POLYMER HANDBOOK

SECOND EDITION

J. BRANDRUP • E. H. IMMERGUT, Editors

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with the collaboration of

W. McDOWELL

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PREFACE

Eight years have passed since the publication of the first edistion of this POLYMER HANDBOOK. This according to many publications is exactly the time it takes for our knowledge in the natural science to double. We can confirm this statement with nearly every table in this Handbook, which indicates that progress is still occurring in all areas of Polymer Science.

This increase in the volume of literature has created a considerable number of practical problems since it was desirable to maintain a one volume Handbook. Therefore, a number of restrictions has to be imposed on the content in addition to enlarging the book format. Firstly, this edition is limited to synthetic polymers plus poly(saccharides) and derivatives. Secondly, spectroscopic data were eliminated since a number of other publications make this information available in the meantime. Within this framework, a number of new tables were added in order to complete the Handbook. Thus, tables on activation volumes, activation enthalpies and entropies of stereocontrol in free radical polymerization, isomorphous polymer pairs, compatible polymers, heat capacities, refractive indices, polymolecularity correction factors, Schulz-Blaschke and Huggins coefficients, Fikentscher K-values relative viscosity converdion tables and tables on several important polymers like poly(vinyl chloride), poly(tetrafluoroethylene), poly(oxymethylene), poly(methyl methacrylate), and poly(amide 6) appear for the first time.

It is the purpose of this Handbook to help in the search for data and constants needed in theoretical and experimental polymer work. This objective sets the framework for the contents of the second edition, as it did for the first one. Therefore, we repeat the following statements from the preface to the first edition:

"First of all, only fundamental constants and parameters were compiled rather than data of interest to the polymer engineer of fabricator. Data of fundamental interest are interpreted as data which are either physical or chemical constants of the polymer molecule within reasonable or predictable limits, or are constants of existing physical laws describing the properties and the behavior of polymers. Constants which depend to a major extent on the particular processing conditions, or sample history, were not compiled as they can be found in existing plastics handbooks and encyclopedias. Within these limits the selection of tables to be compiled was governed by two principles: sufficient data should exist to make a compilation worthwhile, and their scientific basis should be commonly accepted.

No critical evaluation of published values was attempted since this would have been an impossible undertaking within a reasonable time or with the manpower available for the task. Therefore, the authors of the individual tables were urged to list all data found in the literature except values which in their judgement, were obviously erroneous. The reader is requested to use the data with this restriction in mind and to consult the original literature references for details. Whereas a complete compilation of existing data was attempted, there will, no doubt, be some omissions. The users are asked to send to the editors any data they might be aware of but cannot find in the Handbook. This would help to make the Handbook a more reliable information source, and, therefore, an increasingly useful tool for polymer scientists.

The inclusion of the table on practical data of commercial polymers may seem to be inconsistent with the selection principles expressed earlier, but, we felt that a selected listing of such data would remind all of us that polymer "science is not a religion to be worshipped for its own sake. Science is not an ornament on society's chest. It must be woven into the fabric of life to help with the world's needs". (W.J. Sparks - Presidential Address, American Chemical Society Meeting, Detroit, 1965)".

The editors would like to thank everyone who contributed to the second edition either by submitting tables or giving advice, encouragment or support. J.B. thanks Farbwerke Hoechst AG for generous help and for the permission to undertake this task.
Thanks are also due Dr. W. McDowell who helped bear the editorial burden of the second edition by conscienciously proofreading and checking the various tables.

Spring 1974

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COMMENTS TO THE FIRST EDITION

We asked for comments about the first edition and suggestions for improvements. Here they are:

General Comments

The task of reviewing this massive work is similar to setting out to review the ABC rail guide. However, just as the possession of an ABC is vital to those who travel a lot on trains, so is the Polymer Handbook an essential piece of equipment for polymer users.
W. A. Holmes-Walker -

Publication of the Polymer Handbook marks another significant milestone in the growth of macromolecular chemistry since its inception early in this century. . . . . It is a much needed addition to the polymer literature and merits a place besides the standard chemical reference works.
G. M. Kline, Science, September 1966. -

Dieses Handbuch der Polymerchemie kommt einem ausgesprochenen Bedürfnis entgegen, indem es dem Polymerchemiker erstmals die Möglichkeit gibt, die von ihm benötigten Daten nachzuschlagen, statt sie aus der rasch anwachsenden Literatur in mühsamer Arbeit zusammensuchen zu müssen. Es gehört in die Hand jedes Polymerchemikers und wird sich bald als unersetzlich erweisen.
H. Luessi, Chmica, October 1966 -

Das Handbuch ist für die Forschung und das Labor ein hervorragendes zeitsparendes Hilfsmittel.
C. Mierisch, Textil-Praxis, October 1967 -

What Perry's "Chemical Engineers' Handbook" is to the chemical engineer, and the "Handbook of Chemistry and Physics" is to the chemist, the "Polymer Handbook" will be to the polymer scientist. This book will be a gold mine of polymer chemical data for those who know how to use it.
P. F. Bruins, Polytechnic Institute of Booklyn, Modern Plastics, February 1967 -

Dieses Werk ist sowohl für den Synthetiker, den Applikations- und Physiko-Chemiker wie auch für den Analytiker eine sehr wertvolle Zusammenstellung . . . . . .
H. Batzer, Kunststoffe-Plastics, 1966 -

For persons who work with polymers, this handbook will prove to be a valuable addition to the working literature.
W. W. West, Chevron Research Company -

The compilation has been a tremendous effort by a large number of distinguished workers, and the reward for their careful and painstaking work will be the appreciation of their colleagues, whose life will now be made much easier.
C. E. H. Bawn, Nature, 1966 -

