

Organic Compounds

THE MAIN IDEA



Carbon can form a limitless number of chemical structures.

12.1 Hydrocarbons

12.2 Unsaturated Hydrocarbons

12.3 Functional Groups

12.4 Alcohols, Phenols, and Ethers

12.5 Amines and Alkaloids

12.6 Carbonyl Compounds

12.7 Organic Synthesis

12.8 Polymer Chemistry

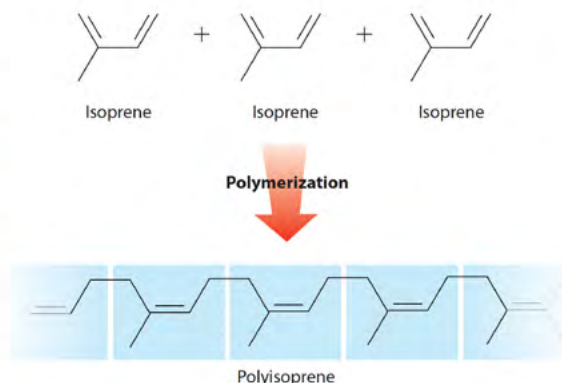
12.9 A Brief History of Plastics



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The search for a lightweight, non-breakable, moldable material began with the invention of vulcanized rubber. This material is derived from natural rubber, which is a semisolid, elastic, natural polymer. The fundamental chemical unit of natural rubber is polyisoprene, which plants produce from isoprene molecules, as shown in **Figure 12.43**. In the 1700s, natural rubber was noted for its ability to rub off pencil marks, which is the origin of the term *rubber*. Natural rubber has few other uses, however, because it turns gooey at warm temperatures and brittle at cold temperatures.

In 1839, an American inventor, Charles Goodyear, discovered *rubber vulcanization*, a process in which natural rubber and sulfur are heated together. The product, vulcanized rubber, is harder than natural rubber and retains its elastic properties over a wide range of temperatures. This is the result of *disulfide cross-linking* between polymer chains, as illustrated in **Figure 12.44**. To help quench our ever-growing thirst for vulcanized rubber, the polymer of rubber (polyisoprene) is now also produced from petroleum.



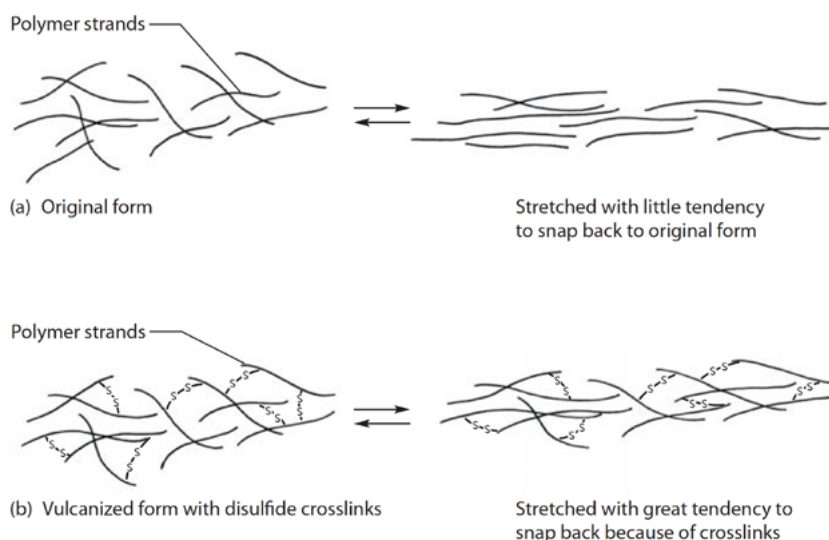
< **Figure 12.43**

Isoprene molecules react with one another to form polyisoprene. Isoprene is the fundamental chemical unit, or monomer, of natural rubber.

Figure 12.44 >

(a) When stretched, the individual polyisoprene strands in natural rubber slip past one another and the rubber stays stretched.

(b) When vulcanized rubber is stretched, the sulfur crosslinks hold the strands together, allowing the rubber to return to its original shape.



