Macromolecular Nomenclature Note No. 18

E. S. Wilks*
Nomenclature Committee
ACS Division of Polymer Chemistry, Inc.

SRUs: Using the Rules

In this Macromolecular Nomenclature Note (MNN) we review the process of how to draw and name correctly the structural repeating unit (SRU) of a structure-based representation of a polymer. In the published literature there are a disturbing number of structure-based representations that are incorrect according to the rules set forth by Chemical Abstracts Service (CAS) and the International Union of Pure and Applied Chemistry (IUPAC). Not only are the pictorial representations frequently incorrect, names are often either omitted, incorrect, or source-based. In a publication, it may admittedly be unnecessary to give the correct structural representation and name of a polymer in order to understand its composition, but continued failure to draw structure-based representations correctly is dangerous because it clearly disseminates the ever-widening belief among authors of publications that either there are no rules, or that it is acceptable to ignore them. There ***are*** rules; to ignore them is to impede proper communication. Failure to learn and adhere to the rules results in decreased uniformity among pictorial representations in publications and frustration for those who search the published literature. Searchers of well-organized databases, such as Chemical Abstracts' Registry File, who don't know the rules become frustrated because they can't find a structure that they seek, and they conclude that: (1) it isn't in the database because they didn't find it; or (2) they suspect it may be in the database, but they can't find it, don't know why, and give up the search; or (3) they know what the problem is but they haven't the skills to circumvent it.

Those who search the CAS Registry File owe it to themselves to learn the rules. The on-screen images of many SRUs appear laterally reversed, which may unfortunately contribute to misunderstandings about correct orientation; the rules for naming SRUs have no connection with their on-screen appearance.

Those who publish papers on polymers owe it to the polymer community to familiarize themselves with the rules and apply them to published structure representations. This introduction provides guidance for some commonly encountered linear polymers; it is ***not*** intended to be a complete course on the subject.

CAS and IUPAC have agreed upon a set of rules for the **identification**, **orientation**, and **naming** of SRUs. CAS publishes them in the *Index Guide*.[1a] The IUPAC recommendations, published in "Nomenclature of Regular Single-Strand Organic Polymers",[2] are based on seminal ACS recommendations from 1968.[3] CAS names a polymer as poly(SRU), whereas IUPAC uses "poly(constitutional repeating unit)" or poly(CRU); the two terms are virtually synonymous. In this MNN we will use SRU. The CAS and IUPAC naming principles are essentially identical, but names of SRUs derived by the two systems are sometimes different; examples are given. Structure-based representation only of polymers is discussed.

The steps involved in the complete process are:

(1) **Identification** of the repeating unit: this is more easily accomplished by drawing a larger segment of the chain that contains at least two repeating units.

(2) **Orientation** of the repeating unit: this is the most difficult step, and precise instructions are given below for some simple SRUs. Complete coverage of all the rules is beyond the scope of this MNN.

(3) **Naming** of the complete repeating unit: the complete SRU is named as a bivalent organic group according to the usual nomenclature rules for organic chemistry. This step is optional but it is usually helpful for those writing publications or executing searches.

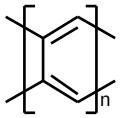
Each of these three steps is now described in more detail.

(1) **Identification**: draw a segment of the chain long enough to contain at least two complete units. Start by placing a left square bracket through any single chain bond between two subunits (also called multivalent radicals) in the chain. Read along the chain (from left to right) until you come to the next occurrence of the same type of subunit to the left of which you placed the left square bracket, and place a right square bracket through the single chain bond to the left of it. Place a sub-*n* outside the right square bracket. This **identifies** the SRU.

Example 1.1: assume that a chain has seven different types of subunit, called (arbitrarily) P, Q, R, S, T, U, and V, and that they are bonded in the order: ..P-R-T-V-U-S-Q-P-R-T-V-U-S-Q-.. .
(a) Place a left square bracket somewhere near the left-hand end of the sequence, e.g. through the single chain bond between T and V. This creates ..P-R-T-[-V-U-S-Q-P-R-T-V-U-S-Q-.. .
(b) Read along the chain (from left to right) as far as the next occurrence of V and place a right square bracket through the single chain bond to the left of it; this creates ..P-R-T-[-V-U-S-Q-P-R-T-]-V-U-S-Q-.. .

