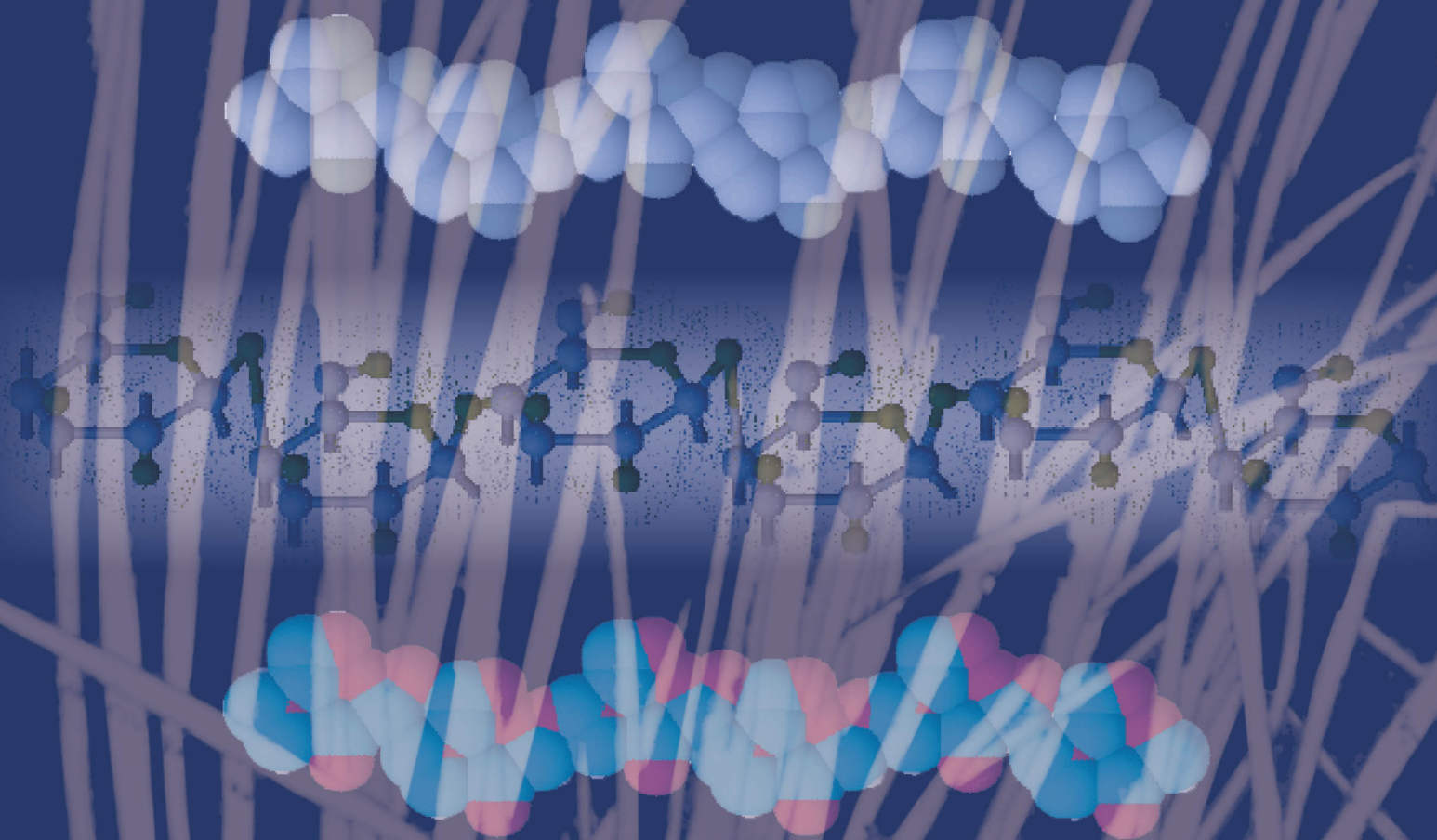


INTRODUCTION TO  
**Polymer  
Chemistry**

FOURTH EDITION



Charles E. Carraher Jr.

 CRC Press  
Taylor & Francis Group

# **Introduction to Polymer Chemistry**

## **Fourth Edition**



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# Introduction to Polymer Chemistry

## Fourth Edition

Charles E. Carraher, Jr.



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# 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.





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# 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

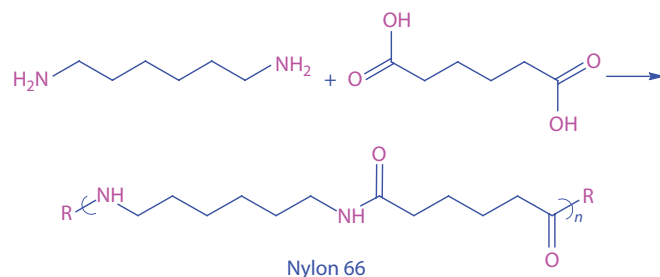
As with most areas, the language of the area is important. Here we will focus on naming polymers with the emphasis on synthetic polymers. Short presentations on how to name proteins and nucleic acids are given when they are covered in Chapter 4 and for nylons in Chapter 5.

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

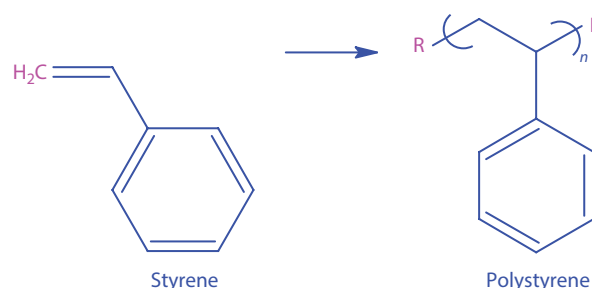
Little rhyme or reason is associated with many of the common names of polymers. Some names are derived from the place of origin of the material, such as *Hevea brasiliensis*—literally “rubber from Brazil”—for natural rubber. Other polymers were named after their discoverer, as is Bakelite, the three-dimensional 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.



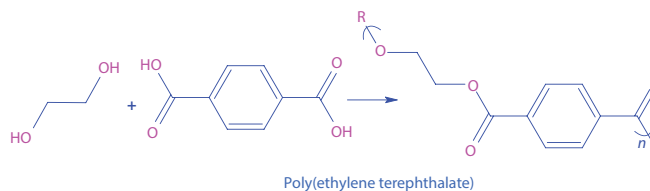
## P.2 SOURCE-BASED NAMES

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.



The vast majority of polymers based on the vinyl group ( $\text{H}_2\text{C}=\text{CHX}$ ) or the vinylidene group ( $\text{H}_2\text{C}=\text{CX}_2$ ) 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.



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 -AAAAAABBBBBBAAAAA-, 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.

### 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.

### 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

**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-methylethylene]
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]

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

Family Name	Linkage	Family Name	Linkage
Polyamide	$\begin{array}{c} \text{O} \\    \\ -\text{N}-\text{C}- \end{array}$	Polyvinyl	$-\text{C}-\text{C}-$
Polyester	$\begin{array}{c} \text{O} \\    \\ -\text{O}-\text{C}- \end{array}$	Polyanhydride	$\begin{array}{c} \text{O} \quad \text{O} \\    \quad    \\ -\text{C}-\text{O}-\text{C}- \end{array}$
Polyurethane	$\begin{array}{c} \text{O} \quad \text{H} \\    \quad   \\ -\text{O}-\text{C}-\text{N}- \end{array}$	Polyurea	$\begin{array}{c} \text{H} \quad \text{O} \quad \text{H} \\   \quad    \quad   \\ -\text{N}-\text{C}-\text{N}- \end{array}$
Polyether	$-\text{O}-$	Polycarbonate	$\begin{array}{c} \text{O} \\    \\ -\text{O}-\text{C}-\text{O}- \end{array}$
Polysiloxane	$-\text{O}-\text{Si}-$	Polysulfide	$-\text{S}-$

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, PVAI	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

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# 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



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# Introduction to Polymers

## 1.1 HISTORY OF POLYMERS

Since most materials are polymeric and most of the recent advances in science and technology involve polymers, some have called this the polymer age. Actually, we have always lived in a polymer age. The ancient Greeks classified all matter as animal, vegetable, and mineral. Minerals were emphasized by the alchemists, but medieval artisans emphasized animal and vegetable matter. All are largely polymeric and are important to life as we know it. Most chemists, biochemists, and chemical engineers are now involved in some phase of polymer science or technology.

The word “polymer” is derived from the Greek *poly* and *meros*, meaning many and parts, respectively. Some scientists prefer to use the word *macromolecule*, or large molecule, instead of polymer. Others maintain that naturally occurring polymers, or *biopolymers*, and synthetic polymers should be studied in different courses. Others name these large molecules simply “giant molecules.” However, the same principles apply to all polymers. If one discounts the end uses, the differences between all polymers, including plastics, fibers, and elastomers, or rubbers, and natural and synthetic, are determined primarily by the intermolecular and intramolecular forces between the molecules and within the individual molecule, respectively, and by the functional groups present, and most of all, by their size allowing an accumulation of these forces.

In addition to being the basis of life itself, protein is used as a source of amino acids and energy. The ancients degraded or depolymerized the protein in meat by aging and cooking, and they denatured egg albumin by heating or adding vinegar to the eggs. Early humans learned how to process, dye, and weave the natural proteinaceous fibers of wool and silk and the carbohydrate fibers from flax and cotton. Early South American civilizations, such as the Aztecs, used natural rubber (*Hevea brasiliensis*) for making elastic articles and for waterproofing fabrics.

There has always been an abundance of natural fibers and elastomers but few plastics. Of course, early humans employed a crude plastic art in tanning the protein in animal skins to make leather and through heating created somewhat “plastic” tortoise shells. They also used naturally occurring tars as caulking materials and extracted shellac from the excrement of small coccid insects (*Coccus lacca*).