Specific Comments and Suggestions

Topic: Nomenclature

Eine weitere Schwierigkeit war die Nomenklatur, die bei weitem nicht einheitlich ist.
Mierisch, Textilpraxis 1967 -

A brief introductory chapter outlines some well thought out rules for polymer nomenclature.
W. W. West, The Vartex -

Es bleibt zu hoffen, daß die Herausgeber in einer folgenden Auflage zu einer einheitlichen Nomenklatur finden.
K. F. Elgert, Kunststoffe, 1968 -

The first problem facing the editors is nomenclature. They have adopted a sensible compromise, adopting several systems, rather than forcing a single system into areas where it was difficult to use.
J. W. S. H. Hearle, Skinners Record, September 1966 -

The book is well arranged, the system of nomenclature is clearly set out, the index is adequate.
Res. Ass. Brit. Paint Colour Varnish Manuf. (England), October 1966 -

An introductory chapter on "Nomenclature rules" provides a useful guide to the system used in classifying and naming the polymers . . . . . This is particularly helpful in the case of the confusing situation with regard to the naming of polyurethanes, polycarbonates, and copolymers.
G. M. Kline, Science, Vol. 153 -

Topic: Selection of Tables

. . . . such topics as the physical properties of monomers and solvents should be omitted, this information is readily available in organic chemistry texts.
D. G. H. Ballard, Polymer, 1966 -

Besonders interessante Kapitel für den Synthetiker und auch den Applikationschemiker dürften sein: . . . . sowie die physikalischen Eigenschaften von einigen wichtigen Polymeren, Oligomeren, Monomeren und Lösungsmitteln.
H. Batzer, Kunststoffe - Plastics, May 1966 -

A remarkable collection of data on polymerization catalysts and inhibitors, properties of monomers and solvents; . . . The above listing does not begin to illustrate the depth or utility of the information available. For example, not only are physical properties of monomers included, but also copolymerization reactivity ratios. . .
P. F. Bruins, Modern Plastics, February 1967 -

Sehr zu begrüßen ist schließlich eine Sammlung von physikalischen Daten von Oligomeren.
Br., Gummi, Asbest, Kunststoffe, March 1967 -

Physical constants of some important polymers. Here are data on eleven materials, but - rather unfortunately - each contribution is by a different author and the treatment correspondingly varies.
W. J. Roff, Textile Inst. Ind., October 1966 -

Den Herausgebern wäre allerdings zu empfehlen, in das Kapitel VI auch Polyamid 6 aufzunehmen.
K. Gehrke, Plaste Kautschuk, December 1966 -

There is also lack of information on polyvinyl chloride, Nylon 6, the higher Nylons and some of the newer materials such as polypyromellitimides
D. G. H. Ballard, Polymer, 1966 -

Ask for more remote data in the field and it still may be there, easily found and attractively tabulated.

. . . . a veritable treasure house of information. . . . The editors aimed to compile only fundamental constants and parameters and so in some ways can be forgiven for paying only sparse attention to data relating to deformation and flow.
D. R. J. Hill, British Plastics, 1967 -

Topic: Form

The authors and editors are to be congratulated on packing so much into a single volume. Yet it would seem . . . . that the same information might have been compressed without loss of anything but blank space, into a still more compact presentation.
W. J. Roff, Textile Inst. Ind., October 1966 -

. . . . thanks to a clear lay-out (and) by following the simple nomenclature rules, information can be extracted with very little difficulty.
W. A. Holmes-Walker -

Die Vielseitigkeit und Fulle des Zahlenmaterials, das dieses Handbuch in wohlgeordneter, konzentrierter Form enthält . . . .
H. Reichert, Faserforsch. Textiltechn., 1966 -

Die Tabellen sind übersichtlich dargestellt und mit kurzen prägnanten Einführungen versehen.
H. Lussi, Chimia, 1966 -

Die Suche ist ohne Frage von Bedeutung als Nachschlagewerk; aber wenn man sich orientieren möchte, stört die kleine Schrift sehr. Ob man daran nichts ändern konnte?
W. Scheele, Kautschuk Gummi, 1967 -

. . . . direct-copy typed manuscript is small but legible.
D. W. West, The Vortex, May 1967 -

They can be forgiven for directly reprinting a large part of the copolymerization section from G. E. Ham "Copolymerization". The type script is so different from the rest of the book that there must be a certain aesthetic displeasure associated with it: it is as if the pages were colored green.
But if the editors saved time and trouble by this method and intend to amend this in their next edition, they surely cannot be blamed.
D. R. J. Hill, British Plastics, February 1967 -

The system of numbering the pages afresh in each section seems to offer no advantages to the reader and probably most users would prefer to see consecutive pagination throughout the book.
W. J. Roff, Textile Inst. Ind., October 1966 -

Die Seitenzahlen sind nicht fortlaufend; dies verbessert die Übersichtlichkeit und erleichtert den Gebrauch.
H. Batzer, Kunststoffe-Plastics, May 1966 -

Topic: Subject Index

An extensive subject index adds greatly to the value of the book.
C. W. H. Bawn, Nature, 1966 -

. . . . ein allerdings sicher noch ausbaufähiges Register . . . . . .
Br., Gummi, Asbest, Kunststoffe, March 1967 -

Ein ausführliches Sachregister am Schluß des Buches erleichtert dem Leser das Auffinden der Konstanten und Daten . . . . .
Melliand Textilberichte, September 1966 -

I. NOMENCLATURE RULES - UNITS

1. Nomenclature Rules

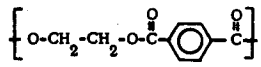
During the time of preparation of the first edition no universally accepted set of rules for naming all classes of polymers existed. We had to devise our own scheme in order to tabulate polymers in an easy way. Since then, the IUPAC Macromolecular Nomenclature Commission has published tentative rules to name regular single-strand organic polymers. These rules have been applied in this Handbook. Since the Commission stated that a number of common names are well-established by usage and that they do not intend to supplant them immediately by structure-based names, we have adhered to these common names as much as possible for simple molecules. Thus, for instance, poly(methyl methacrylate), poly(styrene), and their derivatives are named with their common names. In general, structure-based nomenclature was applied less strictly in smaller tables in order to facilitate ease of reading of these tables. The big advantage of the structure-based nomenclature lies in naming complicated macromolecules. These are mainly condensation type polymers and here we have adhered strictly to the rules given by the Commission.

