

AN INTERNATIONAL HISTORIC
CHEMICAL LANDMARK

The Establishment of Modern Polymer Science By Wallace H. Carothers

WILMINGTON, DELAWARE
NOVEMBER 17, 2000



AMERICAN CHEMICAL SOCIETY
Division of the History of Chemistry and
The Office of Communications



DuPont Experimental Station, Wilmington, Delaware, ca. 1928.

This booklet commemorates the designation of the establishment of modern polymer science by Wallace H. Carothers as an International Historic Chemical Landmark. The designation was conferred by the American Chemical Society (ACS), a nonprofit scientific and educational organization of 161,000 chemists and chemical engineers. A plaque marking the designation was presented to DuPont on November 17, 2000. The inscription reads:

“At this site in 1928, Wallace H. Carothers (1896–1937) began his pioneering studies into the chemistry of giant molecules. He soon confirmed that high molecular weight molecules consist of repeating units of simple molecules (monomers) linked together by chemical bonds to form long chains (polymers), as first proposed in 1920 by German chemist Hermann Staudinger. Carothers excelled at creating polymers, and his work quickly led to the E.I. du Pont de Nemours and Company’s highly successful commercial production of neoprene, the first synthetic rubber made in the United States (1932), and nylon, the world’s first totally synthetic textile fiber (1939).”

On the cover:

Wallace H. Carothers demonstrating the elastic properties of neoprene, early 1930s.

Acknowledgments:

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Marvelous, Mysterious Macromolecules

When Wallace H. Carothers joined the research staff of the U.S. chemical manufacturer E.I. du Pont de Nemours and Company (now DuPont) in early 1928 and launched his pathbreaking studies of polymerization, polymer science was still in its infancy—ill-understood and full of uncertainties.

By the early 20th century, chemists had learned that many materials were polymeric—including such natural substances as proteins, cellulose, and rubber. Other polymers had been synthesized in the laboratory from smaller molecules like styrene, vinyl chloride, and acrylic acid. At least one synthetic polymer, Bakelite, a hard resin produced from phenol and formaldehyde by Leo H. Baekeland about 1907, was a big commercial success. Chemists knew, too, that polymers were molecules of high molecular weight (for example 40,000 or more) made up of huge numbers of smaller chemical units. But how these units were arranged and held together was not clear. Many eminent chemists believed that polymers were aggregates, perhaps colloids, consisting of relatively small molecules held together by some intermolecular force of uncertain nature.

In the early 1920s, the German organic chemist (and 1953 Nobel laureate) Hermann Staudinger postulated that polymers consisted of units linked together by the same covalent bonds found in smaller organic molecules. Throughout the 1920s, Staudinger supported his view with new experimental evidence, and other chemists, among them Karl Freudenberg, Michael Polanyi, Kurt Meyer, and Herman Mark, came up with additional evidence backing Staudinger. The subject, nevertheless, remained controversial well into the 1930s.

Carothers had no direct contact with these chemists, but his ideas were generally in line with those of Staudinger. His research approach, on the other hand, was quite different. Whereas Staudinger focused his study on the analysis of natural polymers, Carothers built up polymers by reacting small organic molecules by means of well-known reactions—for example, by combining dicarboxylic acids with diols or diamines—to form long, macromolecular chains.



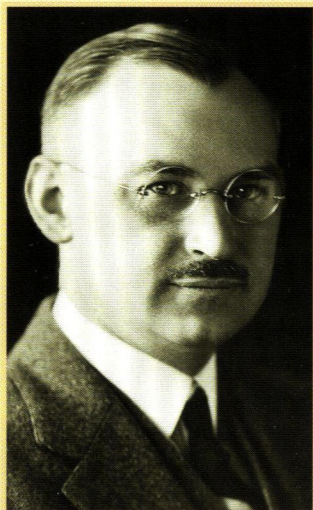
Wallace H. Carothers (1896-1937)

In addition to the many experimental studies, Carothers believed that mathematics could be applied to understand the formation and properties of polymers. To this end, Paul J. Flory was hired in 1934 and introduced to polymers by Carothers. The seminal ideas they advanced provided the foundation of many of the theoretical methods for studying polymers used to this day. Flory's accomplishments were recognized with the 1974 Nobel Prize in chemistry.

The research accomplishment of Staudinger and Carothers, along with that of their colleagues, during the 1920s and 1930s laid the foundations of modern polymer science and today's plastics, synthetic fiber, and rubber industries. Today, approximately half of the industrial chemists in the United States work in some area of polymer chemistry.

