

Macromolecular Nomenclature Note No. 22

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

In this issue, three topics of interest or importance to polymer scientists and engineers are discussed:

1. Use of molar mass versus molecular weight
2. The name for the mathematical term $(R_g^2/M)^{1/2}$
3. The conflict that arises between the “logical” or “traditional” way that most authors use to draw structure-based representations, according to the polymerization reactions, versus what is correct according to:
 - the principles of the American Chemical Society and Chemical Abstracts Service
 - the recommendations of the International Union of Pure and Applied Chemistry (IUPAC)

Topic 1: Which is Correct – Molar Mass or Molecular Weight?

L. H. Sperling^a and E. S. Wilks^b
Nomenclature Committee
ACS Division of Polymer Chemistry, Inc.

An author of a text-book on polymers asked a member of the Nomenclature Committee whether it was more correct to use **molar mass** (MM), a more recently introduced term, or **molecular weight** (MW), an older term still in widespread usage.

There is an important difference; MM is (technically) independent of gravity, whereas MW is not. However, on planet Earth, MM and MW amount to virtually the same thing. Discussion by the members of Nomenclature Committee resulted in the recommendation that authors of textbooks on polymers who choose to discuss this point should write an explanatory paragraph or footnote, at the point in their text at which the first occurrence of either of these expressions occurs, that ties the two expressions together by addition of a statement such as “molar mass is informally referred to as molecular weight”. Then, authors are free to select *one* of the two expressions and – for the sake of consistency – use it for the rest of the book. The International Union of Pure and Applied Chemistry (IUPAC) defines both terms as shown in Table 1.¹

Table 1. IUPAC Definitions for Molar Mass and Molecular Weight¹

Term	Definition
1.1 relative molecular mass, molecular weight	recommended symbol: M_r The ratio of the average mass per formula unit of a substance to 1/12 of the mass of an atom of nuclide ¹² C. <i>Note</i> See Definition 1.2.
1.2 molar mass	recommended symbol: M Mass divided by amount of substance. <i>Notes</i> 1. Molar mass is usually expressed in g/mol or kg/mol units. The g/mol unit is recommended in polymer science, since then the numerical values of the molar mass and the relative molecular mass of a substance are equal.

The Nomenclature Committee conducted a global internet survey by asking polymer scientists and engineers for their opinions on Topic 1. Most respondents were from the US; five said that they use MM, eight said that they use MW, and four were non-committal. Two respondents pointed out that Europeans already use MM. Additional comments came from two of those who use MW; one stated that MM is more correct, and the other stated that (s)he uses MW but would support a change to MM. Only one respondent liked Daltons.

A survey of two issues of the *Eur. Polym. J.*, [2001, 13, issues 10 and 11] yielded the results summarized in Table 2. None of the articles surveyed was a contribution from the North American continent.

Table 2. Summary of Survey of *Eur. Polym. J.*, 2001, 13(10, 11) for Molar Mass vs. Molecular Weight

Molecular Weight	Molar Mass	M_n or M_w^a	η^b	Kilodaltons	Degree of Polymerization	Nil ^c
17	1	6	2	1	1	22

^a M_n means number-average molecular weight; M_w means weight-average molecular weight.

^b η means viscosity; notes were not taken during the survey on whether the viscosity type cited was specified (e.g., inherent, intrinsic, Mooney) or unspecified.

^cNil means that the number of articles surveyed either did not discuss molecular weight, molar mass, etc., or cited no synonyms.

Most of those not reporting any molecular weight (molar mass) data used either industrial samples or crosslinked materials, or natural products. This sample suggests that an overwhelming majority of *European Polymer Journal* scientists and engineers use molecular weight, rather than molar mass.

Conclusions

1. IUPAC recommends the term molar mass (MM), but permits the use of molecular weight (MW)
2. MM and MW are both in use by polymer scientists and engineers
3. MW is preferred on the North American continent
4. MW is preferred by most contributors of articles to the *European Polymer Journal*
5. Complete unanimity is unlikely to be achieved soon

Topic 2: Is There a Name for the Mathematical Term $(R_g^2/M)^{1/2}$?

