Wallace H. Carothers and Fundamental Research at Du Pont

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The discovery of nylon has for many years served as a model for scientifically based industrial research. This revolutionary product originated from research undertaken in 1927 in the newly organized fundamental research program at E. I. du Pont de Nemours. Among those hired by the program's originator Charles M. A. Stine to staff the venture was Wallace H. Carothers, who during his 9 years with Du Pont not only made important contributions to polymer science but also produced nylon and neoprene synthetic rubber. Of course, other scientists have accomplished similar feats; Irving Langmuir at General Electric is but one example. Du Pont's program is interesting because unlike many industrial laboratories, for which it has proved impossible to classify research as "pure" science and "applied" science or technology (*1*), initially Du Pont did separate its pure science research from other types. Carothers agreed to join Du Pont only after he was convinced that he could pursue his interest in theoretical organic chemistry without having to concern himself with what usually was thought of as industrial research. And unlike other young theoretically oriented scientists who entered industry, he never abandoned his pursuit of pure science.

Summary. In the Depression decade, the research group headed by Wallace H. Carothers made two discoveries—neoprene and nylon—that have had an enormous impact on E. I. du Pont de Nemours and industrial research generally. At the same time, Carothers's many publications helped establish the foundations of polymer science. A theoretical organic chemist, he left Harvard University to take part in Du Pont's new fundamental research program. Although founded on the academic model, it soon began to reflect its industrial setting. Some surprising experimental results, the research philosophy of a new research director, and the economic realities of the Great Depression pushed Du Pont's pure scientists toward more practical or mission-oriented goals. Nylon and neoprene emerged from this creative tension between chemists interested in science and management committed to innovation.

In 1930, three events occurred that would make Carothers a renowned, though somewhat reluctant, inventor. In April, chemists in Carothers's group unexpectedly discovered neoprene and the first synthetic fiber. Two months later, Stine was promoted to Du Pont's Executive Committee, and Elmer K. Bolton replaced him as head of the company's central research organization. Bolton was a more traditional industrial research director whose interest was in work that might lead to new products, and Carothers's interesting but impractical synthetic fibers appeared to him to be one such area (*2*). Bolton personally took the responsibility for ensuring that Carothers's scientific investigations were translated into an enormously important new product. Du Pont Chairman Lammot du Pont clearly had Bolton's contribution to nylon in mind when he denied that "the best direction of research is not to direct it. I don't think that is correct in [one] sense . . . . The division between fundamental research in industry and applied research is a subject for direction, and the man who directs fundamental research in industry, and directs it properly, is the one who makes the success in that industry"(*3*).

Fundamental Research at Du Pont

Although Du Pont had been one of a handful of U.S pioneers in industrial research, its research managers had not seriously entertained the idea of doing fundamental research until shortly after Stine became the director of the company's Central Chemical Department. In late 1926, Stine submitted to the company's Executive Committee a proposal that he considered to be "sufficiently radical" to demand a special letter of explanation. In a short memorandum, he requested $20,000 to begin research "with the object of discovering new scientific facts." Stine pointed out that this type of research had been done successfully by German industry and the General Electric Company. He also cited Herbert Hoover, who argued that the rapid growth of industrial research was depleting the reserve of scientific knowledge that formed the basis of technological innovation. As Stine put it, "applied research is facing a shortage of its principal raw materials" (*4*).

Stine listed four reasons why Du Pont should spend its money on a new kind of industrial chemical research. First was the scientific prestige or "advertising value" to be gained through the presentation and publishing of papers. Next, interesting scientific research would improve morale and make the recruiting of Ph.D. chemists easier. Third, the results of Du Pont's pure science work could be used to barter for information about research in other institutions. Stine's fourth reason was that pure science might give rise to practical applications. Although he personally believed that new technology would inevitably result, he felt that his proposal was justified by the first three reasons.

Though intrigued by Stine's request, the Executive Committee wanted more information. Three months later, Stine submitted a more detailed proposal in which he used "fundamental research" in the title of his proposed program instead of pure science. He sought to demonstrate that this program would explore the fundamental science underlying Du Pont's technology. To show how fundamental research would be different, he compared it to what he called "pioneering applied" research, which "might result in something of great value or might come to naught." Fundamental research, Stine argued, "is bound to result in the discovery of new highly useful and in some cases indispensable knowledge." At first, this may seem like a curious distinction. But Stine saw pioneering applied research as a form of gambling—for example, he cited the Organic Chemicals Department's unsuc-

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cessful attempts to make synthetic rubber. According to Stine, the investigation of the scientific foundations of chemical technology inevitably had to yield significant results (*5*).

For fundamental research at Du Pont, Stine proposed the following lines of work: colloid chemistry, catalysis, the generation of physical and chemical data, organic synthesis, and polymerization. He described colloids as "practically a virgin field from a scientific standpoint. . . . Our progress in [their] utilization . . . has been made slowly and painfully, principally by the 'shotgun method.' " Catalysis, Stine noted, "represents probably the most remarkable and most important development in modern chemistry . . . , [yet] the mechanism of the action of catalysis is unknown. There is consequently no scientific basis for selecting the best catalyst for a given process." He expressed similar ideas regarding physical and chemical data and organic synthesis. Regarding polymerization he stressed that almost nothing was "known about the actual mechanism of the change which takes place, so that the methods used are based almost solely on experience." By undertaking fundamental research in polymerization, Stine implied, the company stood a good chance of benefiting materially.

These carefully formulated arguments convinced the company's Executive Committee to give Stine the go-ahead with his program in which he hoped to spend about $250,000 per year on five or six lines of research. Although Stine did not want his fundamental research groups to receive special attention, they would need a new laboratory. When built, the facility promptly became known as "Purity Hall" (*6*).

