Historical Background

Most topics are best introduced from a historical perspective. Although synthetic polymers and the plastics industry is a product of the 20th Century, the history of polymers goes back several centuries. This section presents some of the key materials and people involved in making the polymer industry into what it is known today.

2.1 From Natural to Synthetic Rubber

Natural polymeric materials such as rubber have been in use for several millennia. Natural rubber also known as caoutchouc or gummi elasticum has been used by South American Indians in the manufacture of waterproof containers, shoes, and torches (Fig. 2.1)[1]. When the natives made an incision in the bark of a tree it produced a white colored sap, composed of water and a monomer called isoprene (Fig. 2.2). As the sap dried in air, and in conjunction with the sun's ultraviolet rays, the isoprene polymerizes into long chains or polymers, called polyisoprene (Fig. 2.2). This process turns the liquid into a sticky bouncy mass. Sometimes the natives performed the drying process while dipping a clay container in and out of a bat of rubber tree sap. This way, the container was slowly coated with a layer of polyisoprene, and when the layer was thick enough the clay was broken and washed out. This first dip-coating process produced a light waterproof container to carry liquids. Similarly, the indians produced rubber boots, by dip-coating their feet. A container produced by this method is shown in Fig. 2.3[1].

From a native South American language caucho: cao (wood) and o-chu (tears). In French (caoutchouc) and German (Kautschuk) this word is still used to describe some elastomers.

From the Latin elastic gum.

While a polymer is made from many parts, a monomer is a single entity.
Figure 2.3 Container from the Amazon produced by an early dip-coating technique.

The first Spanish explorers of Haiti and Mexico reported that natives played games on clay courts with rubber balls [2]. Rubber trees were first mentioned in De Orbe Novo, originally published in Latin, by Pietro Martire d’Anghiera in 1516. The French explorer and mathematician Charles Maria de la Condamine, who was sent to Peru by the French Académie des Sciences, brought caoutchouc from South America to Europe in the 1740s. In his report [3] he mentions several rubber items made by native South Americans including a pistonless pump composed of a rubber pear with a hole in the bottom. He points out that the most remarkable property of natural rubber is its great elasticity. The first chemical investigations on gunmi elasticum were published by the Frenchman Macquer in 1761. However, it was not until the 20th Century that the molecular architecture of polymers was well understood. Soon after its introduction to Europe, various uses were found for natural rubber. Gossart manufactured the first polymer tubes in 1768 by wrapping rubber sheets around glass pipes. During the same time period small rubber blocks where introduced to erase lead pencil marks from paper. In fact, the word rubber originates from this specific application—rubbing.

These new materials slowly evolved from being just a novelty thanks to new applications and processing equipment. Although the screw press, which is the predecessor of today’s compression molding press, was patented in 1818 by McPherson Smith [4], the first documented polymer processing machinery dates back to 1820 when Thomas Hancock invented a rubber masticator. The primary use of this masticator, which consisted of a toothed rotor inside a toothed cylindrical cavity [5], was to reclaim rubber scraps which resulted from the manual manufacturing process of elastic straps. In 1833, the development of the vulcanization process by Charles Goodyear [6] greatly enhanced

4 Perhaps the first plastics recycling program.
5 From the Greek Vulcan, god of fire.
6 In 1832, F. Lüdersdorf in Germany had already discovered that when incorporating sulfur into rubber it loses its tackiness if heated.
the properties of natural rubber, and in 1836, Edwin M. Chaffee invented the
two roll steam-heated mill, the predecessor of the present day calender, for
mixing additives into rubber for the continuous manufacturing of rubber
coated textiles and leather. One of the first applications of vulcanized rubber
was a set of rubber tires for Queen Victoria’s carriage, but it took another 25
years for the veterinarian John Boyd Dunlop of Belfast, to develop the
pneumatic tire to make his son’s bicycle ride a little smoother.

As early as 1845, presses and dies were being used to mold buttons, jewelry,
dominoes, and other novelties out of shellac and gutta-percha. Gutta-percha or
gummi plasticum, a gum found in trees similar to rubber, became the first wire
insulation material and was used for ocean cable insulation for many years. A
patent for cable coating was filed in 1846 for trans-gutta-percha and cis-hevea
rubber and the first insulated wire was laid across the Hudson River for the
Morse Telegraph Company in 1849. Charles Goodyear’s brother, Nelson,
patented hard rubber, or ebonite, in 1851 for the manufacturing of dental
prostheses and combs. To allow the continuous coating of wires or textiles, the
ram-type extruder was invented by Henry Bewley and Richard Brooman in
1845. The first polymer processing screw extruder, the most influential element
in polymer processing, was patented by an Englishman named Mathew Gray in
1879 for the purpose of wire coating. Figure 2.4 [7] presents Mathew Gray’s
extruder as illustrated in his patent.

The demand for rubber grew rapidly in a world that was becoming more
industrialized. In the late part of the 19th and early 20th Centuries, most of the
world’s rubber came from the Amazon region of South America. This not only
led to a dependency of the industrialized nations on a few local families and
corporations in a relatively unstable part of the world, but also to horrible
human rights abuses against the natives of the Amazon region by those entities
that controlled the rubber cartel. To free themselves from the Latin-American
rubber cartels, the British had planted rubber trees in Maylasia and other South
East Asian colonies using seeds that had been smuggled out of South America
by the 1920’s. In Germany, to overcome its dependency on rubber from other
countries, other countries’ colonies, the German Kaiser, Wilhelm II,
promised a 25,000 Reichsmark prize to anyone that would invent a synthetic
replacement for natural rubber. By 1909, the German chemist Fritz Hoffmann,
who was working at Bayer in Leverkusen had developed the first synthetic
polyisoprene. The Kaiser’s automobile was the first vehicle to be fitted with
synthetic rubber tires (Fig 2.5[1]). When World War I broke out, the German
government decided that since the war would not last long, it would drop the
idea of building large polymerization plants to make synthetic rubber. Instead,
despite of the British embargo on Germany, the Germans smuggled natural
rubber inside coffee cans from America through neutral countries. After 1916,
the British blockade forced the Germans to produce synthetic rubber. In the
next two years, Germany painstakingly produced 2,500 tons of synthetic rubber
using polymerization processes that took several months.