Until Wohler synthesized urea from inorganic compounds in 1828, there had been little progress in organic chemistry since the alchemists emphasized the transmutation of base metals to gold and believed in a vital force theory. Despite this essential breakthrough, little progress was made in understanding organic compounds until the 1850s when Kekule developed the presently accepted technique for writing structural formulas. However, polymer scientists displayed a talent for making empirical discoveries before the science was developed.

The original connection between rubber and sulfur is often attributed to Nathaniel Hayward, an American. He is reported to have dusted rubber with sulfur powder and exposed the dusted rubber to sunlight as a way to remove the rubber’s stickiness. Hayward patented his discovery. He turned over his discovery to Charles Goodyear who transformed the connection between sulfur and rubber into the rubber industry.

Charles Goodyear grew up in poverty. He was a Connecticut Yankee born in 1800. He began to work in his father’s farm implements business. Later, he moved to Philadelphia where he opened a retail hardware store that soon went bankrupt. Charles then turned to being an inventor. As a child, he had noticed the magic material that formed a rubber bottle he had found. He visited the

Roxbury India Rubber Company to try and interest them in his efforts to improve the properties of rubber. They assured him that there was no need to do so.

He started his experiments with a malodorous gum from South America in debtor's prison. In a small cottage on the grounds of the prison, he blended the gum, the raw rubber called *Hevea* rubber, with anything he could find—ink, soup, castor oil, etc. While rubber-based products were available, they were either sticky or became sticky in the summer's heat. He found that treatment of the raw rubber with nitric acid allowed the material to resist heat and not to adhere to itself. This success attracted backers who helped form a rubber company. After some effort, he obtained a contract to supply the U.S. Post Office with 150 rubber mailbags. He made the bags and stored them in a hot room while he and his family were away. When they returned, they found the bags in a corner of the room, joined together as a single mass. The nitric acid treatment was sufficient to prevent surface stickiness, but the internal rubber remained tacky and susceptible to heat.

While doing experiments in 1839 at a Massachusetts rubber factory, Charles accidentally dropped a lump of rubber mixed with sulfur on the hot stove. The rubber did not melt but rather charred. He had discovered vulcanization, the secret that was to make rubber a commercial success. While he had discovered vulcanization, it would take several years of ongoing experimentation before the process was really commercially useful. During this time, he and his family were near penniless. While he patented the process, the process was too easily copied and pirated so that he was not able to fully profit from his invention and years of hard work. Even so, he was able to develop a number of items.

Charles Goodyear, and his brother Nelson, transformed natural rubber, *Hevea* rubber, from a heat "softenable" thermoplastic to a less-heat-sensitive product through the creation of cross-links between the individual polyisoprene chainlike molecules using sulfur as the cross-linking agent. *Thermoplastics* are 2D molecules that may be softened by heat. *Thermosets* are materials that are 3D networks that cannot be reshaped by heating. Rather than melting, thermosets degrade. As the amount of sulfur was increased, the rubber became harder becoming a hard rubberlike (ebonite) material.

The spring of 1851 found the construction of a remarkable building on the lawns of London's Hyde Park. The building was designed by a maker of greenhouses so it was not unexpected that it had a "greenhouse look." This Crystal Palace was to house almost 14,000 exhibitors from all over the world. It was the chance for exhibitors to show their wares. Charles Goodyear, then 50 years old, used this opportunity to show off his over two decades worth of rubber-related products. He decorated his Vulcanite Court with rubber walls, roof, furniture, buttons, toys, carpet, combs, etc. Above it hung a giant six foot rubber raft and assorted balloons. The European public was introduced to the world of new man-made materials.

Within a little more than a decade, Charles Goodyear was dead. Within a year of his death, the American Civil War broke out. The Union military used about \$27 million worth of rubber products by 1865 helping launch the American rubber industry.

In 1862, Queen Victoria, while in mourning for her recently departed husband Albert, opened the world's fair in London. One of the exhibitors was Alexander Parks. He was displeased with the limited colors available for rubber products—generally dull and dark. In his workshop in Birmingham, England, he was working with nitrocellulose, a material made from the treatment of cotton with nitric and sulfuric acids. Nitrocellulose solutions were made from organic liquids such as ethanol and ether. Thin films and coatings were made by simply pouring the nitrocellulose solutions onto the desired item or surface and allowing the solvent to evaporate. He wanted to make solid objects from nitrocellulose. After years of work, he developed a material he called Parkesine from which he made buttons and combs, and in fact many of the items were made of rubber—except that his materials could be brightly colored, clear, or made to shine like mother-of-pearl. At the London world's fair, he advertised "PATENT PARKESINE of various colours: hard elastic, transparent, opaque, and waterproof." Even with his work he had not developed a material that could be "worked" or was stable and even with his hype, the material never caught on except within exhibition halls.

About this time, John Wesley Hyatt, a printer from Albany, NY, was seeking a \$10,000 prize for anyone who could come up with a material that was a substitute for ivory billiard balls, developed a material that was stable and could be "worked" from shellac and wood pulp. He then turned to nitrocellulose discovering that shredded nitrocellulose could be mixed with camphor, heated

under pressure, to produce a tough white mass that retained its shape. This material, dubbed celluloid, could be made into the usual rubberlike products, but also solid pieces like boxes, wipe-clean linen collars, cuffs, and ping-pong balls. Celluloid could also, like the shellac-wood pulp mixture, be worked—cut, drilled, and sawed. But celluloid was flammable and did not stand up well in hot water. The wearers of celluloid dentures truly could have their “teeth curled” when drinking a hot cup of coffee. One of its best qualities was that it could be made to “look like” other materials—it could be dyed to look like marble and swirled to mimic tortoiseshell and mother-of-pearl and even look and feel like ivory. It did not make good billiard balls. One account has billiard balls hitting and exploding like a shot that caused cowboys to draw their guns.

Both cellulose and cellulose nitrate are linear, or 2D, polymers, but the former cannot be softened because of the presence of multitudinous hydrogen bonds between the chainlike molecules. When used as an explosive, the cellulose nitrate is essentially completely nitrated, but the material used by Parks and Hyatt was a dinitrate, still potentially explosive, but less so. Parks added castor oil and Hyatt added camphor to plasticize—reduce the effect of the hydrogen bonding—the cellulose nitrate allowing it some flexibility.

Worldwide, rubber gained in importance with the invention of the air-filled or pneumatic tires by a Scotsman, John Dunlop in 1888. He had a successful veterinarian practice in Belfast. In his off time, he worked to improve the ride of his son’s tricycle. His invention happened at the right time. The automobile was emerging and the air-filled tires offered a gentler ride. Thus, was begun the tire industry.

All of these inventions utilized natural materials as at least one ingredient. After years of work in his chemistry labs in Yonkers, NY, Leo Baekeland in 1907 announced in an American Chemical Society meeting the synthesis of the first truly synthetic polymeric material latter dubbed Bakelite.

Baekeland was born in Belgium in 1863, the son of an illiterate shoe repairman and a maid. He was bright and received, with highest honors, his doctorate at the age of 20. He could have spent the remaining part of his life in academics in Europe, but heading the words of Benjamin Franklin, he sailed to America. In the 1890s, he developed the first photographic paper, called Velox, which could be developed in synthetic light rather than sunlight. George Eastman saw the importance of this discovery and paid Baekeland \$750,000 for the rights to use this invention.

It was generally recognized by the leading organic chemists of the nineteenth century that phenol would condense with formaldehyde. Since they did not recognize the concept of functionality, Baeyer, Michael, and Kleeberg produced useless cross-linked goos, gunks, and messes and then returned to their research on reactions of monofunctional reactants. However, by the use of a large excess of phenol, Smith, Luft, and Blumer were able to obtain a hard, but meltable thermoplastic material.

With his \$750,000, Baekeland set up a lab next to his home. He then sought to solve the problem of making the hard material made from phenol and formaldehyde soluble. After many failures, he thought about circumventing the problem by placing the reactants in a mold of the desired shape and allowing them to form the intractable solid material. After much effort, he found the conditions under which a hard, clear solid could be made—Bakelite was discovered. Bakelite could be worked, it was resistant to acids and organic liquids, stood up well to heat and electrical charge, and could be dyed to give colorful products. It was used to make bowling balls, phonograph records, telephone housings, gears, and cookware. His materials also made excellent billiard balls. Bakelite also acted as a binder for sawdust, textiles, and paper forming a wide range of composites including Formica laminates, many of which are still used. It was also used as an adhesive giving us plywood.

While there is no evidence that Baekeland recognized what polymers were, he appeared to have a grasp on functionality and how to “use” it to produce thermoplastic materials that could later be converted to thermosets. Through control of the ratio of phenol to formaldehyde, he was able to form a material that was a thermoplastic. He coined the term “*A-stage resole resin*” to describe this thermoplastic. This *A-stage resole resin* was converted to a thermoset cross-link, *C-stage Bakelite*, by additional heating. Baekeland also prepared thermoplastic resins called “*novolacs*” by the condensation of phenol with a lesser amount of formaldehyde under acidic conditions. The thermoplastic novolacs were converted to thermosets by addition of more formaldehyde. While other polymers had been synthesized in the laboratory using a combination of chemicals and



naturally derived materials, Bakelite was the first truly synthetic plastic. The “recipes” used today differ little from the ones developed by Baekeland showing his ingenuity and knowledge of the chemistry of the condensation of the trifunctional phenol and difunctional formaldehyde.

While poly(vinyl chloride) was initially formed by Baumann in 1872, it awaited interest until 1926 when B. F. Goodrich discovered how to make sheets and adhesives from poly(vinyl chloride), and the “vinyl-age” began. While polystyrene was probably first formed by Simon in 1839, it was almost 100 years later, 1930, that the German giant company I. G. Farben placed polystyrene on the market. Polystyrene molded parts became common place. Rohm and Haas bought out plexiglass from a British firm in 1935 and began the production of clear plastic parts and goods including replacements for glass as camera lenses, aircraft windows, clock faces, and car taillights.