(c) Add a sub-*n* outside the right square bracket; this **identifies** the SRU as -[-V-U-S-Q-P-R-T-]*n*- .

Notes: (1) place the square brackets through single chain bonds in preference to multiple chain bonds (see rule F below); (2) if there are no single, acyclic (non-ring) bonds in the chain, the polymer is a ladder type (see example 1.2); their orientation requires a complex set of rules that is outside the scope of this MNN.[1,4]

Example 1.2: 

(2) **Orientation**: orienting the SRU correctly means that it may have to be redrawn. A correctly oriented SRU has the senior subunit placed leftmost, and the rest of the subunits then read left to right, as determined by the procedure described below. In order to orient the SRU identified in the previous step, six important rules (A – F below) are needed.[5]

· **Rule A**: the order of seniority among the types of subunits is: (a) heterocyclic rings; (b) acyclic hetero atoms; (c) carbocyclic rings; and (d) chain containing carbon atoms only. In the examples in this MNN, ">" means "is senior to".

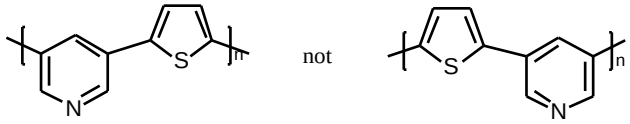
Table 1: Examples to illustrate rule A

Ex. No.	Example[a]	Rule demonstrated
2A1	2,5-thiophenediyloxy (not oxy-2,5-thiophenediyl)	heterocyclic ring > acyclic hetero atom
2A2	oxy-*p*-phenylene (not *p*-phenyleneoxy)	acyclic hetero atom > carbocyclic ring
2A3	*p*-phenylenemethylene (not methylene-*p*-phenylene)	carbocyclic ring > carbon chain
2A4	oxymethylene (not methyleneoxy)	acyclic hetero atom > carbon chain

[a]A lower-case italic letter *p* may be used in place of the numerical locants 1,4 for disubstituted benzene derivatives, but the numerals are preferred.[6]

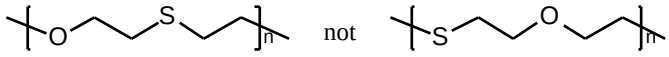
· For chains containing more than one type of heterocyclic ring, there is a further set of rules,[1b] which are too complex to reproduce here, for determining seniority; one example only is given.

Example 2A5: 3,5-pyridinediyl > 2,5-thiophenediyl (nitrogenous heterocycle > non-nitrogenous heterocycle); therefore:



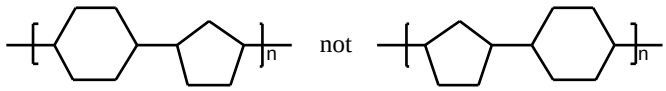
· For chains containing heteroatoms, seniority is as follows: O, S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, Hg.

Example 2A6: -O-C-C-S-C-C-, not -S-C-C-O-C-C-, because O > S; therefore:



· For chains containing more than one type of carbocyclic ring, there is a further set of rules,[1b] which are too complex to reproduce here, for determining seniority. One example only is given.

Example 2A7: 1,4-cyclohexanediyl > 1,3-cyclopentanediyl (larger ring > smaller ring); therefore:



· **Rule B**: from the senior subunit (most preferred multivalent radical), as determined by rule A, proceed by the shortest path (smallest number of atoms) to (a) another occurrence of the same subunit (if present) within the SRU, then (b) to the next most preferred subunit, and so on.[1a] This rule thus indicates the direction in which to read along the chain after the senior subunit has been identified. Table 2 gives some examples.