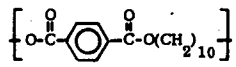
According to these tentative rules (reprinted below with the permission of the publisher) polymers can be named as follows:

(1) Find the constitutional repeating unit (CRU) which is independent of the way it was prepared (rule 1.21, page I-4).

(2) Wherever possible, the CRU should be a bivalent group. This principle of minimizing the number of free valences supersedes all orders of seniority, discussed below (rule 2.12, page I-5).

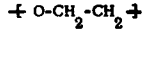
(3) The CRU is written from left to right beginning with the subunit of highest seniority and proceeding in a direction defined by the shortest path to the subunit equal or next in seniority (rule 2.11, page I-5). Ring and chain atoms are counted individually (rule 2.13, page I-6). For subunits of equal path length see rule 2.14, page I-6 and 2.32, page I-9).

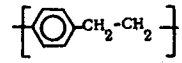
Example:  poly(oxyethyleneoxyterephthaloyl) not poly(oxyterephthaloyloxyethylene)

but:  poly(oxyterephthaloyloxydecamethylene)

(4) Start to name the CRU with the subunit of highest seniority. The descending order of seniority among the types of bivalent groups is
- heterocyclic rings (names according to rule 2.2, page I-7).
- chains containing heteroatoms (names according to rule 2.3, page I-8).
- carbocyclic rings (names according to rule 2.4, page I-9).
- chains containing only carbon

This order is unaffected by the presence of rings, atoms, or groups that are not part of the main chain (rule 2.12, page I-5).

Example:  poly(oxyethylene) not poly(ethyleneoxy)

 poly(1,4-phenyleneethylene) not poly(ethylenephenylene) or poly(methylenephenylenemethylene).

(5) The order of seniority among heterocyclic rings is given in rule 2.23, page I-7.

(6) The descending order of seniority of heteroatoms in the main chain is O, S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, Hg (rule 2.31, page I-8).

(7) The name of the subunit should include in one single name as many as possible of
- the main chain atoms or rings and
- substituents (rule 1.21, page I-4).

Example:  poly(ethylidene) not poly(methylmethylene)

(8) The subunits are named wherever possible according to the definitive rules for nomenclature of organic chemistry (International Union of Pure and Applied Chemistry "Nomenclature of Organic Chemistry". Sections A, B and C combined, Butterworths, London 1971. See also "Tentative Rules for the Nomenclature of Organic Chemistry", Section E, Fundamental Stereochemistry, J. Org. Chem. 35, 2849 (1970)).

Problems still exist in naming three-dimensional polymers, statistical, block- and graft-copolymers. These polymers were named according to their source. Rules of the first edition were applied. Thus, the different components of statistical copolymers and co-condensates are separated by the infix -co-. Components of block-copolymers are separated by the symbol: and the components of graft-copolymers by the symbol +. If monomers yield several polymeric structures a source name was also preferred. Examples are: poly(acrolein), poly(glutardialdehyde), poly(2-formyl-Δ^5-dihydropyran).

NOMENCLATURE OF REGULAR SINGLE-STRAND ORGANIC POLYMERS
TENTATIVE RECOMMENDATION OF IUPAC MACROMOLECULAR DIVISION
IUPAC-INFORMATION BULLETIN NOVEMBER 1972*.

Contents

A single strand polymer is composed of molecules whose constitutional units can be chosen such that all of them have no more than two terminal atoms. See ref. 5.

INTRODUCTION

In 1952, the Subcommission on Nomenclature of the IUPAC Commission on Macromolecules published (1) a report on the nomenclature of macromolecules that included a method for the systematic naming of linear organic polymers on the basis of structure. A later report (2) dealing with steric regularity utilized this system of nomenclature. When the first report was issued, the skeletal rules were adequate for most needs; indeed, most polymers could at that time be reasonably named on the basis of the substance used in producing the polymer. In the intervening years, however, the rapid growth of the polymer field has dictated a need for modification and expansion of the earlier rules. This report presents an updating of those rules. Necessarily, a great many changes in detail were required, since it is desirable that organic polymer nomenclature adhere as much as possible to the Definitive Rules for the Nomenclature of Organic Chemistry (3, 4).

These rules are designed to name, uniquely and unambiguously, the structures of linear regular organic polymers whose repeating structures can be written within the framework of ordinary chemical principles; stereochemistry is not considered in this report. As with organic nomenclature, this nomenclature describes chemical structures rather than substances. It is realized that polymeric substances ordinarily include many structures, and that a complete description of even a single polymer molecule would include an itemization of terminal groups, branching, random impurities, degree of steric regularity, chain imperfections, etc. Nonetheless, it is useful to think of a substance as being represented by a single structure that may itself be hypothetical. To the extent that the polymer structure can be portrayed as a chain of regularly repeating structural or constitutional repeating units (the terms are synonymous), the structure can be named by these rules; in addition, provision has been made for including end groups in the name.