To this time, polymer science was largely empirical, instinctive, and intuitive. Prior to World War I, celluloid, shellac, Galalith (casein), Bakelite, and cellulose acetate plastics; *Hevea* rubber, cotton, wool, and silk rayon fibers; Glyptal polyester coatings; bitumen or asphalt; and coumarone-indene and petroleum resins were all commercially available. However, as evidenced by the chronological data shown in Table 1.1, there was little additional development in polymers prior to World War II because of a general lack of fundamental knowledge of polymers. But the theoretical basis was being built. Only a few of many giants will be mentioned.

Over a century ago, Graham coined the term “colloid” for aggregates with dimensions in the range of  $10^{-9}$  to  $10^{-7}$  m. Unfortunately, the size of many macromolecules is in this range, but it is important to remember that unlike colloids, whose connective forces are ionic and/or secondary forces, polymers are individual molecules whose size cannot be reduced without breaking the covalent bonds that hold the atoms together. In 1860, an oligomer, a small polymer, was prepared from ethylene glycol and its structure correctly given as  $\text{H}-(\text{OCH}_2\text{CH}_2)_n-\text{OH}$ . But when poly(methacrylic acid) was made by Fittig and Engelhorn in 1880, it was incorrectly assigned a cyclic structure. Polymers were thought of as being colloids or cyclic compounds like cyclohexane. By the use of the Raoult and van’t Hoff molecular weight concepts, several scientists obtained high-molecular-weight values for these materials and for a number of other polymeric materials. But since the idea of large molecules was not yet accepted, they concluded that these techniques were not applicable to these molecules rather than accepting the presence of giant molecules.

The initial “tire-track in the sand” with respect to tires was the discovery of vulcanization of rubber by Charles Goodyear in 1844. The first rubber tires appear in the mid-1880s. These tires were solid rubber with the rubber itself absorbing the bumps and potholes. John Dunlop invented the first practical pneumatic or inflatable tire with his patent granted in 1888. Andre Michelin was the first person to use the pneumatic tire for automobiles. The Michelin brothers, Andre and Edouard, equipped a racing car with pneumatic tires and drove it in the 1895 Paris–Bordeaux road race. They did not win but it was sufficient advertising to begin interest in pneumatic tires for automobiles. Further, because they did not cause as much damage to the roads, pneumatic tires were favored by legislation. It is interesting to see that the names of these three pioneers still figure prominently in the tire industry. Even so, another inventor Thompson had actually been given the first patent for a vulcanized rubber pneumatic tire in 1845, but it did not take off. Thompson was a prolific inventor also having patented a fountain pen in 1849 and a steam traction engine in 1867.

A number of the giant tire companies started at the turn of the century. In America, many of these companies centered about Akron, the capital of the rubber tire. In 1898, the Goodyear Tire and Rubber Company started. The Firestone Tire and Rubber Company was started by Harvey Firestone in 1900. Other tire companies shortly followed.

Hermann Staudinger studied the polymerization of isoprene as early as 1910 (Picture 1.1). Intrigued by the difference between this synthetic material and natural rubber, he began to focus more of his studies on such materials. His turn toward these questionable materials, of interest to industry but surly not academically important, was viewed unkindly by his fellow academics. He was told by one of his fellow scientists, “Dear Colleague, Leave the concept of large molecules well alone... There can be no such thing as a macromolecule.”

Staudinger systematically synthesized a variety of polymers. In the paper *Uber Polymerization* in 1920, he summarized his findings and correctly proposed linear structures for such important polymers as polyoxymethylene and polystyrene. X-ray studies of many natural and synthetic

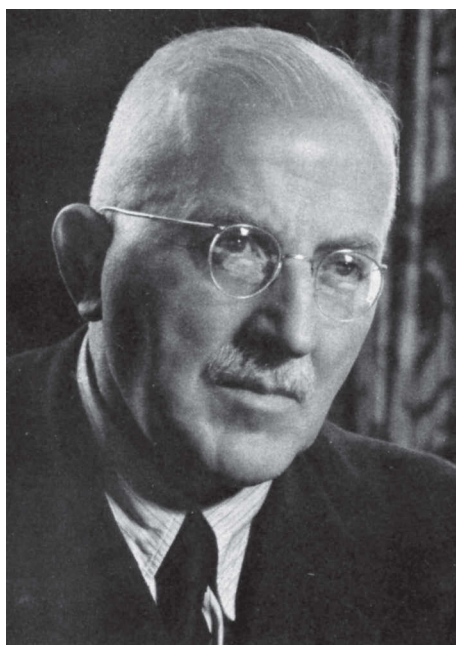
**TABLE 1.1 Chronological Developments of Commercial Polymers (to 1992)**

Before 1800	Cotton, flax, wool, and silk fibers; bitumens caulking materials; glass and hydraulic cements; leather and cellulose sheet (paper); and natural rubber ( <i>Hevea brasiliensis</i> ), gutta-percha, balata, and shellac
1839	Vulcanization of rubber (Charles Goodyear)
1845	Cellulose esters (Schonbein)
1846	Nitration of cellulose (Schonbein)
1851	Ebonite (hard rubber; Nelson Goodyear)
1860	Molding of shellac and gutta-percha
1868	Celluloid (plasticized cellulose nitrate; Hyatt)
1888	Pneumatic tires (Dunlop)
1889	Cellulose nitrate photographic films (Reichenbach)
1890	Cuprammonia rayon fibers (Despeisses)
1892	Viscose rayon fibers (Cross, Bevan, and Beadle)
1903	First tubeless tire (Litchfield of Goodyear Tire Co.)
1897	Poly(phenylene sulfide)
1901	Glyptal polyesters
1907	Phenol-formaldehyde resins (Bakelite; Baekeland)
1908	Cellulose acetate photographic fibers
1912	Regenerated cellulose sheet (cellophane)
1913	Poly(vinyl acetate)
1914	Simultaneous interpenetrating network
1920	Urea-formaldehyde resins
1923	Cellulose nitrate automobile lacquers
1924	Cellulose acetate fibers
1926	Alkyd polyester (Kienle)
1927	Poly(vinyl chloride) wall covering
1927	Cellulose acetate sheet and rods
1927	Graft copolymers
1928	Nylon (Carothers, DuPont)
1929	Polysulfide synthetic elastomer (Thiokol; Patrick)
1929	Urea-formaldehyde resins
1930	Polyethylene (Friedrich/Marvel)
1931	Poly(methyl methacrylate) (PMMA) plastics
1931	Polychloroprene elastomer (Neoprene; Carothers)
1934	Epoxy resins (Schlack)
1935	Ethyl cellulose
1936	Poly(vinyl acetate)
1936	Poly(vinyl butyral) (safety glass)
1937	Polystyrene
1937	Styrene-butadiene (Buna-S) and styrene-acrylonitrile (Buna-N) copolymer elastomers
1939	Melamine-formaldehyde resins
1939	Nylon 6 (Schlack)
1939	Nitrile rubber (NR)
1940	Isobutylene-isoprene elastomer (butyl rubber; Sparks and Thomas)
1941	Low-density polyethylene (LDPE)
1941	Poly(ethylene terephthalate) (PET)
1942	Butyl rubber
1942	Unsaturated polyesters (Ellis and Rust)
1943	Fluorocarbon resins (Teflon; Plunket)
1943	Silicones
1945	SBR
1946	Polysulfide rubber (Thiokol)
1948	Copolymers of acrylonitrile, butadiene, and styrene (ABS)

(Continued)

**TABLE 1.1 (Continued) Chronological Developments of Commercial Polymers (to 1992)**

1949	Cyanoacrylate (Goodrich)
1950	Polyester fibers (Winfield and Dickson)
1950	Polyacrylonitrile fibers
1952	Block copolymers
1953	High-impact polystyrene (HIPS)
1953	Polycarbonates (Whinfield & Dickson)
1956	Poly(phenylene ether); Poly(phenylene oxide) (GE)
1957	High-density polyethylene (HDPE)
1957	Polypropylene
1957	Polycarbonate
1958	Poly(dihydroxymethylcyclohexyl terephthalate) (Kodel, Eastman Kodak)
1960	Ethylene-propylene copolymer elastomers
1961	Aromatic nylons (Aramids, Nomex, DuPont)
1962	Polyimide resins
1964	Poly(phenylene oxide)
1964	Ionomers
1965	Polysulfone
1965	Styrene-butadiene block copolymers
1966	Liquid crystals
1970	Poly(butylene terephthalate)
1974	Polyacetylene
1982	Polyetherimide (GE)
1991	Carbon nanotubes (Iijima; NEC Lab)

**PICTURE 1.1** Herman Staudinger, Father of Polymer Science. (From Wikipedia.)

materials were used as structural proof that polymers existed. Foremost in these efforts were Herman Mark and Linus Pauling. Both of these giants contributed to other important areas of science. Pauling contributed to the fundamental understanding of bonding and the importance of vitamins. Mark helped found the academic and communication (journals, short courses, workshops) basis that would allow polymers to grow from its very diverse roots.

Probably, the first industrial effort aimed at basic or fundamental research in the chemical sciences was by DuPont. Their initial venture in artificial fibers was in 1920 when they purchased a 60% interest in Comptoir des Textiles Artificiels, a French rayon company. The combined company was named the DuPont Fiber Company. DuPont spent considerable effort and money on expanding the properties of rayon. In 1926, Charles M. A. Stine, director of the chemical department, circulated a memo to DuPont's executive committee suggesting that the company move from investing in already existing materials to investigating new materials. This was a radical idea that a company supposedly focused on profit spend some of its effort on basic research. The executive committee approved much of Stine's proposal giving him \$25,000 a month for the venture allowing him to hire 25 chemists for the task. The initial hiring was difficult because academic chemists did not trust DuPont to allow them to do basic research. A year later, he was able to make his central hiring, Wallace Hume Carothers.

Wallace Hume Carothers is the father of synthetic polymer science (Picture 1.2). History is often measured by the change in the flow of grains of sand in the hour glass of existence. Carothers is a granite boulder in this hour glass. Carothers was born, raised, and educated in the Midwest of the United States. In 1920, he left Tarkio College with his BS degree and entered the University of Illinois where he received his MA in 1921. He then taught at the University of South Dakota where he published his first paper. He returned to receive his PhD under Roger Adams in 1924. In 1926, he became an instructor in organic chemistry at Harvard.

