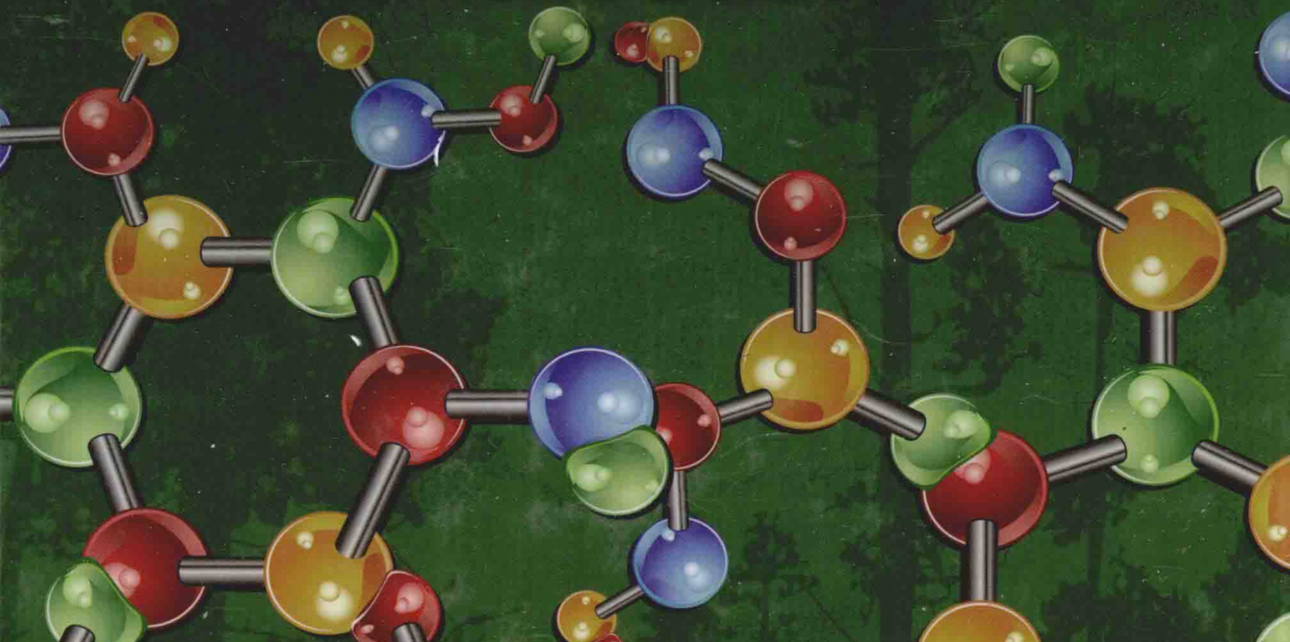
Introduction to POLYMER CHEMISTRY

Second Edition



Charles E. Carraher, Jr.

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Preface

There is an appropriate and necessary move toward green materials and green chemistry. This trend is captured in this book as it is both integrated within the appropriate sections and treated separately in a section on green materials. There also exists a greater awareness of health concerns within our society, and this awareness is also mirrored in this book.

Polymers are all about us and are the basis of life itself; they are used for communication (both natural and synthetic), for our nutrition and clothing, for recording history, and for constructing buildings and highways. In fact it is difficult to imagine society without synthetic polymers, and life without natural polymers. Part of being an educated and responsible citizen involves knowing the correct questions to ask and knowing (possible) the correct answers. In our ever-increasingly technological world, science plays a crucial role in providing solutions to critical problems of food; clean and abundant water, energy, and air; and health. This book provides both the information and the insights that allow a better understanding of these large molecules that are all about us.

Most books on polymers are aimed at either graduate students or are hybrids aimed at both undergraduate, but mostly graduate students. This book is aimed mainly at undergraduate students but can also serve graduate students. Thus, a strong bond is forged between science, history, and the crucible that is today's society. Information gained from the basic core science courses are brought to bear on understanding giant molecules. This information includes factual, theoretical, and practical concepts presented in science. It is of use to those who want to simply be well educated, as well as to those who want to pursue a career in medicine, engineering, physics, chemistry, biomedical sciences, law, and business.