In this report, the fundamental principles and the basic rules of the structure-based nomenclature are given first, accompanied by detailed extensions and applications. An appendix is included containing a limiting list of acceptable source-based names, along with the corresponding structure-based names, of common polymers. The Commission sees no objection to the continued use of such source-based names where they are clear and unambiguous, but prefers the use of the structure-based nomenclature detailed in these rules.

*Reprinted with permission of the publisher.

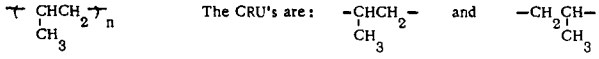
FUNDAMENTAL PRINCIPLES

This nomenclature system rests upon the selection of a preferred constitutional repeating unit (5) (abbreviation: CRU) of which the polymer is a multiple; the name of the polymer is simply the name of this repeating unit prefixed by poly. The unit itself is named wherever possible according to the Definitive Rules for the Nomenclature of Organic Chemistry(3). For single-strand polymers, this unit is a bivalent group.

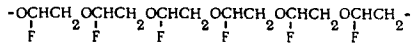
In using this nomenclature, the steps to be followed in sequence are (1) identify the CRU, (2) orient the CRU, and (3) name the CRU. Identification and orientation must always precede the selection of the name of the polymer.

(1) Identification of the Constitutional Repeating Unit

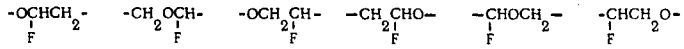
There are many ways to write the CRU for most polymer structures. In simple cases, these units are readily identified:



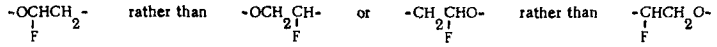
In more complex cases, it is often necessary to draw a large segment of the chain and from it choose all of the possible CRU's. For example, in the polymer



the CRU's are



To allow construction of a unique name, a single CRU must be selected. The rules following have been designed to specify both seniority among subunits, i.e. the point at which to begin writing the CRU, and the direction along the chain in which to continue to the end of the CRU. The preferred constitutional repeating unit will be one beginning with the subunit of highest seniority (see Rule 2). From this subunit, one proceeds toward the subunit next in seniority. In the preceding example, the subunit of highest seniority is an oxygen atom and the subunit next in seniority is a substituted $-CH_2CH_2-$unit. The parent CRU will therefore be either $-OCH_2CH_2-$ or $-CH_2CH_2O-$. Further choice in this case is based on the lowest locant for substitution, so that the CRU is

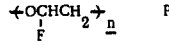


(2) Orientation of the Constitutional Repeating Unit

The CRU is written to read from left to right. In the above example, the preferred CRU is therefore  .

(3) Naming the Constitutional Repeating Unit

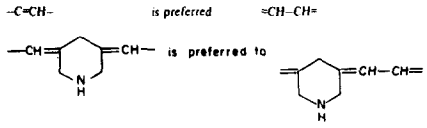
The name of the CRU is formed by citing, in order, the name of the largest subunits within the CRU (Rule 1.21). In the example, the oxygen atom is called oxy and the $-CH_2CH_2-$ (preferred to $-CH_2-$ because it is larger and can be named as a unit) is called ethylene; the latter unit substituted with one fluorine atom is called 1-fluoroethylene. The CRU in question is therefore named oxy(1-fluoroethylene), and the corresponding polymer is


Poly[oxy(1-fluoroethylene)]

The rules that follow are essentially directions for the selection of the CRU in a given polymer.

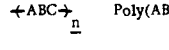
Rule 1. THE BIVALENT CONSTITUTIONAL REPEATING UNIT

Regular single-strand polymer chains can usually be represented as multiples of a bivalent repeating unit which can itself be named. The name of the polymer is poly(bivalent constitutional repeating unit). In those cases in which a choice is possible between a bivalent and a higher-valent CRU, the bivalent unit is always selected. The principle of minimizing the number of free valences in the CRU supersedes all orders of seniority. (See also Rule 2.12).



1.1 The Generic Name

Linear polymers of unspecified chain length will be named by prefixing poly to the name, placed in parentheses or brackets, of the structural repeating unit of the polymer, i.e., the smallest unit of which the polymer is a multiple. If the name of the repeating unit is "ABC", the corresponding polymer name is


Poly(ABC)

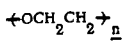
Where it is desired to specify chain length, the appropriate Greek prefix (deca,, docosa, etc.) may be used in place of poly. For a single-strand polymer,

the CRU is a bivalent group and is named within the restriction of directional citation by the IUPAC organic nomenclature rules (3, 4).

1.2 Simple Constitutional Repeating Units

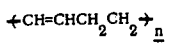
1.21 - The CRU may contain one or more subunits. Among the possible subunits of combinations of adjacent subunits, the largest possible bivalent group, based on main chain atoms and rings only, is to be named (see also Rule 2.11). When the largest bivalent group includes the entire CRU its name, prefixed by **poly**, is the name of the polymer.

Poly(methylene)



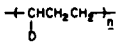
Poly(oxyethylene)

The name of a CRU or any subunit has no relationship to the manner in which the unit was prepared; the name is simply that of the largest identifiable unit and any locants for unsaturation, substituents, etc., are dictated by the structure of the unit.

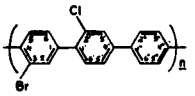


Poly(1-butenylene) (not poly(2-butenylene), which gives a higher locant to the double bond, nor poly(vinyleneethylene), which identifies less than the largest unit in the CRU)

1.22 - Identification of the preferred CRU rests on (a) the kinds of atoms or rings in the main chain or (b) on the location of substituents when there is only one kind of main chain atom or ring. Orientation of the CRU in case (a) is determined by the rules of seniority given in Rule 2; in case (b), lowest locants (except when fixed numbering applies; see Rule 1.24) are given to substituents in alphabetical order (Rule 2.42).

