

Invent or Discover

the art of useful science

[Sample Chapter 3: Nylon]

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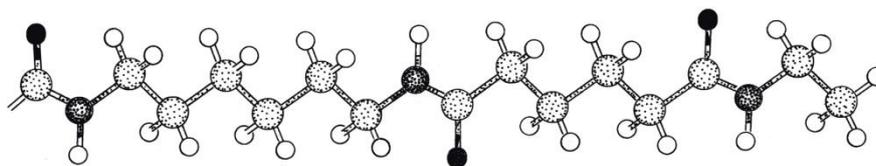
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‘It may be observed that the results described herein furnish a very satisfactory verification of my theory.’

(Wallace Carothers)

Charles Stine, the vice president of du Pont Inc., addressed a gathering of 3,000 members of women’s clubs on the theme of The World of Tomorrow. The venue was New York World’s Fair of 1938. Stine had chosen his audience well: he announced a new textile fiber, made from raw materials such as coal, water and air, transformed into filaments as strong as steel and fine as a spider’s web. At DuPont’s stand in the Fair, fashion models dressed in daring knee-length skirts to reveal their nylon stockings, demonstrated how this new wonder material was tougher than silk. The company had decided to market nylon first to customers for hosiery and textiles; they were following their original strategy of searching for a synthetic substitute for silk. The sales campaign, complete with colossal replicas of a stockinged leg, was so successful that eager customers were soon mobbing the shops.

After the attack on Pearl Harbor supplies of silk from the Far East stopped. Nevertheless, this wonderful new plastic substitute could meet the needs of military mobilization: far stronger and durable than silk, usefully elastic, rot-proof, and easy to clean. Most important of all, it was relatively cheap to make using routine chemical industry stock available in America. Goodbye to nylon stockings for a while; every fiber of nylon made was needed for parachutes, ropes, engineering solids and so on.

This material was something entirely new, not just to so many grateful and admiring customers, but also fundamentally new to technology. Already chemists had developed substitutes for silk: there was viscose fiber made by dissolving wood pulp, transforming the natural cellulose, then spinning fibers from the liquid. But not only was viscose a poor substitute for silk, nobody understood the nature of what it was made of, so the only route to improving it was more trial and error, other natural raw materials and acids, alkalis and solvents off the laboratory shelf to treat them. In those days organic chemists restricted themselves to the simplest carbon-containing compounds and their special characteristics, all amenable to laboratory experimentation. The nature of biological materials such as wool and the proteins of muscle and skin was a mystery fobbed off with a vague explanation of

aggregates of small molecules in the form of colloids. In the 1920s, after 50 years of trial and error development and manufacture of polymer plastics such as styrene and celluloid, colloids were so badly misunderstood that many researchers considered them to be a strange fourth state of matter, along with gases, liquids and solids.

Was there an alternative? Possible the growing theory of macromolecules could help. Its promoters were those who cared far more for large molecules than for what others thought of them. They were convinced the way to test their theory was to construct such a molecule from first principles of chemical bonding, using starting blocks of small simple molecules. Could they prove their theory by synthesizing a radically new macromolecule in the form of a new textile fiber?

DuPont company

The DuPont company originated in France as a manufacturer of explosives, so when it moved to America it flourished by supplying much of the high demand for explosives and gun propellants in that pioneering nation of the late 1800s. DuPont's strategy was to turn cheap raw materials into specialty chemicals of high value for onward sale to manufacturers of finished goods. It was then a family run business and a new generation of directors in a new country decided to diversify to exploit wider opportunities. Viscose fiber was an obvious choice. The American Viscose Company, a subsidiary of Courtaulds Ltd in Britain, was the only manufacturer of viscose as an artificial silk in America in the early 1900s. About 1916 DuPont made a series of complicated deals to buy into this field. In 1924 the viscose fiber was renamed rayon and by 1928 profits were at 33% return on investment per year. Managers at DuPont coupled profits on rayon to the high cost of imported natural silk, a greatly desired commodity that was permanently in short supply because of its laborious production from the cocoons of silk moth caterpillars. They priced rayon at about one third the cost of silk, rather than to its low cost of simple production using wood pulp as raw material.