At the outset Stine felt that his program would succeed only if he could hire the best scientists in each of his proposed areas of research. To lead his organic chemistry group, he offered positions to Roger Adams of Illinois and Henry Gilman of Ohio State, both established academic professors (*7*). After failing to recruit such men, he next attempted to hire "men of exceptional scientific promise but no established reputation" whose lines of research "can largely be determined by us." But Louis F. Fieser and Reynold C. Fuson, both young academics, also declined to join the program (*8*). Stine succeeded in obtaining only two men who had academic experience: Elmer O. Kraemer, a 30-year-old colloid chemist at Wisconsin, and Wallace H. Carothers, a 31-year-old organic chemistry instructor at Harvard.

Recruiting Carothers

Carothers became interested in chemistry in high school in Des Moines, Iowa. After graduation he spent a year completing the course at the Capital City Commercial College where his father taught. In the fall of 1915, he entered Tarkio College in Missouri as a science major, and also assisted first in the Commercial Department there and later in the English Department. Carothers prided himself on his ability to write clear and forceful prose, a skill evident in his scientific papers (*9*). When his chemistry professor, Arthur M. Pardee, left Tarkio for the University of South Dakota, Carothers filled in as the chemistry instructor although still an undergraduate. After graduating in 1920, he studied organic chemistry at the University of Illinois and obtained a masters degree. Then, joining Pardee in South Dakota, Carothers taught courses in analytical and physical chemistry before returning to Illinois for his Ph.D. At South Dakota, Carothers carried out his first original work on the application to organic reactions of G. N. Lewis's theory on the role of electrons in chemical bonding (*10*).

At Illinois in 1922, Carothers worked under Roger Adams on platinum oxides as catalysts for the reduction of organic compounds. He completed his doctorate in 1924 and remained at Illinois as an instructor for 2 years until Harvard hired him. Not long afterwards Stine offered him a position in Du Pont's new fundamental research program (*11*).

Carothers resisted Stine's recruitment efforts until he was assured that fundamental research literally meant pure science. He also asked to continue his work on the thermal decomposition of ethylmetal compounds, looking for evidence of free radicals. "The problem," he explained, "has some . . . explicit bearings on theoretical chemistry, but none so far as I know [will] be of any practical use." Stine replied that at Du Pont Carothers could continue to work on whatever he pleased but the growth of his group would depend on his "capacity for initiating and directing work that we consider worthwhile undertaking." Carothers turned down the job offer without giving any reasons (*12*).

A few days later, however, he wrote a long letter to Stine detailing his major concerns, which were professional, financial, and personal. Carothers said that his overriding concern was for scientific advancement; therefore, he had to weigh Du Pont's offer against his present position. Harvard was getting a new laboratory and more money for research, and Carothers thought his teaching load might be reduced. He worried that at Du Pont he might have to "suppress the development of an investigation." On the other hand, Carothers felt that he would have more and higher quality assistants at Du Pont than at Harvard. Looking at the financial aspect, he did not consider that the increase in salary, $5000 versus $3200 per year paid by Harvard was adequate to compensate for the loss of "the real freedom and independence and stability of a university position." Carothers also wondered how he would fit in at Du Pont, especially since he suffered "from neurotic spells of diminished capacity which might constitute a much more serious handicap there than here." He stressed that he had gone through a difficult period of adjustment in Cambridge and feared something similar if he moved to Wilmington (*13*).

Fig. 1. Wallace H. Carothers stretches a sample of neoprene synthetic rubber, one of two major innovations that resulted from his fundamental studies of polymerization at Du Pont. The other one was nylon.

Stine sent one of his assistants, Hamilton Bradshaw, to Cambridge. In Bradshaw, Carothers found a kindred spirit. They must have talked about the intellectual challenges offered by polymer research and the kind of support that Du Pont promised. Also, Bradshaw must have raised the salary offer. Ten days later, Carothers decided to join the Du Pont Company (*14*).

While finishing the semester at Harvard, Carothers began to contemplate his work at Du Pont and for the first time actively began to consider polymers (*15*). Writing to Bradshaw shortly after accepting the Du Pont position, Carothers set down his ideas about polymerization. His discussion contains the basis of the classic polymer research that he did at Du Pont. At this time, chemists were debating whether polymeric substances were held together by the same forces that operate in smaller molecules or whether some other kind of force peculiar to these substances was involved. In the 1920's, Herman Staudinger began to publish articles asserting that polymeric molecules are practically endless chains held together by ordinary chemical bonds. Carothers espoused this point of view and proposed a way to prove it. As he wrote Bradshaw, "I have been hoping that it might be possible to tackle this problem from the synthetic side. The idea would be to build up some very large molecules by simple and definite reactions in such a way that there could be no doubt about their structures. This idea is no doubt a little fantastic but after all, [Emil] Fischer synthesized an [eighty carbon unit] peptide" (*16*).

Carothers's Work at Du Pont

Carothers moved to Wilmington in February 1928, and his correspondence indicates that his new situation pleased him. He wrote to his closest friend and fellow chemist John R. Johnson:

> A week of the industrial slavery has already elapsed without breaking my proud spirit. Already I am so accustomed to the shackles that I scarcely notice them. Like the child laborers in the spinning factories and the coal mines, I arise before dawn and prepare myself a meagre breakfast. Then off to the terrific grind arriving at 8 just as the birds are beginning to wake up. Harvard was never like this. From then on I occupy myself by thinking, smoking, reading, and talking until five o'clock.