L. H. Sperling^a and E. S. Wilks^b
Nomenclature Committee
ACS Division of Polymer Chemistry, Inc.

A graduate student at Lehigh University, Mr. Aki Kikuchi, suggested the name *chain stiffness* for the term $(R_g^2/M)^{1/2}$, where R_g represents a polymer chain radius of gyration of molecular weight M . Although it appears in virtually all modern polymer textbooks, this term still has **no name**.

The Nomenclature Committee conducted a global internet survey by asking polymer scientists and engineers for their opinions on Topic 2. The results are given in Table 3.

Table 3. Responses to the Question: “What Name would you Propose for the Equation $(R_g^2/M)^{1/2}$?”

Names	Number of Respondents	Comments
Chain flexibility (possibly)	1	Chain stiffness is widely used
Chain frangibility	1	None
Chain persistence	1	None
Chain stiffness	1	Chain stiffness is not too bad
Chain stiffness	3	None
Characteristic ratio	1	Don't like name chain stiffness
No name suggested	1	Chain stiffness is not a good name
No name suggested	1	Chain stiffness might be construed as modulus
No name suggested	1	Expression doesn't equate to chain stiffness
No name suggested	1	Not in favor of chain stiffness per se; suggests qualification by writing “chain stiffness as measured by $(R_g^2/M)^{1/2}$ ”
No name suggested	8	None

The term $(R_g^2/M)^{1/2}$ deserves a name. Chain stiffness, which implies modulus, was recommended by only a few. How about a name that recognizes the name of a pioneer in the field? Polymer science has the Flory θ -temperature and the Mark-Houwink-Sakurada intrinsic viscosity term. Peter Debye^{2,3} did the basic

derivation for the determination of R_g via light-scattering. Would something like the *Debye dimension* for $(R_g^2/M)^{1/2}$ be acceptable? Of course, any term proposed should be both recommended by IUPAC and accepted by the polymer community. Suggestions are welcomed.

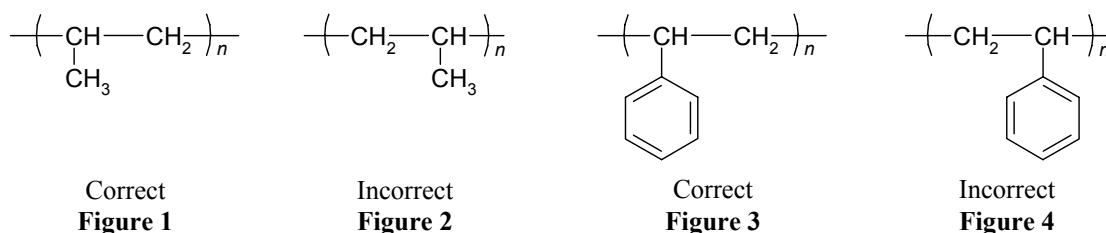
Topic 3: Graphic Representations of Polymers – The Conflict Between Polymerization Mechanisms and Guidelines

E. S. Wilks^b and L. H. Sperling^a
Nomenclature Committee
ACS Division of Polymer Chemistry, Inc.

In 1968, the American Chemical Society⁴ (ACS) proposed structure-based nomenclature and representation for linear polymers in which structural repeating units (SRUs) are named from left to right. The recommendations cover SRUs containing heterocyclic ring systems, acyclic hetero atoms, carbocyclic ring systems, and acyclic carbon chains. A fundamental point of structure-based nomenclature is that any substituents attached to rings or chains are assigned the lowest possible locants. The accompanying graphic representations are consistent with the proposed nomenclature system.

The recommendations of the International Union of Pure and Applied Chemistry (IUPAC) for graphic representations of such SRUs, which IUPAC refers to as constitutional repeating units (CRUs), are fully in accordance with the ACS document and are given in a comprehensive publication.⁵

For example, polypropylene and polystyrene are represented as shown in Figures 1 and 3,⁴ and *not* as shown in figures 2 and 4.



The structure-based names given⁴ for polypropylene and polystyrene were poly(1-methylethylene) (Figure 1) and poly(1-phenylethylene) (Figure 3), respectively;⁶ a key point is that in both names the *lowest* locant, i.e. 1-, is assigned to the substituent.

Figure 5 shows another example – the correct graphic representation for polyamide 66 (nylon 66).