The low prices for rubber after the war -- 17¢ per pound in 1920 -- soon
resulted in a loss of interest in continuing development of synthetic rubber.
However, it did not take long for the rubber cartel to reorganize and as a result,
prices of natural rubber skyrocketed again to a high of $1.21 per pound in 1925.
The high rubber prices as well as being the home of the key polymer chemists
of the time were the main incentives for the German government and industry
to reinvest in their synthetic rubber research program.

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7. From the Malay getah and perija which means rubber and clump, respectively.
8. From the Latin plastic gum.
9. The screw pump is attributed to Archimedes, and the actual invention of the screw extruder by A.G.
DeWolfe of the United States dates back to the early 1860s.
2.2 Cellulose and the $10,000 Idea

If we step back to the 19th Century, in addition to rubber, another natural polymer, cellulose, impacted everyday life. The invention of cellulose plastics, also known as Celluloid, Parkesine, Xylonite, or Ivarite has been attributed to three people: The Swiss professor Christian Schönbein, the English inventor Alexander Parkes, and the American entrepreneur John Wesley Hyatt.

Christian Friedrich Schönbein, a chemistry professor at the University of Basel, loved to perform chemistry experiments in the kitchen of his home, much to his wife’s dismay. Early one morning in the spring of 1845, Schönbein spilled a mixture of nitric and sulfuric acids, part of that day’s experiment, on the kitchen counter. He quickly took one of his wife’s cotton aprons and wiped the mess up, then rinsing it with water before the acid would damage the cloth. As he hung the apron to dry over the hot stove, it went into the air in a loud puff and flame. It had exploded in front of his very eyes. After he recovered from the shock, Schönbein’s curiosity led him to impregnate wads of cotton with the acid mixture. Every time, he was able to ignite the mass, leading to an enormous, uncontrollable explosion. He called his invention guncotton. He had invented cellulose nitrate. Guncotton was three times as powerful as gunpowder and did not leave a black cloud after the explosion. Schönbein sold his patent to the Austrian Empire’s army, but found no buyers in Prussia, Russia, or France. Finally, he sold his patent to John Taylor, his English agent, who immediately began production of guncotton in England. The production ended when his factory exploded, killing 20 workers. Although there were no buyers, several laboratories did spring up across Europe to investigate guncotton; going up into the air faster than they were being built. In addition to its bellicose applications, Schönbein envisioned other uses for the nitrated cotton mass. He added a solvent or plasticizer made of ether and alcohol and found a way to nitrate the cellulose fibers into a less explosive material which he called kollodium, glue in Greek. He reported to his friend Michael Faraday that this mass “is capable of being shaped into all sorts of things and forms…” In the spring of 1846, after accidentally cutting himself on the hand, he covered the wound with a thin elastic translucent film made of kollodium. He sold his idea to the English, who for years supplied the world with the first adhesive bandages. In England, there was one person that took particular interest in the Swiss professor’s inventions. His name was Alexander Parkes.

Alexander Parkes started playing around with cellulose nitrate in 1847, and spent the next 15 years in the laboratory perfecting the formulas and processes to manufacture cellulose nitrate. His final process took the nitrated cotton and added vegetable oils and organic solvents producing a “plastic mass” that was easily molded into any shape or form after it was softened under heat. He called his plastic mass Parkesine. The new applications for this versatile
material, such as combs, knife handles, and decorations, made their debut at the 1862 World Exposition in London. In 1866, Parkes launched the Parkesine Company Ltd. Due to the low quality of its products, parkesine was not a success and the company was liquidated in 1868. The poor mixing of the additives and solvents caused Parkesine products to significantly warp only a few weeks after manufacture. In 1869, Parkes sold his patents to Daniel Spill, his chief engineer, who founded the Xylonite Company and renamed Parkesine, Xylonite. Parkes continued working on his material until his death in 1890 at the age of 77. Alexander Parkes, the inventor and engineer can be credited with improving on Schönbein’s invention, paving the road for the future of the plastics industry. He is also credited with fathering a total of 20 children. A very busy man, to say the least.

At the same time as the plastics industry seemed to be going under in England, in the United States John Wesley Hyatt was launching an enterprise that finally made cellulose nitrate a success, under the name of celluloid. As the story goes, it all began when in 1865 the billiard ball manufacturer Phelan & Collendar placed an add that promised $10,000 to the person who would find a replacement for ivory in the manufacture of billiard balls. Elephants were being slaughtered at a rate of 70,000 per year, which would have led to the extinction of this great animal, exorbitant prices for the “white gold” from Africa, and reduced profits for the billiard ball industry. The $10,000 tag called the 28-year old Hyatt’s attention. After returning home from his job as a printer, he worked on this project until eventually he stumbled upon nitrocellulose in 1869. After finding a way to better mix all the components as well as allowing the solvents to completely evaporate from the mass before solidification, he was soon manufacturing high quality billiard balls. Instead of cashing in on the $10,000 prize, John Hyatt founded the Albany Billiard Ball Company with his brother Isaiah, becoming a direct competitor to Phelan and Collendar. For the next thirty years, until Bakelite replaced celluloid on the billiard table, many guns were pulled in the Wild West when the volatile balls sometimes exploded upon collision. Another immediate application of celluloid were dentures (Fig. 2.6[9]), which up until then were made of hard rubber. In view of loosing a rather profitable business to plastics, the rubber industry started a propaganda campaign against cellulose in all major US newspapers. They falsely claimed that celluloid dentures could easily explode in ones mouth when coming in contact with hot food. This not only cheated people of a much prettier smile, but also started a rivalry between the two industries which has caused them to maintain as completely separate entities to this day. In fact, despite of the materials and processing similarities between plastics and rubber, the plastics industry and the rubber industry have completely separate societies and technical journals. A plastics engineer is likely to be found in meetings organized by the Society of Plastics Engineers (SPE) or the Society of the Plastics Industry (SPI), while a member of the rubber industry

will attend meetings organized by their own society, the Rubber Division of the American Chemical Society.