FRUITFUL FUNDAMENTAL RESEARCH AT PURITY HALL

In late 1926, Charles M. A. Stine, director of the E.I. du Pont de Nemours and Company's chemical department in Wilmington, Delaware, convinced the company's executive committee to establish a continuing program in fundamental research. Only a handful of industrial firms had such farsighted programs. For most firms, research simply meant problem solving and process improvement. Stine argued that DuPont's support of work in pure science would enhance the company's prestige, make recruiting Ph.D. scientists easier, and cement bonds to academic chemistry departments. Finally, he added, something of practical value might come out of it.



Charles M. A. Stine established the basic research program that brought Wallace Carothers and other talented young scientists to DuPont.

Stine chose five lines of study—colloid chemistry, catalysis, the generation of chemical and physical data, organic synthesis, and polymerization—and set out to recruit the very best chemists to head each field. In 1927, he persuaded Wallace H. Carothers, a brilliant young instructor in organic chemistry at Harvard University, to head the program in organic synthesis.

Wallace Carothers was born in Burlington, Iowa, on April 27, 1896, the son of

Presbyterians of modest means. His father taught at the Capital City Commercial College in Des Moines, Iowa, and young Carothers spent a year there. In 1915 he enrolled at Tarkio College, a small Presbyterian-supported school in northwestern Missouri. There he majored in chemistry while helping in the school's floundering commercial department. When the chemist who ran the college's one-man science department departed in 1918, Carothers, then a senior, took over the college's chemistry classes.

After graduating from Tarkio in 1920, Carothers continued his studies at the University of Illinois, at the time the preeminent school in the United States for training organic chemists. There, he earned a

Master's degree in 1921 and a Ph.D. under Roger Adams in 1924. Years later, Adams characterized Carothers as "the best organic chemist in the country."

While an instructor at Illinois, Carothers became interested in the electronic theory of valence to explain how atoms in organic molecules bond together. It was a theory propounded by the physical chemist G. N. Lewis of the University of California at Berkeley. But most organic chemists of the time ignored that theory, if they did not dismiss it outright. Carothers published a paper on the electronic nature of the carbon-carbon double bond in the *Journal of the American Chemical Society* in 1924. It marked his growing interest in theoretical as well as experimental organic chemistry.

In 1926, Carothers accepted a teaching post in organic chemistry at Harvard University, but he was uncomfortable as a classroom lecturer. When DuPont offered Carothers the opportunity to do fundamental research, at first he was reluctant to accept. He agreed to do so once convinced that he would be free to work on whatever interested him and that he would command an ample budget for supplies and equipment. Besides, his \$6,000 a year salary would nearly double what Harvard was paying him.

Shortly after arriving at the newly constructed laboratory (later dubbed "Purity Hall") on February 6, 1928, Carothers began to study the structure and synthesis of polymers. He concluded from the literature that long molecules could be strung together from small organic compounds that had a reactive (functional) group at each end. He called these resulting products "condensation polymers" because another compound (such as water) would be split off as a byproduct. Carothers and a small group of young Ph.D. chemists began by reacting dibasic acids (containing two carboxylic acid, $-\text{COOH}$ groups) with diols (two alcohol, $-\text{OH}$ groups). This reaction, known as esterification, was roughly akin to linking together a chain of paper clips. The resulting long chain molecules were polyesters.

Progress was rapid, and the resulting polymers theoretically interesting. But their molecular weights were 4,000 or less. Carothers was aiming for larger molecules. He concluded that the water formed during the esterification reaction was limiting the chain length.

A New Synthetic Rubber

Meanwhile, in 1930 Carothers had been asked by Elmer Bolton, the new head of DuPont's chemical department, to look into polymers based on acetylene. Unlike Stine, who emphasized pure science, Bolton believed that research should be aimed at clearly defined applications. The free-wheeling days of fundamental research at DuPont were fading.