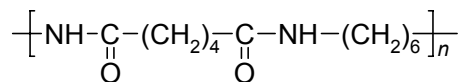


Figure 5

Concerning correct orientation, the ACS principles for SRUs and IUPAC recommendations for CRUs are referred to collectively in this article as *guidelines*; in this article the CRU versus SRU issue will be circumvented by use of RU (for Repeating Unit). The correct orientation for the RU of Figure 5 is determined by the three guidelines listed in Table 4, which are applied in descending order.

Table 4. Guidelines Required to Determine Correct Orientation of the Polyamide 66 RU

Guideline No.	Description of Guideline ^a
(1)	Start at one of the hetero atoms
(2)	Proceed by the shortest possible path to the other hetero atom
(3)	Since (2) offers two possibilities, proceed by the <i>more substituted path</i>

^aThe general guidelines that apply to all RUs are modified here specifically to apply to polyamide 66.

From the point of view of polymer scientists and engineers, the guidelines unfortunately frequently conflict with the chemical processes involved in polymer syntheses. Studies of many articles and chapters, including those specifically about nomenclature, in encyclopedias and text-books by noted scientists and

educators in the polymer field showed that authors prefer to represent polymers graphically according to the way the polymer chains form, rather than according to the guidelines. With some justification, they argue (sometimes vehemently) that, unless the chemistry and the guidelines coincide, graphic representations according to the guidelines confuse the students, who have enough problems with understanding polymer chemistry without having to deal with what are – to them – irrational guidelines that don't conform to the chemistry!

Polystyrene and polyamide 66 (nylon 66), as examples of chain-growth (addition) polymers and step-growth (condensation) polymers, respectively, serve here as polymers suitable for discussion of this conflict.

Polystyrene

Free-radical polymerization of styrene to give polystyrene typically proceeds from reaction of styrene with a free-radical initiator ($R\cdot$), and the growing chain is typically represented in encyclopedias and text-books as shown in Figure 6. Because secondary carbon atom radicals are more stable than primary ones, the chains grow mostly as shown in Figure 6, rather than as shown in Figure 7.

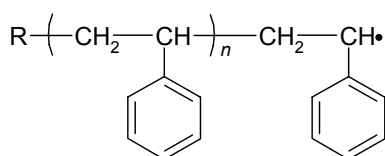


Figure 6

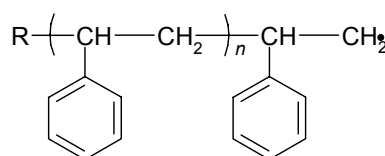


Figure 7

The final polymer, however, should be drawn according to the representation of Figure 3.

Polyamide 66

This polyamide, typically prepared from hexanedioic acid [adipic acid⁸] and 1,6-hexanediamine [hexane-1,6-diamine], is usually represented in encyclopedias and text-books according to Figure 8 or Figure 9, both of which show the moieties derived from the comonomers intact within the chain after the water molecules have been eliminated during the polycondensation reaction.

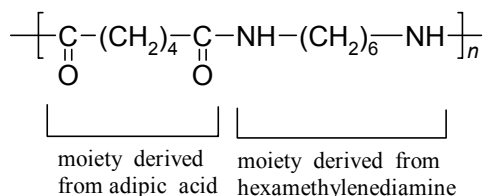


Figure 8

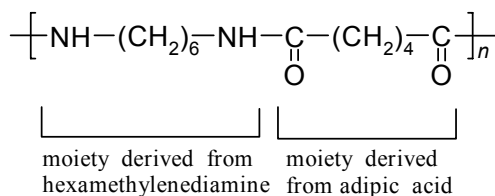


Figure 9

The final polymer, however, should be drawn according to the representation of Figure 5.

In order to reconcile these opposing forces, it is necessary to state two simple but critical related points:

Correct graphic representation of a polymer is:

- achieved by following the guidelines
- not directly related to the polymerization mechanism

While this requires educators, students, and authors of encyclopedias, text-books, and journal articles, to take one additional step, it is not usually a difficult one. Having depicted the RU according to the polymerization mechanism, the writer of an article or chapter is then required to orient it according to the guidelines, which may require that it be redrawn or “rephased” (parentheses or brackets shifted along the chain to the left or to the right) versus the RU drawn according to the polymerization reaction. Again, polystyrene and polyamide 66 (nylon 66) are used as examples to illustrate the steps.