With a new and versatile material, Hyatt and his coworkers needed equipment to mass-produce plastic products. Based on experience from metal injection molding, the Hyatt brothers built and patented the first injection molding machine in 1872, to mold cellulose materials [10], as well as the first blow molding machine, to manufacture hollow products. In the summer of 1869, Hyatt and Spill, respectively, filed for patents dealing with the manufacture of nitrocellulose materials. This started a lengthy and costly litigation that eventually ruled in Hyatt’s favor in 1876. Spill died soon after, at age 55, of complications from diabetes. John Wesley Hyatt lived another 44 productive years in which he invented the injection molding and the blow molding machines with which he processed celluloid products. He can certainly be credited for being the first person to successfully mold a plastic mass into a useful, high quality final product. However, above all, we should credit him for saving the elephant on the road to a $10,000 prize he never claimed.

Figure 2.6  Celluloid dentures.

With the mass production of rubber, gutta-percha, cellulose, and shellac articles during the height of the industrial revolution, the polymer processing industry after 1870 saw the invention and development of internal kneading and mixing machines for the processing and preparation of raw materials [11]. One of the most notable inventions was the Banbury mixer, developed by Fernley Banbury in 1916. This mixer, with some modifications, is still in use today for rubber compounding.
2.3 Galalith -- The Milk Stone

Galalith, a popular plastic at the beginning of the 20th century, owes its discovery to a cat, a chemist, and an industrialist. Casein formaldehyde, a milk protein-based polymer is better known as casein plastic or by various trade names of which the most memorable ones are Galalith, Aladdinite, Erinoid, and Lactoid. As an industrial material it has come and gone, and all there is left are beautiful casein jewelry pieces, buttons, museum exhibits, and memories for plastic historians.

As the story goes, one night in 1897, the German chemist Adolf Spitteler's cat knocked over a small bottle of formaldehyde. The formaldehyde dripped from the chemist's counter down to the floor into the cat's milk dish. The next morning, when Spitteler returned to his laboratory, he found that the formaldehyde that had dripped into the dish, had caused the milk to curdle and turn into a hard horn-like substance, much like celluloid. In fact, his cat had just invented the first semi-synthetic plastic since cellulose. Soon, Spitteler started experimenting with cheese curds (casein) and formaldehyde, and he found that the milk protein was rendered water-insoluble by letting it sit in a formaldehyde solution for extended periods of time.

Around the same time, Ernst W. Krische, who owned a small book binding and school supplies manufacturing company in Hanover, Germany, received a request from Turkey for washable, white writing boards. Pedagogists of the end of the 19th century believed that it would be better to teach children to write with black chalk on white boards rather than the other way around. However, the whiteboard had not been invented yet. Krische started experimenting by coating cardboard with casein. Casein, easily made by letting milk curdle, had been used for over 100 years as an adhesive, possibly also in Krische's book binding operation. In fact, the use of casein for non-food applications goes back even further, to at least 2 centuries B.C.E., in Egypt, where it was used as a binder for color pigments in the manufacture of paint. However, all these applications, which were well known at the end of the 19th century, did not require a water-insoluble material. In addition, there were many other hurdles that Krische had to overcome, such as the cracking and warpage which both resulted during the drying process of the wet casein.

Luckily, somehow Spitteler and Krische found each other. The chemist and the business man started playing with various materials that would soften or plasticize casein, such as glycerin and borax, and with various amounts and solutions of formaldehyde that would render the mass water-insoluble. Finally, in 1899 they were able to patent their invention. They were not only able to produce the washable whiteboards but soon their moldable plastic mass was marketed under the trade name of Galalith, from the Greek words for milk (gala) and stone (lithos). In Britain it was marketed under the trade name of Erinoid, derived from the Gaelic word for Ireland, the source of most of the British cheese curds required in the manufacture of the new plastic mass.

Beautiful products were produced using this new semi-synthetic material. Bright colored artifacts, such as fountain pens, buttons, clock cases, combs, faux jewelry, etc., were all made out of this polymer. In addition to pigments, fish scales were often blended with casein to produce a pearlised effect. By the late 1920s, the height of casein formaldehyde production, over 10,000 tons per year of dry casein were being absorbed by the plastics industry worldwide. At the same time, 35,000 tons of cellulose were being transformed into plastic products every year. But the end of casein plastics was around the corner. In addition to phenol formaldehyde, the advent of synthetic polymers caused the casein industry to slowly disappear. The new materials were less expensive and easier to process.

Today, the use of casein as well as other protein-based polymers is very small. However, it is still, for example, possible to find very exclusive buttons being made of casein formaldehyde. Although most people regard Galalith as a historic material, the fact that protein-based plastics are made of renewable resources, offering us an unlimited supply of raw materials, should not be ignored.

2.4 Leo Baekeland and the Plastics Industry

Leo Hendrik Baekeland is well known for inventing the first synthetic polymer and for being the father of today's plastics industry. Dr. Baekeland, the chemist and inventor, refined and made possible Bakelite, also known as phenolic. Leo Baekeland, the sometimes mischievous, boyish, Belgian immigrant of modest origins, was an entrepreneur who created and gave momentum to what is known today as the plastics industry.

