Macromolecular Nomenclature Note No. 21

[The Nomenclature Committee of the ACS Division of Polymer Chemistry (E. S. Wilks, chairman) presents a joint contribution.]

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Proposed Shorthand Notation for Nomenclature and Graphic Representation of Modified Polymers

In the last twenty years, a significant percentage of modified polymers has become commercially available. The published literature also contains many papers discussing modified polymers. In this article, "modified" is defined as referring specifically to post-treated polymers, especially those subjected to chemical post-treatment; it excludes copolymers described as "modified" by addition of a comonomer, e.g. for property enhancement. Table 1 lists some modified polymers.

Table 1. Examples of Modified Polymers

Source Material	Chemical or Physical Modification Process
Alkylene copolymers	Chlorination to form adhesion promoters; partial neutralization to form ionomers
Fluoropolymers with $-SO_2F$ groups	Hydrolysis of $-SO_2F$ groups to $-SO_3H$ groups or their salts
Melt processible rubbers	Cross-linked during compounding
Poly(methylene)	Modification by chlorination or chlorosulfonation
Poly(oxymethylene)	Acetylation of hydroxy end groups enhances polymer stability
Poly(vinyl acetate)	Hydrolysis to form poly(vinyl alcohol) monomeric units
Poly(vinyl alcohol)	Partially cyclized by reaction with aldehydes
Polyesters	Radiation of surfaces (e.g. corona treatment) to provide writable/wettable surfaces
Polyolefins, polyacrylics	Grafting of maleic anhydride to provide reactive sites for grafting or cross-linking
Polysiloxanes	Comb polymers from grafting to siloxanes of the type $-(-O-SiHMe-)_n-$
Polystyrene	Bromination to form fire-retardants; chloromethylation to provide reactive sites for grafting or cross-linking
Homo- and copolymers of C_2F_4	Post-fluorination to enhance chemical stability

There is a growing need for a concise, unambiguous, and uniform way of representing such modifications in terms of both graphic representations and nomenclature. Standards have been proposed for neither nomenclature nor graphic representations of partially modified polymers. The International Union of Pure and Applied Chemistry (IUPAC) has an active nomenclature project on this subject[1] in which use of the connective *-mod-* is tentatively proposed for use within names of modified polymers; in contrast, Chemical Abstracts Service uses the general expression "post-treated",[2] and the DuPont company uses the expression "aftertreated to".[4]

The conventional way of expressing modification of polymers is to write a chemical equation that cites the original polymer, an arrow (→), and the modified polymer. Thus, for poly(A) ***completely*** modified to poly(J) (where A and J are the names or chemical formulas of the repeating units), the change is expressed by the structure-based polymer names as poly(A) → poly(J) or by the graphic representation shown in Figure 1.

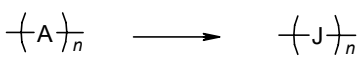

Figure 1

Source-based polymer names such as poly(A′) → poly(J′) can also be used (where A′ and J′ are the names of the real or hypothetical monomers).
Similarly, for poly(A′) ***partially*** modified to poly(A′-*co*-J′), the change is expressed by poly(A′) → poly(A′-*co*-J′) or by the graphic representation shown in Figure 2.

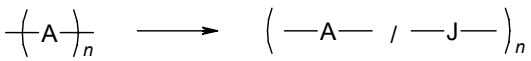

Figure 2

The conventional arrow → has thus been used for both partial and complete reactions, i.e. there has been no way of distinguishing graphically between partial and complete modification except by use of modifying text. Furthermore, this presents a conflict; the traditional arrow symbol → usually conveys the concept of a ***complete*** reaction, so to write "partial" in conjunction with its use, e.g. by drawing a modified symbol such as partial >, creates an oxymoron.

A symbol specifically intended to denote ***partial*** modification of one polymer into another is therefore needed; it is hoped that this will be discussed at an IUPAC Macromolecular Nomenclature Commission meeting in the near future. The requirements are that the symbol must be novel, unambiguous, easy to write or draw, and readily created with a minimum of keystrokes on a standard computer keyboard, and it must never have been used previously in the field of chemistry.

The new symbol tentatively proposed is a combination of a tilde and a "greater than" sign to give the symbol ~>. The expression A~>J (or A′~>J′) means that some repeating units of (A) are modified into repeating units of (J) so that A and J coexist in the polymer chain. In contrast, conventional expressions such as poly(A/J)[6] or $(\text{-A-/-J-})_n$ give no indication of how (J) was formed. If it is desired to include a degree of modification, the ~> symbol may be written as ~(x%)~>, in which x% indicates the mole percent of modification. For partial modifications in which an indication of the weight percent is more useful than mole percent, such as in the bromination of polystyrene or the chlorination of polyethylene, the symbol may be written as ~(x wt%)~>, in which x wt% denotes the weight percent of halogen added to the polymer.