To achieve uniformity in structural representations is sometimes, as in the case of polystyrene (Figures 3 and 7), a simple matter. The polystyrene backbone comprises only one subunit – asymmetrically

substituted 1,2-ethanediyl [ethylene].⁹ Correct orientation is achieved by “rephasing” it so that the phenyl substituent has the lowest locant.

While the case of polyamide 66 (nylon 66) (Figure 5) requires slightly more work, inspection shows that there are four subunits, but only three types of subunit; these are depicted in Figure 10. Although they are arranged alphabetically, it is the *structural characteristics* of each subunit that determine the final order in the complete SRU.

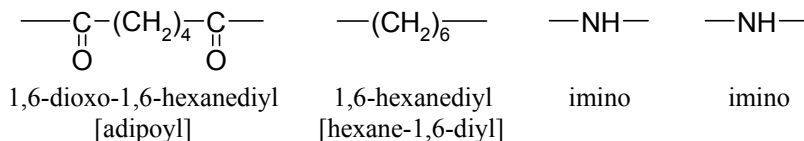


Figure 10

According to the first principle listed in Table 4, one imino subunit is selected first. Choice of the next subunit cannot be determined by the second principle alone, since the 1,6-dioxo-1,6-hexanediyl [adipoyl] and 1,6-hexanediyl [hexane-1,6-diyl] subunits are of equal length – both are six carbon atoms long. The third principle is therefore applied in order to resolve the situation. This results in choice of 1,6-dioxo-1,6-hexanediyl [adipoyl], the more highly substituted subunit, to be drawn to the right of the first imino subunit selected. The rest of the RU then “falls into place” – selection of the second imino subunit, followed by the 1,6-hexanediyl [hexane-1,6-diyl] subunit.

While this may seem overly pedantic, especially because the result is different from the “intuitive” one obtained by merely “stringing together monomeric units and removing water molecules to form the final RU”, discipline is needed even in a relatively simple case such as polyamide 66. Many RUs are much more complex than this, and the possible variants in a complex RU may result in hundreds of permutations, i.e., ways of combining subunits. It is *fundamental* to the creation of databases used for storage of structure representations that order and method be applied; reliable retrieval of specified polymers can be achieved only by using one standard way of structuring and naming RUs.

Once uniformity of representation is accomplished, there is surely satisfaction to be gained from knowing that everyone else who follows the guidelines will also draw the RU for any given polymer in the same way.

The result of global uniformity is enhanced ease of communication about polymers. There is an additional benefit; nomenclature is frequently difficult for many polymer scientists and engineers, and representing RUs incorrectly simply adds to their frustration. The chances of naming correctly an incorrectly oriented RU are bleak, whereas a correctly oriented RU has a good chance of being named correctly.

The challenge, therefore, to polymer scientists and engineers all over the world, is to take that extra step, to make that additional effort; the rewards are there! References are available for the identification, orientation, and naming of repeating units for structure-based representations of polymers.¹⁰⁻¹⁴

Authors’ Closing Comments

In an effort to reduce the dichotomy depicted above, the IUPAC Commission on Macromolecular Nomenclature (or its successor after January 1, 2002) should consider ways of condoning both chain-growth and step-growth mer structures, as drawn by most polymer scientists and engineers. While IUPAC should – and does – provide leadership in nomenclature, it also has an obligation to:

- recognize wide-spread, well-used, and traditional nomenclature and terminology terms
- find ways to reconcile principles and practice

References and Notes

1. IUPAC: (a) “Note on the Terminology for Molar Masses in Polymer Science”. *J. Polym. Sci., Polym. Lett. Ed.* **1984**, 22, 57; (b) “Definitions of Terms Relating to Individual Macromolecules, Their Assemblies, and Dilute Polymer Solutions (Recommendations 1988)”. *Pure Appl. Chem.*, **1989**, 61, 211-241. Reprinted as Chapter 3 in Ref. 13.

