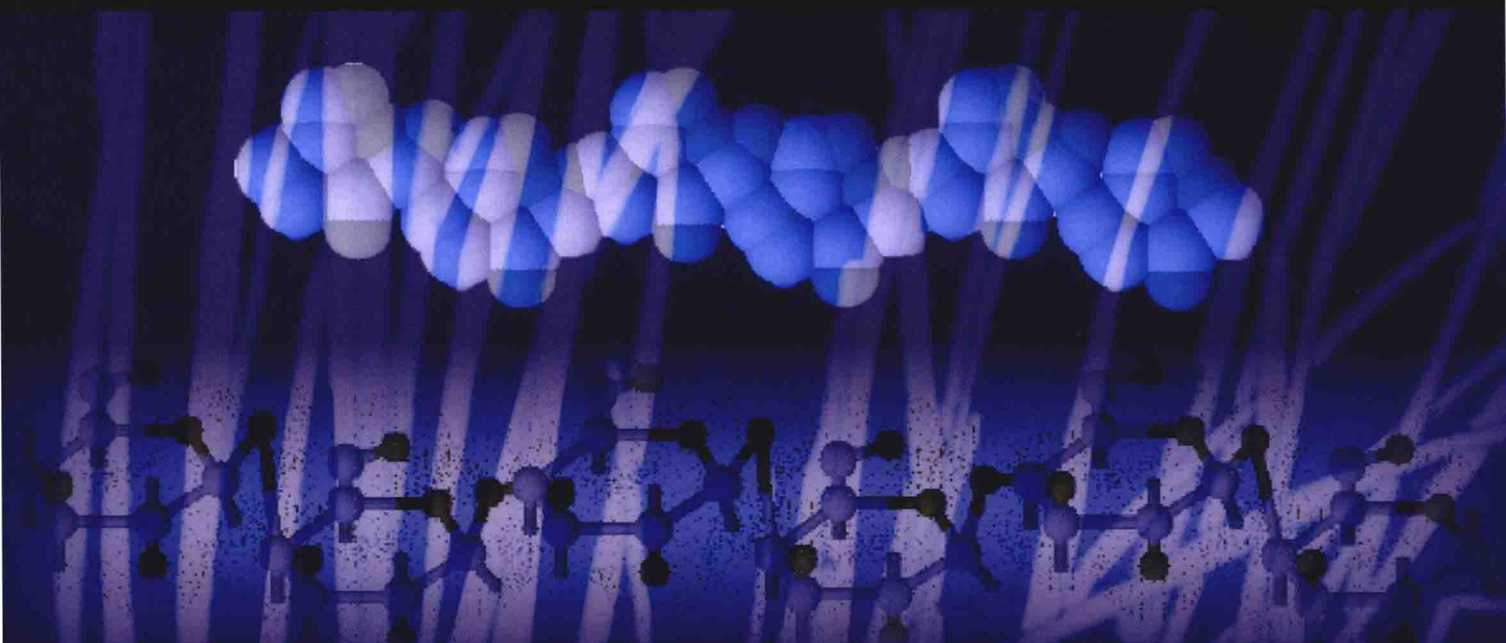
INTRODUCTION TO

# Polymer Chemistry

FOURTH EDITION



Charles E. Carraher Jr.

CRC Press
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POLYMER SCIENCE

# INTRODUCTION TO Polymer Chemistry

## FOURTH EDITION

Continuing the tradition of its previous editions, the fourth edition of *Introduction to Polymer Chemistry* provides a well-rounded presentation of the principles and applications of natural, synthetic, inorganic, and organic polymers. This edition offers detailed coverage of natural and synthetic giant molecules, inorganic and organic polymers, biomacromolecules, elastomers, adhesives, bio-based materials, coatings, fibers, plastics, blends, caulks, natural composites, and ceramics.

Using simple fundamentals based on other chemistry core courses, the book demonstrates how the basic principles of one polymer group can be applied to all of the other groups. It covers reactivities, synthesis and polymerization reactions, techniques for characterization and analysis, energy absorption and thermal conductivity, physical and optical properties, and practical applications. This edition addresses environmental concerns and green polymeric materials, including biodegradable polymers and biobased materials and problems related to introducing new materials. Case studies woven within the text illustrate various developments and the societal and scientific contexts in which these changes occurred.

Now in four color, *Introduction to Polymer Chemistry, Fourth Edition* remains the premier book for understanding the behavior of polymers. Building on undergraduate work in foundational courses, the text fulfills the American Chemical Society Committee on Professional Training (ACS CPT) in-depth course requirement that macromolecule material be present in the curriculum for all approved undergraduate programs. Since the ACS-CPT now requires that macromolecule material be present in the curriculum for all approved undergraduate programs, it is more important that students be exposed to this material. This book fulfills this new requirement.