This book provides a detailed coverage of polymers including natural and synthetic giant molecules; inorganic and organic polymers; and elastomers, adhesives, coatings, fibers, plastics, blends, caulks, composites, and ceramics. The basic principles that apply to one polymer group apply to all of the other groups when used with some simple fundamentals. These fundamentals are integrated into the fabric of this book.

We have kept in mind the saying that we should be students of history so we do not repeat the same mistakes; at the same time we should also be students of history so that we might repeat the successes. Brief case studies are woven within the fabric of this book as historical accounts illustrating the purposes in back of change as well as the societal and scientific contexts within which these changes occurred.

Acknowledgments

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Author

Charles E. Carraher, Jr. is a professor of chemistry and biochemistry, Florida Atlantic University, Boca Raton, FL and an associate director of the Florida Center for Environmental Studies, Palm Beach Gardens, FL. He has been recognized as an outstanding chemist in the southeast United States (1992) by the American Chemical Society (ACS) and was the recipient of a distinguished service award for his efforts in science education (1995) from the ACS's Divisions of Polymer Chemistry and Polymeric Materials: Science and Engineering. He is also a fellow of the American Institute of Chemists and the American Chemical Society-PMSE. Currently, he serves as a cochair of the ACS's joint Polymer Education Committee and on the board of the Intersocietal Polymer Education Committee; he has also been a member of the ACS's Committee on Professional Training. He is an associate editor of the *Journal of Polymeric Materials* and serves on the board of the *Journal of Inorganic and Organometallic Polymers and Materials*. He has authored/coauthored nearly 60 books and over 1000 articles and has chaired/cochaired numerous national and international symposia. His research has led to the synthesis of over 75 new families of polymers. In 1984, he received the Outstanding Scientist and Engineering Award from the Engineers and Scientists Affiliate Societies Council for his work in science education and research, and in 1992 he received the Saltarilli Sigma Xi Award for his research efforts. Dr. Carraher was the recipient of the 2002 Distinguished Researcher Award from Allied Technologies.

How to Study Polymers

Studying polymers is similar to studying any other science. The following text provides some ideas that may prove to be helpful in your study.

Much of science is abstract. While much of the study of polymers is abstract, it is easier to conceptualize and create mental pictures of what a polymer is and how it should behave than it is in many other areas of science. In the case of linear polymers, think of a string or a rope. Long ropes often get entangled with themselves or with other ropes. In the same way, polymer chains get entangled with themselves and with chains of other polymers that are brought into contact with them. **Thus, create mental pictures of the polymer molecules as you study them.**

Polymers are real and they are all about us. We can look at giant molecules at a microscopic or an atomic level, or at a macroscopic level. The PET bottles we have may be composed of long chains of poly(ethylene terephthate) (PET) chains; the aramid tire cord is composed of aromatic polyamide chains; even our hair is made up of complex bundles of fibrous proteins, again polyamides. **Polymers are related to the real world in which we live. We experience these "large molecules" at the macroscopic level every day of our lives and this macroscopic behavior is a direct consequence of the atomic-level structure and behavior.** Make pictures in your mind that allow you to relate the atomic world to the macroscopic world.

At the introductory level, we often examine only the primary factors that may cause particular giant molecule behaviors. Other factors may assume importance only under particular conditions. **The polymer molecules you study at times examine only the primary factors that impact polymer behavior and structure. Even so, these primary factors form the basis for both complex and simple structure–property behavior.**

The structure–property relationships you will be studying are based on well-known basic chemical and physical relationships. **Such relationships build upon one another and need to be studied in an ongoing manner. Understand as you go along. Read the material BEFORE you go to class.**

This course is an introductory-level course. Each chapter or topic emphasizes knowledge about one or more areas. **The science and excitement of polymers has its own language. It is a language that requires you to understand and memorize certain key concepts.** Our memory can be short term or long term. Short-term memory may be considered as that used by an actor or actress for a TV drama. It really does not need to be totally understood, nor retained after the final "take." **Long-term memory is required when studying giant molecules since it will be used repeatedly to understand other concepts (i.e., it is built upon).**

When memorizing, learn how you do this best, i.e., time of day, setting, etc. Use as many senses as necessary—**be active**, read your assignment, write out what is needed to be known, say it, and listen to yourself say it. Also, look for patterns, create mnemonic devices, avoid cramming too much into too small a time, practice associations in all directions, and test yourself. **Memorization is hard work.**

While knowledge involves recalling memorized material, to really "know" something involves more than simple recall—it involves **comprehension**, **application**, **evaluation**, and **integration** of the **knowledge.** Comprehension is the interpretation of this knowledge—making predictions, applying it to different situations. Analysis involves the evaluation of the information and comparing it with other information, and synthesis (integration) has to do with integration of the information with other information.