Charles Goodyear was the classic eccentric inventor. He lived most of his life in poverty, obsessed with transforming rubber into a useful material. Goodyear was a man of ill health who died in debt, yet he remained stubbornly optimistic. The present-day Goodyear Corporation was founded not by Goodyear, but by others who sought to pay tribute to his name 15 years after he died.

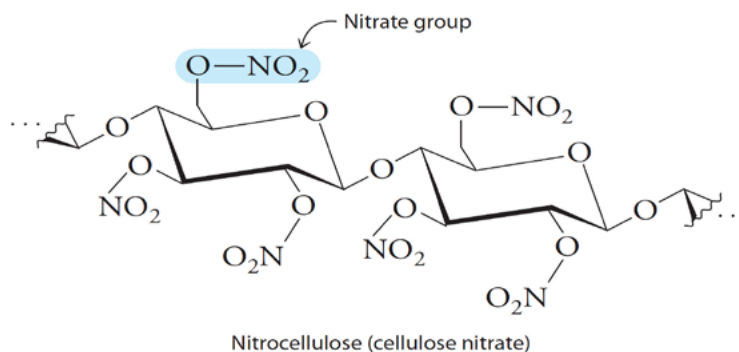
In 1845, as vulcanized rubber was becoming popular, the Swiss chemistry professor Christian Schönbein wiped up a spilled mixture of nitric and sulfuric acids with a cotton rag that he then hung up to dry. Within a few minutes, the rag burst into flames and then vanished, leaving only a tiny bit of ash. Schönbein had discovered nitrocellulose, in which most of the hydroxyl groups in cellulose are bonded to nitrate groups, as **Figure 12.45** illustrates. Schönbein's attempts to market nitrocellulose as a smokeless gunpowder (*guncotton*) were unsuccessful, mainly because of a number of lethal explosions at plants producing the material. Researchers in France discovered that solvents such as diethyl ether and alcohol transformed nitrocellulose to a gel that could be molded into various shapes. This workable nitrocellulose material was dubbed *collodion*, and its first application was as a medical dressing for cuts.

**CHEMICAL CONNECTIONS**

How is celluloid connected to the many exits now in movie theaters?

Figure 12.45 >

Nitrocellulose, also known as cellulose nitrate, is highly combustible because of its many nitrate groups, which facilitate oxidation.



In 1870, John Hyatt, a young inventor from Albany, New York, discovered that collodion's moldable properties were vastly improved by using camphor as a solvent. This camphor-based nitrocellulose material was named *celluloid*, and it became the plastic of choice for the manufacture of many household items, such as combs and hair fasteners. In addition, thin transparent films of celluloid made excellent supports for photosensitive compounds, a boon to the photography industry and a first step in the development of motion pictures.

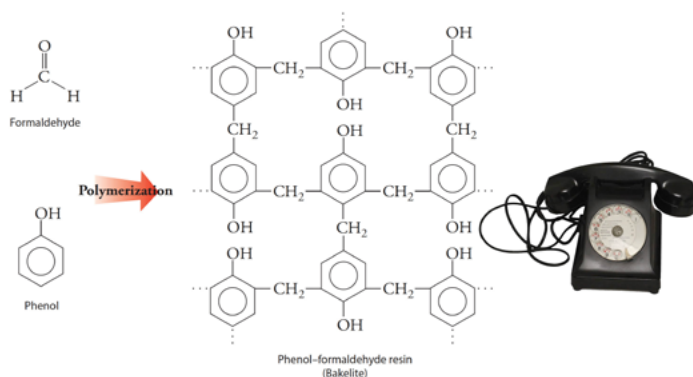
As wonderful as celluloid was, it still had the major drawback of being highly flammable. Today, one of the few commercially available products made of celluloid is Ping-Pong balls, shown in **Figure 12.46**.