Table 2: Examples to illustrate rule B

Ex. no.	Example	Rule demonstrated
2B1	-O-C-O-C-C- (not -O-C-C-O-C-)	B(a): shortest path to another occurrence of same subunit
2B2	-O-C-S-C-C- (not -O-C-C-S-C-)	B(b): from senior subunit to next most preferred subunit

If application of rule B results in more than one possible path, the situation is resolved by taking the most highly substituted path; nylon 66 is a good example (see table 3).

Table 3: Resolution of "Equal Path Length" Situation

Ex. no.	Example	Rule demonstrated
2B3	-NH-CO-$(CH_2)_4$-CO-NH-$(CH_2)_6$- (not -NH-$(CH_2)_6$-NH-CO-$(CH_2)_4$-CO-, not -CO-$(CH_2)_4$-CO-NH-$(CH_2)_6$-NH-)	N-to-N path-lengths are the same via adipoyl or hexamethylene; the more highly substituted path, i.e. via adipoyl, is preferred.

· **Rule C**: for any given arrangement of atoms in a subunit, unsaturation is senior to saturation.[1a]

Table 4: Examples to illustrate rule C

Ex. no.	Example
2C1	-CF=CF-CH=CH- > -CF=CF-CH_2-CH_2- > -CHF-CHF-CH_2-CH_2-
2C2	1,4-phenylene > 2,5-cyclohexadiene-1,4-diyl > 2-cyclohexene-1,4-diyl > cyclohexane-1,4-diyl
2C3	2,5-furandiyl > 2,5-dihydro-2,5-furandiyl > tetrahydro-2,5-furandiyl

· **Rule D**: if substituents are present, otherwise identical parent subunits (radicals) in the SRU are chosen by the principles, in turn, of (a) maximum number, (b) lowest locants, and (c) earliest alphabetical order of substituents.[1a]

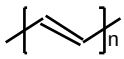
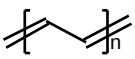
Table 5: Examples to illustrate rule D

Ex. no.	Example	Substituents rule demonstrated
2D1	**2,5-di**chloro-*p*-phenylene > **2**-bromo-*p*-phenylene	D(a): max number
2D2	**2,5-**dimethyl-*p*-phenylene > **2,6-**dichloro-*p*-phenylene	D(b): lowest locants
2D3	**2-bromo**-*p*-phenylene > **2-chloro**-*p*-phenylene	D(c): earliest alphabetical order

· **Rule E**: multiple bonds in carbon chains take the lowest possible locants, if there is a choice and no conflict with the SRU orientation rule.[1a]

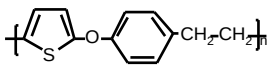
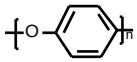
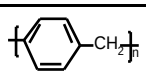
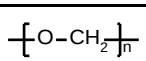
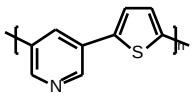
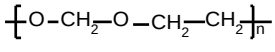
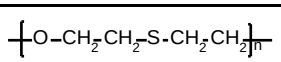
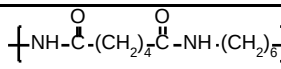
Examples to illustrate rule E: (1) poly(1,3-butadiene) obtained by polymerization of 1,3-butadiene in the so-called "1,4" mode is frequently misdrawn in publications as -(CH_2-CH=CH-CH_2)$_n$-; it should be drawn as -(CH=CH-CH_2-CH_2)$_n$-, i.e. the double bond must be assigned the lowest locant possible, and its CAS SRU name is poly(1-butene-1,4-diyl); (2) poly(2-methyl-1,3-butadiene), also called "polyisoprene", should be drawn as -[C(CH_3)=CH-CH_2-CH_2]$_n$-; (3) similarly, -(-O-CH_2-CH=CH-CH_2-CH_2-CH_2-)$_n$- is preferred to -(-O-CH_2-CH_2-CH_2-CH=CH-CH_2-)$_n$- (O is still head atom; double bond takes lowest possible locant).

· **Rule F**: when defining an SRU, parentheses are never drawn through a multiple chain bond if they can be drawn through a single chain bond (CAS doesn't state this as a rule, but cites this example[1a]).