More seriously but enthusiastically, he continued (*17*):

> Regarding funds, the sky is the limit. I can spend as much as I please. . . . Nobody asks any question as to how I am spending my time or what my plans are for the future. Apparently it is all up to me. So even though it was somewhat of a wrench to leave Harvard when the time finally came, the new job looks just as good from this side as it did from the other.

Carothers talents and interests included art, sports, politics, and music, and he quickly made many friends in Wilmington. Almost everyone liked and admired him. Carothers appeared to be a stereotypical odd-ball genius only to those who did not know him well. (*18*).

Seeking to resolve the controversy regarding polymerization, Carothers proposed to build long-chain molecules, one step at a time, by carrying out well-understood reactions between standard kinds of organic chemicals. He chose one of the simplest reactions to test his hypothesis: alcohols reacting with acids to form esters. He added a new twist, though. Carothers reasoned as follows: If each molecule has only one alcohol or acid group, then one reaction is all that can occur. But if the molecules have one group capable of reaction on each end, then the molecules can continue to react, building up a long chain in the process (*19*).

Carothers thought of using this esterification reaction during his first visit to Du Pont upon learning that the company made resinous polymers for paints by a similar process (*20*). Reacting compounds with alcohol groups on each end with analogous acids, he made polyesters that contained up to 25 alcohol-acid pairs and had molecular weights between 1500 and 4000.

Studying these and other related types of compounds, Carothers produced a thorough, logical, and massively documented case showing that polymers were just ordinary molecules, only longer. As his co-worker Julian Hill later recalled, this work "finally laid to rest the ghost . . . that polymers were mysterious aggregates of small entities rather than true molecules." Carothers published his findings in a landmark paper on polymerization in *Chemical Reviews* (*21*).

By the end of 1929, Stine felt that his fundamental research program had been "marked by excellent progress," since "publication of results has occasioned favorable comment from numerous sources, and several of our men are earning increasing recognition in the scientific world." Also, his group leaders were acting as internal consultants in their special fields. However, the so-called "academic era" of fundamental research at Du Pont would soon come to an end (*22*).

The Miraculous Month

Within weeks of each other in April 1930, chemists in Carothers's group unexpectedly produced neoprene synthetic rubber and the first laboratory synthesized fiber. These results were not the stated or implicit goals of Carothers's research, but in retrospect, the discovery of the fiber was the more predictable outcome of the experiments then in progress.

Neoprene was discovered incidentally during a project initiated to study the chemistry of an unusual compound, a short polymer consisting of three acetylene molecules, divinylacetylene (DVA). Several years earlier, researchers in Du Pont's Dyestuffs Department had tried unsuccessfully to make synthetic rubber from DVA. In early 1930, Carothers was asked to explore its chemistry by the new assistant director of the Central Chemical Department, Elmer K. Bolton, who as director of research for the Dyestuffs Department had originally obtained the rights to the catalyst needed to make this compound. While preparing pure DVA, one of Carothers's assistants, Arnold M. Collins, discovered an unexpected and unknown impurity. When isolated, this new liquid, later called chloroprene, polymerized spontaneously to give a rubber-like solid—neoprene. While others in the company developed neoprene into a commercial product, Carothers and his associates systematically determined the chemistry of chloroprene and related compounds. This work resulted in 23 papers that Carothers described as "abundant in quantity but a little disappointing in quality" (*23*). They were not nearly as significant as his work on condensation polymers that eventually led to nylon.

Another member of Carothers's research group, Julian W. Hill, discovered a synthetic fiber while attempting to produce superpolymers, that is, chains longer than anyone had ever prepared. At the end of 1929, the polymers built by Carothers and his group seemed to have hit a size limit at molecular weights between 5000 and 6000. After considering several factors that might be halting chain growth, Carothers decided that the water formed by the reaction could create a chemical equilibrium and stop the reaction (*20*). The key to building longer molecules, then, was to find some way of removing that water. At a conference several years earlier Carothers had heard of what now seemed like the appropriate device—a molecular still. After constructing a modified version of this instrument, Hill began heating an unusual acid-alcohol pair. He and Carothers had decided that the reaction of a 16-carbon-chain with a short, 3-carbon-chain alcohol would promote the formation of longer molecules. While removing a sample of the resultant product from the still, Hill observed that the molten polymer could be drawn into fibers, and then, after cooling, these pliable filaments could be stretched or "cold drawn" to form very strong fibers. Further tests on the sample showed that it had a molecular weight of over 12,000, far beyond any condensation polymer prepared previously.

Encouraged by this result, new combinations were tried. Enough polymer was made to evaluate the so-called 3-16 polyester and other related ones. These polyesters proved to be unsuitable for textile fibers, primarily because they melted below 100°C. Because theoretical considerations indicated to Carothers that the polyamides would melt at higher temperatures than polyesters, he and Hill tried to make fibers from a few compounds of this type. Nylon is a polyamide, but in 1930 Carothers and his group failed to produce satisfactory fibers with their new techniques. (Only later was it shown that a sample prepared in July 1930 would have yielded a strong nylon fiber.)

Given these negative results and some theoretical speculation, Carothers decided that polyamides probably would not make good fibers and instructed his assistants to prepare polymers containing mixtures of polyamides and polyesters. These experiments produced no fibers with outstanding properties. Carothers expressed little concern about this failure; his theories had all proven correct and his interests were heading in other directions (*24*). By this time, however, the invention of neoprene and promising but impractical synthetic fibers helped alter Du Pont research management's expectations of its fundamental research effort.

