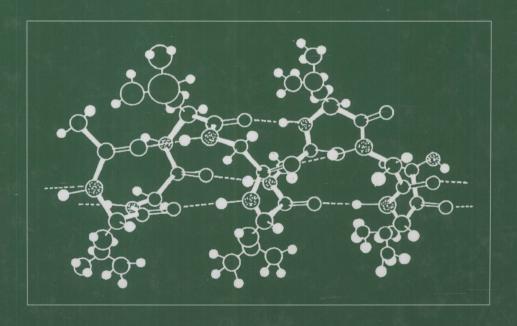
Seymour/Carraher's

Polymer Chemistry

Seventh Edition



Charles E. Carraher, Jr.



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CRC Press Taylor & Francis Group 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742

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International Standard Book Number-10: 1-4200-5102-4 (Hardcover) International Standard Book Number-13: 978-1-4200-5102-5 (Hardcover)

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Library of Congress Cataloging-in-Publication Data

Carraher, Charles E.

Seymour/Carraher's polymer chemistry. -- Seventh edition / by Charles E. Carraher, Jr.

p. cm

Includes bibliographical references and index.

ISBN-13: 978-1-4200-5102-5

ISBN-10: 1-4200-5102-4

1. Polymers. 2. Polymerization. I. Seymour, Raymond Benedict, 1912- II. Title. III. Title: Polymer chemistry.

QD381.S483 2007 547'.7--dc22

2007002479

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Foreword

Polymer science and technology have developed tremendously over the last few decades, and the production of polymers and plastics products has increased at a remarkable pace. By the end of 2000, nearly 200 million tons per year of plastic materials were produced worldwide (about 2% of the wood used, and nearly 5% of the oil harvested) to fulfill the ever-growing needs of the *plastic age*; in the industrialized world plastic materials are used at a rate of nearly 100 kg per person per year. Plastic materials with over \$250 billion per year contribute about 4% to the gross domestic product in the United States. Plastics have no counterpart in other materials in terms of weight, ease of fabrication, efficient utilization, and economics.

It is no wonder that the demand and the need for teaching in polymer science and technology have increased rapidly. To teach polymer science, a readable and up-to-date introductory textbook is required that covers the entire field of polymer science, engineering, technology, and the commercial aspect of the field. This goal has been achieved in Carraher's textbook. It is eminently useful for teaching polymer science in departments of chemistry, chemical engineering, and material science, and also for teaching polymer science and technology in polymer science institutes, which concentrate entirely on the science and technologies of polymers.

This seventh edition addresses the important subject of polymer science and technology, with emphasis on making it understandable to students. The book is ideally suited not only for graduate courses but also for an undergraduate curriculum. It has not become more voluminous simply by the addition of information—in each edition less important subjects have been removed and more important issues introduced.

Polymer science and technology is not only a fundamental science but also important from the industrial and commercial point of view. The author has interwoven discussion of these subjects with the basics in polymer science and technology. Testimony to the high acceptance of this book is that early demand required reprinting and updating of each of the previous editions. We see the result in this new significantly changed and improved edition.

Otto Vogl

Herman F. Mark Professor Emeritus Department of Polymer Science and Engineering University of Massachusetts Amherst, Massachusetts

Preface

As with most science, and chemistry in particular, there is an explosive broadening and importance of the application of foundational principles of polymers. This broadening is seen in ever-increasing vistas allowing the promotion of our increasingly technologically dependent society and solutions to society's most important problems in areas such as the environment and medicine. Some of this broadening is the result of extended understanding and application of already known principles but also includes the development of basic principles and materials known to us hardly a decade ago. Most of the advancements in communication, computers, medicine, air and water purity are linked to macromolecules and a fundamental understanding of the principles that govern their behavior. Much of this revolution is of a fundamental nature and is explored in this seventh edition. The text contains these basic principles and also touches on their application to real-life situations. Technology is the application of scientific principles. In polymers there is little if any division between science and technology.