In 1927, the DuPont Company reached a decision to begin a program of fundamental research "without any regard or reference to commercial objectives." This was a radical departure since the bottom line was previously products marketed and not papers published. Charles Stine, director of DuPont's chemical department, was interested in pursuing fundamental research in the areas of colloid chemistry, catalysis, organic synthesis, and polymer formation and convinced the Board to hire the best chemists in each field to lead this research. Stine visited with many in the academic community including then president of Harvard, one of my uncles, J.B. Conant, an outstanding chemist himself, who told him about Carothers. Carothers was persuaded to join the DuPont group attracted by a generous research budget and an approximate doubling of his academic salary to \$6000. This was the birth of the Experimental Station at Wilmington, Delaware.

Up to this point, it was considered that universities were where discoveries were made and industry was where they were put to some practical use. This separation between basic and applied



**PICTURE 1.2** Wallace Hume Carothers, one of the pioneers of polymer science. (From Wikipedia.)

work was quite prominent at this juncture and continues in many areas even today in some fields of work though the difference has decreased. But in polymers, most of the basic research was done in industry having as its inception the decision by DuPont to bridge this “unnatural” gap between fundamental knowledge and application. In truth, they can be considered as the two hands of an individual and in order to do manual work both hands are important.

Staudinger believed that large molecules were based on the jointing, through covalent bonding, of large numbers of atoms. Essentially, he and fellow scientists like Karl Freudenberg, Herman Mark, Michael Polanyi, and Kurt Myer looked at already existing natural polymers. Carothers, however, looked at the construction of these giant molecules from small molecules forming synthetic polymers. His intention was to prepare molecules of known structure through the use of known organic chemistry and to “investigate how the properties of these substances depended on constitution.” Early work included the study of polyester formation through reaction of diacids with diols forming polyesters. But he could not achieve molecular weights greater than about 4000 below the size where many of the interesting so-called polymeric properties appear.

DuPont was looking for a synthetic rubber. Carothers assigned Arnold Collins to this task. Collins’ initial task was to produce pure divinylacetylene. While performing the distillation of an acetylene reaction, in 1930, he obtained a small amount of an unknown liquid that he set aside in a test tube. After several days, the liquid turned to a solid. The solid bounced and eventually was shown to be a synthetic rubber polychloroprene whose properties were similar to those of vulcanized rubber but it was superior in its resistance to ozone, ordinary oxidation, and to most organic liquids. It was sold under its generic name “neoprene” and the trade name “Duprene.”

As you read through this book, you will see that there were many so-called “accidental” discoveries. But as Louis Pasteur wrote “In the fields of observation, chance favors only the mind that is prepared.” So while results from a given experiment may be unexpected, we are able to profit from them only as far as we are prepared to look at the significance of the observation and place it in context with other knowledge, that is, the prepared mind.

Also in 1930, Carothers and Julian Hill designed a process to remove water that was formed during the esterification reaction. Essentially, they simply froze the water as it was removed using another recent invention called a molecular still (basically a heating plate coupled to vacuum) allowing the formation longer chains. In April, Hill synthesized a polyester using this approach and touched a glass stirring rod to the hot mass and then pulled the rod away effectively forming strong fibers, the pulling helping reorient the somewhat mobile polyester chains. The polyester had a molecular weight of about 12,000. Additional strength was achieved by again pulling the cooled fibers. Further reorienting occurred. This process of “drawing” or pulling to produce stronger fibers is now known as “cold drawing” and is widely used in the formation of fibers today. The process of “cold drawing” was discovered by Carothers’ group. While interesting, the fibers were not considered to be of commercial use. Carothers and his group then moved to look at the reaction of diacids with diamines instead of diols. Again, fibers were formed but these initial materials were deemed not to be particularly interesting.

In 1934, Paul Flory was hired to work with Carothers to help gain a mathematical understanding of the polymerization process and relationships. Thus, there was an early association between theory and practice or structure–property relationships.

In 1934, Donald Coffman, a member of the Carothers team, pulled a fiber from an aminoethyl-ester (polyamide) polymer. The fiber retained the elastic properties of the polyesters previously investigated but had a higher melting point sufficiently high as to allow clothing made from it to be laundered and ironed. The field of candidates for further investigation was narrowed to two-polyamide 5,10 made from 1,5-pentamethylene diamine and sebacic acid, and polyamide 6,6 synthesized from 1,6-hexamethylenediamine and adipic acid. Polyamide 6,6 won because the monomers could be made from benzene, a readily available feedstock from coal tar.

The polyamide fiber project was begun in earnest using the reaction of adipic acid with hexamethylenediamine. They called the polyamide fiber 66 because each carbon-containing unit had six carbons. It formed a strong, elastic, largely insoluble fiber with a relatively high melt temperature. DuPont chose this material for production. These polyamides were given the name “nylons.” Thus, was born nylon 66. It was the first synthetic material whose properties equaled or exceeded the natural analog, namely, silk. (In reality, this may not be the truth, but at the time, it was believed to be true.)



The researchers had several names for polyamide 6,6 including rayon 66, fiber 66, and Duparon derived from “Dupont pulls a rabbit out [of] the hat nitrogen/nature/nature/nozzle/naphtha.” The original “official” name was “Nuron” that implied newness and also spelled “on run” somewhat backward. This name was too close to other trademarked names and was renamed “Norton” and eventually to what we know today as “Nylon.”

As women’s hemlines rose in the 1930s, silk stockings were in great demand but were very expensive. Nylon changed this. Nylon could be woven into sheer hosiery. The initial presentation of nylon hose to the public was by Stine at a forum of women’s club members in New York City on October 24, 1938. Nearly 800,000 pairs were sold on May 15, 1940, alone—the first day they were on the market. By 1941, nylon hosiery held 30% of the market but by December 1941, nylon was diverted to make parachutes, etc.

From these studies, Carothers established several concepts. First, polymers could be formed by employing already known organic reactions but with reactants that had more than one reactive group per molecule. Second, the forces that bring together the individual polymer units are the same as those that hold together the starting materials, namely, primary covalent bonds. Many of the polymer chemistry names and ideas that permeate polymer science today were standardized through his efforts.

America is a melting pot for immigrants and during World War II, it profited from the immigration of a number of scientists including Herman Mark. Because of over 5 years of service as a combat soldier in the elite k.k. Kaiserschutzen Regiment Nr. II Imperial Austrian Army during World War I, Mark did not receive his PhD until the age of 26 in 1919. He was highly decorated and the Austrian hero of the Battle of Mount Ortigara in 1917. He accepted a position at the University of Berlin with many other well-known chemists including Max Bergmann, Hermann Leuchs, Emil Fisher, and Carl Harries. He moved to industry becoming head of research in a division of I. G. Farben.

When the Nazis came to power, he moved to Austria. Though Lutheran, Mark was of Jewish descent so by early 1938 began planning to leave Austria. He started converting his wealth into platinum wire which he made into hangers. His wife knitted hanger covers. When Hitler’s troops invaded Austria, he was stripped of his passport. He retrieved the passport through a bribe and obtained a visa to visit Canada. In April 1938, he mounted a Nazi flag on the radiator of their car, strapped ski equipment onto the car’s roof, and drove across the border. Supposedly, he was asked by a border guard if he had any wealth to declare. He replied that he had only the clothes on his back and the hangers upon which they hung. From Zurich, he traveled to France, then England, and then Canada and finally the United States where he joined the Brooklyn Polytechnic.

While at Brooklyn Polytechnic, he consulted for DuPont and was involved in much of the pioneering work that occurred there. His students included many polymer pioneers including Turner Alfrey, Paul Doty, Isidor Fankuchen, Arthur Tobolsky, W. Hohenstein, and Bruno Zimm. During the war, regular meetings of the chemistry community were organized at Brooklyn Poly focusing mainly on polymers but allowing communication to occur between the academic and industrial scientists. During the war, he worked with the military on a number of projects including creation of a land and sea vehicle, and the use of icebergs to transport large amounts of cargo past the German U-Boats. His first course at Brooklyn Poly was “general polymer chemistry” that attracted many local industrial scientists. He started the long-running Interscience (Wiley) book series on polymers as well as the *Journal of Polymer Science*, again with Wiley. The Institute of Polymer Research was started in 1946 with the creation of a letterhead and located in a vacant razor blade factory.

He worked on x-ray diffraction and Linus Pauling learned x-ray diffraction from Mark leading to Pauling’s seminal work on protein structure. He worked with Albert Einstein using the powerful x-ray tubes available to Mark to verify the Compton effect that provided confirmation of Einstein’s light quantum theory.

In the 1950s and 1960s, he was famous for volunteering to give talks at various colleges about the country showing up with a suitcase and lots of enthusiasm. He was the missionary for polymers.

Representing the true multidisciplinary nature of polymers, early important contributions were also made by physicists, engineers, and those from biology, medicine, and mathematics including W. H. Bragg, Peter Debye, Albert Einstein, and R. Simha.

World War II helped shape the future of polymers. Wartime demands and shortages encouraged scientists to seek substitutes and materials that even excelled currently available materials. Polycarbonate (Kevlar), which could stop a “speeding bullet,” was developed as was polytetrafluoroethylene (Teflon) that was super slick. New materials were developed spurred on by the needs of the military, electronics industry, food industry, etc. The creation of new materials continues today at an even accelerated pace brought on by the need for materials with specific properties and the growing ability to tailor—make giant molecules, macromolecules—polymers.

Unlike other areas of chemistry, most of the basic research has been done in industry so that there is often a close tie between discoveries and their commercialization. Table 1.2 lists some of the dates of commercialization for some important synthetic polymer discoveries.

A number of Nobel Prizes have been given for polymer work. Table 1.3 contains winners whose efforts are related to synthetic polymers. In truth, there are many more since most of the prizes given out in medicine and biology deal with giant molecules.