After the promotion of Stine in June 1930, Bolton played a major role in the reorientation of the program (*25*). Bolton had joined Du Pont in 1915 and was intimately involved in the company's struggle to become a profitable dyestuffs producer. As research director of the Dyestuffs Department in the 1920's, Bolton had become adept at quickly converting research results into commercial reality. Most of the time he was under considerable pressure to do this "in the shortest time with the minimum expenditure of money." Bolton's longtime boss in the Dyestuffs Department, Willis F. Harrington, later recalled that he frequently greeted Bolton with the question, "What have you to show in the way of accomplishment today to justify your existence? Why should your research organization be continued?" Bolton, apparently suspicious of fundamental research in industry, had opposed Stine's program at its inception (*26*). Now it was his responsibility.

Unlike Stine, Bolton wanted to direct or manage fundamental research closely to give Du Pont competitive advantages. In his opinion, the company could not afford to allow an elite group of chemists to pursue purely theoretical results since in both academia and industry "every field of chemistry is being searched for new ideas that can be harnessed to practical applications" (*27*). Whereas Stine had maintained that fundamental research was justified by the scientific prestige that it would bring to Du Pont, Bolton emphasized Stine's fourth and originally nonessential reason, "practical applications." Whereas Stine envisioned fundamental research as the scientific rationalization of existing chemical technology, Bolton saw it as the necessary first step in the creation of new industries. Bolton's administration of the fundamental research program differed from Stine's in one other important respect. When Stine created the program, the nation's economy was expanding and appeared healthy; when Bolton succeeded Stine, the Great Depression had begun to affect thinking throughout Du Pont.

As the economic situation deteriorated in 1932, Bolton tightened the reins on the fundamental research groups. By this time, they had begun to devote much more time to applied subjects. Generally, the elite group of chemists that Stine had set up in Purity Hall were losing their special status. In his 1932 annual report, Bolton stated that "our research program as a whole, particularly our fundamental and pioneering applied research, has been materially revamped with the object of effecting a close relationship between the ultimate objectives of our work and the interests of the company" (*28*). This change had not gone unnoticed. Carothers had already begun to complain about the new order of things.

When Carothers decided to publish his synthetic fiber findings, he encountered opposition from Bolton's new assistant, Ernest B. Benger, who had been a rayon research manager. Like Carothers, Benger did not expect anything of practical significance to emerge from the studies of linear polyesters, but Benger acknowledged that "on the basis of the possible great importance of the work, if successful, . . . I have taken the attitude that the work should not be published and that our position should be protected by a well planned patent program." Carothers responded to Benger by suggesting that he had made, unilaterally, a rather important change in policy and remarked that he was now uncertain about the future course of his work on polymerization. To clarify matters, Benger looked up Stine's original documents, which stressed the importance of publication, and sent them to Bolton (*29*). Carothers waited another year before submitting his paper for publication; in the meantime, Du Pont filed a very broad and admittedly weak patent application (*30*).

Carothers had a better opportunity to express his concerns when Bolton requested a summary of the first 5 years of the fundamental research program with "special reference to its relevance to the commercial interests of the company." After listing the activities and accomplishments of his group, Carothers wrote a thoughtful answer to his own rhetorical question, "What is fundamental research?" (*31*). He stated that before accepting Du Pont's offer, he had come to the conclusion, "through considerable conversation and correspondence" with Stine and Bradshaw, that fundamental research was pure research with its object to increase the body of scientific knowledge and that "any financial profit that might accrue would be so much gravy." In terms of its scientific contributions, his group had been very successful, Carothers asserted, but his "understanding of present policy toward fundamental research is that it is expected to pay its own way." Although his group had not generated any direct profits, it had initiated some developments that might pay off with returns many times the original investment. Nevertheless, Carothers had formulated his program on the assumption that scientific results were the singular goal. "If I had been asked to do research on anything that I pleased with the mutual understanding that the object was to develop something that would bring in a direct profit, I should never have accepted the job," he argued; furthermore, "there are certainly people that do have this ability, but I think that they are rather rare, and I doubt that there are any on the present fundamental research staff."

The "pay-your-way" signals that Bolton was sending out to the groups in Purity Hall, Carothers contended, were causing a great deal of confusion and anxiety. He wrote, "The only guide we have for formulating and criticizing our own research problems is the rather desperate feeling that they should show a profit at the end. As a result, I think that our problems are being undertaken in a spirit of uncertainty and skepticism without any faith in a successful outcome or even without any clear idea of what would create a successful outcome."

In conclusion, Carothers suggested that to put things back on the right course, fundamental research should be guided by scientific, not commercial, considerations. He was skeptical that "pure research in chemistry can be made to pay any direct and sizable returns." In his opinion, pure science researchers should keep the company up to date on the latest analytical techniques and equipment, perform quick evaluations of ideas, and act as internal consultants for problems anywhere in the company. And if changes were necessary, then Du Pont should scale down but not eliminate its effort. After all, he argued, the company spent a considerable sum of money each year supporting academic research; similar work in-house should be at least as productive. Bolton did not take this advice, but Carothers continued his pursuit of pure science.

Following his theoretical interests in the mechanism of polymerization, Carothers moved his research away from linear superpolymers, which formed fibers, and toward the study of cyclic compounds consisting of between 8 and 20 carbon-atom rings. These compounds had been exceedingly difficult to synthesize before Carothers found that they could be made by heating linear polymers in the molecular still. This technique permitted him to determine the effects of molecular geometry on bonding and explain the paucity of naturally occurring compounds containing 9- to 15-member rings (*32*).