Thus, the name of partially modified poly(A) is given by poly(A~>J) (structure-based) or poly(A′~>J′) (source-based), and its graphic representation shown in Figure 3.

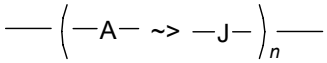

Figure 3

In contrast to the solidus, which has no implied directionality and is used merely to separate the units in graphic representations of copolymers,[5] the ~> symbol is direction-specific; thus, within a graphic representation, (A~>J) indicates partial modification of repeating unit (A) to repeating unit (J), whereas (J~>A) indicates partial modification of repeating unit (J) to repeating unit (A). To avoid confusion, it is suggested that graphic representations of partially modified polymers should never be written in the style (J<~A); i.e. the modified unit should never be written on the left of the original unit and connected to it via a left-facing or backward-pointing <~ symbol.

This shorthand notation may be extended to copolymers. Thus, for poly(A/B), i.e. poly(A′-*co*-B′), when (A) is partially modified to (J), the product is poly(A/J/B), i.e. a terpolymer containing (A), (J), and (B). The graphic representation for the reaction is shown in Figure 4.

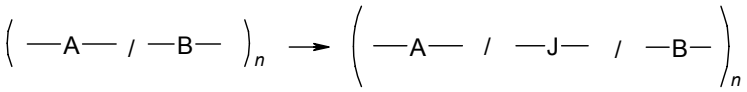

Figure 4

The product, however, is more concisely and more precisely expressed by the shorthand notation, which indicates more precisely that (J) is produced from (A). The name of the polymer is poly[(A~>J)/B] or poly[(A′~>J′)-*co*-B′] and its graphic representation shown in Figure 5.

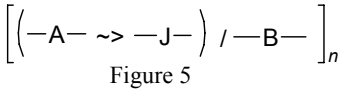

Figure 5

Correspondingly, when (B) is partially modified to (J) in the copolymer poly(A/B), i.e. poly(A′-*co*-B′), the product is also a terpolymer containing (A), (B), and (J). The polymer name may be written according to the generic format poly[A/(B~>J)]. The proposed formal accompanying graphic representation is shown in Figure 6.

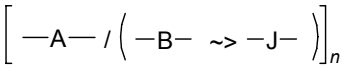

Figure 6

When the degree of modification is unknown, the new symbol should ***not*** be written as ~(partial)~> in an attempt to emphasize the point; the ~> symbol *per se* is designed expressly to indicate partial modification, and requires no further embellishment.

Use of the proposed shorthand notation is further illustrated by three examples.

Example 1: the name for the modified homopolymer in which poly(vinyl alcohol) is partially cyclized to a poly(vinyl acetal) by reaction with benzaldehyde may be written poly{(1-hydroxyethylene)~>[(2-phenyl-1,3-dioxane-4,6-diyl)methylene]} (no source-based name can be given), and the proposed (idealized) compact graphic representation is shown in Figure 7.

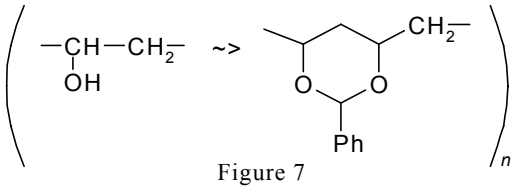

Figure 7

In cyclizations such as the one shown in Example 1, statistically there will be some hydroxy groups that remain uncyclized because their adjacent hydroxy groups are already cyclized. Theoretical calculation suggests that the highest achievable degree of cyclization is 83-85 %. This value can be considered as "complete" from the viewpoint of reactivity but "partial" from the viewpoint of stoichiometry. For a poly(vinyl alcohol) sample known to be 85% cyclized, it is therefore appropriate to draw Figure 8.

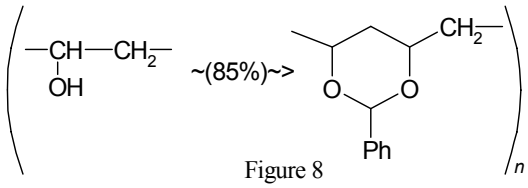

Figure 8

Example 2: the name for post-chlorinated poly(methylene), in which random hydrogen atoms are replaced by chlorine atoms to give a product containing 16% by weight of chlorine, may be written poly[methylene~(16wt%)~>(chloromethylene/dichloromethylene)]. The proposed (idealized) compact graphic representation is shown in Figure 9.