There are also a number of Nobel Prizes given for advances contributing to polymers. The 2010 Nobel Prize in chemistry was given to Richard Heck, Ei-ichi Negishi, and Akira Suzuki for their work on palladium-catalyzed cross-coupling reactions employed to synthesize pi-conjugated oligomers, dendrimers, and polymers.

Throughout this text, advances are placed in some historical setting. This adds some texture to the topics as well as acting as case histories that are widely used in subject areas such as business and medicine.

**TABLE 1.2 Commercialization of Selected Polymers**

Polymer	Year	Company
Bakelite	1909	General Bakelite Corp.
Rayon	1910	American Viscose Company
Poly(vinyl chloride)	1927	Goodrich
Styrene-butadiene copolymer	1929	I.G. Farben
Polystyrene	1929/1930	I.G. Farben & Dow
Neoprene	1931	DuPont
Poly(methyl methacrylate)	1936	Rohm & Haas
Nylon 66	1939/1940	DuPont
Polyethylene (LDPE)	1939	ICI
Poly(dimethyl siloxane)	1943	Dow Corning
Acrylic fiber	1950	DuPont
Poly(ethylene terephthalate), PET	1953/1954	DuPont/ICI
Polyurethane block copolymers (Spandex)	1959	DuPont
Poly(phenylene terephthalamide)	1960	DuPont

**TABLE 1.3 Nobel Prize Winners for Their Work with Synthetic Polymers**

Scientist(s)	Year	Area
Herman Staudinger	1953	Polymer hypothesis
Karl Ziegler and Giulio Natta	1963	Stereoregulation of polymer structure
Paul Flory	1974	Organization of polymer chains
Bruce Merrifield	1984	Synthesis on a solid matrix
Pierre de Gennes	1991	Polymer structure and control at interfaces
A. J. Heeger, Alan MacDiarmid, and H. Shirakawa	2000	Conductive polymers
Y. Chauvin, R. H. Grubbs, and R.R. Schrock	2005	Metathesis
R. Heck, E. Negishi, and A. Suzuki	2010	Palladium-catalyzed cross-coupling reactions

## 1.2 WHY POLYMERS?

Polymers are all about us. They serve as the very basis of both plant and animal life as proteins, nucleic acids, and polysaccharides. In construction, they serve as the basic building blocks as concrete, insulation, and wooden and composite beams. At home, they are found as the materials for our rugs, curtains, coatings, wastepaper baskets, water pipes, window glass, ice cube trays, and pillows. In transportation, they are present in ever-increasing amounts in our aircraft, automobiles, ships, and trucks. In communication, they form critical components in our telephones, TVs, computers, CDs, newspaper, optical fibers, and cell phones. Plastics act as favorite materials for our toys such as toy soldiers, plastic models, toy cars, dolls, skip ropes, hula hoops, and corvettes. Our food is polymer intense as meats, vegetables, breads, and cookies. In history, polymers have been the vehicle for the Magna Carta, Torah, Bible, Koran, and our Declaration of Independence. Outside our homes, they are present in our flowers, trees, soil, spider webs, and beaches. In fact, it is improbable that a polymer is not involved in your present activity—reading a paper book, holding a plastic-intense writing device, sitting on a cloth-covered chair or bed, and if your eyes need corrective vision, glasses, and contact lenses of one variety or another.

Polymers gain their importance because of their size. Many polymers are made from inexpensive and readily available materials allowing vast quantities of products to be made for a high increase in value, but they are typically inexpensive compared to nonpolymer alternatives. They also often have desirable physical and chemical properties. Some polymers are stronger on a weight basis than steel. Most are resistant to rapid degradation and rusting. You will learn more about these essential materials for life and living in this text.

Polymers are often divided according to whether they can be melted and reshaped through application of heat and pressure. These materials are called “**thermoplastics**.” The second general classification belongs to compounds that decompose before they can be melted or reshaped. These polymers are called “**thermosets**.” While both thermoset and thermoplastic polymers can be recycled, because thermoplastics can be reshaped simply through application of heat and pressure, recycling of thermoplastics is easier and more widespread.

In general groups, synthetic polymers are often described by their “use” and “appearance” as fibers, elastomers, plastics, adhesives, and coatings. A common toothbrush illustrates the three major physical forms of synthetic polymers—the rubbery (elastomeric) grips, plastic shaft, and fibrous bristles. The rubbery grips have a relatively soft touch; the plastic shaft is somewhat flexible and hard; and the bristles are highly flexible. Another illustration of the breath of polymers about us is given in Table 1.4 where polymers are divided according to source.

To get an idea of the pervasiveness of polymers in our everyday life, we can look at containers. Most containers are polymeric—glass, paper, and synthetic polymer. It is relatively easy to identify each of these general categories. Even, within the synthetic polymer grouping, it has become relatively easy to identify the particular polymer used in some applications such as with disposable containers. Most of these synthetic polymers are identified by an “identification code” that is imprinted somewhere on the plastic container, generally on their bottom. The numbers and letters are described in Figure 1.1. The recycling code was developed by the Society of Plastics Industry for use with containers. Today, the “chasing arrows” triangle is being used more widely for recycling by the public. A colorless somewhat hazy water container has a “2” within the “chasing” arrows and underneath it “HDPE” both indicating the bottle is made of high-density polyethylene. The clear, less flexible soda bottle has a “1” and “PETE” both signifying that the container is made out of poly(ethylene terephthalate), a polyester. A brownish clear medicine or DVD container has a “5” and the letters “PP” on its bottom conveying the information that the bottle is made of polypropylene (Picture 1.3). Thus, ready identification of some common items is easy.

But because of the use of many more complex combinations of polymers for many other items, such identification and identification schemes are not as straightforward. For some items, such as clothing and rugs, labels are present that tell us the major materials in the product. Thus, a T-shirt might have “cotton” on its label signifying that the T-shirt is largely made of cotton. A dress shirt’s label may say 55% cotton and 45% polyester meaning it is made from two polymers. Some items are identified by trade names. Thus, a dress advertised as being made from Fortrel (where “Fortrel” is a trade name) means it is made largely of a polyester material, probably the same










**TABLE 1.4 Common Polymers**

Material/Name	Typical Polymer	Chapters
Styrofoam	Polystyrene	7
PVC pipe	Poly(vinyl chloride)	7
Nylon stockings	Polyamide, Nylon 66	5
Concrete	Cement	10
Meat	Protein	4
Plexiglass	Poly(methyl methacrylate)	7
Automotive bumpers/side panels	Polyethylene and polyethylene/polypropylene blends	6 and 8
Potatoes	Starch	4
Compact discs (case)	Polycarbonate (polystyrene)	5
Hula Hoop	Polypropylene, polyethylene	6
Diamond	Carbon	10
Silicon sealants	Polydimethylsiloxane	9
Bakelite	Phenol-formaldehyde cross-linked	5
Super glue	Poly(ethyl cyanoacrylate)	16
Cotton T-shirt	Cellulose	4
Fiberglass	Composite	14
Saran wrap	PVC copolymer	8
Velcro	Polyamide	5
Rubber band	Natural rubber	4
Soda bottle	Poly(ethylene terephthalate), PET	5
Teflon	Polytetrafluoroethylene	7
Orlon sweater	Polyacrylonitrile	7
Sand	Silicon dioxide	10
Pillow stuffing	Polyurethane	5
Wood, paper	Cellulose	4
Human genome	Nucleic acids	4

polyester (PET or PETE) that our soda bottle is made from. Some everyday items are a complex of many materials only some or none noted. This is true for many running shoes and tires. Tires will often be described as being polyester (again, probably the same PETE) or nylon (or aramid). This describes only the composition of the tire cord but does not tell us what other materials are included in the tire's composition. Yet those that deal with tires generally know what materials are used in the manufacture of the tire in addition to the "stated ingredients." You will be introduced, gently, to the identification of the main polymers that are present in many everyday items, either through looking at labels, researching on the web, simply knowing what certain items are generally composed of, through the feel and gross physical properties (such as flexibility and stiffness) of the material, etc.

Further, the properties of essentially the same polymer can be varied through small structural changes giving materials with different properties and uses. There is a match between desired properties and the particular material used. For instance, for plastic bags, strength and flexibility are needed. The bag material should be somewhat strong, inexpensive (since many bags are "throwaway" items), and readily available in large quantities. Increased strength is easily gained from increasing thickness. But with increased thickness comes decreased flexibility, increased cost since more material is needed to make the thicker bags, and increased transportation (because of the additional weight) and storage costs. Thus, there is a balance between many competing factors. Plastic bags are typically made from three polymers, high-density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE) (actually a copolymer with largely ethylene units). These different polyethylene polymers are similar differing only in the amount of branching that results in differing tendencies to form ordered (crystalline) and less ordered (amorphous) chain arrangements. You will learn more about them in Chapter 6. Grocery bags are generally made from HDPE, which is largely a linear polymer that

	<b>Poly(ethylene terephthalate)—PET or PETE</b> PET is the plastic used to package the majority of soft drinks. It is also used for some liquor bottles, peanut butter jars, and edible-oil bottles. About one-quarter of plastic bottles are PET. PET bottles can be clear; they are tough and hold carbon dioxide well.
	<b>High-density polyethylene—HDPE</b> HDPE is a largely linear form of polyethylene. It accounts for over 50% of the plastic bottle market and is used to contain milk, juices, margarine, and some grocery snacks. It is easily formed through application of heat and pressure and is relatively rigid and low cost.
	<b>Poly(vinyl chloride)—PVC or V</b> PVC is used “pure” or as a blend to make a wide variety of products including PVC pipes, food packaging film, and containers for window cleaners, edible oils, and solid detergents. It accounts for only 5% of the container market.
	<b>Low-density polyethylene—LDPE</b> LDPE has branching and is less crystalline, more flexible, and not as strong as HDPE. The greater amount of amorphous character makes it more porous than HDPE, but it offers a good inert barrier to moisture. It is a major material for films from which trash bags and bread bags are made.
	<b>Polypropylene—PP</b> PP has good chemical and fatigue resistance. Films and fibers are made from it. Few containers are made of PP. It is used to make some screw-on caps, lids, yogurt tubs, margarine cups, straws, and syrup bottles.
	<b>Polystyrene—PS</b> PS is used to make a wide variety of containers, including those known as “Styrofoam” plates, dishes, cups, etc. Cups, yogurt containers, egg cartons, meat trays, and plates are made from PS.
	<b>Other plastics</b> A wide variety of other plastics are coming to the marketplace including copolymers, blends, and multilayered combinations.

