chain of "A" units looks ridiculously simple, but even here there can be complications, for when we say "A" can be anything, we mean just that—including the sterically or geometrically oriented forms of "A." As soon as branches are introduced, a new structural factor arises. The group at the intersection of the

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branch is different from the other A's. The A's might well be $-CH_2-$, while B is shy one hydrogen and is $-\overset{|}{C}H-$. If the branches connect to another chain, we have a crosslink, and these crosslinks can be random or regular; a form of the latter is the so-called "ladder" polymer. Additional forms of these chains might be a regular comb, where the teeth are the branches, or a star with a cyclopentane ring at the center.

If these are not enough, the situation is even more complicated in copolymers. In a sense, some of the structures in Figure 1 are copolymers. Some other copolymer types are shown in Figure 2. Any one of the A's, B's, etc., can themselves be polymers and any one of them can have some sort of stereoregular configuration.

$\sim$AABABBBAABAAAABAB$\sim$ Random

$\sim$ABABABABAB$\sim$ Alternating

$\sim A_nB_mA_nB_mA_nB_m\sim$ Block

$\sim A_nBA_nBA_nB\sim$ Coupled Block

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~AAAAAABAAABAAAAAABAA~
      C   C     C
      C   C     C
      C   C     C
      C~  C~    C~
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Graft

Figure 2. Copolymers

Vastly simplified, this is the problem: Name all of these and many other kinds of structures in some rational way so that we don't have to draw pictures in the air while we talk or spend half an hour describing how it was made to avoid calling it anything.

THE USERS

Whether these substances are called anything at all depends entirely on the user. Some users may wish to keep the whole thing a secret; a marketing man may want to identify a good product with a company. If he is with the Chromatic Chemical Co., "polychromatol" might be a perfect name for the colored plastic he pushes.

Scientists usually like to communicate a little more information. The needs of these and other users will overlap in many cases. The users can be the research and development people, who exchange information with those who correlate it and make it available in some form, such as in indexes, punched cards, or tapes. All of these various users may have to communicate their information to people who are not chemists at all—the lawyers and the management people or the readers of the Sunday supplements, for instance. This means that your language has to be rather explicit to allow only one interpretation (and a correct interpretation, at that) to someone not well-versed in the words of some field.

IDEAL POLYMER NOMENCLATURE

What are the requirements of all these users, and how can they be matched to the naming of the structures which we have or will have in hand? First, let us examine the properties of an ideal nomenclature for polymers. The adjectives which apply to any kind of nomenclature are systematic, descriptive, and unambiguous. These properties are not necessarily compatible in the case of polymers, unfortunately. Attempts to describe a series of polymers differing only in the number of branches along the same kind of chains can lead to a systematic nomenclature. But if another system has evolved which is based on the chemical nature of those branches, the one cannot easily be described in terms of the other. Any system must include provision for *all* of the things which need to be described, and the problem becomes one of where to cut off description.

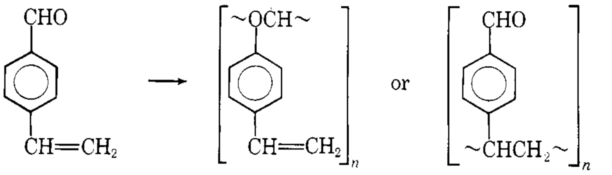
In general, the ideal is probably better approached from the point of view of improvement of systematization rather than description. The reason is soon apparent in polymers as complexity increases just a little bit, and any describable chemical property or chemical group, such as "acidity" or "carboxylic acid" is lost in the maze of other properties or groups. Thus, the aim is better to *identify* the structure in terms understandable by as many users as possible and forget description. This identification must be such that not only any imaginable polymer can be clearly delineated, but the system should be able to take care of polymers which haven't yet been imagined! In all cases, ambiguity is to be avoided. If two things have the same name, how do you tell them apart? If two people call the same thing different names, how do they talk to each other?

PRESENT PRACTICE

How closely do we approach this so-called ideal systematic, unambiguous, and somewhat descriptive nomenclature in the case of polymers? The answer, sad to say, is "not very," and it's to the detriment of almost all concerned. It would almost seem that for each new series of polymers a new system of nomenclature was devised. Thus, polymer nomenclature has grown largely as a matter of convenience. The results are generally incapable of handling the new materials being synthesized every day, and not infrequently lead a reader or listener to an incorrect conclusion as to just what substance is under discussion.