Polymers are found in the organic natural world as the building blocks for life itself. They are also found as inorganic building blocks that allow construction of homes, skyscrapers, and roads. Synthetic polymers serve as basic building blocks of society now and in the future. This text includes all three of these critical segments of polymeric materials.

A basic understanding of polymers is essential to the training of today's science, biomedical, and engineering students. *Polymer Chemistry* complies with the American Chemical Society's Committee on Professional Training old and revised guidelines as an advanced or in-depth course. It naturally integrates and interweaves the important core areas since polymers are critical to all of the core areas, which in turn contribute to the growth of polymer science. Most of the fundamental principles of polymers extend and enhance similar principles found throughout the undergraduate and graduate training of students. This allows students to integrate their chemical knowledge illustrating the connection between fundamental and applied chemical information. Thus, along with the theoretical information, application is integrated as an essential part of the information. As in other areas such as business and medicine, short case studies are integrated as historical material.

While this text is primarily written as an introductory graduate-level text, it can also be used as an undergraduate text, or as an introductory undergraduate—graduate text. The topics are arranged so that the order and inclusion or exclusion of chapters or parts of chapters will still allow students an adequate understanding of the science of polymers. Most of the chapters begin with the theory followed by application. The most important topics are generally at the beginning of the chapter followed by important, but less critical, sections. Some may choose to study the synthesis-intense chapters first, others the analytical/analysis/properties chapters, and yet others to simply read the chapters as they appear in the book. All of the elements of an introductory text with synthesis, property, application and characterization are present, allowing this to be the only polymer course taken by an individual or the first in a series of polymer-related courses taken by the student.

This edition continues in the "user-friendly" mode with special sections in each chapter containing definitions, learning objectives, questions, and further reading. Application and theory are integrated so that they reinforce one another. There is a continued emphasis on pictorializing, reinforcing, interweaving, and integrating basic concepts. The initial chapter is short, allowing students to become acclimated. Other chapters can be covered in about a

week's time or less. Where possible, difficult topics are distributed and reinforced over several topics.

The basic principles that apply to synthetic polymers apply equally to inorganic and biological polymers and are present in each of the chapters covering these important polymer groupings.

The updating of analytical, physical, and special characterization techniques continues. The chapter on biological polymers has been expanded so that it is now two chapters. The chapter on organometallic and inorganic polymers has likewise been greatly upgraded. An additional chapter covering the important area of composites has been added. Topics such as blends, multiviscosity oils, cross-linking, microfibers, protein folding, protein site identification, aerogels, carbon nanotubes, breakage of polymer chains, permeability and diffusion, mass spectroscopy, polyethers and epoxies, synthetic rubbers, poly(methyl methacrylate), polyacrylonitrile, and polyurethanes have been added or greatly enhanced. A number of new selected topics have been added including nonlinear optical behavior, photo physics, drug design and activity, flame retardants, textiles, water-soluble polymers, hydrogels, and anaerobic adhesives. The emphasis on the molecular behavior of materials has been expanded as has been the emphasis on nanotechnology and nanomaterials. The practice of including a number of appendices has continued, including an enlargement of the trade names appendix.

Acknowledgments

The author gratefully acknowledges the contributions and assistance of the following in preparing this text: John Droske, Charles Pittman, Edward Kresge, Gerry Kirshenbaum, Sukumar Maiti, Alan MacDiarmid, Les Sperling, Eckhard Hellmuth, Mike Jaffe, Otto Vogl, Thomas Miranda, Murry Morello, and Graham Allan; and a number of our children who assisted in giving suggestions for the text: Charles Carraher III, Shawn Carraher, Colleen Carraher-Schwarz, Erin Carraher, and Cara Carraher—to Erin for discussions on materials, Cara for her help with the biomedical material, and Shawn for his help in relating the business and industrial aspects. Special thanks to Gerry Kirshenbaum for his kind permission to utilize portions of my articles that appeared in *Polymer News*. This book could not have been written except for those who have gone before us, especially Raymond Seymour, Herman Mark, Charles Gebelein, Paul Flory, and Linus Pauling; all of these friends shepherded and helped me. My thanks to them.