**FIGURE 1.1** The Society of Plastics Industry recycling codes utilizing the numbers 1–7 and bold, capital letters to designate the material utilized to construct the container.



**PICTURE 1.3** Chasing arrows and number for the top of a DVD container made from polypropylene.

has a high degree of crystallinity. Here, in comparison to LDPE film with the same strength, the bags are thinner allowing a decrease in cost of materials, transportation cost, and storage space. The thinness allows good flexibility. LDPE is used for dry cleaning garment bags where simply covering the garments is the main objective rather than strength. The LDPE is less crystalline and weaker, but more flexible, because of the presence of more branching in comparison to HDPE. The thicker glossy shopping bags from malls are often LLDPE, which, like HDPE, is largely linear. This increased thickness results in the bags being less flexible. These bags can be used many times.

Thus, most of the common items about us are polymeric. Table 1.4 gives a brief listing of some of these materials along with the locations where they will be dealt with in the book.

With the electronic age we can access the web to gather lots of general information about most of the topics including polymers. This book allows you to have a greater appreciation and understanding of such information and the products about us, including our own bodies.

### 1.3 TODAY'S MARKETPLACE

As noted earlier, polymers are all around us. Over 100 billion pounds (50 million tons) of synthetic polymers is produced annually in the United States (Tables 1.5 through 1.9), and the growth of the industry is continuing at a fast rate. There is every reason to believe that this polymer age will continue as long as petroleum and other feedstocks are available and as long as consumers continue to enjoy the comfort, protection, and health benefits provided by elastomers, fibers, plastics, adhesives, and coatings. The 100 billion pounds of synthetic polymers consumed each year in the United States translates to over 300 pounds for every man, woman, and child in the United States. This does not include paper and wood-related products (Table 1.10; over 500 pounds/person/year), natural polymers such as cotton and wool, or inorganic polymers (Table 1.11).

Polymers are all about us. The soils we grow our foods from are largely polymeric as are the foods we eat. The plants about us are largely polymeric. We are walking exhibitionist as to the widespread nature of polymers—from our hair and finger nails, our skin, bones, tendons, and muscles; our clothing like socks, shoes, glasses, undergarments; the morning newspaper; major amounts of our automobiles, airplanes, trucks, boats, and spacecraft; our chairs, wastepaper baskets, pencils,

**TABLE 1.5 U.S. Production of Plastics (Millions of Pounds; 2013)**

<i>Thermosetting resins</i>	
Epoxies	500
Ureas, melamines, and phenolics; Misc.	14,500
Total	15,000
<i>Thermoplastics</i>	
Polyethylenes	
Low density	7,000
High density	17,900
Linear low density	13,900
Polypropylene	16,400
Polystyrene	
Polystyrene	4,500
Acrylonitrile-butadiene-styrene and styrene-acrylonitrile	2,600
Polyamides, nylons	1,200
Poly(vinyl chloride) and copolymers	15,400
Other thermoplastics	15,400
Total thermoplastics	93,000
<i>Grand total</i>	108,000

Source: American Chemistry Council, Washington, DC.

**TABLE 1.6 Thermoplastic Sales by Major Market (Millions of Pounds; 2013)**

Transportation	2,800
Building and construction	12,200
Furniture and furnishings	1,500
Electrical and electronic	1,700
Packaging	25,700
Industrial and machinery	850
Adhesives, inks, and coatings	350
Consumer and institutional	15,000
Other	1,300
Exports	14,200
Total	75,700

Source: American Chemistry Council, Washington, DC.

**TABLE 1.7 U.S. Production of Man-Made Fibers (Millions of Pounds; 2014)**

<i>Noncellulosic</i>	
Nylons	1300
Olefins	2200
Polyesters	2900
<i>Cellulosic</i>	
Acetate	55
Lyocell (rayon)	120

Source: Fiber Economics Bureau, Arlington, VA.

**TABLE 1.8 U.S. Coatings Consumption (Billion Dry Pounds; 2015; Estimated)**

<b>Year</b>	<b>1996</b>	<b>2001</b>	<b>2006</b>	<b>2011</b>	<b>2015</b>
<i>Consumption by segment</i>					
Architectural	3.6	3.9	4.9	3.9	4.5
Original equipment manufacturers	2.1	2.3	2.4	1.0	2.2
Special purpose	1.8	2.0	2.2	2.0	2.1
<i>Total</i>	7.5	8.2	9.5	7.8	8.8
<i>Consumption by technology</i>					
Water-based					
Architectural	2.8	3.0	3.8	3.1	3.7
Industrial	0.9	1.1	1.4	1.3	1.4
Solvent-based					
Architectural	0.9	0.9	1.2	0.8	0.8
Industrial	2.3	2.2	2.1	1.8	1.9
Powder	0.3	0.4	0.5	0.4	0.5
Other solids	0.4	0.4	0.4	0.3	0.4
Radiation cured	0.05	0.09	0.1	0.09	1.3
<i>Total</i>	7.5	8.2	9.5	7.8	8.8

Source: Kusumgar, Nerfi, and Growney 2015, U.S. Paint & Coatings Industry, Elmwood Park, NJ.

**TABLE 1.9 U.S. Production of Synthetic Rubber  
(Millions of Pounds)**

	2008	2014
Styrene-butadiene	1750	1400
Polybutadiene	1210	900
Nitrile	180	51
Ethylene-propylene	540	960
Other	1100	1700

Source: International Institute of Synthetic Rubber Producers, Houston, TX.

**TABLE 1.10 U.S. Production of Paper and Paperboard  
(Million Metric Tons; 2012)**

Type	Amount
Total pulp/paper/paperboard	75.5
Corrugated/packaging	45.9
Newsprint	2.9
Writing/printing	16.1
Others	10.6
Recovered paper	46.4

Source: Paper and Paperboard Recovery, Institute of Scrap Recycling Industries, Washington, DC. June 6, 2013. <http://www.paperonweb.com/USA.htm>.

**TABLE 1.11 Polymer Classes: Natural and Synthetic**

Polymeric Materials				
Inorganic			Organic	
Natural	Synthetic	Organic/Inorganic	Natural	Synthetic
Clays	Fibrous glass	Siloxanes	Proteins	Polyethylene
Cement	Poly(sulfur nitride)	Polyphosphazenes	Nucleic acids	Polystyrene
Pottery	Poly(boron nitride)	Polyphosphate esters	Lignins	Nylons
Bricks	Silicon carbide	Polysilanes	Polysaccharides	Polyesters
Sands		Sol-gel networks	Melanins	Polyurethanes
Glasses			Polyisoprenes	Poly(methyl methacrylate)
Rocklike				Polytetrafluoroethylene
Agate				Polyurethane
Talc				Poly(vinyl chloride)
Zirconia				Polycarbonate
Mica				Polypropylene
Asbestos				Poly(vinyl alcohol)
Quartz				
Ceramics				
Graphite/diamond				
Silicas				

**TABLE 1.12 U.S. Chemical Trade: Imports and Exports (Millions of Dollars)**

Business Sector	2004 Exports	2004 Import	2014 Export	2014 Import	2014 Trade Balance
Total chemistry business	105,000	109,000	191,000	197,000	−5,200
Pharmaceuticals	27,000	53,000	52,000	93,000	−42,000
Chemicals excluding pharmaceuticals	78,000	72,000	140,000	103,000	37,000
Agricultural chemicals	4,400	6,300	8,300	12,000	−3,700
Consumer products	5,400	4,600	12,000	9,700	1,900
Basic chemicals	52,000	34,000	92,000	61,000	31,000
Inorganics	6,700	6,300	13,000	9,800	3,100
Bulk petrochemicals and intermediates	24,000	17,000	41,000	32,000	8,500
Plastic resins	16,000	7,700	32,000	14,000	17,000
Synthetic rubber	2,500	1,300	4,400	2,600	1,800
Synthetic fibers	1,900	1,800	2,700	2,500	200
Specialties	17,000	12,000	28,000	20,000	7,400
Coatings	1,600	700	2,900	1,100	1,700
Other specialties	15,000	12,000	25,000	18,000	5,700

Source: Department of Commerce and American Chemistry Council, Washington, DC.

tables, pictures, coaches, curtains, and glass windows; the roads we drive on, the houses we live in, and the buildings we work in; the tapes and CDs we listen to music on; and packaging—all are either totally polymeric or contain a large amount of polymeric materials. Table 1.10 lists some general groupings of important polymers. Welcome to the wonderful world of polymer science.

The number of professional chemists directly employed with polymers as part of their interest and assignment is estimated to be 40%–60% of all the chemists. As the diversity of chemistry increases, the dispersion of those dealing with polymers increases. Polymer chemistry is a major tool applied in biomedical research, synthesis, manufacturing, chemical engineering, pharmaceutical efforts, the environment, communications, etc. “As it was in the beginning,” polymers continue to draw strength from those with diverse training allowing polymers to directly contribute to solutions for most of our technological problems including fuel and transportation, building and construction, communication, and medicine and dentistry. Analytical chemistry is applied to the analysis of materials; inorganic to the catalysts employed in the synthesis of natural and synthetic polymers; organic to the synthesis of diverse materials; physical to describe the kinetics, thermodynamics, and properties of macromolecules; and biological chemistry that deals intently with biopolymers.

Polymeric materials, along with most other chemical industrial products, contribute positively to the balance of trade (Table 1.12). Thus, polymers play a positive role in our balance of trade.