Example 2F1:  not 

(1) **Naming**: name the subunits in the order in which they occur in the oriented SRU (from left to right); write the names of the subunits in order (left to right); enclose them in parentheses or brackets; and preface the assembled subunits with "poly". Since CAS and IUPAC nomenclature differ somewhat, the examples given above in tables 1, 2, and 3 are repeated in table 6 with both CAS and IUPAC names for comparison.

Table 6: Comparison of CAS 9CI[a] and IUPAC Names for some Polymers

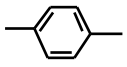
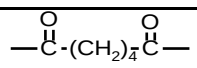
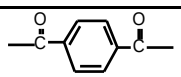
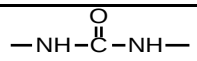
Ex. No.	Structure	CAS Polymer Name[a]	IUPAC Polymer Name
2A1		poly(2-5-thiophenediyloxy-1,4-phenylene-1,2-ethanediyl)	poly(thiophene-2,5-diyloxy-*p*-phenyleneethylene)
2A2		poly(oxy-1,4-phenylene)	poly(oxy-*p*-phenylene)
2A3		poly(1,4-phenylenemethylene)	poly(*p*-phenylenemethylene)
2A4		poly(oxymethylene)	poly(oxymethylene)
2A5		poly(3,5-pyridinediyl-2,5-thiophenediyl)	poly(pyridine-3,5-diylthiophene-2,5-diyl)
2B1		poly(oxymethyleneoxy-1,2-ethanediyl)	poly(oxymethyleneoxyeth=ylene)[b]
2B2		poly(oxy-1,2-ethanediylthio-1,2-ethanediyl)	poly(oxyethylenethioethyl=ene)[b]
2B3		poly[imino(1,6-dioxo-1,6-hex=anediyl)imino-1,6-hexanediyl][b]	poly(iminoadipoylhexane-1,6-diyl)

[a]The CAS nomenclature used in this MNN is the so-called "9CI nomenclature", which was introduced at the beginning of the Ninth Collective Index period (1972). The reasons for its adoption were set forth in the Ninth Collective *Index Guide* and in a journal article.[7]

[b] An equals sign, "=", is used to indicate that the name segment continues on the next line with no space or hyphen.

Since this part of the procedure necessarily involves knowledge of names for subunits, a long list of these would be helpful for those unfamiliar with them, but this is clearly impossible here; as stated above, this is an introduction, not a complete course. For guidance, a few examples only are included in table 7. CAS has published a larger (but still incomplete) list,[1c] many of which are usable as names of subunits in SRU nomenclature. Notice two key points in table 7: (1) the CAS and IUPAC names for some biradicals are identical whereas others are not (compare lines 1–11); (2) CAS has discontinued use of trivial names for moieties comprising two or more subunits,[8] whereas IUPAC has not (compare lines 12–14).

Table 7: Comparison of CAS 9CI and IUPAC Names for frequently encountered Bivalent Radicals

Ex. No.	Structure	CAS 9CI Name	IUPAC Name
1	-O-	oxy	oxy
2	-S-	thio	thio
3	-NH-	imino	imino
4	-N=	nitrilo	nitrilo
5	$-CH_2-$	methylene	methylene
6	-CH=	methylidyne	methylidyne
7	$-CH_2-CH_2-$	1,2-ethanediyl	ethylene
8	$-CH_2-CH_2-CH_2-$	1,3-propanediyl	propane-1,3-diyl
9	$-CH_2-CH_2-CH_2-CH_2-$	1,4-butanediyl	butane-1,4-diyl
10	-CH=CH-	1,2-ethenediyl	vinylene
11		1,4-phenylene[a]	*p*-phenylene[a]
12		(1,6-dioxo-1,6-hexanediyl)[b]	adipoyl[d]
13		carbonyl-1,4-phenylenecarbonyl[c]	terephthaloyl[c,d]
14		iminocarbonylimino[8]	ureylene[d]

[a]The other two in this series are 1,2-phenylene (= *o*-phenylene) and 1,3-phenylene (= *m*-phenylene).