I thank Girish Barot, Amitabh Battin, and Randy Doucette, for their assistance in proofing. I also thank my wife Mary Carraher for her help in proofing and allowing this edition to be written.

Polymer Nomenclature

As with most areas, the language of the area is important. Here we will focus on naming polymers with the emphasis on synthetic polymers. Short presentations on how to name proteins and nucleic acids are given in Chapter 10 and for nylons in Chapter 5.

The fact that synthetic polymer science grew in many venues before nomenclature groups were present to assist in standardization of the naming approach resulted in many popular polymers having several names including common names. Many polymer scientists have not yet accepted the guidelines given by the official naming committee of the International Union of Pure and Applied Chemistry (IUPAC), because the common names have gained such widespread acceptance. Although there is a wide diversity in the practice of naming polymers, we will concentrate on the most utilized systems.

COMMON NAMES

Little rhyme or reason is associated with many of the common names of polymers. Some names are derived from the place of origin of the material, such as *Hevea brasilliensis*—literally "rubber from Brazil"—for natural rubber. Other polymers are named after their discoverer, as is Bakelite, the three-dimensional polymer produced by condensation of phenol and formaldehyde, which was commercialized by Leo Baekeland in 1905.

For some important groups of polymers, special names and systems of nomenclature were developed. For instance, the nylons were named according to the number of carbons in the diamine and dicarboxylic acid reactants used in their synthesis. The nylon produced by the condensation of 1,6-hexamethylenediamine (6 carbons) and adipic acid (6 carbons) is called nylon-6,6. Even here, there is no set standard as to how nylon-6,6 is to be written with alternatives including nylon-66 and nylon-6.6.

SOURCE-BASED NAMES

Most common names are source-based, i.e., they are based on the common name of the reactant monomer, preceded by the prefix "poly." For example, polystyrene is the most

frequently used name for the polymer derived from the monomer 1-phenylethene, which has the common name styrene.

The vast majority of commercial polymers based on the vinyl group ($H_2C=CHX$) or the vinylidene group ($H_2C=CX_2$) as the repeat unit are known by their source-based names. Thus, polyethylene is the name of the polymer synthesized from the monomer ethylene; poly(vinyl chloride) from the monomer vinyl chloride, and poly(methyl methacrylate) from methyl methacrylate.

Many condensation polymers are also named in this manner. In the case of poly(ethylene terephthalate), the glycol portion of the name of the monomer, ethylene glycol, is used in constructing the polymer name, so that the name is actually a hybrid of a source-based and a structure-based name.

Poly(ethylene terephthalate)

This polymer is well known by a number of trade names, such as Dacron, its common grouping, polyester, and by an abbreviation, PET.

Although it is often suggested that parentheses be used in naming polymers of more than one word [like poly(vinyl chloride)], but not for single-word polymers (like polyethylene), some authors entirely omit the use of parentheses for either case (like polyvinyl chloride), so even here there exist a variety of practices. We will employ parentheses for naming polymers of more than one word.

Copolymers are composed of two or more monomers. Source-based names are conveniently employed to describe copolymers using an appropriate term between the names of the monomers. Any of half a dozen or so connecting terms may be used depending on what is known about the structure of the copolymer. When no information is known or intended to be conveyed, the connective term "co" is employed in the general format poly(A-co-B), where A and B are the names of the two monomers. An unspecified copolymer of styrene and methyl methacrylate would be called poly[styrene-co-(methyl methacrylate)].

Kraton, the yellow rubber-like material often found on the bottom of running shoes, is a copolymer whose structural information is known. It is formed from a group of styrene units, i.e., a "block" of polystyrene, attached to a group of butadiene units, or a block of

polybutadiene, which is attached to another block of polystyrene forming a triblock copolymer. The general representation of such a block might be —AAAAAAABBBBBBB-AAAAAAAA, where each A and B represents an individual monomer unit. The proper source-based name for Kraton is polystyrene-block-polybutadiene-block-polystyrene, or poly-block-styrene-block-polybutadiene-block-polystyrene, with the prefix "poly" being retained for each block. Again, some authors will omit the "poly," giving polystyrene-block-butadiene-block-styrene.