2. Debye, P. *J. Appl. Phys.*, **1944**, *15*, 338.
3. Debye, P. *J. Phys. Colloid Chem.*, **1947**, *51*, 18.
4. American Chemical Society: "A Structure-Based Nomenclature for Linear Polymers". *Macromolecules* **1968**, *1*, 193-198.
5. IUPAC: "Graphic Representations (Chemical Formulae) of Macromolecules (Recommendations 1994)". *Pure Appl. Chem.*, **1994**, *66*, 2469-2482. For a more comprehensive listing of published articles on polymer nomenclature, see Ref. 11.
6. Chemical Abstracts Service introduced the so-called "9CI nomenclature" at the beginning of the Ninth Collective Index period (1972). Application of 9CI nomenclature principles to the names poly(1-methylethylene) and poly(1-phenylethylene) results in changes to poly(1-methyl-1,2-ethanediyl) and poly(1-phenyl-1,2-ethanediyl), respectively [IUPAC still recommends poly(1-methylethylene) and poly(1-phenylethylene)]. The reasons for adoption of the 9CI nomenclature were set forth in the Chemical Abstracts Ninth Collective *Index Guide* and in a journal article; see Ref. 7.
7. Donaldson, N.; Powell, W. H.; Rowlett, R. J.; White, R. W.; Yorka, K. V. "Chemical Abstracts Index Names for Chemical Substances in the Ninth Collective Period (1972-1976)". *J. Chem. Doc.* **1974**, *14*, 3-15.
8. Where an IUPAC name differs from a Chemical Abstracts index name, it is enclosed within square brackets after the Chemical Abstracts index name.
9. A subunit is a segment or moiety of the backbone of the complete SRU. In linear single-strand SRUs, typical subunits are: (a) heterocyclic ring systems (e.g., 3,5-pyridinediyl [pyridine-3,5-diyl]); (b) acyclic hetero atoms [e.g., oxy (-O-) and imino (-NH-)]; (c) carbocyclic ring systems (e.g., 1,4-phenylene); (d) acyclic carbon chains (e.g., 1,6-hexanediyl [hexane-1,6-diyl], -(CH₂)₆-, which must not be divided into smaller subunits. Thus, 1,2-ethanediyl [ethylene], -CH₂-CH₂-, must not be treated as "methylenemethylene".
10. Wilks, E. S. "Macromolecular Nomenclature Note No. 18. SRUs: Using the Rules". *Polym. Prepr.* **2000**, *41*(1), 6a-11a. Also available at: <http://www.chem.umn.edu/~poly/nomenclature.html>.
11. Wilks, E. S. "Macromolecular Nomenclature Note No. 17. Whither Nomenclature?" *Polym. Prepr.* **1999**, *40*(2), 6-11. Also available at: <http://www.chem.umn.edu/~poly/nomenclature.html>. This article lists the most significant documents on polymer nomenclature published during the second half of the twentieth century.
12. Chemical Abstracts Service (CAS): *Index Guide*, Appendix IV (© 2002). Chemical Abstracts Service, 2540 Olentangy River Road, P.O. Box 3012, Columbus, OH 43210-0012; see Section F, Subsection 222: Description of CAS Polymer Indexing Rules. Appendix IV is also available as a reprint entitled "Naming and Indexing of Chemical Substances for Chemical Abstracts"; free reprints are available by writing to Marketing Communications, Chemical Abstracts Service, P.O. Box 3012, Columbus, OH 43210-0012. Section F, Subsection 222 is also available at: <http://www.cas.org/EO/polymers.pdf>.
13. *Compendium of Macromolecular Nomenclature* (The Purple Book), W. V. Metanomski, (Ed.), Blackwell Scientific Publications, Oxford, 1991. The paper edition is out of print; an online version is available at: <http://www.iupac.org/publications/books/author/metanomski.html>.
14. A list of valid IUPAC and other recommendations on macromolecular terminology and nomenclature is published twice yearly in Polymer Preprints; see, for example, *Polym. Prepr.* **2000**, *41*(2), 14a-15a. The list is also available at: <http://www.iupac.org/divisions/IV/IV.1/index.html>. Most of these references, as well as a cumulative list of all previously published Macromolecular Nomenclature Notes, are also available at: <http://www.chem.umn.edu/~poly/nomenclature.html#rec>.

^aMailing address: Departments of Chemical Engineering and Materials Science and Engineering, Materials Research Center, Center for Polymer Science and Engineering, and Polymer Interfaces Center, Lehigh University, 5 E. Packer Ave., Bethlehem, PA 18015-3194. E-mail address: lhs0@Lehigh.edu.

^bMailing address: 113 Meriden Drive, Canterbury Hills, Hockessin, DE 19707. E-mail address: tedwilks@juno.com.