Bakelite Was the First Widely Used Plastic

About 1899, Leo Baekeland, a chemist who had immigrated to the United States from Belgium, developed an emulsion for photographic paper that was exceptional in its sensitivity to light. He sold his invention to George Eastman, who had made a fortune selling celluloid-based photographic film along with his portable Kodak camera. Expecting no more than \$50,000 for his invention, Baekeland was shocked at Eastman's initial offer of \$750,000 (in today's dollars, that would be about \$25 million). Suddenly a very wealthy man, Baekeland was free to pursue his chemical interests.

Baekeland explored a tar-like solid once produced in the laboratories of Alfred von Baeyer, the German chemist who played a role in the development of aspirin. Whereas Baeyer had dismissed the solid as worthless, Baekeland saw it as a virtual gold mine. After several years, he produced a resin that, when poured into a mold and then heated under pressure, solidified into a transparent positive of the mold. Baekeland's resin was a mixture of formaldehyde and a phenol that polymerized into the complex network shown in **Figure 12.47**.

The solidified material, which he called *Bakelite*, was impervious to harsh acids or bases, wide temperature extremes, and just about any solvent. Bakelite quickly replaced celluloid as a molding medium, finding a wide variety of uses for several decades. It wasn't until the 1930s that alternative thermoset polymers began to challenge Bakelite's dominance in the evolving plastics industry.



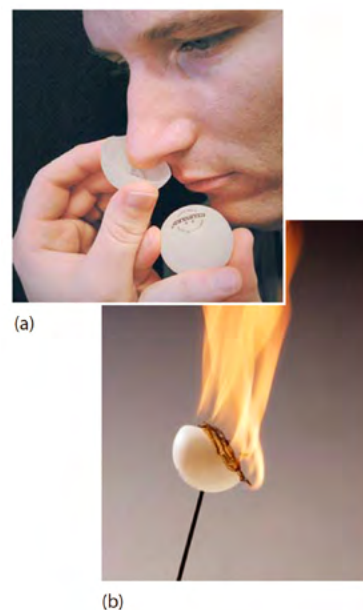
▲ Figure 12.47

The molecular network of Bakelite shown in two dimensions. (The actual structure projects in all three dimensions.) (b) The first handset telephones were made of Bakelite.



READING CHECK

What was a major drawback of celluloid?

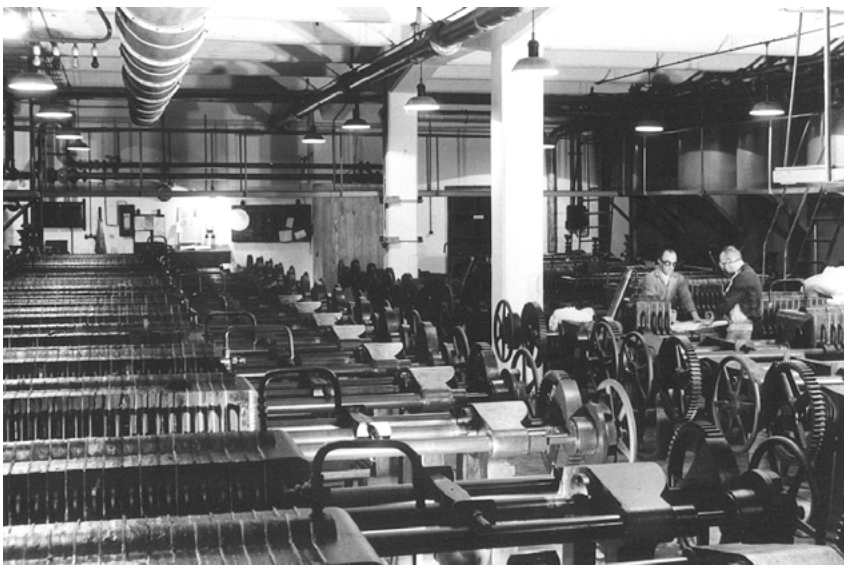


▲ Figure 12.46

(a) Smell a freshly cut Ping-Pong ball, and you will note the distinct odor of camphor, which is the same smell that arises from heat cream for sore muscles. This camphor comes from the celluloid from which the ball is made. (b) Ping-Pong balls burn rapidly because they are made of nitrocellulose.