STRUCTURE-BASED NAMES

Although source-based names are generally employed for simple polymers, IUPAC has published a number of reports for naming polymers. These reports are being widely accepted for the naming of complex polymers. A listing of such reports is given in the references section. A listing of source- and structure-based names for some common polymers is given in Table 1.

LINKAGE-BASED NAMES

Many polymer "families" are referred to by the name of the particular linkage that connects the polymers (Table 2). The family name is "poly" followed by the linkage name. Thus, those polymers that contain an ester linkage are known as polyesters; those with an ether linkage are called polyethers, etc.

TRADE NAMES, BRAND NAMES, AND ABBREVIATIONS

Trade (and/or brand) names and abbreviations are often used to describe a particular material or a group of materials. They may be used to identify the product of a manufacturer, processor, or fabricator, and may be associated with a particular product or with a material or modified material, or a material grouping. Trade names are used to describe specific groups of materials that are produced by a specific company or under license of that company. Bakelite is the trade name given for the phenol–formaldehyde condensation developed by Baekeland. A sweater whose material is described as containing Orlon contains polyacrylonitrile fibers that are "protected" under the Orlon trademark and produced or licensed to be produced by the holder of the Orlon trademark. Carina, Cobex, Dacovin,

TABLE 1 Source- and Structure-Based Names

Source-Based Names Structure-Based Names

Polyacrylonitrile Poly(1-cyanoethylene)
Poly(ethylene oxide) Polyoxyethylene
Poly(ethylene terephthalate) Polyoxyethyleneoxyterephthaloyl

Polyisobutylene Poly(1,1-dimethylethylene)

Poly(methyl methacrylate) Poly[(1-methoxycarbonyl)-1-metylethylene]
Polypropylene Poly(1-methylethylene)
Poly(1-phenylethylene)

Polytetrafluoroethylene Polydifluoromethylene
Poly(vinylacetate) Poly(1-acetoxyethylene)
Poly(vinyl alcohol) Poly(1-hydroxyethylene)
Poly(vinyl chloride) Poly(1-chloroethylene)

Poly(vinyl butyral) Poly[(2-propyl-1,3-dioxane-4,6-diyl)methylene]

TABLE 2 Linkage-Based Names

Family Name	Linkage	Family Name	Linkage
D.L. 'I	O 	D.I.e.'e.I	G G
Polyamide	–N–C–	Polyvinyl	-C-C-
Polyester	-O-C-	Polyanhydride	-C-O-C-
Polyurethane	O H -O-C-N-	Polyurea	H O H -N-C-N-
Polyether	-0-	Polycarbonate	-O-C-O-
Polysiloxane	-O-Si-	Polysulfide	-S

Darvic, Elvic, Geon, Koroseal, Marvinol, Mipolam, Opalon, Pliofex, Rucon, Solvic, Trulon, Velon, Vinoflex, Vygen, and Vyram are all trade names for poly(vinyl chloride) manufactured by different companies. Some polymers are better known by their trade name than their generic name. For instance, polytetrafluoroethylene is better known as Teflon, the trade name held by DuPont.

Abbreviations, generally initials in capital letters, are also employed to describe polymers. Table 3 contains a listing of some of the more widely used abbreviations and the polymer associated with the abbreviation.