Leo Hendrik Baekeland was born November 14, 1863, in Ghent, Belgium, to poor illiterate parents. He excelled at school and at age 17 enrolled as the youngest student at the University of Ghent, where he studied chemistry. After only two years he finished his Baccalaureate in chemistry, and at age 21 he received a doctorate summa cum laude. Shortly after receiving his doctorate, he taught chemistry at the University of Bruges, until he was offered a professorship at the University of Ghent. That same year he married his major professor's daughter, Céline, much to the old professor's dismay. Baekeland would recount years later: "The most important discovery that I ever made was Céline." In the end, a displeased senior faculty member, and a traveling
fellowship to the United States was enough incentive for the young professor to embark for New York. During his visit, Professor Chandler at Columbia University encouraged Baekeland to stay in the United States. The 25-year-old Leo was now well aware that an academic career was not his calling. He was an entrepreneur at heart; even while an academic in Ghent he had started a small business that manufactured dry photographic plates, an enterprise that also satisfied his passion for photography. From New York, Baekeland telegraphed his resignation to the University of Ghent and soon after was offered a position as a chemist at A. & H.T. Anthony & Company, a large photographic supply house where he worked for two years. He then decided to try it on his own as a chemical consultant.

The next few years were very difficult for Baekeland. The country went into a deep recession, which adversely affected his consulting business. Worries about his finances and his future mounted, affecting Leo’s health to the point that he was bedridden for an extended period of time. After recovering, he decided he would concentrate all his energies on one project where he knew he could strike it big. He returned to his old hobby, photography, and developed a photographic paper that was so light sensitive that it could be exposed using artificial light. Sunlight was the only light intense enough to expose the photographic plates of the late 1890s. Velox, the name he gave to his new product, was an instant success. It caught George Eastman’s attention, who invited Baekeland to Rochester, NY, to negotiate the rights to this revolutionary photographic product. Baekeland had decided that he would ask Eastman for $50,000 for the rights of Velox, but he was willing to go as low as $25,000. Before Baekeland was allowed to state his demands, the overpowering magnate took over the meeting and on the spot offered the young scientist $1 million for his invention. The year was 1899. Ten years after his arrival in the United States, the 35-year-old Leo Baekeland was wealthy beyond his wildest dreams.

Baekeland now had the necessary funds to embark on the research that would eventually lead to the development of Bakelite, the first synthetic plastic. Bakelite, also known as phenolic, results when phenol and formaldehyde undergo a condensation polymerization reaction. The reaction between these two readily available materials had been well known since 1872, when Adolf von Baeyer first reported it. Baekeland’s contribution was converting the sticky useless material of the late 1800s into the chemically-resistant stiff product that could easily be shaped into any imaginable geometry during the 20th century.

Bakelite not only helped shape the streamlined pre-WWII years, but it also presented a material that made it possible to mass-produce items that made life easier in the home, office, street, field, and factory. The ability to mass-produce plastic products helped create the myth that plastics are a cheap replacement for materials of higher quality. The reality is that phenolic is a material of superior mechanical and electrical properties with higher chemical resistance than those materials it replaced. For example, tough, lightweight, and stiff phenolic-cloth composite propellers replaced wooden aircraft propellers that easily cracked, causing catastrophic failures in the early years of aviation. In another case, Bakelite replaced wood as the material of choice for radio housings (Fig. 2.7), not because it was a cheaper material, but because it was easier and faster to form into its finished shape. In addition, phenolic offered the freedom to experiment with design and esthetics, while at the same time made products, that were previously considered luxuries, available to everyone.

Figure 2.7 Bakelite radios. (The Kölsh Collection).

While president of the American Chemical Society, Baekeland once said: “If academics are given the opportunities to cut their teeth on some practical problems, they may grow to be of decidedly greater service to their science or its applications.” Baekeland gave himself that opportunity and certainly grew greater than anyone before or after him in the plastics industry. He died at age 80 in Beacon, New York, on February 23, 1944.

2.5 Herman Mark and the American Polymer Education

Herman Francis Mark has been credited for being one of the founders of the field of polymer science and for being the father of polymer education in the United States. Over his long and productive lifetime, Herman Mark published 20 books and over 500 articles. His Institute of Polymer Science at the Brooklyn Polytechnic University in New York served as the incubator for some of the most notable polymer scientists of the second half of the twentieth century.
Herman Mark was born in Vienna, Austria, on May 3, 1895, to a Jewish father and a Lutheran mother. He spent his formative years in the Viennese fourth district where his father, a physician, and his mother welcomed many turn-of-the-century intellectuals into their home. One can only imagine the impact on young Mark when among his parent’s friends were the musician Johan Strauss, Sigmund Freud and Theodor Herzl, who with Chaim Weizmann went on to found the Zionist movement. As a twelve-year-old, his life and world changed during a visit to a university laboratory. When he got home, the excited boy reported of “glass bottles and glass beakers, blue flames and Bunsen burners, bubbling liquids and those long rubber tubes through which vapors are diverted.” Soon after, Herman built his own laboratory in his room, where he conducted his own analyses and syntheses, starting a love affair with chemistry that lasted over 80 years.

World War I forced him into adulthood (Fig.2.8[9]). He served as a combat soldier on various fronts for a period of five years. During this time he had two short stays in Vienna, the first to recover from a bullet wound. As usual, making the most of his time, during each stay he completed a semester of chemistry at the university. During the war, his many acts of bravery made Herman Mark a national hero. On one occasion, Mark single-handedly held a dozen Russian soldiers at bay until his whole commando reached safety. At the end of the war, after a short imprisonment in Italy, Mark, now the most decorated officer of the Austrian Army, continued his chemistry studies at the University of Vienna.

After Graduating summa cum laude with a Ph.D. in chemistry in the summer of 1921, he moved to Berlin with his advisor Wilhelm Schlenk who succeeded Professor Emil Fischer at the University of Berlin. The year 1922 was an eventful year for Mark: he married Marie Schramek (Mimi) and joined the Kaiser Wilhelm Institute for fiber chemistry (today the Max Planck Institute), directed by R. O. Herzog. In Berlin, Mark co-authored over 30 papers, which included his work on applying the field of X-ray diffraction when analyzing crystal structures. His stay in the postwar, inflation ridden Prussian capital gave him the opportunity to work and fraternize with people of various backgrounds and nationalities, broadening his intellect and interests. He always felt that a highlight of his years in Berlin was when he conducted experiments for Albert Einstein to confirm Einstein’s light-quantum hypothesis.