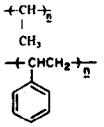


Poly(trimethylene-$\underline{d}_1$)



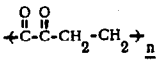
Poly(3-bromo-2'-chloro-$\underline{p}$-terphenyl-4,4''-ylene)

After the CRU and its orientation, reading left to right, have been established, the CRU or its constituent subunits are named to include as many as possible, in order, of (a) the main chain atoms or rings and (b) the substituents within a single name (see also Rule 3.1).

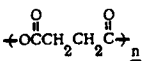


Poly(ethylidene) (not poly(methylmethylene))

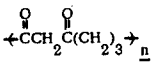
Poly(1-phenylethylene) (not poly(benzylidenemethylene) or poly(1-phenyldimethylene))



Poly(1,2-dioxotetramethylene) (not poly(succinyl), since substituent positions 1,2 are preferred to 1,4, and identification and orientation of the CRU precede formation of the name)

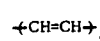


Poly(oxysuccinyl) (not poly[oxy(1,4-dioxotetramethylene)], since succinyl is an approved name (3))



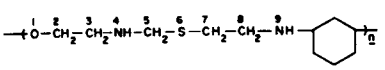
Poly(1,3-dioxohexamethylene) (not poly(malonyltrimethylene) because the six-carbon chain is the largest unit that can itself be named)

Unsaturation in an acyclic repeating unit is indicated wherever possible by the use of an unsaturated bivalent group name rather than a saturated multivalent group name. This procedure will lead to a name for the group having the minimum number of free valences (see Rule 2.12).



Poly(vinylene) (not  , poly(ethanediylidene))

1.23 - If, after identification and orientation, the CRU is found to contain one or more acyclic bivalent groups having more than two hetero atoms in the main chain, these groups may often be advantageously named by replacement nomenclature (3). The main chain of the group is named and numbered as though the entire chain was an acyclic hydrocarbon and the hetero atoms named by means of prefixes "aza", "oxa", etc., with locants to fix their positions.



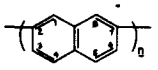
Replacement name: Poly(1-oxa-6-thia-4,9-diaza-1,9-nonanediyi-1,3-cyclohexylene)
Systematic name: Poly(oxyethyleneiminomethylenethioethyleneimino-1,3-cyclohexylene)

See Rules 2.14 and 2.32 for other examples of the use of replacement nomenclature.

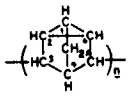
1.24 - Bivalent groups having fixed numbering retain that numbering in naming the CRU (see also Rules 2.22 and 2.41).

Poly(2,4-pyridinediyl)

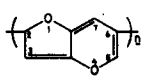
For most acyclic and monocarbocyclic bivalent groups, preference in lowest numbers is given to the carbon atoms having the free valences. In other families of compounds, notably the polycyclic hydrocarbons, bridged hydrocarbons, spiro hydrocarbons, and heterocyclic ring systems, numbering is fixed for the ring system. Free valences in groups are numbered as low as possible, consistent with the fixed numbering. Since direction through the bivalent group is a requisite parameter in naming polymers, the same fixed numbering is retained for either direction of progress through the group in generating the polymer name.



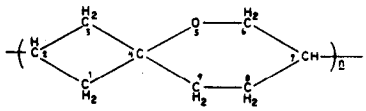
Poly(2,7-naphthylene) (not poly(7,2-naphthylene) or poly(3,6-naphthylene))



Poly(tricyclo[2.2.1.$0^{2,6}$]hept-3,5-ylene)



Poly(2H-furo[3,2-b]pyran-2,6-diyl)



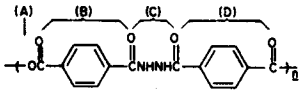
Poly(5-oxaspiro[3.5]non-2,7-ylene)

Rule 2. BIVALENT CONSTITUTIONAL REPEATING UNITS HAVING TWO OR MORE SUBUNITS

Many regular single-strand polymers can be represented as multiples of bivalent repeating units, such as -ABC-, that consist of a series of smaller subunits, -A-, -B-, and -C-. The prototype name of the polymer is poly-(ABC), where (ABC) stands for the names of A, B, and C, taken in that order. This rule is concerned with the seniority fo subunits in identifying the preferred CRU for a given polymer structure.

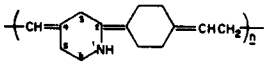
2.1 Seniority of Subunits and Direction of Citation

2.11 - Polymers having CRU's containing two or more subunits are named with the prefix poly followed in parentheses or brackets by the names of the largest possible subunits cited in order from left to right as they appear in the CRU. The CRU is written from left to right beginning with the subunit of highest seniority and proceeding in a direction defined by the shorter path to the subunit next in seniority.



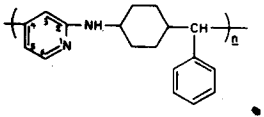
Poly(oxyterephthaloylhydrazoterephthaloyl) (not poly(oxycarbonyl-1,4-phenylenebicarbamoyl-1,4-phenylenecarbonyl))

2.12- The principle of minimizing the number of free valences in the CRU supersedes all orders of seniority. Wherever possible, the CRU in a linear polymer should be a bivalent group. The starting point for the unit is at a single free valence adjacent or nearest to the subunit of highest seniority and citation will be in the direction of the shorter path toward that subunit or subunit combinations of highest seniority.