CHEMICAL ABSTRACTS-BASED POLYMER NOMENCLATURE

The most complete indexing of any scientific discipline is found in chemistry and is done by Chemical Abstracts (CA). Almost all of the modern searching tools for chemicals and

TABLE 3
Abbreviations for Selected Polymeric Materials

Abbreviation	Polymer	Abbreviation	Polymer
ABS	Acrylonitrile-butadiene-styrene terpolymer	CA	Cellulose acetate
EP	Epoxy	HIPS	High-impact polystyrene
MF	Melamine-formaldehyde	PAA	Poly(acrylic acid)
PAN	Polyacrylonitrile	SBR	Butadiene-styrene copolymer
PBT	Poly(butylene terephthalate)	PC	Polycarbonate
PE	Polyethylene	PET	Poly(ethylene terephthalate)
PF	Phenyl-formaldehyde	PMMA	Poly(methyl methacrylate)
PP	Polypropylene	PPO	Poly(phenylene oxide)
PS	Polystyrene	PTFE	Polytetrafluoroethylene
PU	Polyurethane	PVA, PVAc	Poly(vinyl acetate)
PVA, PVAl	Poly(vinyl alcohol)	PVB	Poly(vinyl butyral)
PVC	Poly(vinyl chloride)	SAN	Styrene-acrylonitrile
UF	Urea-formaldehyde		

chemical information are based on CA for at least some information. It is critical for polymer chemists to have some grasp of how CA names chemical compounds. The full description of the guidelines governing the naming of chemical compounds and related properties is given in Appendix IV at the end of the CA *Index Guide*. This description covers about 200 pages. While small changes are made with each new edition, the main part has remained largely unchanged since about 1972. Today, there are computer programs, including that associated with SciFinder Scholar, that name materials once the structure is given. For small molecules this is straight forward, but for polymers care must be taken. Experiments must be carried out with simple polymers before moving to more complex macromolecules. If the Chemical Abstract Service Number (CAS #) is known, this can be entered and names investigated for appropriateness for your use.

CA organizes the naming of materials into 12 major arrangements that tie together about 200 subtopics. These main headings are:

- A. Nomenclature systems and general principles
- B. Molecular skeletons
- C. Principle chemical groups
- D. Compound classes
- E. Stereochemistry and stereoparents
- F. Specialized substances
- G. Chemical substance names for retrospective searches
- H. Illustrative list of substitute prefixes
- J. Selective bibliography of nomenclature of chemical substances
- K. Chemical prefixes
- L. Chemical structural diagrams from CA Index Names
- M. Index

The section dealing with polymers is subtopic 222. Polymers. The subsection dealing with polymers builds on the foundations given earlier, and thus some of the guidelines appear to be confusing and counterproductive to the naming of polymers but the rules were developed for the naming of small molecules. Following is a description of the guidelines that are most important to polymer chemists. Additional descriptions are found in the CA Appendix IV itself and in articles given in the Further reading. Appendix IV concentrates on linear polymers. A discussion of other more complex polymeric materials is also found in articles cited in the Further Reading.

General Rules

In the chemical literature, in particular systems based on CA, searches for particular polymers can be conducted using the CAS # (where known), or by repeat unit. The IUPAC and CAS have agreed upon a set of guidelines for the identification, orientation, and naming of polymers based on the structural repeat unit (SRU). IUPAC names polymers as "poly(constitutional repeat unit)" while CAS utilizes a "poly(structural repeating unit)." These two approaches typically give similar results.

Here we will practice using the sequence "identification, orientation, and naming" first by giving some general principles and finally by using specific examples.

In the identification step, the structure is drawn, usually employing at least two repeat units. Next, in the orientation step, the guidelines are applied. Here we will concentrate on basic guidelines. Within these guidelines are subsets of guidelines that are beyond our scope.

Structures will be generally drawn in the order, from left to right, in which they are to be named.

Seniority

The starting point for the naming of a polymer unit involves determining seniority among the subunits.

A. This order is:

Heterocyclic rings>

Greatest number of most preferred acyclic heteroatoms>

Carbocyclic rings>

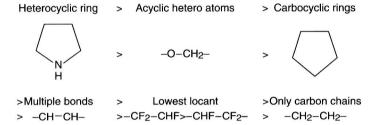
Greatest number of multiple bonds>

Lowest or closest route (or lowest locant) to these substituents>

Chains containing only carbon atoms

with the symbol ">" indicating "is senior to."

This is illustrated below.