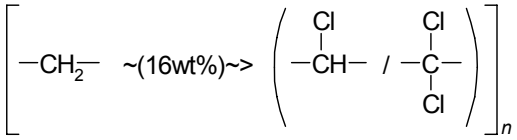

Figure 9

In this example, it is not possible to define "complete" modification based on structures such as poly(vinyl chloride), poly(vinylidene dichloride), or poly(1,2-dichloroethylene) because the products cannot be expressed by simple structures. Furthermore, poly(tetrachloroethylene) cannot be the basic structure, because steric hindrance of the chlorine atoms precludes its existence. However, from a formal viewpoint, it is possible to define "complete" modification based on this hypothetical polymer; any modification of polyethylene by chlorination is therefore partial.

Example 3: the name for the modified copolymer in which 75% hydrolysis of the methoxycarbonyl functionality of methyl acrylate structural units in poly[styrene/(methyl acrylate)] occurs to form 1-carboxyethylene (i.e. in situ acrylic acid) structural units may be written poly{[(1-acetoxyethylene)~(75%)~>(1-hydroxyethylene)]/(1-phenylethylene)} (or poly[(methyl acrylate)~(75%)~>(acrylic acid)]; source-based name). The proposed (idealized) compact graphic representation is shown in Figure 10.

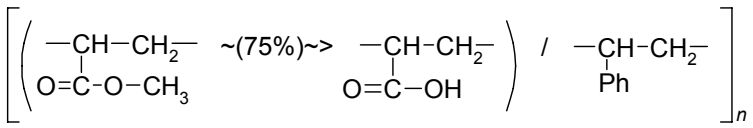

Figure 10

As shown by these examples, the proposed notation makes nomenclature and graphic representation of modified polymers a very rapid, facile, and unambiguous process.

References and Notes

1. Wilks, E. S. "Process-Based Nomenclature for Modified Polymers (IUPAC Recommendations)", Project No. 1999-051-1-400 [990511/400/00]. Url: http://www. iupac. org/projects/1999/1999-051-1-400. html. [Original title: Source-Based Nomenclature for Modified Polymers (IUPAC Recommendations)"]

2. A typical Chemical Abstracts Service (CAS) post-treated polymer is named thus: Ethene, homopolymer, chlorinated, [64754-90-1*]. Whenever a CAS RN appears followed by an asterisk, it is accompanied by the following message: "* Use of this CAS Registry Number alone as a search term in other STN files may result in incomplete search results. For additional information, enter HELP RN* at an online arrow prompt (=>). " Records with registry numbers marked with an asterisk do ***not*** represent CAS indexing and naming policies. These numbers and names are created by CAS for regulatory agencies to meet their need in identifying articles of commerce.[3] Such registry numbers usually have few or no postings in bibliographic files such as File CA or File CA Plus.

3. Metanomski, W. V. Chemical Abstracts Service, personal communication to E. S. Wilks, 1996.

4. Wilks, E. S. “Polymer Nomenclature: The Controversy Between Source-Based and Structure-Based Representations (A Personal Perspective)”. *Prog. Polym. Sci.,* **2000**, *25*, 9-100.

5. IUPAC: “Graphic Representations (Chemical Formulae) of Macromolecules (Recommendations 1994)”. *Pure Appl. Chem*., **1994**, *66*, 2469-2482.

6. IUPAC: “Structure-Based Nomenclature for Irregular Single-Strand Organic Polymers (Recommendations 1994)” *Pure Appl. Chem.,* **1994**, *66***,** 872; 873-889.

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Title: Proposed Shorthand Notation for Nomenclature and Graphic Representation of Modified Polymers

Abstract (explanation of article, for DuPont only; not part of the article; will not be published)

In the last twenty years, a significant percentage of modified polymers has become commercially available, and the published literature also contains many papers discussing modified polymers. There is therefore a growing need for a concise, unambiguous, and uniform way of representing such modifications in terms of both graphic representations and nomenclature. The usual way of indicating a completely modified polymer is to write a conventional equation such as poly(A) → poly(J) [in which poly(A) is completely converted to poly(J)]. Standards have been proposed for neither nomenclature nor graphic representations of ***partially*** modified polymers. This article proposes use of a novel symbol, ~>, to indicate partially modified polymers. Thus, the expression A~>J (where A and J are structural repeating units) means that some repeating units of (A) are modified into repeating units of (J) so that A and J coexist in the polymer chain. For source-based representations the expression is poly(A′~>J′) (where A′ and J′ are monomeric units). The name of partially modified poly(A) is given by poly(A~>J) (structure-based) or poly(A′~>J′) (source-based); the corresponding graphic representation is -(-A- ~> -J-)$_n$-. If it is desired to include a degree of modification, the ~> symbol may be written as ~(x%)~>, in which x% indicates the mole percent of modification. For partial modifications in which an indication of the weight percent is more useful than mole percent, such as in the bromination of polystyrene or the chlorination of polyethylene, the symbol may be written as ~(x wt%)~>, in which x wt% denotes the weight percent of halogen added to the polymer.