Figure 12.48 >

Viscose is still used today in the manufacture of fibers used to make the synthetic fabric called rayon. The fibers are formed as viscose and extruded through holes in metal dies. Shown here is a viscose factory from the early 1900s.

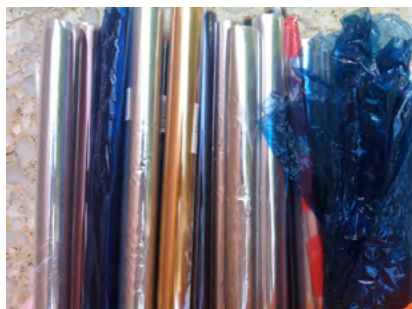


The First Plastic Wrap Was Cellophane

Cellophane had its beginnings in 1892, when Charles Cross and Edward Bevan of England found that treating cellulose with concentrated sodium hydroxide, NaOH, followed by carbon disulfide, CS₂, created a thick, syrupy yellow liquid they called *viscose*. Extruding the viscose into an acidic solution generated a tough cellulose filament that could be used to make a synthetic silky cloth today called *rayon* (Figure 12.48).

In 1904, Jacques Brandenberger, a Swiss textile chemist, observed restaurant workers discarding fine tablecloths that had only slight stains on them. Working with viscose at the time, he had the idea of extruding it not as a fiber, but as a thin, transparent sheet that might be adhered to tablecloths and provide an easy-to-clean surface. By 1913, Brandenberger had perfected the manufacture of a viscose-derived, thin, transparent sheet of cellulose, which he named *cellophane*.

Within several years, the Du Pont Corporation bought the rights to cellophane. Hermetically sealed by cellophane, a product could be kept free of dust and germs. And unlike paper or tin foil—the alternatives of the day—cellophane was transparent and thus allowed the consumer to view the packaged contents. With properties such as these, cellophane played a great role in the success of supermarkets, which first appeared in the 1930s. Perhaps cellophane's greatest appeal to the consumer, however, was its shine. As marketing people soon discovered, nearly any product—soaps, canned goods, and golf balls—would sell faster when wrapped in *cellophane* (Figure 12.49).

**^ Figure 12.49**

Colored cellophane samples. In the early 1900s, cellophane transformed the way foods and other items were marketed.

Polymers Win in World War II

In the 1930s, more than 90 percent of the natural rubber used in the United States came from Malaysia. In the days after Pearl Harbor was attacked in December 1941 and the United States entered World War II, however, Japan captured Malaysia. As a result, the United States—the land with plenty of everything, except rubber—faced its first natural resource crisis. The military implications were devastating because without rubber for tires, military airplanes and jeeps were useless. Petroleum-based synthetic rubber had been developed in 1930 by Du Pont chemist Wallace Carothers but was not widely used because it was much more expensive than natural rubber.

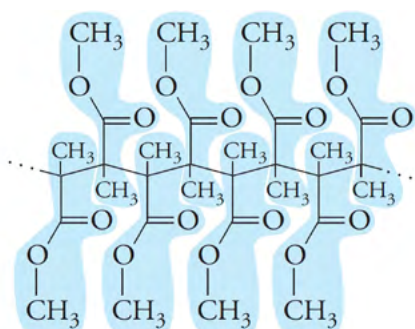
With Malaysian rubber impossible to get and a war on, however, cost was no longer an issue. Synthetic rubber factories were constructed across the nation, and within a few years, the annual production of synthetic rubber rose from 2000 tons to about 800,000 tons.

Also, in the 1930s, British scientists developed radar as a way to track thunderstorms. With war approaching, these scientists turned their attention to the idea that military planes could be equipped with radar. To make the radar equipment light enough to fly on an airplane, however, they needed the wires of the device coated with some sort of electrical insulator. Fortunately, the polymer polyethylene, recently developed in Britain, turned out to be an ideal electrical insulator. The radar-equipped planes were slow, but flying at night or in poor weather, they could detect, intercept, and destroy enemy aircraft.