This order is partially derived from guidelines found, for example, in section 133 Compound Radicals, where the following order is given:

Greatest number of acyclic heteroatoms>

Greatest number of skeletal atoms>

Greatest number of most preferred acyclic heteroatoms>

Greatest number of multiple bonds>

Lowest locants or shortest distance to nonsaturated carbons

The lowest locant or shortest distance refers to the number of atoms from one senior subunit to the next most senior subunit when there is only one occurrence of the senior subunit.

This order refers to the backbone and not to substitutions. Thus, polystyrene and poly (vinyl chloride) are contained within the "chains containing only carbon atoms" grouping. B. For ring systems the overall seniority is

Heterocyclic> Carbocyclic

but within the rings there is also an ordering (section 138), which is:

Nitrogenous heterocyclic>

Heterocyclic>

Largest number of rings>

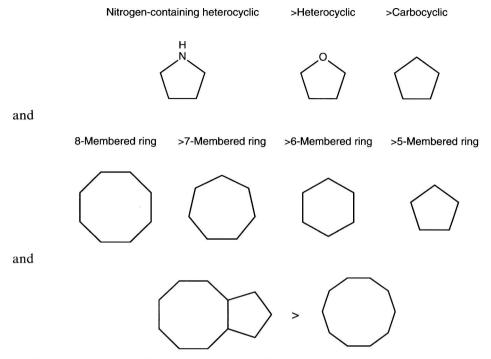
Cyclic system occurring earliest in the following list of systems: spiro, bridges fused,

bridges nonfused, fused>

Largest individual ring (applies to fused carbocyclic systems)>

Greatest number of ring atoms

For example,



C. For heteroatomed linear chains or cyclic rings the order of seniority is O > S > Se > Te > N > P > As > Sb > Bi > Si > Ge > Sn > Pb > B > Hg.

Thus, because $-O-CH_2-$ is senior to $-S-CH_2-$, it would be named first in a polymer that contained both $-O-CH_2-$ and $-S-CH_2-$ segments. Further, a polymer containing these alternating units would not be poly(thiomethyleneoxymethylene) but would be named poly (oxymethylenethiomethylene).

Another example,

$$O \\ \parallel \\ -(-O-C-CH_{2}-)_{n}-$$

is named poly[oxy(1-oxy-1,2-ethanediyl)] or less preferred poly[oxy (1-oxoethylene)] but not poly[(2-oxo-1,2-ethanediyl)oxy] or poly[(2-oxoethylene)oxy].

D. Unsaturation is senior to saturation. The more the unsaturation, the greater the seniority, with all other items being equal. Thus, 1,4-phenylene is senior to 2,5-cyclohexadiene-1,4-diyl, which is senior to 2-cyclohexene-1,4-diyl, which in turn is senior to cyclohexane-1,4-diyl. For linear chains -CH=CH-CH=CH—is senior to -CH=CH-CH₂-CH₂- which is in turn senior to the totally saturated chain segment.

Route

A. From the senior subunit determined from "seniority" take the shortest path (smallest number of atoms) to another like or identical unit or to the next most preferred subunit. Thus, for the homo polymer poly(oxymethylene) it is simply going from one oxygen to the next oxygen and recognizing that this is the repeat unit. For a more complex ether this means going on in the shortest direction from the senior unit or atom to the next most senior unit or

atom until the chain begins to repeat itself. Thus, -O-C-C-O-C-C-is named oxy-1,2-ethanediyloxy-1,3-propanedily rather than oxy-1,3-propanediyloxy-1,2-ethanediyl.

B. Where the paths are equal, such as in some nylons, the repeat unit is named so that the heteroatom "N" appears first and the more highly substituted (carbonyl) unit appears next. Thus nylon 3,3 with the structure

is named poly[imino(1,3-dioxo-1,3-propanediyl)imino-1,3-propanediyl].