In the summer of 1926, Professor Kurt H. Meyer, one of the research leaders at the I.G. Farbenindustrie chemical giant’s BASF labs in Ludwigshafen, visited Mark in Berlin and proposed that the young scientist move to industry to apply his basic research abilities to industrial problems. Mark accepted Meyer’s offer and in January of 1927, moved to Mannheim, where he and his family would live for the next five years. This dramatic change, along with Mark’s association with Meyer, his immediate boss at I.G. Farben, and his continuing collaboration with Hermann Staudinger and other German academic scientists of the time, served as one of the catalysts that propelled the field of polymer science into the spotlight. In 1924, Hermann Staudinger had proposed a model that described polymers as linear molecular chains. Once this model was accepted by other scientists, the concept used to synthesize new materials was realized. For his idea of giant molecules, Staudinger was ridiculed by his conservative peers, who at the time were still convinced that polymers such as natural rubber (polysisoprene) were made of colloids. It took until 1953 for Staudinger to receive the Nobel prize for his pioneering work on polymers. The young and open-minded Hermann Mark understood Staudinger’s theories from the beginning. In 1928, Mark and Meyer proposed a crystal structure for cellulose, rubber, and silk, nearly identical to the ones still accepted today. Their theory was supportive of Staudinger’s high molecular weight theory and refuted the commonly accepted colloidal association theory of the time. Mark’s model for polymer molecules differed from Staudinger’s in that the molecules were flexible, not rigid, as Staudinger suggested. Time would prove Mark right. In the relatively short time at I.G. Farben, Mark produced an impressive list of publications, which included over 80 papers, 17 patents and 3 books.

Figure 2.8 Hermann Mark in 1917.

The idea that polymers were formed by macromolecules was not well received by his peers at first. However, for this work Staudinger received the 1953 Nobel prize in chemistry.
With the political winds in Germany shifting to the right, and because of his Jewish ancestry, both Mark's and Kurt Meyer's positions at IG Farben became uncertain in the summer of 1932. The advice that came from the top of the company was that Mark look for an academic position, preferably outside of Germany. However, since IG Farben did not want to lose a certain degree of control on Mark's research, he was promised financial support for his future academic work. And so, Herman Mark, his wife, Mimi, and two young children moved to Vienna in the fall of 1932, where he became director of the first Chemistry Institute at the University of Vienna. His friend and closest collaborator, Kurt Meyer, moved to Geneva that same year. With IG Farben funds, Mark was able to assemble an impressive team of scientists that included Eugene Guth, Robert Simha, and Fritz Eirich. In Vienna, Mark published many fundamental papers on polymer physics including groundbreaking theories on polymer relaxation, polymerization kinetics and molecular weight distribution. However, leaving Germany was not enough; during the thirties, the Austrian political air also started turning brown, culminating March 15, 1938, when the Nazis marched into Vienna. Mark was arrested the following day, and released without his passport four days later. The next eight weeks were spent recovering his passport and securing a position in Canada, in order to get Canadian and Swiss visas. To finance his trip to North America, the resourceful Mark purchased over one kilogram of platinum wire that he carefully wrapped around coat hangers. With visas in-hand, and their precious currency, the Marks and their niece attached a Nazi flag on the hood of their car and placed rope and skis to the roof and headed up the Alps. They drove into Switzerland on May 10, 1938. After bribing their household possessions out of Austria, the Marks spent the summer in Switzerland, France, and England. Mark started his new position at the Canadian International Paper Company in September of 1938.

After almost two years in Canada, Mark moved to New York in the summer of 1940 where he founded The Institute of Polymer Science at the Brooklyn Polytechnic University in New York. This marks the official start of polymer science education in the United States. The Institute of Polymer Science was the first American institution to award the Ph.D. degree in polymer science, and thus, became the incubator of many American scientists and educators. He advised over 100 scientists that included Fritz Eirich, Edmund Immergut, Herbert Morawetz, and Charles Overberger. Some of his students went on as educators, multiplying the polymer science education all over the world. Eirich stayed at Brooklyn, Guth went to Notre Dame, Simha to Caltech and later to Case Western. Other pupils of Mark served as editors and writers such as Immergut, who had several editorial positions, including with Hansen Publishers between 1980 and 1997, which resulted in a vast polymer engineering and science book library, that has served as a reference and resource to many students, engineers, and scientists. During his years at Brooklyn, Mark wrote hundreds of papers, many books and was the founder and editor of various journals including the Journal of Polymer Science. He also served as a consultant to DuPont, Polaroid, and others, and maintained relations with industry in his native Austria.

Herman Mark's lifetime achievements were recognized by many: he received 17 honorary doctorates, numerous medals and awards, and served as an honorary member to dozens of scientific academies and professional societies. Herman Mark, the war hero, scientist and teacher, died at age 96 in April of 1992.

2.6 Wallace Hume Carothers and Synthetic Polymers

Wallace Hume Carothers is perhaps the most influential American character in the history of polymers. Already as a child he was greatly admired by his grade school friends, who called him "Doc" for his ability to make, among other things, crystal radios. This was only the beginning of a short but productive life in a time when the field of polymer chemistry was still in its infancy. He went on to author over 50 technical papers, file over 100 U.S. and foreign patents, and above all, invent nylon, the world's first synthetic fiber. This specific contribution of Carothers opened the floodgates of invention in the field of thermoplastic polymers.

Born on April 27, 1896, in Burlington Iowa, Carothers was raised in Des Moines where his father taught at the Capital Cities Commercial College, which he attended after high school. He then went to Tarkio College in Missouri where he received a degree in Chemistry at age 24. From Tarkio he moved to the University of Illinois at Urbana-Champaign where he studied under Professor Roger Adams. In the summer of 1921 he received a science degree in chemistry and, after a one year teaching position at the University of South Dakota, defended his Ph.D. in the late spring of 1924. After two years as an instructor at Illinois, Carothers was recruited to teach at Harvard.