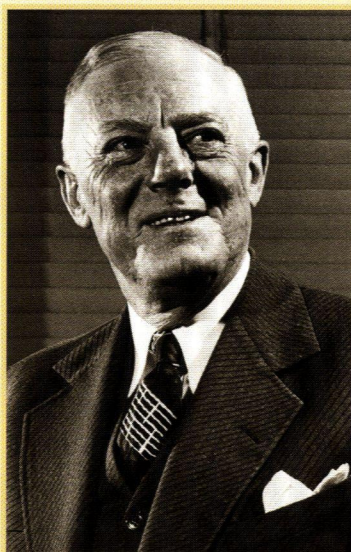
Bolton, who previously had headed DuPont's research on dyes, had long been interested in producing a synthetic rubber. In the late 1920s he had followed the research of Father Julius Nieuwland of Notre Dame University, who used a cuprous chloride catalyst to combine two or three acetylenes into mono- or divinylacetylene. Bolton realized that these compounds were similar to isoprene, the molecule that is the basic structural unit of natural rubber.

Carothers assigned Arnold Collins to make a very pure sample of divinylacetylene. While distilling the products of the acetylene reaction in March 1930, Collins obtained a small amount of an unknown liquid, which he put aside in stoppered test tubes. A few days later he found that the liquid had congealed into a clear homogenous mass. When Collins dislodged the mass from its container, it bounced. Analysis showed that the mass was a polymer of chloroprene, formed with chlorine from the cuprous chloride catalyst. Accidentally, Collins had prepared a new synthetic rubber.

DuPont began large-scale production of polychloroprene, marketed under the name Duprene (later changed to neoprene), in 1932. Neoprene was difficult and expensive to manufacture, however, and it didn't really rival natural rubber, which was selling for only a few cents per pound in the early 1930s. Neoprene—which was resistant to weather, oil, chemicals, and heat—found several relatively small but profitable uses.

Nylon: A Synthetic Fiber Stronger Than Silk

1930 was a banner year for Carothers' research group. While Collins, through his careful observation, was uncovering the polymer that would become neoprene, Carothers and his closest



Elmer K. Bolton succeeded Stine as DuPont's chemical research director. Bolton provided the direction that led to the development of nylon and the commercialization of neoprene.

research associate, Julian Hill, had found that the unwanted water formed during esterification could be removed by running the reaction in a molecular still, a recently invented device. In late April 1930, Hill synthesized a polyester in the still, touched the hot mass with a glass rod, and stretched "this festoon of fiber." He

had formed a polyester with a much higher molecular weight than before, about 12,000. Moreover, the cooled fibers became strong and elastic when pulled out farther. This "cold drawing" process orients the previously helter-skelter polymer molecules along a single axis. The first synthetic fibers had been created.

Hill then produced a wide array of polyester fibers, which, although they were scientific marvels, were of no practical value. All of the fibers melted in boiling water, and they dissolved in many organic liquids. Carothers and Hill turned to polymerizing dibasic acids with diamines—compounds that had amino ($-\text{NH}_2$) groups at either end. Although the products had very high melting points and were relatively insoluble, they proved no more useful as fibers than the polyesters. For a while, Carothers stopped working on such polymers, but Bolton was convinced that a viable fiber was possible.

In early 1934 the polyamide fiber project got back in gear. A wide variety of dibasic acid and diamine polymers were prepared. One of these, synthesized from adipic acid and hexamethylenediamine on February 28, 1935, was called fiber 66 because each of its components had six carbon



Entrance to the DuPont Experimental Station, ca. 1939.

atoms. It formed fibers that, after cold drawing, were strong, elastic, unaffected by water or most solvents, and had a high melting point. DuPont chose this fiber in July 1935 for full-scale production.

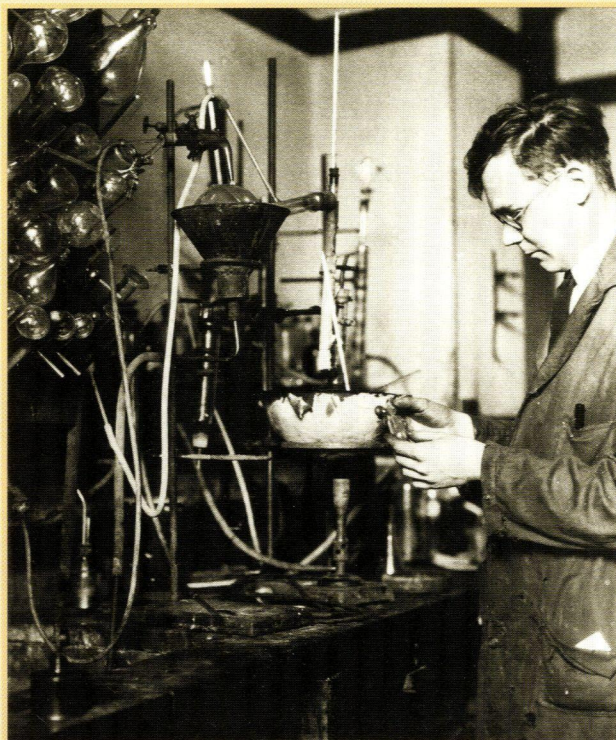
Much development work remained.