When studying giant molecules please consider doing the following:

- Skim the text BEFORE the lecture
- Attend the lecture and take notes
- Organize your notes and relate information
- Read and study the assigned material
- Study your notes and the assigned material
- Review and self-test

Learning takes time and effort. Study by daily skimming the text and other material, think about it, visualize key points and concepts, write down important material, make outlines, take notes, and study sample problems. All of these help, but some may help you more than others; hence, focus on these modes of learning, but not at the exclusion of the other aspects.

When preparing for an exam, consider the following:

- Accomplish the above—DO NOT wait until the day before the exam to begin studying; create good study habits.
- Study wisely—study how YOU study best, i.e., time of day, surroundings, etc.
- Take care of yourself—get plenty of sleep the night before the exam.
- Attend to last-minute details—Is your calculator working, is it the right kind, do I have the needed pencils? Review the material once again.
- Know what kind of test it will be, if possible.
- Get copies of old exams, if possible; talk to others who might have already undergone the course.

During the test

- Stay cool, do NOT PANIC
- Read the directions, try to understand what is being asked for
- In an essay or similar exam, work for at least partial credit; plan your answers
- In a multiple choice or T/F exam, eliminate obviously wrong choices
- Look over the entire exam; work questions that you are sure of then go to less sure questions; check answers if time permits

The study of polymer molecules contains several types of content:

- **Facts**—the term *polymer* means "many" (poly) "units" (mers)
- **Concepts**—linear polymers are long molecules such as strings
- **Rules**—solutions that contain polymer chains are more viscous and slower flowing than solutions that do not contain polymers
- **Problems**—what is the approximate molecular weight of a single polystyrene chain that has 1000 styrene units in it?

These varied types of contents are often integrated within any topic. In this introduction to polymer molecules, the emphasis is often on concepts but all the aspects are equally important.

Polymer Nomenclature

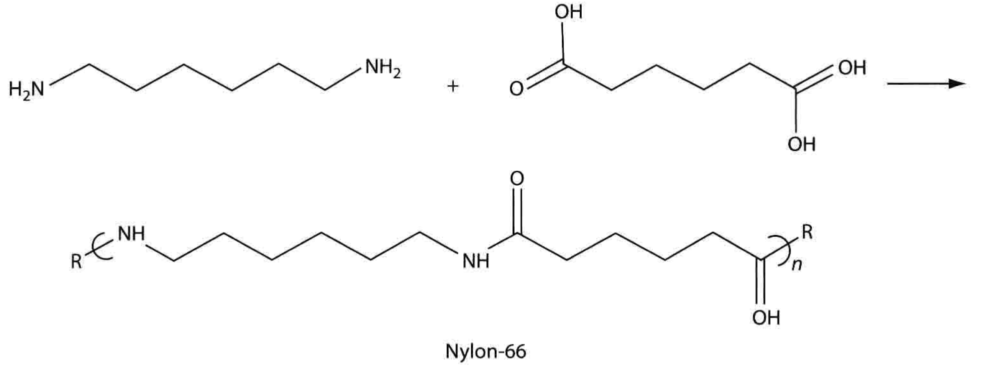
As with most areas, the language of the area is important. Here we will focus on naming polymers with an emphasis on synthetic polymers. Short presentations on how to name proteins and nucleic acids are provided in Chapter 4 and for nylons in Chapter 5.

As synthetic polymer science developed in many venues before standard nomenclature groups were present to assist in the standardization of the naming approach, many popular polymers took on several names including common names. Many polymer scientists have not yet accepted the guidelines laid out 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 used ones.

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 were named after their discoverer, e.g., Bakelite, the three-dimensional polymer produced by condensation of phenol and formaldehyde, which was commercialized by Leo Baekeland in 1905.