Essentially, all of the industrially advanced countries of the world have major chemical producers. These producers are involved directly and/or indirectly with some form of synthetic polymers. Table 1.13 contains a partial listing of these companies. Chemistry and polymer chemistry are represented in many other applied chemistry areas including pharmaceuticals and biopharmaceuticals. Table 1.14 contains the top 25 pharmaceutical companies according to global sales.

Thus, polymers play a critical role in our everyday lives, actually forming the basis for both plant and animal life, and represent an area where chemists and other scientists and engineers continue to make important contributions.

## 1.4 ENVIRONMENTAL ASSESSMENT

Daily, we are becoming more aware of the importance of environmental planning and good environmental actions (practices) and their effect on us. This emphasis is being driven by a number of pressures including federal and state laws and initiatives, industrial consciousness, reality,

**TABLE 1.13 Top 50 Global Major Chemical Producers  
Based on (Net) Sales (in Millions of  
U.S. Dollars; 2014)**

<i>Africa</i>	
South Africa	
Sasol	10,000
<i>Asia</i>	
China	
Sinope	43,000
India	
Reliance Inds.	16,000
Japan	
Mitsubishi Chem	26,000
Sumitomo Chem	18,000
Mitsui Chem	17,000
Toray Inds.	17,000
Shin-Etsu Chem	12,000
Asahi Kasei	11,000
DIC	8,200
Tosoh	7,700
South Korea	
LG Chem	21,000
Lotte Chem	14,000
SK Innovation	12,000
Hanwha Chem	7,700
Thailand	
Siam Cement	7,600
Indorama	7,500
Twain	
Formosa plastics	37,000
PTT Global Chem	10,000
<i>Europe</i>	
Austria	
Borealis	11,000
Belgium	
Solvay	14,000
France	
Air Liquide	19,000
Arkema	7,900
Germany	
BASF	79,000
Bayer	28,000
Linde	19,000
Evonik Inds.	17,000
Lanxess	11,000
The Netherlands	
LyondellBasell Inds.	35,000
Shell	25,000
AkzoNobel	19,000
DSM	12,000
Norway	
Yara	15,000

(Continued)

**TABLE 1.13 (Continued) Top 50 Global Major Chemical Producers Based on (Net) Sales (in Millions of U.S. Dollars; 2014)**

Switzerland	
Ineos	30,000
Syngenta	11,000
UK	
BP	7,300
Johnson Matthey	7,200
<i>Middle East</i>	
Saudi Arabia	
SABIC	43,000
<i>South America</i>	
Brazil	
Braskem	20,000
<i>United States</i>	
DOW Chemical	58,000
ExxonMobil	38,000
DuPont	30,000
PPG Inds.	14,000
Chevron Phillips Chem	13,000
Praxair	12,000
Huntsman	12,000
Air Products and Chem	10,000
Eastman Chem	10,000
Mosaic	9,100
Ecolab	7,200

Source: C & EN, 92 (30), July 28, 2014.

international efforts, and individual actions. Chemistry, chemists, and the chemical industry have been directing much effort in this direction for over several decades with this effort magnified over the past several years. This textbook highlights some of these efforts in polymers. Here a number of terms will be introduced related to these efforts. While these terms are described individually, the environmental activity is a matrix of actions and activities each one dependent on others to be successful. Many of these studies and assessments are governed somewhat by procedures described by the International Organization for Standardization (ISO). (More about ISO can be found on the web and in Appendix D.)

#### 1.4.1 ENVIRONMENTAL IMPACT ASSESSMENT

An environmental impact assessment (EIA) is simply an assessment of the possible impact that a project or material may have on the natural environment. This possible impact may be positive or negative and often is a combination of positive and negative impacts. The intension of such EIAs is to identify where changes can and should be made and to make us aware of these instances. The International Association for Impact Assessment describes such impact assessments as a process for “identifying, predicting, evaluating, and mitigating the biophysical, social, and other relevant effects of development proposals prior to major decisions being taken and commitments made” (Petts, 1999). The need and specifications for EIAs depend on the particular country. For the United States, it originated as part of the National Environmental Policy Act of 1970. States may also have other requirements.



**TABLE 1.14 Top 25 Pharmaceutical Companies Based on Global Sales (in Millions of U.S. Dollars; 2014)**

<b>Company</b>	<b>Sales (Millions US\$)</b>
Novartis	47,000
Pfizer	46,000
Roche	39,000
Sanofi	36,000
Merck & Co.	36,000
Johnson & Johnson	32,000
GlaxoSmithKline	30,000
Astra Zeneca	26,000
Gilead Sciences	24,000
Takeda	20,000
AbbVie	20,000
Amgen	19,000
Teva	18,000
Lilly	17,000
Bristol-Myers Squibb	16,000
Bayer	15,000
Novo Nordisk	15,000
Astellas	14,000
Boehringer Ingelheim	14,000
Actavis	13,000
Otsuka	11,000
Daiichi Sankyo	10,000
Biogen Idec	9,400
Baxter	8,800
Merck KGaA	7,700

Source: Global Data in Chemical and Engineering News, Washington, DC.

### 1.4.2 ECOLOGICAL FOOTPRINT

The ecological footprint is a measure of our demand on the Earth's ecosystems. It includes our demand on both natural resources and on the ability for these resources to be regenerated. In the past, the methods and items to be measured varied widely, often based on factors suiting the particular sector making the footprint assessment. Today, more homogeneous standards are emerging. It is intended to reflect a measure of the land, freshwater, and ocean area required to produce, for instance, a product. Such footprints are often calculated to reflect other average measures. One such measure is a per capita ecological footprint that compares consumption and lifestyles with the natural ability to provide this consumption.

### 1.4.3 LIFE CYCLE ASSESSMENT

A life cycle assessment (LCA) investigates and evaluates the environmental impact of a product or service. It is also referred to as an ecobalance analysis, cradle-to-grave analysis, and life cycle analysis. Such assessments are intended to measure the effects of the cascade of technologies related to products and services. Here we will restrict our comments to products. "Life cycle" can refer to a holistic assessment of raw material used in the production of a product including energy consumption for procurement and transport of the material, manufacture, distribution, use, and finally disposal (including recycling if possible) environmental costs. Often, guesses and averages are included in these studies. Thus, the cost of transportation

could include some proportion of the truck or train construction, road or rail construction, and the deterioration and repair of same.

According to ISO 14040 and 14044 standards, an LCA contains four distinct phases. These phases are goal and scope, inventory analysis, impact assessment, and interpretation of the first three phases. In the “goal and scope” phase, the functional unit is described with effort focused on defining the boundaries of the system or product to be studied. It includes describing the methods used for assessing possible environmental impacts and which impact categories are to be included in the study. In the “inventory” phase, data are collected including the description and verification of the data along with various modeling programs to be used. Generally, items considered include inputs such as quantities of materials, land usage, and energy and outputs such as air emission, solid waste, and water emissions. Software packages have been developed, and are being developed, to assist in such evaluations. The “impact” phase is intended to describe contributions to more global situations such as global warming and acidification. The final phase, “interpretation,” brings together the other three phases and conclusions are made.

There are varying types of LCA studies that act to limit or define the type of LCA study being made. The *cradle-to-grave* assessment is a full LCA study from manufacture (cradle) to the disposal (grave) of a product. A *cradle-to-gate* study looks at the life cycle from manufacture (cradle) to factory gate (before it is sent to the consumer). These assessments are often used as a basis for environmental product declarations. A *cradle-to-cradle* assessment involves products where the product is recycled so the study terminates when a new product is made from the recycled original product. A *life cycle energy analysis* looks at all energy inputs to a product and not solely direct energy inputs during manufacture including energy necessary to produce components and materials needed for the manufacturing process.

## 1.5 MANAGING SUSTAINABILITY

Earth, air, fire, and water, not the music group but rather the Greek classical elements, representing the critical elements of global sustainability. Our ability to manage these elements will determine the sustainability of human life as we know it. The need for sustainability is not a recent phenomenon but one on the “front burner.” The most cited definition of sustainability is from the UN World Commission on Environment and Development (Brundtland Commission) that says “Sustainable development is development that meets the needs of the present without compromising the ability of future generations to meet their own needs.”

*Earth* represents food, EPA sites, etc.; *air*, our atmosphere and need for breathable air; *water*, the necessity for safe drinking water; and *fire*, our energy. Currently, we are sinking further toward and past the “tipping point” for each of these. A tipping point is generally defined as when some feature reaches a point where various “feedback” loops are not able to compensate for unwanted movement toward (here unwanted) consequences and the movement toward these unwanted consequences becomes more rapid and/or permanent.

The magnitude of the problem or opportunity is great. More than 80 countries and 1 billion people do not have a good source of safe water. About 87 million barrels of nonrenewable crude oil are pumped daily resulting in over 3.5 billion gallons each day with most of this employed as fuel with the remaining used for the production of plastics, drugs, rubbers, paints, fibers, etc.

The polymer industry is part of this challenge and polymers play an essential role in solutions as the materials that allow us to perform the needed tasks to allow us to have safe water and air, efficient use of fuel and an earth that allows us to thrive. Polymers are integral parts of filtering systems for water and air; lighter components for transportation systems and serve as the basis for more fuel efficient engines; polymeric growth hormones and gene engineered seeds can help feed us.

Our reply to issues of sustainability is critical and involves many stakeholders. Managing this reply is critical. The following illustrates some of the inner-relationships and complexity related to the “elements” and their management.

The Florida peninsula receives unwanted mercury from three major sources. The three sources are natural, past agricultural practices, and atmospheric. The atmospheric mercury comes from two main sources. The first is the result of gold retrieval when gold ore is heated with mercury

in open containers in South America allowing mercury to escape into air. The second source is Europe and is connected to ore production and coal burning. The atmospheric mercury finds its way over Florida and is deposited from the sky during violent summer storms. This example illustrates several key factors in addressing sustainability. First, the sources are identified through research highlighting the need for science to contribute to sustainability solutions. Second, there are no governing and enforcement agencies that successfully control such emissions. Third, globalization is a feature since the mercury is moved from country and continent to country and continent. Fourth, the problem is complex and not easily solved. Fifth, environmental problems are often comprised of past and present practices.