Despite such pricing, rayon failed as a big earner because fabrics made from it tend toward untidiness unless carefully handled. Rayon remains a good fiber for garments such as skirts styled for drape and sheen. Apart from the competition from other manufacturers, patent protection of the fiber itself had expired, so the only route to better profits was incremental improvement in manufacturing technique. Such options, however, are much harder to patent and this was unfavorable to DuPont's new business strategy. The company bosses sought a trading image based on novel goods for their customers developed from a well publicized technical base and protected by impregnable patents. They had much work ahead to achieve this, but chemical manufacture in the 1920s was booming worldwide so there was enough cash to invest in researchers and laboratories.

This branch of industry was based almost entirely on technological knowledge acquired by slow trial and error testing, starting with imitation of natural products and heading to a more manageable version of the same basic material. The familiar

household and industrial plastic polystyrene dates back to 1839 when Eduard Simon in Germany found by chance a sample of benzoin resin from *Styrax* trees had polymerized into a hard material he named styrol oxide. More deliberately, Alexander Parkes in Britain about 1855 used solvents to transform wood chips into a hard uniform solid that could be molded to smooth shapes. Parkesine it became known as, or later as the more generic celluloid. None of the chemists involved knew the nature of their materials at the molecular or atomic level. Did these new plastics do a useful job was sufficient to ask.

Charles M.A. Stine was director of the Chemical Department at DuPont in 1926. He was well aware of this primitive state of affairs and wanted to advance from trial and error procedures to innovation based on scientific understanding of the nature of these strange substances. Stine moved boldly toward his ambition. He set out to persuade the executive of DuPont to support generously science research within a conventional chemical manufacturing firm. Stine listed four reasons for DuPont to spend its own money on science research: scientific prestige for the advertising value of presenting and publishing papers to the science research community; interesting research would raise morale and make recruiting of scientists easier; results of DuPont's science research could be used to barter for information from others; and that science research might lead to practical applications. Although Stine personally believed that practical results would inevitably ensue, he felt that his proposal was totally justified by the first three reasons.

Charles Stine wanted to change DuPont's approach to research and development away from what he called the 'shotgun method' in which an exhaustive screening effort was made in the hope of finding useful new chemicals. The German chemical industry preferred to describe this approach as massive-scientific-teamwork. During the 1880's the firm BASF (Badische Anilin und Soda Fabrik) tested several thousand potential dyes each year, with only tens of them ever reaching market. The same approach was used in other chemical manufacturing countries and remains routine in many technological fields. Stine identified colloids as a virgin field from a scientific standpoint and wished to recruit highly talented scientists to work on them under conditions of ample pay and resources and much freedom to inquire and publish. His application to an open minded executive board caught their imagination and they responded amply.



Wallace H. Carothers had been the sort of schoolboy who read, at his home in Des Moines, popular science books about wondrous discoveries being made about molecules, atoms and electrons. Books with titles as brave as *The New Knowledge: a popular account of the new physics and the new chemistry in their relation to the new theory of matter*, were being written just after the turn of the century by Robert K. Duncan, professor of chemistry at Washington and Jefferson College. By the time Carothers read them, they were out of date in that very rapidly moving field, but even now they are a wistfully inspiring read, full of awe and optimism, all trenchantly expressed.

Soon Carothers got his hands on some research kit at Tarkio College, Missouri. Arthur Pardee, who had studied under Duncan in Washington, had recently set up there a laboratory in the basement (not the same Pardee as in Chapter 1). Initially Pardee was away completing his doctorate studies and by the time Carothers was in his senior year Pardee had moved back to Washington and Jefferson College. Carothers struggled on with Pardee's job of teaching chemistry. He spent the two years before finally graduating in control of the lab in the basement, with rows of brown bottles, wooden benches littered with retorts, burettes and flasks, permeated with that brew of acrid and aromatic smells lingering evermore. Pardee, however, remembered his most talented student and persuaded him to enroll as a graduate student at the Department of Chemistry of the University of Illinois, at Urbana. Good advice, for this was one of the best in the country.