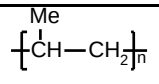
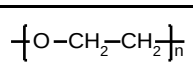
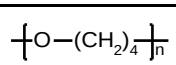
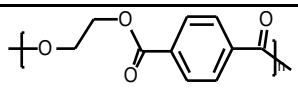
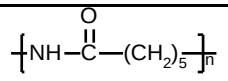
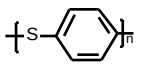
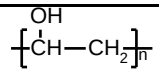
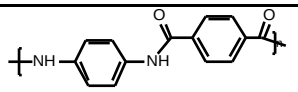
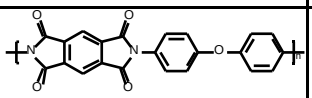
[b]Names for others in this series may be safely deduced, e.g. (1,2-dioxo-1,2-ethanediyl) = oxalyl; (1,3-dioxo-1,3-propanediyl) = glutaryl; etc. Compound (i.e. "complex") expressions such as these, which contain substituents, must be parenthesized.

[c]The other two in this series are carbonyl-1,2-phenylenecarbonyl (= phthaloyl) and carbonyl-1,3-phenylenecarbonyl (= isophthaloyl).

[d] IUPAC names such as adipoyl, terephthaloyl, ureylene, etc., are allowed only if they do not conflict with the orientation rule.

By way of further examples, table 8 gives the correct SRU representations and IUPAC names for several commercially available polymers. CAS names are given only where applicable; CAS's policy for acetylenic, acrylic, methacrylic, ethylenic, and vinyl polymers is to use source-based representation, and they are named accordingly. Thus, the CAS name for poly(vinyl alcohol) (line 8) is ethenol, homopolymer; the CAS representation is $(CH_2=CH\text{-}OH)_x$, i.e. source-based not structure-based.

Table 8: Examples of Commercially Available Polymers (see also example 2B3 in table 6)

No.	SRU	Trivial Name; CAS Polymer Name[a]	Typical IUPAC Polymer Name
1		Polyethylene; Not structured or named as an SRU	poly(methylene)
2		Polypropylene; Not structured or named as an SRU	poly(1-methylethylene)
3		poly(oxy-1,2-ethanediyl)	poly(oxyethylene)
4		poly(oxy-1,4-butanediyl)	poly(oxybutane-1,4-diyl)
5		Poly(ethylene terephthalate) (PET); poly(oxy-1,2-ethanediyloxycarb=onyl-1,4-phenylenecarbonyl)[b]	poly(oxyethyleneoxyterephth=aloyl)
6		Nylon-6; poly[imino(1-oxo-1,6-hexanediyl)]	poly[imino(1-oxohexane-1,6-diyl)]
7		RYTON® PPS;[c] poly(phenylene sulfide); poly(thio-1,4-phenylene)	poly(thio-*p*-phenylene)
8		Elvanol®;[c] poly(vinyl alcohol); Not structured or named as an SRU	poly(1-hydroxyethylene)
9		Kevlar®;[c] poly(imino-1,4-phenyleneimino=carbonyl-1,4-phenylenecarbonyl)	poly(imino-*p*-phenyleneimino=terephthaloyl)
10		Kapton®;[c] poly[(5,7-dihydro-1,3,5,7-tetraoxobenzo[1,2-*c*:4,5-*c*′]dipyrrole-2,6(1*H*,3*H*)-diyl)-1,4-phenyleneoxy-1,4-phenylene]	poly[(5,7-dihydro-1,3,5,7-tet=raoxobenzo[1,2-*c*:4,5-*c*′]dipyr=role-2,6(1*H*,3*H*)-diyl)-*p*-phen=yleneoxy-*p*-phenylene]

[a]Searchers need to know that in the Registry File, CAS frequently indexes both source-based and structure-based representations for 1- and 2-component condensation polymers. The two records are not usually cross-referenced to each other (for an exception, see note *b*). Thus, the polyamide on line 9 has two representations (source-based and structure-based), each with its own CAS Registry Number (RN). To ensure complete retrieval of references, it is necessary to search ***both*** RNs.