Carothers' success was also due in great part to the vision of Dr. Charles M. Stine, the Director of DuPont's Chemical Department. In 1927 Stine used his influence to accomplish something that was unheard of in a corporation of any size; he convinced the company's executive committee to fund research in pure science at the experimental station in Wilmington. With a $25,000 per month budget, Stine lured Carothers from Harvard were he had been teaching for about two years. With this practically unlimited budget and after assembling a team of extremely bright coworkers, including Paul Flory and Julian Hill, Carothers was ready, to begin his 10-year tenure at DuPont. Building on his
experience as a physical chemist and on the research of his contemporaries, such as Adams, Marvel, Staudinger and Mark, Carothers and his team developed polychloroprene, polyester, and of course polyamide 6 and polyamide 66. During that time he coined the terms so widely used today: addition polymerization and condensation polymerization. Polychloroprene (Fig. 2.9), an elastomer, was polymerized by addition polymerization, similar to the polymerization of polyisoprene in Fig. 2.2. Polyamide 66 is polymerized by condensation polymerization as shown in Fig. 2.10.

**Figure 2.9** Wallace Carothers stretching a sheet of polychloroprene.

\[ n \text{ HOOC - (CH}_2\text{)}_4\text{-COOH} + n \text{ H}_2\text{N-(CH}_2\text{)}_6\text{-NH}_2 \]

Adipic acid Hexamethylenediamine

\[ \rightarrow \text{HO} - \text{OC - (CH}_2\text{)}_4\text{-CO-NH - (CH}_2\text{)}_6\text{-NH} \quad \text{H} + (2n-1)\text{H}_2\text{O} \]

Polyamide 66 Water

**Figure 2.10** Condensation polymerization of polyamide 66.

Unfortunately, Carothers never saw the dramatic impact of his inventions. He suffered from two illnesses that in the 1930s were still considered deadly: he was both a manic-depressive and an alcoholic. And so, in spite of his own efforts, and the constant care of friends, family, and doctors, the demons finally took over. Two days after his 41st birthday he was found dead in a Philadelphia hotel room. He had taken cyanide.

In 1938, a year after Carothers's death, nylon was introduced to the world, primarily as a replacement for silk in hose and stockings and as toothbrush bristles. As the story goes, nylon is not an acronym for New York and London, as many people often believe. It evolved from the suggested name norun (a descriptive word that was inaccurate, since fiber 66 stockings did run), to nuron (which sounded too brainy), to nylon (which would have been hard to market as the new nuron), to nilon (two possible pronunciations) to, finally, nylon. In the heated pre-WWII years, it was even suggested that the word nylon was an insulting acronym for the Japanese. Though this is doubtful, it is certain that its invention gravely affected the Japanese trade balance, and in consequence, the overall position of the Japanese industry in world markets at the threshold of World War II. The influence of this miracle fiber is indisputable. Allied use of nylon in parachutes during the invasion of Normandy may have played a decisive role in the war's military outcome. The most obvious influence may come from its impact on consumer consumption. A comical example of this came after the war, the day a department store in Washington offered to sell a pair of nylon stockings to the first 1000 callers. As a result the entire phone system in the D.C. area was flooded and collapsed. This phone system had always resisted collapse, including the day Pearl Harbor was bombed, the day the war ended, and every historically significant day since. This suggests the real power of Carothers' invention: a public whose lives have been changed forever with the advent of thermoplastic polymers.

As Wallace Hume Carothers once said, he had done enough for one lifetime.
2.7 Polyethylene - A Product of Brain and Brawn

By the 1930s Staudinger, Carothers and Mark had paved the road of synthetic polymers for the chemical industry. At the ICI laboratories in Winsington, England, in addition to knowledge in polymers and polymerization, it took muscle power and risk-taking youths, to invent polyethylene, today's highest volume commodity plastic.

Eric William Fawcett and Reginald Oswald Gibson are the two young British scientists who can be credited with polymerizing the first few grams of polyethylene at the Winsington ICI laboratories in England. Fawcett was a young Oxford graduate who was only twenty years old and had to have his father come to the Winsington laboratories to sign for him his employment contract with ICI. Gibson had just returned from Amsterdam, where he had worked with Professor Anton Michels, the world-leading expert on high-pressure vessel design. They both worked in Lab Z, a small ICI laboratory that housed a pressure vessel that everyone called "the bomb." It was no coincidence that the assistants that worked in Lab Z were all young men in great physical shape. It took significant muscle power to operate the hand pump that could pressurize the bomb to up to 2,500 atmospheres (almost 37,000 psi). After pressurizing various liquids and finding that they remained unfazed, they decided to switch to gases, which they hoped would lead to more exiting reactions.

Late on a Friday afternoon, March 24 of 1933, they filled the bomb with ethylene gas, raised the temperature to 170 °C and pressurized it to 1,900 atmospheres. They turned off the lights and went home for the weekend. Since they couldn't wait all weekend for their results, Fawcett and Gibson went back to the lab on Saturday morning and found that the pressure inside the vessel had dropped to 100 atmospheres, a sure sign for a chemical reaction having taken place. Again they pumped the bomb up to 1,900 atmospheres, and left for the remainder of the weekend. On Monday, they found the pressure dials marking 0 atmospheres. They found out that, in addition to the polymerization reaction that took place inside the vessel, the pressure drop was also due to a leak that sprang around an oil tube connection. After opening the vessel, they saw that its inside was covered with a waxy white powder, of which they were able to scrape out 0.4 grams; the first 0.4 grams of polyethylene. They quickly fixed the leak and repeated the experiment, recovering a total of 4 grams of polyethylene. They now had collected enough material that they were able to spin a couple of fibers and form a small thin film. In the third try, the bomb exploded. Even though the explosion did not harm anyone, the managers did not find these experiments as important as Fawcett and Gibson knew they were, and Lab Z was put to rest and the young men were given other tasks.