This work on large ring compounds completed Carothers's classic researches on polymerization and marked the end of his major scientific studies. He soon began casting about for new research areas and even briefly considered leaving Du Pont. Upon hearing of James B. Conant's election to the presidency of Harvard, Carothers dashed off a note to Roger Adams asking him to inquire if he might be considered for the position of professor of organic chemistry. Carothers shared his intellectual discontent with Adams: "problems in this period have fallen into an unsatisfactory, indefinable class, they are neither theoretical nor practical. . . . I haven't any confidence about practical problems, but enough nice theoretical ones have turned up during the past two years to last a long time." Ten days later, he wrote Adams asking him to forget this "brainstorm that flew over rather quickly." Besides, he had just bought a house so that his parents, who had been hard hit by the Depression, could move from Iowa to Delaware. And he had too many loose ends to tie up, especially in the matter of getting things ready for publication (*33*).

Nylon

Bolton saw Carothers's vacillation over research topics as an opportunity to encourage him to renew work on synthetic fibers. After a period of sporadic activity, the fiber work had come to a halt in the middle of 1933. Following Bolton's request, Carothers again began to think about new approaches to a practical synthetic fiber (*34*). He reasoned that the obstacles that blocked the pathway earlier could be overcome by starting with a long-chain amino ester. On 23 March 1934, he suggested to one of his assistants, Donald D. Coffman, that he attempt to prepare a fiber from an aminonanoic ester. After 5 weeks spent preparing this compound, Coffman quickly polymerized it. One day later he pulled silk-like fibers from the molten polymer. Work at the laboratory bench then shifted to a systematic canvassing of diamine-dibasic acid pairs to determine which ones gave the best combination of properties. By the spring of 1935, Carothers had decided that the polyamide made from pentamethylene diamine and sebacic acid, called 5-10 nylon because the amine and acid have 5 and 10 carbon chains, respectively, was the best candidate for a synthetic textile fiber. Bolton, however, insisted that the high cost of its basic raw materials and its relatively low melting point overrode any other advantages the 5-10 polymer might have. He favored 6-6 polymer, which could be made from a cheap starting compound, benzene, even though 5-10 could be much more easily manufactured and spun into fibers (*35*). With Bolton's decision to push the development of the 6-6 polymer, all other objectives of Carothers's group were abandoned. While confronting the myriad difficulties involved in developing an entirely new technology, Carothers became pessimistic about the future of fundamental research at Du Pont.

Before rejecting an offer to become chairman of the chemistry department at the University of Chicago, made when the nylon work had reached "an exciting stage," Carothers carefully considered the advantages that he would have in a university and no longer enjoyed in industry: "complete freedom in the selection of problems and the aiming of the work directly toward scientific contributions." At Du Pont he felt that the choice of problems had become limited and he now had to "regard scientific contributions as an occasional and accidental byproduct. . ." (*36*).

Carothers did not live to see nylon become the tremendously successful product that it quickly proved to be. He died before it was even announced to the public. Not long after Coffman prepared the first polyamide fiber, Carothers had an unusually severe attack of depression. Despite psychiatric care, his attacks became more frequent and severe during the next 2 years, culminating in the summer of 1936 in a major breakdown from which he never recovered. Personal problems, including the sudden death of his favorite sister, compounded his difficulties. Finally, on 29 April 1937, 3 weeks after the basic nylon patent had been filed and 2 days after his 41st birthday, Carothers committed suicide with cyanide in a Philadelphia hotel room (*37*). In the years just before his death, Carothers had become obsessed with the idea that he was a failure as a scientist (*38*).

Elected to the National Academy of Sciences in 1936 and a potential Nobel Prize candidate, Carothers stood with a select few, very near the pinnacle of his profession. Adams described Carothers as "the best organic chemist in the country" (*39*). Bolton stated that "Carothers read from the depths of organic chemistry such as I have never seen." Yet it seems unlikely that, had Bolton been the chemical director in 1927, Du Pont would have initiated a fundamental research program or any research program sufficiently attractive to recruit Carothers. Stine's contribution to Du Pont research was not just deciding to pursue fundamental research but to package it in an appealing way.

Bolton's New Research Program

Carothers's illness and the manpower needs of nylon development gave Bolton the opportunity to bring Stine's fundamental research division back into the fold of Du Pont's standard industrial research practice. Soon, it was "reported, reviewed, supervised, and administered in much the same manner as other lines of work." Du Pont no longer recruited personnel exclusively for fundamental research. Chemists were shifted back and forth between applied and fundamental research subjects. There were no longer any specially designated groups (*40, 41*). Since each research group in the central research laboratory could now do some fundamental research, Bolton essentially democratized the "radical" program that Stine had set up in 1927.

The case of nylon, however, suggests one important fact often overlooked in studies about basic research in industry. Stine's fundamental research program proved to be necessary to attract Carothers to an industrial laboratory. But had Carothers been left entirely to his own work, as Stine had envisioned, nylon—and perhaps neoprene—would probably not have been discovered and developed. Bolton, the chemist with an industrial mind-set, played a critical role in the transformation of scientific theories into important innovations. Clearly, tension existed between the idealist Carothers and the pragmatist Bolton, but nylon emerged from this tension. Ironically, Carothers agreed to work for Du Pont only after repeated assurances that he would not be expected to produce tangible results. However, the Great Depression, Stine's promotion, and the early commercially promising discoveries combined to prevent Carothers from the scientific career that he desired.