[b]An unusual situation exists with this polymer; the RN for the SRU, 25038-59-9, is the **preferred** registration number (PR); the Registry File record also cites three RNs in the alternate registration (AR) field and many deleted RNs (DRs). A search of the PR in the Registry File to create a line number, followed by a search of that line number in File CAPlus, retrieves all references for the PR record, the AR records, and all DR records. A search of the PR alone, or the PR plus the three ARs, does ***not*** ensure complete retrieval.

[c]Registered trademarks: Phillips Petroleum Company (RYTON® PPS); DuPont (Elvanol®, Kevlar®, Kapton®).

End groups of SRUs, when known, are specified by means of appropriate radical names, together with Greek letters "α–" and "ω–" in the name. In the CAS preferred name of a polymer, called the index name, expressions for the end groups are added after the name of the polymer. The α–end group is the group attached to the left end of the SRU when the structure is ordered according to the rules given above; it is cited first, regardless of alphabetic order.[1a] Examples are given in table 9.

Table 9: Examples of SRUs with End Groups

Ex. No.	SRU	CAS Polymer Name[a]	IUPAC Polymer Name
1	H-(O-CH_2-CH_2)$_n$-OH	α-hydro-ω-hydroxypoly(oxy-1,2-ethanediyl)	α-hydro-ω-hydroxypoly=(oxyethylene)
2	Cl-(CH_2)$_n$-CCl_3	α-chloro-ω-(trichloromethyl)=poly(methylene)	α-chloro-ω-(trichloromethyl)=poly(methylene)
3	Cl_3C-(CF_2-CH_2-)$_n$-Cl	α-(trichloromethyl)-ω-chloro=poly(1,1-difluoro-1,2-ethanediyl)	α-(trichloromethyl)-ω-chloro=poly(1,1-difluoroethylene)

[a]CAS uninverted names are given here for easier comparison with IUPAC names; CAS index names of the polymers are typically inverted, e.g. poly(oxy-1,2-ethanediyl), α-hydro-ω-hydroxy-.

References

1. CAS: Index Guide, Appendix IV (© 1998). Chemical Abstracts Service, 2540 Olentangy River Road, P.O. Box 3012, Columbus, OH 43210: (a) Section 222 – Description of CAS Polymer Indexing Rules; (b) Section 138 – Description of Ring Seniority; (c) Section 294 – Illustrative List of Substituent Prefixes.
2. IUPAC. "Nomenclature of Regular Single-Strand Organic Polymers". *Pure Appl. Chem.* **1976**, *48*, 373-385. Reprinted as Chapter 5 in "Compendium of Macromolecular Nomenclature" (The Purple Book). Blackwell Scientific Publications, Oxford, 1991.
3. ACS. "A Structure-Based Nomenclature for Linear Polymers". *Macromolecules* **1968**, *1*, 193-198.
4. IUPAC. "Nomenclature of Regular Double-Strand (Ladder and Spiro) Organic Polymers". *Pure Appl. Chem.* **1993**, *65*, 1561-1580.
5. These rules are lettered solely for clarity during discussion within this MNN; they are not so identified by either CAS or IUPAC.
6. Panico, R.; Powell, W. H.; Richer, J.-C. "A Guide to IUPAC Nomenclature of Organic Compounds (recommendations 1993)". Blackwell Scientific Publications, Oxford, 1993 [ISBN 0-63203-488-2]; see section R-0.1.6.1.
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. Some of the compound or "complex" names given in Section 294 (see ref. 1c) are intended for use as doubling radicals in substitutive nomenclature, rather than as a succession of SRU subunits; for example, the -NHCONH- moiety is named (carbonyldiimino); this would be used in a name such as (carbonyldiimino)diacetic acid. This name has nothing to do with naming the -NH-C(=O)-NH- sequence of subunits in an SRU. Use caution, therefore, with names taken from Section 294.

[*]Mailing address: CR&DD, Barley Mill Plaza P-14/1288, E. I. du Pont de Nemours and Co. (Inc.), P. O. Box 80014, Wilmington, DE 19880-0014.