Other polymers that had a significant impact on the outcome of World War II included Nylon[®], Plexiglas[®], PVC, Saran[™], and Teflon[®]. Nylon[®] was invented in 1937 and, as discussed in the previous section, found great use in the manufacture of ropes, parachutes, and clothing. Interestingly, tear-resistant Nylon[®] stockings, which had just been introduced, were extremely popular during the war and often used as a commodity for favors or to repay debts among soldiers. Plexiglas[®], shown in **Figure 12.50**, is a polymer known to chemists as poly(methyl methacrylate). This glass-like but moldable and lightweight material made excellent domes for the gunner's nests on fighter planes and bombers.

Polyvinyl chloride (PVC) had been developed by a number of chemical companies in the 1920s. The problem with this material, however, was that it lost resiliency when heated. In 1929, Waldo Semon, a chemist at BFGoodrich, found that PVC could be made into a workable material by the addition of a *plasticizer*. Semon got the idea of using plasticized PVC as a shower curtain when he observed his wife sewing together a shower curtain made of rubberized cotton. Other uses for PVC were slow to appear, however, and it wasn't until World War II that this material became recognized as an ideal waterproof material for tents and rain gear. After the war, PVC replaced Bakelite as the medium for making phonograph records.

Originally designed as a covering to protect theater seats from chewing gum, Saran[™] found great use in World War II as a protective wrapping for artillery equipment during sea voyages. (Before Saran[™], the standard operating procedure had been to disassemble and grease the artillery to avoid corrosion.) After the war, this polymer soon pushed cellophane aside



Poly(methyl methacrylate)



< **Figure 12.50**

The bulky side groups in poly(methyl methacrylate) prevent the polymer chains from aligning with one another. This makes it easy for light to pass through the material, which is tough, transparent, lightweight, and moldable, perfect for the creation of sneeze-guards that became popular during the Covid pandemic. (Plexiglas[®] is a registered trademark belonging to ATOFINA.)



▲ Figure 12.51

The now-familiar plastic food wrap carton with a cutting edge was introduced in 1953 by Dow Chemical for its Saran™ Wrap brand.

to become the most popular food wrap of all time (**Figure 12.51**). Because of environmental issues associated with Saran™, polyethylene now holds the title of most widely used food wrap.

In the late 1930s, the discoverers of Teflon® were impressed by the long list of things this new material would not do. It would not burn, and it would not completely melt. Instead, at 620°F it congealed into a gel that could be conveniently molded. It would not conduct electricity, and it was impervious to attack by mold or fungus. No solvent, acid, or base could dissolve or corrode it. And most remarkably, nothing would stick to it, not even chewing gum.

Because of all the things Teflon® would not do, DuPont was not quite sure what to do with it. Then in 1944, the company was approached by governmental researchers in desperate need of a highly inert material to line the valves and ducts of an apparatus being built to isolate uranium-235 in the manufacture of the first nuclear bomb. Thus, Teflon® found its first application, and one year later, World War II came to a close with the nuclear bombing of Japan.

Attitudes about Plastics Have Changed

With a record of wartime successes, plastics were readily embraced in the postwar years. In the 1950s, Dacron polyester was introduced as a substitute for wool. Also, the 1950s were the decade during which the entrepreneur Earl Tupper created a line of polyethylene food containers, known as Tupperware®. By the 1960s, a decade of environmental awakening, many people began to recognize the negative attributes of plastics. Being inexpensive, disposable, and non-biodegradable, plastic readily accumulated as litter and as landfill. With petroleum so readily available and inexpensive, however, and with a growing population of plastic-dependent baby boomers, little stood in the way of an ever-expanding array of plastic consumer products. By 1977, plastics surpassed steel as the number-one material produced in the United States. Environmental concerns also continued to grow, and in the 1980s, plastics recycling programs began to appear. Some 40 years later, however, still less than 10 percent of plastics are recycled. Our attitudes toward plastics have certainly changed over the years. One might argue from excitement to fear to boredom. Given the nature of plastics

CONCEPT CHECK

Name at least four polymers that had a significant impact on the effectiveness of Allied forces in World War II.

CHECK YOUR ANSWER Here are six: synthetic rubber, polyethylene, Nylon, Plexiglas, PVC, Saran, and Teflon.