Another feature that should be recognized is unintended consequences. One of the initial efforts at producing genetically engineered corn was dropped because the genetically engineered plant killed butterflies that were a chief means of pollinating the corn. For several decades, no new petroleum refining plants have been constructed mainly because of the seemingly excessive cost associated with meeting the “new” environmental regulations.

We will take a moment to describe the situation with respect to biofuels. While ethanol production helps decrease our dependence on “foreign” oil, it is not our answer to energy independence. Ethanol can be made from corn, but this approach suffers from several problems. While corn is a renewable source of ethanol fuel, it is also a source of food; so as corn production for food is diverted to fuel production, the price of corn products increases. Only about a net 20% energy is realized from the production of ethanol from corn when including the energy needed for its production. The production of ethanol is water intensive. Further, calculations show ethanol production from corn is acre limited with only a reasonable 10% of our overall fuel consumption possible through this venue. The problem of supplying ethanol as a fuel is partially solved with the blending of ethanol with regular petroleum-based fuels. The long-range fuel reduction and automotive performance and care have not yet been established.

Research shows some alternatives to the present ethanol production from corn. One alternative is the production of plants that give greater fuel production for acre. Another alternative, and one where the energy tab is low, employs especially designed microbes, mainly bacteria, which convert carbohydrate biomasses into alcohols, mainly ethanol and methanol. These alternatives illustrate other possible solutions. “Total” solutions are often complex with multiple “solutions” needed. Energy solutions must depend on many sources including coal, biofuels, nuclear, direct solar, hydrogeological, and biosolar.

Global warming illustrates the political nature of most sustainability issues. While the press is fully convinced that global warming is a fact and that we are responsible, many scientists are not totally on board with this conclusion. There are abundant scientific studies to support both sides. Even so, with a sustainability issue that can have such dramatic consequence affecting all of humanity, it is better to treat it as real until it is overwhelmingly shown to be false. Thus, there is sufficient scientific information that supports global warming, whether it is a majority or not, as a fact it must be dealt with in a reasonable manner. Note the “reasonable” clause. Today, there are emerging countries, as well as first-world nations, which must act as responsible citizens of earth, but this means that the emerging countries be allowed to “emerge” and the current first-world countries be allowed to exist without great damage to them. This is a balancing act and points out another factor that is important as we address global issues. This factor is to allow some independence of nations while recognizing their interdependence.

All of the major sustainability issues influence our personal health and our business and industrial economies.

We now move toward managing sustainability. The stakeholders are many. Here we will assume the most important stakeholders are you and me. We contribute by influencing legislation, voting, membership in groups, etc. We also contribute through recycling, use of reduced energy consuming transportation, lights, appliances, etc. Sociological and psychological components are also important.

The important stakeholders include

1. Research
2. Business and industry

3. Governmental and legislative including enforcement
4. Environmental and related groups
5. Us

Thus far, all of these stakeholders have shown an inability to effect needed positive change on a global basis. On the research side, while lots of research is being done, it is not globally focused and it has not been shown to appropriately interact with some of the other major stakeholders. Most scientific (including engineering) organizations are small, national, and poorly funded. The largest single discipline organization is the American Chemical Society with 160,000 members, mostly in the United States. It is mainly funded by membership dues and information-related activities. While it attempts to highlight sustainability issues and has a governmental action arm, it lacks sufficient funding and legislative connections. Multidiscipline organizations such as Sigma Xi also suffer from inadequate funding, industrial and business, and legislative governmental connections.

Business and industry is already global and must play a critical role in managing sustainability. They have the multinational ability to influence change on a global way. They lack the primary focus, legislative, and enforcement power as well as “free” funds to assist in the research necessary to understand and influence sustainability.

Governmental and legislative stakeholders have shown an inability to manage sustainability. While some good has come from such entities as the UN and World Bank, they lack the power and funds to adequately manage sustainability. Environmental and related groups are without sufficient funds and research capability. Even so, they are a critical stakeholder often influencing needed legislation that in turn acts as an incentive to obey directives.

Thus, each stakeholder is important and currently all lack some crucial aspect to lead in the management of sustainability.

There is a related question. Are we willing to pay for sustainability and “green” products? Many automobiles that are supposedly green, such as hybrid models, often cost 10%–20% higher than a similar model that burns regular petrol-based fuel. Based on savings on fuel alone, it takes a few years to break even and by then the battery or other “green” energy-producing “motor” parts may need replacing. In studies with bioplastic containers, it appears that consumers are not willing to pay more for their food and drinks coming from biobased containers. In 2010, Stonyfield switched from polystyrene yogurt-derived containers opting to go with “green” poly(lactic acid)-derived yogurt containers that offer a 48% global warming potential savings compared with petrol-based packaging. It was found that consumers, that is, us, were unwilling to pay extra for the container. In 2011, Stonyfield switched from petrobased polyethylene to biobased polyethylene for their smoothie bottles. This switch offered a 65% reduction in warming potential but consumers were not willing to pay extra for the green poly(lactic acid) material. A similar result was observed by Coca-Cola with their bottled water derived from biobased produced ethylene glycol. In order to compete, the price of the biobased polymer was reduced allowing the container price to remain the same. As the cost of biobased materials decreases, this should become less of a problem, but it does raise a question: how much are we willing to pay to be “green?”

Hopefully, this text will allow you both to see where polymers are part of the solution to sustainability and to allow you to become informed in one of the most scientifically important disciplines, polymer science, which will supply many of the materials and knowledge needed to allow a sustainable world.

## SUMMARY

After reading this chapter, you should understand the following concepts:

1. Polymers or macromolecules are giant molecules with large structures and high molecular weights. In spite of their varieties, they are governed by the same laws that apply to small molecules.
2. If we disregard metals and some inorganic compounds, practically everything else in this world is polymeric. Polymers form the basis for life itself and for our communications,

transportation, buildings, food, etc. Polymers include protein and nucleic acids in our bodies, the fibers (natural and synthetic) we use for clothing, the protein and starch we eat, the elastomers in our automotive tires, the paint, plastic wall and floor coverings, foam insulation, dishes, furniture, and pipes.

3. There are some systems in place that allow us to readily identify the nature of many polymeric materials including clothing and containers.
4. Early developments in polymers were largely empirical because of a lack of knowledge of polymer science. Advancements in polymers were rapid in the 1930s and 1940s because of the theories developed by Staudinger, Carothers, Mark, and many other scientists.
5. This is truly the age of the macromolecule. Essentially, every important problem and advance includes polymers including synthetic (such as carbon nanotubes) and biological (such as the human genome and proteins). There are more chemists working with synthetic polymers than in all of the other areas of chemistry combined.
6. The so-called green chemistry is becoming increasingly important in today's chemical industry. The use of naturally derived monomers and polymers is increasing. We are part of the overall solution as informed citizens and scientists.

## GLOSSARY

**ABS:** A polymer produced by the copolymerization of acrylonitrile, butadiene, and styrene.

**Bakelite:** A polymer produced by the condensation of phenol and formaldehyde.

**Cellulose:** A naturally occurring carbohydrate polymer.

**Ecological footprint:** A measure of our demand on the Earth's ecosystems.

**Elastomer:** A rubber.

**Environmental impact assessment, EIA:** An assessment of the possible impact that a project or material may have on the natural environment.

**Filament:** The individual extrudate emerging from the holes in a spinneret; forms fibers.

**Functionality:** The number of reactive groups.

**Intermolecular forces:** Secondary forces between macromolecules.

**Intramolecular forces:** Secondary forces within the same macromolecular chain.

**Life cycle assessment, LCA:** Investigation and evaluation of the environmental impact of a product or service. It is also referred to as an ecobalance analysis, cradle-to-grave analysis, and life cycle analysis.

**Linear:** A continuous chain.

**Macromolecule:** A polymer. Large chained molecular structure.

**Natural rubber (NR):** Polyisoprene obtained from rubber plants. *Hevea brasiliensis*.

**Nylon 66:** A polyamide produced from the condensation of adipic acid and 1,6-hexanediamine. Nylon 66 is also given a number of other similar names such as nylon-6,6, nylon-66, and nylon 6,6.

**Oligomer:** Low-molecular-weight polymer with generally 2–10 repeat units.

**Plasticizer:** An additive that reduces intermolecular forces in polymers making it more flexible.

**Polymer:** A giant molecule, macromolecule, made up of multiple repeating units where the backbone is connected by covalent bonds.

**Protein:** A natural polyamide composed of many amino acid-derived repeat units.

**Rayon:** Regenerated cellulose in the form of filaments.

**Sustainability:** Development that meets the needs of the present without compromising the ability of future generations to meet their own needs.

**Thermoplastic:** A linear polymer that softens when heated.

**Thermoset:** A network polymer containing chemical cross-linking that does not soften when heated.

**Vital force concept:** A hypothesis that stated that organic compounds can be produced only by natural processes and not in the laboratory.

**Vulcanization:** Process where elastomers such as natural rubber are cross-linked by heating with sulfur.

## EXERCISES

1. Name six polymers that you encounter daily.
2. Why are there more chemists that work with polymers than with other areas?
3. Why are there so many outstanding polymer chemists alive today?
4. Which of the following are polymeric or contain polymers as major components?  
(a) Water, (b) Wood, (c) Meat, (d) Cotton, (e) Tires, and (f) Paint
5. Name three inorganic polymers.
6. Name three synthetic polymers.
7. Look at the bottom of several containers. Identify what the bottles are made of from the following recycling codes found on their bottoms: (a) 4 with the letters LDPE, (b) 6 with the letters PS, and (c) 5 and the letters PP.
8. Why is there a time delay between discovering a new polymer and commercializing it?
9. What are some advantages of polymers over metals?
10. It has been said that we are walking exhibitions of the importance of polymers. Explain.
11. Why are polymer-intensive industries often located in the same geographical area?
12. Why might simple identification codes such as those employed for containers fail for objects such as sneakers and tires?
13. How can we become more environmentally responsible?

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