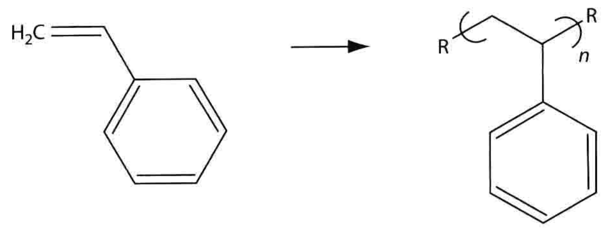
For some important groups of polymers, special names and systems of nomenclature were developed. For instance, nylons were named according to the number of carbons in the diamine and dicarboxylic acid reactants used in their syntheses. The nylon produced by the condensation of 1,6-hexamethylenediamine (six carbons) and adipic acid (six carbons) is called nylon-66. Even here, there is not a set standard as to how nylon-66 is to be written with alternatives including nylon-66 and nylon-6,6.



Nylon-66

SOURCE-BASED NAMES

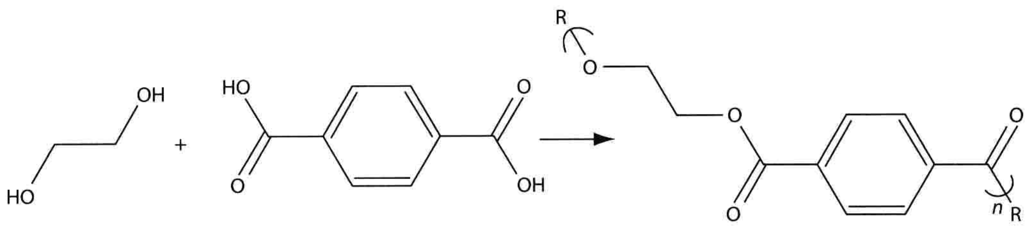
Most common names are source based, i.e., they are based on the common name of the reactant monomer, preceded by the prefix "poly." For example, polystyrene is the most frequently used name for the polymer derived from the monomer 1-phenylethene, which has the common name styrene.



Styrene Polystyrene

The vast majority of 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 the monomer 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- 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 (e.g., poly(vinyl chloride)), but not for single-word polymers (e.g., polyethylene), some authors entirely omit the use of parentheses for either case (e.g., polyvinyl chloride); thus even here there exists a variety of practices. We will employ the use of parentheses for naming polymers of more than one word.

Copolymers are composed of two or more monomers. Source-based names are conveniently used to describe copolymers using an appropriate term between the names of the monomers. Any of a half 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 rubberlike material often found on the bottom of running shoes, is a copolymer where 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 –AAAAAAAABBBBBBBAAAAAAAA–, 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 use of "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 widely accepted for the naming of complex polymers. A listing of such names 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.

TABLE 1
Source-Based 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-methylethylene]
Polypropylene	Poly(1-methylethylene)
Polystyrene	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
Polyamide	–N–C(=O)–	Polyvinyl	–C–C–
Polyester	–O–C(=O)–	Polyanhydride	–C(=O)–O–C(=O)–
Polyurethane	–O–C(=O)–N(H)–	Polyurea	–N(H)–C(=O)–N(H)–
Polyether	–O–	Polycarbonate	–O–C(=O)–O–
Polysiloxane	–O–Si–	Polysulfide	–S–

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		
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	SBR	Butadiene–styrene copolymer

TRADE NAMES, BRAND NAMES, AND ABBREVIATIONS

Trade (and/or brand) names and abbreviations are often used to describe material. 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 (or tradenames) are also used to describe specific groups of materials that are produced by a specific company or under license of that company. Bakelite is the tradename given for the phenol–formaldehyde condensation developed by Baekeland. A sweater whose contents are 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, Darvic, Elvic, Geon, Koroseal, Marvinol, Mipolam, Opalon, Pliofex, Rucon, Solvic, Trulon, Velon, Vinoflex, Vygen, and Vyram are all tradenames 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.

SUMMARY

While there are several important approaches to the naming of polymers, we will use common and source-based names because these are the names that are most commonly utilized by polymer scientists and the general public, and these names, in particular the source-based names, allow a good vehicle to convey structure–property relationships.

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