A most common method of naming polymers, especially addition polymers, involves a presumed monomer. Polystyrene is the name given to the polymer made from styrene and can be considered to be a contraction of that phrase. Poly-X is the polymer made from X. Indexers are often forced to resort to the same device, and we find "X, polymer of." This way of naming polymers falls completely apart on several counts. First, there may be many X's and therefore many possible names for what amounts to the same substance. The classic example is the polymer commonly made from ethylene oxide and called, therefore, poly(ethylene oxide). Of course, this polymer conceivably could also be made by the dehydration of ethylene glycol, the dehydrochlorination of ethylene chlorohydrin, or even a Würtz reaction from bis(chloromethyl)ether. Should it have those names?

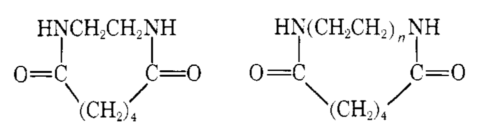
An even more ambiguous situation exists when one monomer can lead to more than one polymer. An example is the polymerization of *p*-vinylbenzaldehyde, which can lead to two different substances:



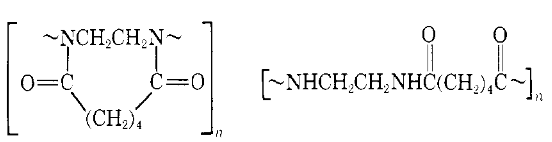
Under the source system, these would both be called poly(vinylbenzaldehyde).

A third problem arises in the case of condensation polymers. What it the monomer corresponding to the polymer made from hexamethylenediamine and adipoyl chloride? Or adipic acid, which would lead to the same polymer? Obviously, there is no monomer, and another system must be devised to name such materials. Poly(vinyl alcohol) is the name of an addition polymer for which no monomer exists.

A second nomenclature system used with polymers makes, and usually fails in, an attempt to name the repeating structural unit. This system has been applied primarily to condensation polymers. A good example is the polymer which might have its origin in terephthalic acid and ethylene glycol. It has been called poly(ethylene terephthalate), and anyone with knowledge of organic nomenclature is supposed to know that "poly" spreads ethylene terephthalate, a cyclic compound, out into linear chains! A wonderful side effect in this type of name is that you can forget the parentheses and get a whole new polymer: polyethylene terephthalate, a macrocycle. A name similar to this is poly(hexamethylene adipamide). Another might be a polymer made somehow from ethylene adipamide; the product could be either of the two poly(ethylene adipamide)s:



Ethylene adipamide   Polyethylene adipamide



Poly(ethylene adipamide)

or the macrocycle polyethylene adipamide.

In the case of some hydrocarbon polymers, structurally accurate names have been used: polymethylene, poly-1,4-phenylene, and poly(*p*-xylylene) actually name correctly the repeating unit by conventional organic nomenclature. Polyethylene and polypropylene are fortuitously correct in the same sense, but most chemists think of these as names based on source.

Many polymers are given names which describe neither source nor structure. The omission of parentheses can further complicate matters. Polyethylene glycol, I, has been used as a name for II, but this polymer

$$HO(CH_2CH_2)_nOH \qquad HO(CH_2CH_2O)_nH$$

I   II

is rarely made from ethylene glycol. Usually, II is produced from ethylene oxide, and by the source system, it is properly called poly(ethylene oxide). Neither of these names gives any indication of chemical structure. Other examples are poly(hydroxyacetic acid) (III) and poly(caproamide) or poly(ϵ-aminocaproic acid) (IV).

$$[\sim OCH_2C(O)\sim]_n \qquad [\sim NH(CH_2)_5C(O)\sim]_n$$

III   IV

Actually, probably more people call structure IV nylon-6 than anything else. This is an example of a trade name or a trade name turned generic name, which is, at best, an expedient of extremely limited usefulness. If one is concerned only with condensation polymers of the amide type such as can be obtained from the condensation of diamines with acid dichlorides, and the reaction is restricted to aliphatic straight-chain reactants, then the product polymers can be named by the term "nylon" followed by two numbers, the first giving the number of carbon atoms in the diamine, the second the number in the acid.

$$\sim NH(CH_2)_6NHCO(CH_2)_8CO\sim$$

nylon-6,10 or nylon 610

polyamide-6-10

6-10 polyamide

A more, scientific sounding but less useful (because it conveys misinformation) variant is to append the same numbers to either end of "polyamide." The moment you stray from the straight and narrow chain, you are lost for a name. If the punctuation is omitted, there is trouble; nylon-6 has 6 C-atoms from nitrogen to nitrogen, so nylon-610 should have 610 C-atoms between the nitrogens. Thus, a "system" such as this is not only limited in scope but fraught with danger. In truth, unless you are pushing a product, such names should be ignored.