Two years later, Fawcett attended The Faraday Society of London polymer congress in Cambridge where Wallace Carothers, Herman Mark, Kurt Meyer, and Hermann Staudinger were the main guests and speakers. In the proceedings, Fawcett saw how the future Nobel Prize winner Staudinger claimed that it was not possible to polymerize ethylene. Fawcett got his courage together and went up to Staudinger's room at the University Arms Hotel to attempt to set him straight. There he told the prominent scientist that under certain conditions it was possible to polymerize ethylene. Staudinger ignored him and gave his talk as planned. After the talk Mark even supported Staudinger's findings. Undaunted by the prominence and belief of his opponents the young man rose and told the audience that ethylene polymerizes if maintained at 170 °C under very high pressures. This bold move impressed Carothers, then a well-known American scientist, who offered Fawcett a job and took him to the DuPont laboratories in Wilmington, Delaware.

Soon after, ICI resumed their high-pressure vessel work, reproducing Fawcett and Gibson's experiments and patenting polyethylene in February of 1936. ICI continued to produce polyethylene using their high-pressure polymerization process. Soon, their operation had been scaled-up sufficient to produce several kilograms of polyethylene every hour. In the meantime they had also discovered that this new plastic had excellent dielectric properties, which made it ideal for insulating thin wires for telecommunications applications.

In 1940, the British were at war. The Germans were bombing major English cities, and although ground radars detected the bombers, it was usually too late. A major breakthrough came when the British were able to reduce the weight of a radar from several tons to just under 600 pounds with the use of polyethylene as a wire insulator. This allowed them to place radars inside their fighter planes, enabling them to detect Nazi planes, before they saw them, shooting them out of the air at the same rate as they were crossing the British Channel. This put the British at an advantage, saving their cities from destruction. Similarly, the radar rendered the German submarine fleet obsolete, protecting the life saving sea transports, from the U.S.A. to England. As a result, hardly any submarines returned to Germany after 1943.

Twenty years after Fawcett and Gibson produced polyethylene inside the bomb, the German professor and future Nobel Prize winner Karl Ziegler found a way to polymerize ethylene at low pressures using catalysts. His catalysts where metal based compounds that act as vehicles as they drive through a sea of ethylene, picking up each monomer in an orderly fashion resulting in long chains of polyethylene. One was now able to produce this versatile material at much higher rates, under safer conditions, and at lower energy costs. Ziegler sold his patent to several resin producers who immediately jumped into production. However, they soon found out that their new process produced
polyethylene that cracked easily, rendering the first few thousand tons of high-density polyethylene useless. Luckily, in 1957 along came a small Californian toy manufacturer, The Wham-O Company, who proposed to use the inferior HDPE on their new toy: the Hula-Hoop (Fig. 2.11). While Wham-O was using up the world supply of imperfect polyethylene, and America was buying the hoops by the millions, the chemical companies were successfully working out the kinks in their polymerization processes. One of Ziegler's occasional co-workers, the Italian chemical engineer Giulio Natta, extended Ziegler's research on organometallic catalysts to discover polypropylene. Both, Ziegler and Natta received the Nobel Prize in chemistry in 1963, and today, Ziegler-Natta catalysts are still in use.

Figure 2.11 The Hula-Hoop.

Soon, polyethylene Hula-Hoops, Tupperware, and plastic bags became everyday items. As the years passed, catalysts not only produced other polymers but also allowed us to tailor an ultra-high molecular weight high-density polyethylene that can be spun into fibers that are stronger than steel. Today, UHMWHDPE is used to manufacture artificial hip joint replacements that have given many people a quality of life otherwise thought to be impossible.

Other thermoplastics were also developed during that time and in the years that followed. Polyvinyl chloride (PVC) was made into a useful material in 1927 [12]. Due to its higher wear resistance, polyvinyl chloride replaced shellac as the material of choice for phonograph records in the early 1930s. Polyvinyl acetate, acrylic polymers, polystyrene (PS), polyurethanes, and polymethyl methacrylate (PMMA) were also developed in the 1930s [13], and polycarbonate (PC) in the 1950s. And the list goes on. Today, developing and synthesizing new polymeric materials has become increasingly expensive and difficult. Hence, developing new engineering materials by blending or mixing two or more polymers or by modifying existing ones with plasticizers has become a widely accepted procedure.

2.8 The Super Fiber and the Woman Who Invented It

When Stephanie Louise Kwolek (Fig. 2.12) discovered a low viscosity and cloudy polymer in 1964, she did not discard it as a contaminated and useless polymer solution, but continued experimenting with it. Polymers in the melt state are usually not only highly viscous but also amorphous and therefore transparent or clear. Kwolek's curiosity and persistence soon showed her that she had discovered a polymer that was crystalline in the melt state; she had discovered liquid crystalline polymers or LCP's. This invention soon resulted in the discovery of Aramid fibers, probably better known by their trade name Kevlar fibers.

Kwolek, who was born in 1923 in New Kensington, Pennsylvania, had an early passion for fabrics and fashion design, which resulted in new clothes for her dolls. However, she never imagined that some day people's lives would be saved with bullet proof vests made with fabrics woven out of her fibers. The super fibers that Stephanie Kwolek discovered were five times stronger than steel but were only a fifth of its density. Kwolek studied chemistry and biology at what is today known as Carnegie Mellon University. She wanted to continue her studies in medicine, but could not afford the high costs of medical school. To allow her to save some money, she decided to take a job at the DuPont Company. However, she soon became enamored with the work and shortly thereafter transferred to DuPont's Pioneering Research Laboratory of the Textile Fibers Department. She was in the perfect environment, working for a company that had discovered and made a name with synthetic polymer fibers. In 1964 she found herself working with a group of researchers whose main task was to develop an ultra strong fiber. The main application for this fiber would be the manufacture of lighter tires that would help reduce fuel consumption, motivated by early predictions of gasoline shortages. The main breakthrough came that same year when she discovered that extended-chain aromatic polyamides could be made into liquid crystalline solutions. These polymers could in turn be spun into fibers whose molecules were highly oriented, rendering a very stiff and strong final product.