- C. In otherwise identical subunits, there are three items to be considered in decreasing order of importance:
 - 1. Maximum substitution: thus, 2,3,5-trichloro-*p*-phenylene is senior to 2,5-dichloro-*p*-phenylene, which in turn is senior to 2-chloro-*p*-phyenylene.
 - 2. Lowest locants: thus, 2,3-dichloro-*p*-phenylene is senior to 2,5-dichloro-*p*-phenylene.
 - 3. Earliest alphabetical order: thus, 2-bromo-*p*-phenylene is senior to 2-chloro-*p*-phenylene, which is senior to 2-iodo-*p*-phenylene.
- D. Where there is no conflict with other guidelines, triple bonds are senior to double bonds, which in turn are senior to single bonds; multiple bonds should be assigned the lowest possible locants. Thus, the polymer from 1,3-butanediene polymerized in the "1,4-" mode is usually indicated as -(-C-C=C-C-)-but is named as though it were -(-C=C-C-C-)-and named poly(1-butene-1,4-diyl) with the appropriate *cis* or *trans*-designation. Polyisoprene, typically drawn as $-(-CH_2-C(CH_3)=CH-CH_2-)_n$ is frequently named poly(2-methyl-1,3-butadiene) but is named as though its structure were $-(C(CH_3)=CH-CH_2-CH_2-)_n$ with the name poly(1-methyl-1-butene-1,4-diyl).

Substituents are named as one of several classes. The most important ones are dealt with here. For monoatomic radicals from borane, methane, silane (and other Group IVA elements) they are named by replacing the "ane" ending by "yl," i.e., "ylene" and "ylidyne," to denote the loss of one, two, or three hydrogen atoms, respectively:

$$H_2B$$
- boryl H_3C - methyl H_2C = methylene HC \equiv methylidyne

Acyclic hydrocarbon radicals are named from the skeletons by replacing "ane," "ene," and "yne" suffixes with "yl," "enyl," and "ynyl", respectively:

Table 4 contains the names of selected bivalent radicals that may be of use to polymer chemists.

Searching

Searching is made much simpler with computer systems such as SciFinder Scholar where the name or CAS # can be entered, and references related to that compound obtained.

TABLE 4 Names of Select Bivalent Radicals

Names of Select Bivalent Ra	adicals	
"Common" or "Trivial" Name	CAS Name	Structure
Adipyl, adipoly 1,4-Butanediyl Carbonyl Diglycoloyl Ethylene Imino Iminodisulfonyl Methene, methylene Oxybis(methylenecarbonylimino) Pentamethylene	1,6-Dioxo-1,6-hexanediyl 1,4-Butanediyl Carbonyl Oxybis(1-oxo-2,1-ethanediyl) 1,2-Ethanediyl Imino Iminobis(sulfonyl) Methylene Oxybis[((1-oxo-2,1-ethanediyl)imino)] 1,5-Pentanediyl	-CO - (CH ₂) ₄ - CO - -(CH ₂) ₄ - -CO - -CO - CH ₂ - O - CH ₂ - CO - -CH ₂ - CH ₂ - -NH - -SO ₂ - NH - SO ₂ - -CH ₂ - -NHCO - CH ₂ - O - CH ₂ - CO - N - -(CH ₂) ₅ -
Phenylene	1,4-Phenylene	
Phenylenedimethylene	1,4-Phenylenebis(methylene)	HCH-
Phenylenedioxy	1,4-Phenylenebis(oxy)	-0-
Sebacoyl	1,10-Dioxo-1,10-decanediyl	-CO-(CH ₂) ₈ CO-
Styrenyl	1-Phenyl-1,2-ethanediyl	-CH-HCH-
Sulfonyl, sulfuryl Tartaroyl	Sulfonyl 2,3-Dihydroxy-1,4-dioxo-1,4-butanediyl	-SO ₂ - -CO-CH(OH)-CH(OH)-CO-
Terephthaloyl	1,4-Phenylenedicarbonyl	-co-
Thio Thionyl Ureylene Vinylene	Thio Sulfinyl Carbonyldiimino 1,2-Ethenediyl	-S- -SO- -NH-CO-NH- -CH=CH-