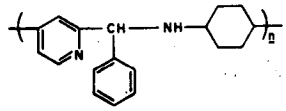
Poly(methylidyne-4,2-piperidinediylidene-1,4-cyclohexanediylidene-2-ethanyl-1-ylidene)

For citation of the first subunit, the order of seniority among the types of bivalent groups is (1) heterocyclic rings (see Rule 2.2), followed by (2) chains containing hetero atoms (see Rule 2.3), (3) carbocyclic rings (see Rule 2.4), and (4) chains containing only carbon, in that order. This order is unaffected by the presence of rings, atoms, or groups that are not part of the main chain, even though such substituents could be expressed as part of a trivial name for a bivalent group.



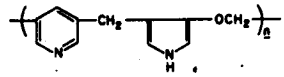
Poly(4,2-pyridinediyl-imino-1,4-cyclohexylene-benzylidene)

2.13 - Choice of direction along the main chain of the CRU is determined by the shorter path, counting ring and chain atoms individually, from the subunit of highest seniority to the subunit next in seniority.



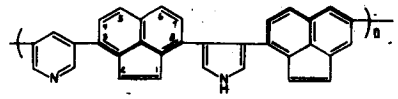
Poly(4,2-pyridinediylbenzylideneimino-1,4-cyclohexylene)

The possible paths between subunits of first and second seniority necessarily involve subunits of lesser seniority. Except in cases where two paths are of equal length (see Rule 2.14), the number rather than the nature of the atoms involved is the determining factor.



Poly(3,5-pyridinediylmethylene-3,4-pyrrolediyloxymethylene) (not poly-(3,5-pyridinediylmethyleneoxy-3,4-pyrrolediylmethylene), in which the longer $-CH_2O-$ path between rings is followed)

Where a ring constitutes all or part of a path, the shortest continuous chain of atoms in the ring is selected



Poly(3,5-pyridinediyl-3,8-acenaphthylenylene-3,4-pyrrolediyl-3,7-acenaphthylenylene) (heavy line denotes path followed)

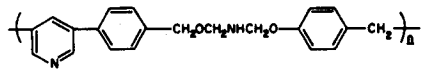
2.14 - When the choice of path determining direction of citation involves paths of equal length to subunits of equal seniority in the normal order of precedence, the choice of path depends upon the kind of subunits in the paths themselves. This condition applies to chains typified by the following generalized structures, where A, B, and C are subunits in that order of decreasing seniority, separated by paths of differing lengths x and y that contain units of lower seniority than C:

-C-y-B-x-A-x-B-y-C-

-B-y-A-x-A-y-B-

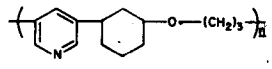
-B-y-A-x-A-x-A-y-B-

The choice of direction is from a subunit A to the nearest part of a path x having highest seniority, or if two paths x are identical in every respect, to the nearest part of path y having highest seniority, etc., until some point of difference is encountered. (See also Rules 2.24 and 2.32).
Examples of direction of citation based on the constituent parts of paths of equal length:



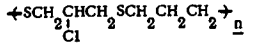
Poly(3,5-pyridinediyl-1,4-phenylenemethyleneoxymethyleneiminomethyleneoxy-1,4-phenylenemethylene) (choice of path from heterocyclic ring to O determined by position of phenylene)

Poly(oxymethyleneoxymethyleneiminoethylenethiomethyleneiminoethylene) or Poly(1,3-dioxa-8-thia-5,10-diazo dodecamethylene (choice of path from O to S determined by position of NH)

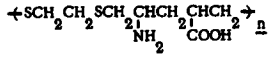


Poly(3,5-pyridinediyl-1,3-cyclohexyleneoxytrimethylene) (a portion of a cyclic structure is senior to carbon chain of equal length)

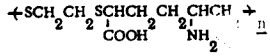
Where substituents controle the choice of CRU, the order of seniority is that given in Rule 2.42.



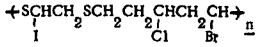
Poly[thio(2-chlorotrimethylene)thiotrimethylene]



Poly[thioethylenethio(2-amino-4-carboxypentamethylene)] (direction determined by alphabetical order)



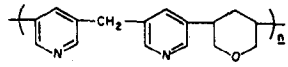
Poly[thioethylenethio(4-amino-1-carboxypentamethylene)] (direction determined by lowest locants takes precedence over alphabetical order)



Poly[thio(1-iodoethylene)thio(5-bromo-3-chloropentamethylene)] (direction determined by the lower locant in the cited subunit after beginning the CRU)

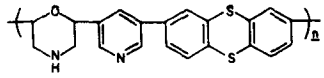
2.2 Heterocyclic Rings

2.21 - Bivalent CRU's having two or more subunits that include a heterocyclic ring system in the main chain are named by citing first the heterocyclic ring bivalent group of highest seniority and proceeding by the shorter path in descending order of preference to (a) another of the same heterocyclic ring (see Rule 2.24)



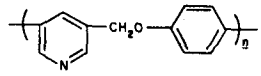
Poly [3,5-pyridinediylmethylene-3,5-pyridinediyl(tetrahydro-2H-pyran-3,5-diyl)]

(b) the heterocyclic ring next in seniority (see Rule 2.23)



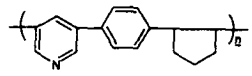
Poly(2,6-morpholinediyl-3,5-pyridinediyl-2,8-thianthrenediyl)

(c) the senior acyclic bivalent group containing a hetero atom in the main chain (see Rule 2.31)



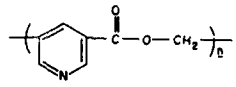
Poly(3,5-pyridinediylmethyleneoxy-1,4-phenylene)

(d) the senior carbocyclic ring system (see Rule 2.41)



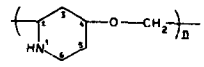
Poly(3,5-pyridinediyl-1,4-phenylene-1,2-cyclopentylene)

and (e) the senior acyclic bivalent group containing only carbon in the main chain (see Rule 2.42)

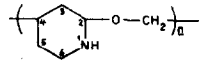


Poly(3,5-pyridinediylcarbonyloxymethylene)

2.22 - Consistent with the fixed numbering of heterocyclic rings, the points of attachment to the main chain of the CRU should have the lowest permissible locants.