The motivation for using shortened names like nylon-6 often stems from a desire to save space in a communication or possibly from the mistaken notion that comprehensibility is somehow improved. A further extension of this is seen in the use of abbreviations. Very likely, things like PMMA for poly(methyl methacrylate) will always be with us. Sometimes, the letters become so well known that many forget what they stand for and fail to define their abbreviations in a paper. It is a short step to using the abbreviation as the basis of a nomenclature; if PS is polystyrene, why not *p*-ClPS for poly(*p*-chlorostyrene)?

There is a bright spot in current polymer nomenclature practice. This is in the naming of stereoregular polymers. The field is new enough and the complexities evident enough that attempts were made almost from the outset to introduce systematic organic names into the picture. The IUPAC Subcommission has been largely responsible for this, and their recommendations (*1*) are sufficiently well-founded that they can be applied to almost any really general structure-based system of polymer nomenclature.

With the difficulties encountered in attempts to name simple polymers, it is not hard to imagine that naming complex polymers is well-nigh impossible, no matter how much stretching and tugging you do with any of the so-called systems of nomenclature just mentioned. The trouble is that most of these systems don't really *name* the polymer. With few exceptions, the appellation is one which gives a little history of the materials, tells what might have been its origin, or pins on it a pseudochemical name of the sort we find on drugs these days. Only rarely does the name accurately describe the polymer; examples are polymethylene (a polymer of repeating methylene units), poly(oxymethylene), polyphenylene, etc.

PROPOSALS

What does organic nomenclature attempt to do? There has been noted the goal of naming a molecule in terms of its structure, and in such a systematic way that all structures could be named and related to each other. The same goal should apply to organic polymers—in fact, to all polymers for which a structure can be written. To convey a notion of a description of a polymer whose structure has been written, we must describe the structure, not the polymer. And what structure is involved? It is the repeating structural unit called a "mer." If the mer can be named, a description of the substance requires only a prefix such as "poly" for an indeterminate number of repetitions or some other numerical prefix, like "deca," for a definite chain length.

As might be guessed, most of the ways to name a polymer structure fall into the realm of proposals, for none has yet been universally accepted. They all work for simple polymers for which the established names will be difficult to dislodge. In principle, these proposals also work for complex polymers, except that usually they have not been sufficiently well developed that they can be applied in detail to any structure that turns up. One fault applies generally: A complex polymer will get a complex name; sometimes it seems harder to name the substance than to synthesize it, just as it might be with organic compounds. The rules, too, must necessarily be complex, and this is a drawback to use.

A few of the broader proposals which have been made for naming polymer structures may be outlined. All of these are beset by a common problem: the definition of the repeating structural unit. By way of illustration, take a condensation polymer:

$$\sim NH(CH_2)_6NHCO(CH_2)_4CO\ [NH(CH_2)_6NHCO(CH_2)_4CO]_nNH(CH_2)_6\sim$$

From left to right, there are six different ways to write the mer in this polymer. Most of us choose the one we do based on some irrelevant habit or a random basis. Thus, the choice is really arbitrary; but nonetheless, rules must be devised so that the structure can be written the same by all who wish to name it. Once the structure has been written, any one of the systems proposed can be applied.

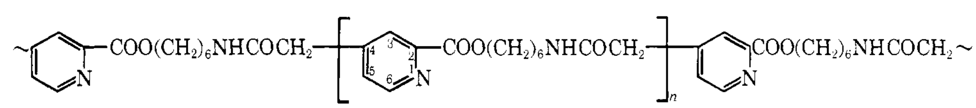
As far as is known, only one proposal has been made in which rules have been sufficiently detailed to allow a strict delineation of the structure of the repeat unit in linear polymers. These rules have been devised to accomodate a system now being developed by the Committee on Nomenclature of the Polymer Division of the American Chemical Society. Under this system, the repeating unit is named as a polyvalent radical by conventional organic nomenclature. In a single-strand linear polymer, this radical is bivalent. The name of the bivalent radical is prefixed by "poly" to give the polymer name. The radical itself is simply a recitation of the names of smaller bivalent radicals which go to make up a more complex mer:

$$\sim CH_2[-CH_2-]_nCH_2\sim$$

polymethylene

$$\sim OCH_2CH_2[-OCH_2CH_2-]_nOCH_2CH_2\sim$$

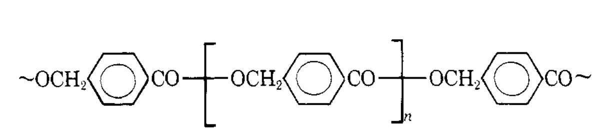
poly(oxyethylene)



poly(4,2-pyridinediylcarbonyloxyhexamethyleneiminocarbonylmethylene)