**FEATURES**

- Covers organic intensive chapters up front, before physical aspects
- Discusses the analytical and physical nature of materials
- Addresses sustainability related to green products
- Includes new subsections on natural composites and less expensive feedstock solutions
- Contains updated exercises, learning summaries, glossaries, and suggestions for further reading

Providing a well-rounded presentation, this book covers the principles and applications of natural, synthetic, inorganic, and organic polymers. Using simple fundamentals, the author shows how the basic principles of one polymer group can be applied to all other groups. Updated brief case studies illustrate various developments and the societal and scientific contexts in which these changes occurred. Each chapter contains careful updates.

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# Fourth Edition

Charles E. Carraher, Jr.

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Cover: Cellulose unit structures are superimposed onto cattails presented in a mixed media of pen and ink and water color drawn by the author.

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# Introduction to Polymer Chemistry
# Fourth Edition

# Preface

Polymers are all about us and are responsible for life itself, for communication (both natural and synthetic), for our nutrition, clothing, recording history, buildings and highways, and numerous other applications. 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) 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; environment; and health. This text provides both the information and insights that allow a better understanding of these large molecules that are all about us. This text includes the elements required by the American Chemical Society Committee on Professional Training in their current guidelines with respect to the requirement that polymers be included in the undergraduate curriculum.

There is an appropriate and necessary move toward green materials and green chemistry. This trend is captured in the present book, within the appropriate sections and with the addition of a separate section on green materials. There also exists a greater awareness of health concerns within our society, and this awareness is mirrored in this text.

Most polymer texts are aimed at either graduate students or are hybrids aimed at both the undergraduate and, mostly, graduate students. This text is aimed mainly at undergraduate students and is suitable for students pursuing fields outside of chemistry. Information gained from the basic core science courses is applied for understanding giant molecules. This information includes factual, theoretical, and practical concepts present in polymer science. This text is useful to those that simply want to be well educated, as well as those wanting to pursue medicine, engineering, physics, chemistry, environmental sciences, biomedical sciences, law, and business.

This text is inclusive in the treatment of polymers including natural and synthetic giant molecules; inorganic and organic polymers; biomacromolecules; and elastomers, adhesives, coatings, fibers, plastics, blends, caulks, composites, and ceramics. The basic principles that apply to one polymer grouping apply to all of the other groupings when applied with some simple fundamentals. These fundamentals are integrated into the fabric of this text.

We remember the saying "we should be students of history so we do not repeat the same mistakes"; we should also be students of history so that we might repeat the successes. Thus, a strong bond is forged between science, history, and the crucible that is today's society. Brief case studies are woven within the fabric of the text as historical accounts illustrating the purposes in back of change as well as the societal and scientific context within which these changes occurred.

This edition is in full color. The use of color is intended to aid in describing basic concepts. It also contains many photographs that allow the reader to grasp the importance of polymers in our everyday lives.

About the cover: Cellulose unit structures are superimposed onto cattails presented in a mixed media of pen and ink and water color drawn by the author.

# Acknowledgments

The author gratefully acknowledges the contributions and assistance of the following in preparing this text: John Droske, Eli Pearce, Charles Pittman, Edward Kresge, Gerry Kirshenbaum, Sukumar Maiti, Alan MacDiarmid, Les Sperling, Eckhard Hellmuth, Mike Jaffe, Otto Vogel, Thomas Miranda, Murry Morello, Graham Allan, and a number of our children who assisted in giving suggestions for the text—Charles Carraher III, Shawn Carraher, Colleen Carraher, Erin Carraher, and Cara Carraher, to Erin for discussions on materials, Cara for her help with the biomedical material, and to Shawn for his help in relating the business and industrial aspects. Special thanks to Gerry Kirshenbaum for his kind permission to use portions of articles by me that appeared in *Polymer News*. This book could not have been written without those that 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 my wife Mary Carraher for her help in proofing and allowing this edition to be written. I thank my researchers for their help in proofing—Jessica Frank, Neil Sookdeo, Paul Slawek, Francesca Mosca, Jeffrey Einkauf, Dhruvin Patel, Loretta Chen, and Elohise St-Fort. Any errors that remain are entirely my fault and I welcome any feedback that you may have.