Although adipic acid was being made in Germany, hexamethylenediamine was only a laboratory curiosity. DuPont engineers had to devise ways to make both chemicals, find a means of extruding the molten polymer through tiny holes (spinnerets) into fine filaments, and design and construct a new production plant. By the time DuPont started building its first plant in Seaford, Delaware, in 1938, more than 230 chemists and engineers had worked on the project at one time or another at a cost of \$27 million.

The new fiber, by then named nylon, was announced to the public by Charles Stine at the *Herald Tribune* forum in New York City on October 27, 1938. Because of the product's silk-like qualities, DuPont planned to target it toward women's hosiery (actually, small amounts also were used as bristles in Dr. West's toothbrushes by 1938). Sample stockings were sold to company office employees in Wilmington in March 1939, and a limited quantity was sold to the public in Wilmington later that year. Demand was overwhelming. The first day nylon stockings were introduced nationwide, May 15, 1940, nearly 800,000 pairs were sold. By 1941, nylon had captured over 30% of the hosiery market. When the United States entered World War II in December 1941, however, all nylon output was diverted to military needs.

An Extraordinary But Brief Career

While at DuPont, Carothers enjoyed varied interests beyond his research, including art, music, poetry, politics, and sports, and he made many friends in Wilmington. In 1936, he married Helen Sweetman, a chemist in the patent department at DuPont. The same year he became the first industrial organic chemist elected to the National Academy of Sciences. Toward the end of his career, Carothers was subject to increasing periods of depression and, in April 1937, he took his own life.



Wallace Carothers in his laboratory at the DuPont Experimental Station, ca. 1930.

Carothers confirmed the basic structure of polymers, demonstrating that they were ordinary molecules, only longer. His synthesis of polymers led to the development of nylon, the world's first fully synthetic fiber, and neoprene, a highly resistant synthetic rubber. His early work with polyesters supported the establishment of the polyester fibers industry. These materials remain important articles of commerce to this day.

Despite Carothers' relatively brief career, it was an extraordinarily productive one, both in terms of fundamental advances in chemistry and nearly unparalleled commercial success.

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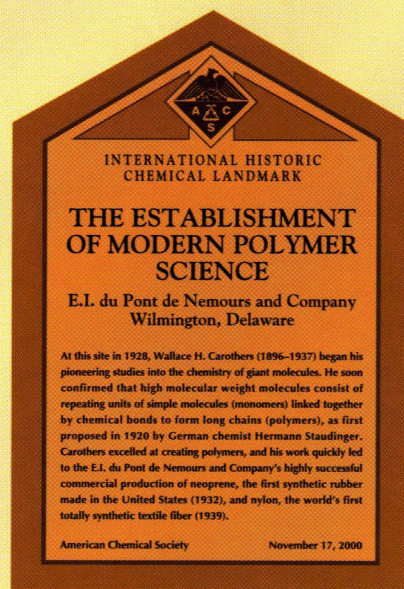
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The National Historic Chemical Landmarks Program recognizes our scientific and technical heritage and encourages the preservation of historically important sites, artifacts, and collections in chemistry, chemical engineering, and the chemical process industries. It provides an annotated roster to remind chemists, chemical engineers, students, educators, historians, and travelers of an inspiring heritage that illuminates both where we have been and where we might go when traveling the diverse paths to discovery.

An historic chemical landmark represents a distinctive step in the evolution of chemical science and technology. Designations of sites and artifacts note events or developments of clear historical importance to chemists and chemical engineers. Collections mark the contributions of a number of objects with special significance to the historical development of chemistry and chemical engineering. The Division of the History of Chemistry began this program in 1992.

An international ACS committee, composed of chemists, chemical engineers, and historians of science and technology, works with the Office of Communications and is assisted by the Chemical Heritage Foundation. Together, these organizations provide a public service by examining, noting, recording, and acknowledging particularly significant achievements in chemistry and chemical engineering. For further information, please contact the ACS Office of Communications, 1155 Sixteenth Street, N.W., Washington, D.C. 20036; 800-227-5558, ext. 6274; e-mail: nhclp@acs.org.



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