References and Notes

1. On Langmuir see G. Wise, *Technol. Cult.* **21**, 408 (1980); L. S. Reich, *ibid.* **24**, 199 (1983). A more complicated case is that of Thomas Midgley at General Motors. Midgley established his reputation at G.M. with the discovery that tetraethyllead suppressed knock in automotive engines. In 1926, when rubber prices soared to over $1 per pound, Midgley began investigating the structure and composition of natural rubber, with the goal of finding the key to making a satisfactory synthetic rubber. Two years later the G.M. management stopped funding this research. Midgley continued this work part-time at Cornell, spending the remainder of his time at G.M. In this period, he devoted several weeks to the study of refrigerants, which led to the development of Freon. Although remaining an executive in G.M. subsidiaries, after 1930 Midgley moved his research to Ohio State University. At G.M., Midgley was free to work on projects with specific goals, but the corporation proved unwilling to support sustained research on more scientific long-range studies [S. W. Leslie, *Bus. Hist. Rev.* **54**, 480 (1980)].
2. See R. M. Joyce, *Natl. Acad. Sci. Biogr. Mem.* **54**, 51 (1983).
3. L. du Pont, *The Future of Industrial Research* (Standard Oil Development Company, New York, 1945), pp. 65–66.
4. C. M. A. Stine to the Executive Committee, "Pure science work," 26 December 1926, Acc. 1784, Box 16, Hagley Museum and Library (HML); H. Hoover, *Mech. Eng.* **48**, 6 (January 1926).
5. C. M. A. Stine to the Executive Committee, "Fundamental research by the Du Pont Company," 31 March 1927, Acc. 1784, Box 16.
6. The Executive Committee "approved in principle" Stine's proposal on 6 April 1927. M. D. Fischer, "Fundamental research by the Du Pont Company," Advice of Action of the Executive Committee, 7 April 1927. Stine discussed funding in C. M. A. Stine to the Executive Committee in "Expenditures for fundamental research during the year 1927," 16 April 1927. (Notes without complete specification refer to Du Pont Company–held documents.)
7. R. Adams, interviews by J. B. Mellecker, 20 November 1964, 12 February 1965, and 15 March 1963, tape 2, side 2, Adams Papers, Box 9, University of Illinois Archives (UILA); H. Gilman to A. P. Tanberg, 10 September 1927, and Tanberg to Gilman, 13 September 1927, Acc. 1784, Box 16.
8. A. P. Tanberg to R. C. Fuson, 24 March 1928, Fuson Papers, Box 1, UILA; L. F. Fieser to J. B. Conant, 26 November 1927, Conant Papers, Box 5, Harvard University Archives.
9. W. H. Carothers to P. G. Beery, 4 April 1932. He read books such as R. K. Duncan's *The New Knowledge: A Popular Account of the New Physics and Chemistry in their Relation to the New Theory of Matter* (Barnes, New York, 1905). Adams wrote, "He expresses himself in writing as well as any scientific man I know regardless of field; he is exact, concise, and has a pleasing style. If I am in doubt about any of my own manuscripts . . . I prefer criticism from Carothers on the scientific reasoning involved as well as in the mode of presentation to that of any other man." R. Adams to F. Woodward, 8 November 1934, Presidential Papers, Box 101, Folder 3, University of Chicago Archives.
10. On Carothers's activities at South Dakota, see A. M. Pardee to R. Adams, 19 February 1938, Adams Papers, Box 54, UILA. For Carothers's papers see *J. Am. Chem. Soc.* **46**, 2226 (1924).
11. For biographical information about Carothers see R. Adams, *Natl. Acad. Sci. Biogr. Mem.* **20**, 293 (1939); J. W. Hill, *Proceedings of the Robert A. Welch Foundation Conferences on Chemical Research 20, American Chemistry Bicentennial*, W. O. Mulligan, Ed. (Welch Foundation, Houston, 1977).
12. The job was offered in a letter, from C. M. A. Stine to W. H. Carothers, 20 September 1927. Carothers replied on 23 September 1927. Another exchange of letters (26 September 1927 and 9 October 1927) led to Carothers's rejection of the offer.
13. W. H. Carothers to A. P. Tanberg, 13 October 1927. Possibly out of concern for Carothers's mental health, Illinois offered him a position in the spring of 1927. J. B. Conant to R. Adams, 8 March 1927, Conant Papers, Box 3, Harvard University Archives.
14. W. H. Carothers to H. Bradshaw, 31 October 1927. There is no evidence that Du Pont raised its salary offer. However, in his project proposal, Stine gave $5,000 as the average salary for assistants and from $8,000 to $15,000 for group leaders. Since Carothers did ask for more money, and Stine had offered him a very low figure, Du Pont probably raised its offer. Carothers's decision surprised Adams since he had written that he was contented at Harvard (R. Adams to J. B. Conant, 17 October 1927, Conant Papers, Box, 5, Harvard University Archives).
15. Carothers later stated that he had begun thinking about polymers shortly before his first visit to Du Pont in September 1927, and "in a rather vague way planned some experiments" (*20*). He made a similar statement four years earlier (*31*). Stine later wrote to Adams that Carothers's interest in polymerization was "one of the principal reasons why I wanted to employ [him]. He had been giving thought and study to polymerization and polymeric molecules" (C. M. A. Stine to R. Adams, 2 December 1938, Adams Papers, Box 54, UILA). Independent of the origin of his ideas, Carothers was strongly encouraged by Stine and Bradshaw to study polymerization (A. P. Tanberg to W. H. Carothers, 16 November 1927).
16. W. H. Carothers to H. Bradshaw, 9 November 1927. For the history of this controversy over polymers, see Y. Furukawa, thesis, University of Oklahoma, Norman (1983).