# Author

**Charles E. Carraher, Jr.** is professor of chemistry and biochemistry, Florida Atlantic University, Boca Raton. Recognized as outstanding chemist in the Southeast United States (1992) by the American Chemical Society and 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 a fellow of the American Institutes of Chemists (1975), Polymeric Materials (2006), Polymer Chemistry (2010), and the American Chemical Society (2010). Currently, he serves as cochair of the ACS's Joint Polymer Education Committee and on the Board of the Intersocietal Polymer Education Committee and has been a member of the ACS's Committee on Professional Training (CPT). He is associate editor of the *Journal of Polymeric Materials* and on the board of the *Journal of Inorganic and Organometallic Polymers and Materials* and the *International Journal of Polymeric Materials and Polymeric Biomaterials*. The author or coauthor of over 75 books and over 1000 articles, he 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 the Saltarilli Sigma Xi Award for his research efforts. Dr. Carraher was the recipient of the 2002 Distinguished Researcher Award from Allied Technologies. In 2016, he was awarded the Distinguished Service Award in Polymer Science by the Polymer Division.

# How to Study Polymers

Studying about polymers is similar to studying any science. Following are some ideas that may assist you as you study.

Much of science is abstract. While much of the study of polymers is abstract, it is easier to conceptualize, make mind pictures, of what a polymer is and how it should behave compared to many other areas of science. For linear polymers, think of a string or rope. Long ropes get entangled with themselves and other ropes. In the same way, polymer chains entangle 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 all about us. We can look at giant molecules on a micro or atomic level or on a macroscopic level. The disposable bottles we use may be composed of long chains of poly(ethylene terephthalate [PET]) chains. The aramid tire cord is composed of aromatic polyamide chains. Our hair is made up of complex bundles of fibrous proteins, again polyamides. *The polymers you study 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 and macroscopic worlds.

At the introductory level we often examine only the primary factors that may cause particular giant molecule behavior. Other factors may become important 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 chemistry and physical relationships. *Such relationships build upon one another and as such you need to study these 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 area. *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 in studying about giant molecules since it will be used repeatedly and is used to understand other concepts (that is, it is built upon).*

In memorizing, learn how you do this best 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, listen to yourself say it. Also, look for patterns, create mnemonic devices, avoid cramming too much into too less 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 evaluation of the information and comparing it with other information and synthesis has to do with integration of the information with other information.

In studying about giant molecules, 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 daily, skimming the text and other study material, think about it, visualize key points and concepts, write down important material, make outlines, take notes, study sample problems, etc. All of these help. Some may help you more than others, so focus on these modes of learning, but not at the exclusion of the other aspects.

In preparing for an exam, consider the following:

- *Accomplish the above: DO NOT wait until the day before the exam to begin studying; inculcate good study habits.*
- *Study wisely: Study how YOU study best—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, etc.*

- *Know what kind of test it will be, if possible, and get copies of old exams if possible; talk to others that might have already had 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 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 like a string.
- *Rules*: Solutions containing polymer chains are more viscous, slower flowing, than solutions that do not contain polymers.

# Polymer Nomenclature

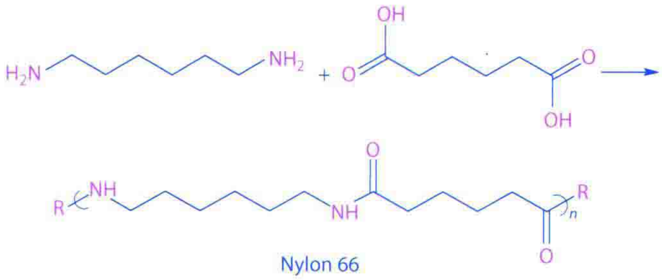
As with most areas, the language of the area is important. Here we will focus on naming polymers with the emphasis on synthetic polymers. Short presentations on how to name proteins and nucleic acids are given when they are covered in Chapter 4 and for nylons in Chapter 5.

The fact that synthetic polymer science grew in many venues before standard 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.

## P.1 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, as is Bakelite, the three-dimensional polymer produced by condensation of phenol and formaldehyde, which was commercialized by Leo Baekeland in 1905.

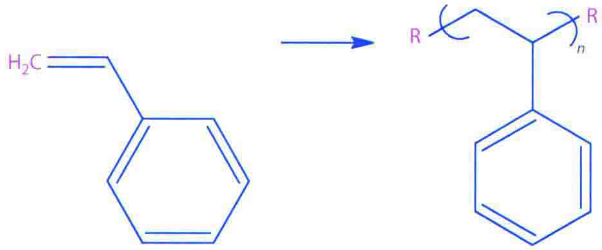
For some important groups of polymers, special names and systems of nomenclature were developed. For instance, the nylons were named according to the number of carbons in the diamine and dicarboxylic acid reactants used in their synthesis. The nylon produced by the condensation of 1,6-hexamethylenediamine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



Nylon 66

## P.2 SOURCE-BASED NAMES

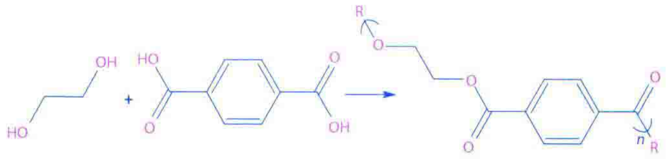
Most common names are source based, that is, they are based on the common name of the reactant monomer, preceded by the prefix "poly." For example, polystyrene is the most frequently used name for the polymer derived from the monomer 1-phenylethene, which has the common name styrene.