The first two structures look familiar, but the last is something new, and it cannot be named by any accepted system. Admittedly, the name is a bit long, but so is the mer. Such a name is readily adaptable to an index, and is easily translated back to the structure. Some knowledge of organic nomenclature must be assumed, but given that, any linear structure can be named. The system has no conflicts with existing nomenclature, and it appears to us to be far and away the simplest to apply, as well as having the capability of general extension to copolymers, inorganic polymers, or crosslinked polymers.

Another way to name the repeating unit on a structural basis requires a little more imagination in some cases. Many of the names are identical with those obtained as just mentioned, especially with the simpler polymers. By this system, "poly" is assumed to indicate a linear chain, and the name of the repeat unit is derived by substituting further and further back from one end of the unit. Polymethylene and poly(oxyethylene) come out the same as with the proposal given above but the last example becomes poly[*N*-[6-(4,2-pyridinediylformyloxy)-hexyl]carbamoylmethyl]. Other examples are



poly(*p*-oxymethylbenzoyl)

$$\sim(CH_2)_6CO(CH_2)_4CO-[-(CH_2)_6CO(CH_2)_4CO-]_n\ (CH_2)_6CO(CH_2)_4CO\sim$$

poly(hexamethylene adipate)

In 1952 (2) the IUPAC recommended a somewhat synthetic structure-based system which interposed an abbreviated organic bivalent radical name between "poly" and "amer."

$\sim CH_2 \sim$

polymethamer

$\sim CH_2CH_2O \sim$

polyethoxamer

$\sim NH(CH_2)_6NHCO(CH_2)_4CO \sim$

poly(azihexazamer-*alt*-adipylamer)

or poly(hexamer-*alt*-adipamidamer)

or polyhexiadipamidamer

This system at the present time is too poorly defined and too incompatible with conventional nomenclature to be adopted for general use, and it has not been accepted by the average polymer chemist.

Other systems have been proposed from time to time. For example, every linear polymer could be conceived of having been derived by the removal of hydrogen from each end of a compound, which, minus the hydrogen, is the repeating unit. Such a system would lead to some of the same problems as resulted from names based on source, such as multiple monomers giving a single polymer.

CONCLUSION

There is little doubt but that polymer nomenclature is fraught with problems, if not near-chaos. While names such as polystyrene are unambiguous and will certainly not be discarded in the near future, it must be realized that even the unambiguous names of current practice generally are simply nouns. If you know their meanings, they are part of your vocabulary. There is little that can be done to extend such names to other structures without introducing new ambiguity.

To assure rational communication in the polymer field, a structure-based nomenclature system is necessary. Such systems have been devised. As in the case of organic compounds, complex polymer structures will be given complex names. The rules for the formation of these names will be complex, also, and this acts as a deterrent to use. Usage of nomenclature in this field not only depends upon the polymer chemist, but perhaps more importantly, absolutely depends upon journal editors and the indexers in the polymer field.

LITERATURE CITED

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(2) *J. Polymer Sci.* **8**, 272 (1952).

Carbohydrate Nomenclature*

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The history and development of the Carbohydrate Nomenclature Committee of the Division of Carbohydrate Chemistry of the American Chemical Society is reviewed briefly and its present status is outlined. The work of this committee has been carried out jointly with a corresponding committee of The Chemical Society (London). The rules currently approved are presently under consideration by the Organic Nomenclature Commission of the International Union of Pure and Applied Chemistry. Extensions of these rules are currently needed and are under consideration.

The nomenclature of carbohydrate chemistry presents many problems. The carbohydrates are the only organic compounds which have an array of adjacent asymmetrically substituted carbon atoms of established configurational relationship. Their basic nomenclature was established by Emil Fischer in his classic work on carbohydrate structure. Fischer rejected a completely rational system, based upon the Geneva conventions, as being too cumbersome. He devised instead a system of common or trivial names denoting configurations of adjacent asymmetric centers through a series of four such centers.

It has become necessary to extend his system to meet structural conditions experimentally established after the work of this great master was closed; we may mention here such points as ring size, anomerism, and oligosaccharide structure. To accomplish this end, a set of basic or stem names are used, to which suitable prefixes or suffixes are added. It was in these needed extensions that great confusion resulted in the carbohydrate organic chemical literature. This situation became especially apparent in the editing of the "Advances in Carbohydrate

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