17. W. H. Carothers to J. R. Johnson, 14 February 1928, Acc. 1842, HML.
18. Adams mentions Carothers's broad interests in his memoir of Carothers.
19. Carothers first wrote out his ideas to Stine in detail in "Proposed research on condensed or polymerized substances," 1 March 1928.
20. W. H. Carothers to A. P. Tanberg, "Early history of polyamide fibers," 19 February 1936.
21. Carothers called the new molecules "condensation polymers" to distinguish them from those formed from double bonds, which he called "addition polymers" [J. Hill in (*11*)]; W. H. Carothers, *Chem. Rev.* **8**, 353 (1931). Earlier he had published a similar paper [*J. Am. Chem. Soc.* **51**, 2548 (1929)].
22. The quotes are from C. M. A. Stine to the Executive Committee, 15 January 1930. The phrase, "academic era," was used by L. G. Wise and N. G. Fisher ("History, activities, and accomplishments of fundamental research in the Chemical Department of the Du Pont Company, 1926–1939 inclusive," 14 August 1940, p. 15).
23. Carothers made this statement in (*31*). For a detailed account of the discovery of neoprene see J. K. Smith, "The ten-year invention: Neoprene and Du Pont research, 1930–1939," *Technol. Cult.* (January 1985).
24. Carothers summarized this work in (*20*): "In retrospect it seems that the decision not to make further immediate attacks on the amides was rather foolish. But there were several factors involved: The aminocaproic acid polymer should have been a relatively favorable case but apparently failed; we suspected that the . . . [viscosity] . . . was so high that [the] reaction stopped prematurely; we had had some previous experience with polyamides . . . and were impressed with the unexpectedly low molecular weight of the products and the difficulty of doing anything with them [because of their insolubility and high melting points]."
25. In this era, Du Pont's Executive Committee did not concern itself with the internal operation of the departments. It approved budgets, mediated disputes, and established broad policies. For this and personal reasons, Stine appears to have left the management of the Chemical Department entirely to Bolton. Stine became increasingly preoccupied with publishing articles and making speeches extolling scientific research in industry.
26. Harrington's recollection is in Acc. 1813, Box 2, HML. Stine pointed out Bolton's opposition because Adams's draft of Carothers's biographical memoir read as if Bolton had initiated fundamental research at Du Pont. C. M. A. Stine to R. Adams, 2 December 1938. On Bolton, see (*2*).
27. E. K. Bolton to the Executive Committee, 14 January 1931.
28. ———, *ibid.*, 6 January 1933.
29. This controversy is discussed in E. B. Benger to E. K. Bolton, "Fundamental research policy," 7 November 1930.
30. By filing an application so early in the project, Du Pont could not make very specific claims, so the patent that it received (U.S. Patent 2,071,350) was a weak one.
31. W. H. Carothers "Fundamental research in organic chemistry at the experimental station—a review," 5 August 1932, Acc. 1784, Box 16.
32. See J. Hill in (*11*); see also H. Mark and G. S. Whitby, Eds., *Collected Papers of Wallace Hume Carothers on High Polymeric Substances* (Interscience, New York, 1940). On the practical side, these compounds turned out to have an odor similar to that of musk. Du Pont prepared a few hundred pounds of one such compound but had difficulty selling it.
33. W. H. Carothers to R. Adams, 10 May 1933 and 21 May 1933, Adams Papers, Box 7, UILA.
34. In his 1936 review of his work on polyamide fibers, Carothers wrote, ". . . in early 1934 I decided it was worth one more effort . . . " (*20*). The evidence that Bolton encouraged him to take another look at fibers comes from bonus recommendations for the nylon development. Then Vice President Stine prepared a statement on Bolton's contribution to nylon in which he said, "In January or February 1934 Dr. Bolton told Dr. Carothers that he wanted Dr. Carothers to think again about synthetic fibers . . ." (C. M. A. Stine, " 'A' Bonus Memorandum," 8 May 1941). In a similar document, Bolton asserted that "in 1934, Carothers was encouraged to reattack the problem of developing a synthetic fiber based on superpolymers" (E. K. Bolton to L. A. Yerkes, 27 June 1941). Twenty years later, Bolton, in an oral history interview, claimed to have continually prodded Carothers to take another look at fibers. Then, Bolton stated, "he came in one day and said, 'I think that I have got some new ideas' " (E. K. Bolton, interview by A. D. Chandler, R. D. Williams, and N. B. Wilkinson, 1961, Acc. 1689, HML).
35. The two problems Carothers faced were (i) the intractability of the molecular still and (ii) the melting points of polyamides were apparently too high for them to be spun into fibers by existing technology. To solve the first problem, Carothers thought that a superpolymer could be prepared without using the still if he used a carefully purified amino acid ester. To lower the melting point, Carothers suggested using a long-chain acid (*20*): he chose aminonanoic ester, $H_2N(CH_2)_8CO_2C_2H_5$. Coffman recorded Carothers's initial instructions in a laboratory notebook. Central Chemical Department Laboratory Notebook No. 1293, p. 39. The experiments are recorded in Notebook No. 2150, pp. 140–146. The so-called 5-10 polymer was first prepared in July 1934. Carothers's group concentrated on preparing every conceivable combination. Nylon 6-6, from hexamethylene diamine and adipic acid, was prepared by Gerard Berchet on 28 February 1935 (*20*). The chemical reaction to make a polyamide is