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 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 the abbreviation PET.

Although it is often suggested that parentheses be used in naming polymers of more than one word, for example, poly(vinyl chloride), but not for single word-polymers, such as polyethylene, some authors entirely omit the use of parentheses for either case (polyvinyl chloride), so even here a variety of practices exist. In this book, we use parentheses for naming polymers that contain 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, rubber-like 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, that is, 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 represent 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" use giving polystyrene-block-butadiene-block-styrene.

## P.3 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 names is given in the references section. A listing of source- and structure-based names for some common polymers is given in Table P.1.

**TABLE P.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(1methylethylene) |
| 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] |

## P.4 LINKAGE-BASED NAMES

Many polymer "families" are referred to by the name of the particular linkage that connects the polymers (Table P.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.

**TABLE P.2 Linkage-Based Names**

| Family Name | Linkage | Family Name | Linkage |
|---|---|---|---|
| Polyamide | O<br>‖<br>–N–C– | Polyvinyl | –C–C– |
| Polyester | O<br>‖<br>–O–C– | Polyanhydride | O O<br>‖ ‖<br>–C–O–C– |
| Polyurethane | O H<br>‖ \|<br>–O–C–N– | Polyurea | H O H<br>\| ‖ \|<br>–N–C–N– |
| Polyether | –O– | Polycarbonate | O<br>‖<br>–O–C–O– |
| Polysiloxane | –O–Si– | Polysulfide | –S– |

## P.5 TRADENAMES, 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. Tradenames (or 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 tradename given for the phenol-formaldehyde condensation product 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 tradename than their generic name. For instance, polytetrafluoroethylene is better known as Teflon, the tradename held by Dupont.

**TABLE P.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, PETE | 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 | | |

Abbreviations, generally initials in capital letters, are also employed to describe polymers. Table P.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 used 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.

## SELECTED READINGS

Bikales, N. M. (1987): Nomenclature, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., Vol. 10, Wiley, NY, p. 191.

Carraher, C. (2011): *Polymer Chemistry*, 9th ed., CRC Press, Boca Raton, FL.

*Compendium of Macromolecular Nomenclature*, CRC Press, Boca Raton, FL, 1991.

Jenkins, A. D., Loening, K. L. (1989): Nomenclature, in *Comprehensive Polymer Science*, Vol. 1, Oxford, U.K., pp. 13–54.

# American Chemistry Society Committee on Professional Training Requirements

The recent requirements for accredited programs by the ACS CPT include a polymer component that can be fulfilled by either a course in polymers, which this text fulfills, and/or integration of polymer topics into the foundation courses. The CPT guidelines state the following:

The Committee had lengthy discussions about the possibility of instituting a polymer requirement. "Inclusion of a polymer requirement was under consideration because of the recognition that the properties of large molecules and aggregated systems are different from those of small molecules.... Based on the feedback, the Committee decided that the principles that govern macromolecular, supramolecular, mesoscale, and nanoscale systems must now be part of the curriculum for certified graduates. Furthermore, instruction must cover the preparation, characterization, and physical properties of at least two of the following: synthetic polymers, biological macromolecules, supramolecular aggregates, meso- and/or nanoscale materials. We expect that most departments will meet this requirement through coverage distributed across multiple course required for the certified degree. In that case, the coverage should constitute the equivalent of approximately one-fourth of a standard semester course. An alternative option is to offer a stand-alone course that is required for the certified degree." This text also supplies material that allows this to occur.

The following gives locations within the text that apply integration of polymer material into each foundational course as well as locations for the other topic areas mentioned in the CPT requirements.

*Organic*:

Cpt 5-Step-Reaction sections 1, 4–15
Cpt 6-Ionic Chain-Reaction sections 3–9
Cpt 7 Free Radical sections 4–9
Cpt 8 Copolymerization sections 4–14
Cpt 15 Synthesis of Reactants and Intermediates for Polymers

*Inorganic*:

Cpt 9 Organometallic and Metalloid Polymers
Cpt 10 Inorganic Polymers (includes nanoscale materials including carbon nanotubes)

*Physical*:

Cpt 2 Polymer Structure
Cpt 3 Molecular Weight
Cpt 5 Step-Reaction sections 1–4

# Contents