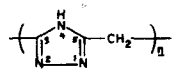


Poly(2,4-piperidinediyloxymethylene)



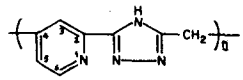
Poly(4,2-piperidinediyloxymethylene)

Where there is a choice, the point of attachment at the left side of the ring should have the lowest permissible number.



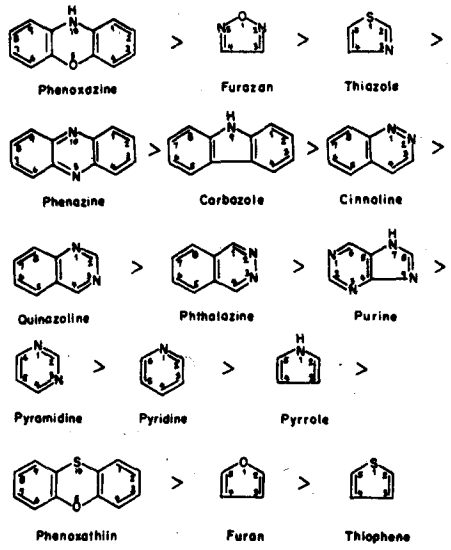
Poly(4H-1,2,4-triazole-3,5-diylmethylene)

2.23 - Among heterocyclic ring systems, the descending order of seniority is (a) a ring system with nitrogen in the ring; (b) a ring system containing nitrogen and a hetero atom other than nitrogen as high as possible in the order given in Rule 2.31; (c) a ring system containing the greatest number of rings; (d) a ring system having the largest individual ring; (e) a ring system having the largest number of hetero atoms; (f) a ring system containing the greatest variety of hetero atoms; and (g) the ring system having the greatest number of hetero atoms highest in the order given in Rule 2.31. This order is that followed in Rule B-2 of the IUPAC Rules (3).

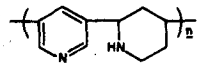


Poly(4,2-pyridinediyl-4H-1,2,4-triazole-3,5-diylmethylene)

Further examples of the application of seniority in heterocyclic ring systems are

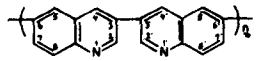


When two heterocyclic subunits differ only in degree of unsaturation, the senior subunit is that having the least hydrogenated ring system.



Poly(3,5-pyridinediyl-2,4-piperidinediyl)

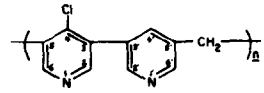
Among assemblies of identical heterocyclic rings, the ring of highest seniority is that having lowest numbers for the points of attachment between the rings within the assembly consistent with the fixed numbering of the parent ring.



Poly[(3,3'-biquinoline)-6,6'-diyl] (not poly[(6,6'-biquinoline)-3,3'-diyl])

Poly[(2,3'-bipyridine)-4,5'-diyl] (not poly[(3,2'-bipyridine)-5,4'-diyl] or poly[(4,3'-bipyridine)-2,5'-diyl])

Further choice is based on the number and kind of substituting groups (see Rule 2.42).



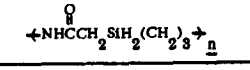
Poly[(4-chloro-3,3'-bipyridine-5,5'-diyl)methylene]

2.24 - When the CRU contains two identical rings of highest seniority or more than two such rings of highest seniority separated by identical paths, the direction of citation is determined by the shorter path to the subunit of second seniority. Further choice is based on the shorter path from that subunit to the subunit of third seniority, etc., as indicated in the order of seniority in Rule 2.21.

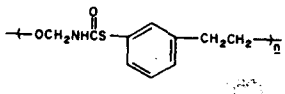
Poly(4,2-piperidinediylmethylene-4,2-piperidinediyl-1,2-cyclopentylene-ethylene-1,2-cyclopentylenemethylene) (numbers in rings show order of preference in formation of name)

2.3 Hetero Atoms in Chains

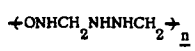
2.31 - Complex bivalent CRU's in which the senior subunit is a hetero atom or an acyclic chain with a hetero atom in the main chain are named by citing first the hetero atom of highest seniority and proceeding by the shorter path in descending order of seniority to (a) another hetero atom of the same kind; (b) the hetero atom next in seniority; (c) the senior carbocyclic ring system (see Rule 2.41); and (d) the senior acyclic bivalent group containing only carbon in the main chain (see Rule 2.42). For the most common hetero atoms the descending order of seniority is O, S, Se, Te, N, P, As, Sb, Bi, Si, Ge, Sn, Pb, B, and Hg; other hetero atoms may be placed within this order as indicated by their positions in the periodic table.



Poly[imino(1-oxoethylene)silylenetrimethylene]



Poly(oxymethylene-iminocarbonylthio-1,3-*phenyleneethyl*-ene)

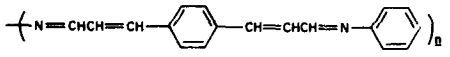


Poly(oxyiminomethylenehydrazomethylene)

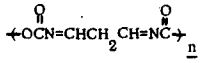
Parentheses must be used in some cases to prevent ambiguity.