$$H_2N(CH_2)_xNH_2 + HOOC(CH_2)_yCOOH \rightarrow [HN(CH_2)_xNHCO(CH_2)_yCO]$$

For nylon 5-10, $x = 5$ and $y = 10$; for nylon 6-6, $x = 6$ and $y = 6$. On 11 July 1935, Bolton decided to push 6-6 because benzene, which is a 6-carbon ring, was available in large quantities. At this time the 10-carbon dibasic acid came only from castor oil (see C. M. A. Stine, " 'A' Bonus Memorandum," 8 May 1941).
36. W. H. Carothers to R. M. Hutchins, 4 November 1934, Presidential Papers, University of Chicago, Box 101, Folder 3.
37. In late July 1934, Carothers lost all his interest in chemistry during a nervous collapse, (W. H. Carothers to R. Adams, 22 July 1934, Adams Papers, Box 7, UILA). In June 1936, he suffered a major nervous breakdown and spent 5 weeks at the Philadelphia Institute, (W. H. Carothers to J. R. Johnson, 9 July 1936, Acc. 1842). In September, Carothers returned to work to start

some new work "in the field lying between organic and inorganic chemistry, and perhaps involving the newer but less fanciful ideas of valency" (W. H. Carothers to J. R. Johnson, 21 September 1936, Acc. 1842). He never seemed to be able to get going, though. The death of his sister, Isabel Carothers Berolzheimer on 7 January 1937, dealt him a severe blow from which he never recovered [see R. Adams in (*11*)]. The date of her death is erroneously listed as 1936. Her obituary was in the *New York Times* of 9 January 1937. What precipitated Carothers's suicide is not known. His obituary was in the *Wilmington Journal Every Evening* on 30 April 1937.
38. Carothers's obsession that he was a failure has been noted by many of his friends and associates. His psychiatrist in Philadelphia concurred in this assessment. I. H. Carothers to R. Adams, 2 December 1937, Adams Papers, Box 54, UILA.
39. See E. K. Bolton, interview, in (*34*); R. Adams to F. Woodward, 8 November 1934, in (*9*).
40. See L. Wise and N. Fisher in (*22*), pp. 15–17.
41. We thank the members of our Du Pont and Academic Advisory Committees for their criticism. Thanks also to L. B. Gortler.

RESEARCH ARTICLE

Mainbelt Asteroids: Dual-Polarization Radar Observations

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Abstract. *Observations of 20 asteroids in the main belt between Mars and Jupiter provide information about the nature of these objects' surfaces at centimeter-to-kilometer scales. At least one asteroid (Pallas) is extremely smooth at centimeter-to-meter scales. Each asteroid appears much rougher than the Moon at some scale between several meters and many kilometers. The range of asteroid radar albedos is very broad and implies substantial variations in porosity or metal concentration (or both). The highest albedo estimate, for the asteroid Psyche, is consistent with a surface having porosities typical of lunar soil and a composition nearly entirely metallic.*

Asteroids comprise an enormous, variegated population of solid bodies and new information concerning them is essential to our understanding of the origin and evolution of the solar system. They may be examples of the first material to accrete from condensates in the solar nebula that existed about 4.6 billion years ago, but some asteroids apparently have undergone varying degrees of chemical differentiation, geologic evolution, and collisional modification. Apart from their scientific significance, asteroids also have economic potential as sources of water, organic compounds, and free metal for the industrialization in space envisioned for the next century.

During the last decade, the number of catalogued asteroids has grown from 2000 to more than 3200, and physical studies of these diminutive objects have expanded dramatically. Observations in the visible and infrared (VIS/IR) parts of the spectrum have demonstrated that the distributions of asteroid sizes and rotation periods span several orders of magnitude and suggest that the compositional diversity of asteroids exceeds that of our meteorite sample. However, asteroids generally cannot be resolved by ground-based optical telescopes and have yet to be examined by spacecraft; and therefore, with very few exceptions, their fundamental physical properties remain poorly known.

Radar observations can provide spatial resolution of a target in a manner that is independent of the target's apparent angular size and, because of the radio wavelengths employed, can also provide information about surface structure at scales much larger than those probed optically but still much smaller than typical asteroid dimensions. During the 12 years after the first radar detection of an asteroid (in 1968), the potential contributions of radar observations of asteroids were realized most fully for the Earth-approaching objects 433 Eros (*1*) and 1685 Toro (*2*). But until 1980, the high signal-to-noise ratios and dual-polarization measurements that yielded useful information about these objects' physical properties were not available for asteroids in the main belt between Mars and Jupiter.

Here we discuss results of 13-cm wavelength, dual-polarization radar observations of 20 mainbelt asteroids, conducted at the Arecibo Observatory in Puerto Rico during 1980 to 1985. Our measurements provide information on asteroid surface characteristics at scales between several centimeters and several kilometers, and also furnish unique constraints on surface bulk density and metal concentration, neither of which is tightly constrained by optical methods.

Observations. Table 1 lists each target's geocentric coordinates for a convenient epoch near the weighted midpoint of the observation dates. Radar system characteristics and our observational, data-acquisition, and data-reduction techniques were nearly identical to those described in (*2*). Echo power spectra were obtained in the same rotational sense of circular polarization as transmitted (that is, the SC sense) as well as in the opposite (OC) sense. Since the handedness of a circularly polarized wave is reversed on normal reflection from a smooth dielectric interface, the OC sense dominates echoes from planetary surfaces that look smooth at the observing wavelength, λ. (A single dielectric interface with minimum radius of curvature $>> \lambda$ would look smooth.) The presence of an SC component can be caused by multiple scattering from smooth interfaces or by reflections from interfaces that are rough at small ($\sim\lambda$) scales. The ratio of SC to OC echo power is thus a useful indicator of near-surface, small-scale "roughness."

Each of our spectra consists of ~400 independent estimates of echo power density at frequency intervals of Δf Hz (Table 1). Figure 1 shows weighted-mean OC and SC echo spectra for our 15 targets with the strongest echoes. Table 1 lists estimates of the OC radar cross section, σ_{OC}, obtained by integrating the power spectra, and of the circular polarization ratio, $\mu_c \equiv \sigma_{SC}/\sigma_{OC}$ (*3*).

Polarization ratio: Small-scale structure. For each asteroid, most of the echo

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