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12 The preparation of PVC was first recorded in 1835 by H.V. Regnault.
while production of metals has barely doubled. However, to be fair, in the popularity contest between metals and plastics we can always present the data differently, namely by weight. This way, the tonnage of metals produced worldwide is over twice the tonnage production of polymers. Nevertheless, this is a book about polymers, and we like to point to the fact that today the volume of polymers produced is three times larger than that of metals.

In fact, the world's annual production of polymer resins has experienced a steady growth since the beginning of the century, with growth predicted way into the 21st century. This can be seen in Fig. 2.13 [14] which presents the world's annual polymer production in millions of tons. There has been a steady increase throughout the years, with slight dips during the oil crisis in the mid 1970s and during the recession in the early 1980s. In developed countries, the growth in annual polymer production has diminished somewhat in recent years. However, developing countries in South America and Asia are now starting to experience tremendous growth. With the exception of the recession years, the growth in US polymer production has been declining in the past 20 years to approximately 4% of annual growth rate. Since 1970, China has seen the highest annual growth in the world, ranging from a maximum approximately 50% between 1976 and 1977 to a low of 2% between 1980 and 1981.

In recent years, there has been a rapid increase in the demand for polymeric materials in developing countries such as Colombia. The demand for polymers in Colombia grew from 295,000 tons in 1992 to 389,000 tons in 1993. Although this number seems small when compared to the 34.4 million tons produced in

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Figure 2.12  Stephanie Louise Kwolek showing an Aramid molecule model.

After continued research refining her discovery, Kevlar was introduced to the market in 1971. Today, in addition to bullet proof vests, the super fiber can be found in brake pads of automobiles, trains, and aircraft as well as in safety helmets, skis, and numerous other applications.

2.9 One Last Word — Plastics

The year 1967 was a significant year for plastics. One event, related to American pop culture and one that some of us tend to remember, is the advise given to the young graduate played by Dustin Hoffman in the movie The Graduate. The prophetic words told to the new graduate —"I just want to say one word to you, Ben. Just one word — plastics"— where a symbol of the times and a sign of things to come. The same year that the movie was showing in the theaters, the volume of plastics' production surpassed that of all metals combined. Today, almost forty years later, plastics production is six times higher than in 1967.
the US in 1993, Colombia has a 32% annual growth compared to the US 4% growth. It should be pointed out that Colombia produces PE, PP, PS and PVC for its own consumption and for export to other Latin American countries, while it imports most of the needed engineering thermoplastics such as SAN, ABS, PC, etc. [15] from developed countries such as the US and Germany. Similar trends exist in other Latin American countries.

There are over 18,000 different grades of polymers, available today in the US alone13. As pointed out in Chapter 1, they can be divided into two general categories—thermosetting and thermoplastic polymers. In 1993, 90% of polymer produced in the United States were thermoplastics. However, in a 1995 worldwide projection, thermoplastics account for 83% of the total polymer production [16]. Figure 2.1314 shows a percentage break down of US polymer production into major polymer categories. These categories include polyethylene, polypropylene, polystyrene, polyvinyl chloride, and thermosets. Polyethylene is by far the most widely used polymeric material, accounting for 41% of the US plastic production.

![Figure 2.14 Break down of US polymer production into major polymer categories.](image)

Packaging accounts for over one-third of the captive use of thermoplastics as graphically depicted in Fig. 2.15, whereas construction accounts for about half that number, and transportation accounts for only 4% of the total captive use of thermoplastics. On the other hand, 69% of thermosets are used in building and construction, followed by 8% used in transportation. The transportation sector is one of the fastest growing areas of application for both thermoplastic and thermosetting resins. It should also be noted that 12% of the 1994 US polymer raw material production was exported.

It cannot be argued that, for some time now, polymers have become an indispensable material in everyday life. From sports to medicine, and from electronics to transportation, polymers are not only a material that is often used, but also the material that in many cases make it possible. One can sum it up with Hans Uwe Schenck’s often quoted phrase — “Without natural polymers, there would be no life; without synthetic polymers, no standard of living.”

![Figure 2.15 Break down of U.S. polymer production into major areas of application.](image)

References

3.1 Macromolecular Structure of Polymers

Polymers are macromolecular structures that are generated synthetically or through natural processes. Cotton, silk, natural rubber, ivory, amber, and wood are a few materials that occur naturally with an organic macromolecular structure, whereas natural inorganic materials include quartz and glass. The other class of organic materials with a macromolecular structure are synthetic polymers, which are generated through addition or chain growth polymerization, and condensation or radical initiated polymerization.

In addition polymerization, monomers are added to each other by breaking the double-bonds that exist between carbon atoms, allowing them to link to neighboring carbon atoms to form long chains. The simplest example is the addition of ethylene monomers, schematically shown in Fig. 3.1, to form polyethylene molecules as shown in Fig. 3.2. The schematic shown in Fig. 3.2 can also be written symbolically as shown in Fig. 3.3. Here, the subscript n represents the number of repeat units which determines the molecular weight of a polymer. The number of repeat units is more commonly referred to as the degree of polymerization. Other examples of addition polymerization include polypropylene, polyvinyl chloride and polystyrene. The side groups, such as CH₃ for polypropylene and Cl for polyvinyl chloride, are sometimes referred to as the X groups.

Another technique to produce macromolecular materials is condensation polymerization. Condensation polymerization occurs when two components with end-groups that react with each other are mixed. When they are stoichiometric, these end-groups react, linking them to chains leaving a by-product such as water. A common polymer made by condensation polymerization is polyamide where diamine and diacid groups react to form polyamide and water, as explained in Chapter 2.