Poly[thio(carbonyl)] ("carbonyl" is enclosed in parentheses to differentiate the structure from  , poly(thiocarbonyl))

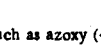
The direction of bonding in unsymmetrical single-atom radicals (e.g. =N- or -N= for nitrilo) is indicated by the endings of the names of the adjacent subunits in the CRU

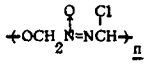


Poly(nitrilo-2-propen-3-yl-1-ylidene-1,4-phenylene-1-propen-1-yl-3-ylidenenitrilo-1,4-phenylene)



Poly(oxycarbonylnitrilo-1,3-propanediylidenenitrilocarbonyl)

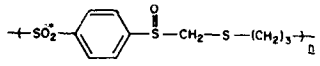
Direction in a bivalent group such as azoxy ( or) is indicated by the prefixes ONN or NNO, respectively, in that order of seniority.



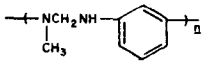
Poly[oxymethylene-ONN-azoxy(chloromethylene)]

The unsymmetrical bivalent group -N=N-NH-, designated "diazoamino" under the IUPAC Organic Rules (3), in the present directional nomenclature for polymers is called "azoimino".

Among hetero atoms of the same kind, the hetero atom of highest seniority is the one most highly substituted, with the order of substituent seniority being that given in Rule 2.42.

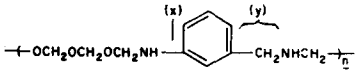


Poly(sulfonyl-1,4-phenylenesulfinylmethylenethiotrimethylene)



Poly[(methylimino)methyleneimino-1,3-phenylene)]

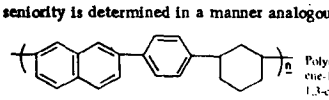
2.32 - If the CRU contains two or more hetero atoms of highest seniority or more than two such hetero atoms separated by identical paths, the direction of citation is determined by the shorter path to the subunit of second seniority. Further choice is based on the shorter path from that subunit to the subunit of third seniority, etc., as indicated in the order of seniority in Rule 2.31.



Poly(oxymethyleneoxymethyleneoxymethyleneimino-1,3-phenylenemethyleneiminomethylene) or poly(1,3,5-trioxa-7-azaheptamethylene-1,3-phenylene-2-azatrimethylene) (the shorter path x between the NH group and the ring has been taken)

2.4 Carbocyclic Rings and Carbon Chains

2.41 - **Constitutional repeating units in which the senior subunit is a carbocyclic ring system** are named by citing first the carbocyclic ring of highest seniority **and proceeding by the shorter path, in descending order of seniority,** to (a) another of the same carbocycle; (b) the carbocyclic system next in seniority; and (c) **the acyclic bivalent group appearing earliest in the alphabet. Carbocyclic ring system seniority is based on complexity, with the ring system of highest seniority being that containing the largest number of rings. Further order of seniority is based on (a) the largest individual ring at the first point of difference; (b) the largest number of atoms common to the rings; (c) the lowest locant numbers at the first point of difference for ring junctions, and (d) the least hydrogenated ring. The basis for further choice is found in Rule C-14.1 of the IUPAC Rules (3). The direction of citation in CRU's having two or more carbocycles of highest seniority is determined in a manner analogous to that of Rule 2.32.**



Poly(2,7-naphthylene-1,4-phenylene-1,3-cyclohexylene)

Examples of the application of seniority rules in carbocyclic ring systems:

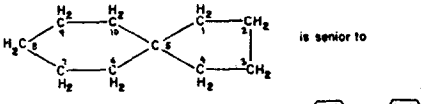
(a) **Largest number of rings:**

Fluorene — Benzocyclooctene

(b) **Largest individual ring at the first point of difference**

Naphthalene — Indene

(c) **Largest number of atoms common to the rings:**

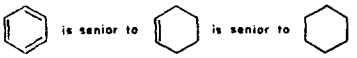


Spiro[4.5]decane — Biphenyl

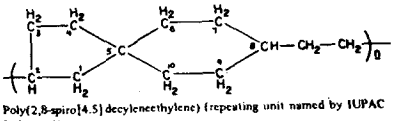
(d) **Lowest locant numbers at the first point of difference for ring junctions:**

Phenanthrene — Anthracene

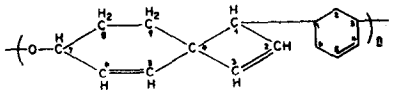
(e) **Lowest state of hydrogenation:**



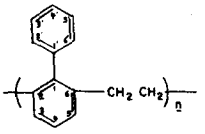
More than one numbering method may be in use in certain ring systems, such as the spiro hydrocarbons. Generally, in a specific ring system, a ring with unprimed locants is senior to one with primed locants. Points of attachment to the main chain of the CRU receive lowest permissible numbers.



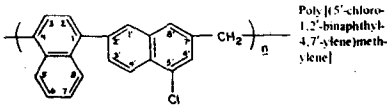
Poly(2,8-spiro[4.5]decyleneethylene) (repeating unit named by IUPAC Rule A-41)



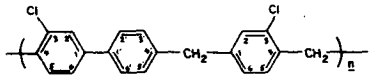
Poly(oxyspiro[3.5]nona-2,5-dien-7,1-ylenecyclohex-4-en-1,3-ylene)



Poly(2,6-biphenylyleneethylene)



Poly[(5'-chloro-1,2'-binaphthyl-4,7'-ylene)methylene]



Poly[(3-chloro-4,4'-biphenylylene)methylene(3-chloro-1,4-phenylene)methylene] (not poly[(3'-chloro-4,4'-biphenylylene)methylene(2-chloro-1,4-phenylene)methylene]: the substituent in the preferred ring determines the direction)