Furthermore, chemical companies in America were enjoying intensified local demand and government support for strategic reasons during the first world war, when the products of German chemical industry were embargoed. Roger Adams as head of organic chemistry in the department deftly exploited this by persuading students to prepare specialty chemicals for sale to local manufacturers, thus combining instruction with profit. Carothers's university did not expect him to do experimental work for his masters degree but he fell in with Carl Marvel, then a doctoral student, who worked late in the laboratory with alarming concoctions of phenol and bromine using carbon disulfide as diluent. Amid such dangers they calmly mused late into the night about the workings of molecules.

Short of money, Carothers accepted a job as instructor offered by Pardee, who by then was a member of faculty at the University of South Dakota. At last Carothers, now with an inspiration of how to start, could satisfy his yearning for discoveries about molecules. The oily compound diazobenzene-imide was then known by an equivocal atomic formula: both versions of the formula had a benzene ring with six carbon atoms and five hydrogen atoms. Attached to this at one point to a carbon atom were three nitrogen atoms that could be represented either as a straight chain or as a triangle. He compared the physical properties of this compound with a closely similar one of confirmed formula, phenyl isocyanate, which has a similar chain of one atom each of carbon, nitrogen and oxygen. The essence of Carothers's study was the new system for explaining how electrons are associated in groups with atoms and how atoms interact by sharing of these shell-like groups.

The existence of previously hypothetical electrons had been proved twenty-six years earlier by Joseph J. Thomson in Britain. Ideas about how electrons acted within molecules were being proposed by Gilbert Lewis of the University of California and Irving Langmuir of the General Electric Company at Schenectady, New York State. Carothers's first published research paper, in 1923, set out his investigation for his peers. He found that the three nitrogen atoms of the imide group must be held together by two double bonds, as are the nitrogen, carbon and oxygen atom of the isocyanate group.

For the first published paper, by an instructor with a masters degree working on a short contract in a minor department, this was ambitious stuff. He went straight to the crucial procedure for contributing to a verification of the hottest chemistry topic. He made a precise prediction based on the theory; he chose simple materials and methods to test the prediction, and did that repeatedly and accurately. He demonstrated his intention to operate at the core of his subject, asking how nature works, not what it looks like observed from the margins. He wanted to know how these strange entities called electrons inside compounds hold together or push apart the constituent atoms.

Carothers re-enrolled at Illinois to complete his doctorate studies on catalytic reductions, which he wrote up in a perfunctory publication in the same year as his diaminobenzene paper. He continued at Illinois for two years as a faculty assistant. The fertile imagination of Carothers was inspired by the hot topic of how electrons might be arranged around the nuclei of elements like shells, and that much of chemistry could be explained by interactions between different shells of eight electrons (now the Lewis-Langmuir octet rule). Carothers strayed way beyond the empirical studies of Adams and Marvel. One year later, 1924, he published a paper titled with the carefree boldness of youth: 'The Double Bond.' His style was splendidly direct: 'In this paper it is proposed to show how this idea together with other specific assumptions of the octet theory may be used to account for the reactions of the double bond.'

Scientists in those days enjoyed the luxury of writing in plain language, unburdened by modern fashion for gobbledygook. This eleven page tour de force in the primary journal of American chemistry must have brought him to the attention of every academic chemist in the country, even if they had missed his first paper. Carothers was a man with a mission already heading down the path of a fundamental change in chemistry. But for a missionary Carothers was sometimes strangely ambivalent about what to do next. He needed a job, so accepted a teaching position at Harvard despite his poor performance in the lecture theatre at South Dakota. Only one modest published paper resulted from his two years there.

Macromolecules

Ambitious researchers in chemistry learnt German to keep up with the trends created by the dynamic schools and companies of chemists in Europe. Carothers specially wanted to read the prolific output the organic chemist Hermann Staudinger, of the University of Freiburg im Breisgau, southwestern Germany. Staudinger had started work in 1912 at the Technical University of Zurich where he studied simple molecules of low molecular weight. When he moved to Freiburg fourteen years later he boldly concentrated on polymers; substances reputedly of high molecular weight that were generally ignored by academic chemists at that time. They disdained investigations on such materials as 'grease chemistry'.

What was the problem with these colloids and so called polymers? Most chemists did not believe they were composed of molecules of very high molecular weight,

and some of them would tenaciously deny the existence of such molecules every time the proposition was raised. Historical context is useful for us now to understand this. In 1858 the Swiss botanist Carl Nägeli described the grains of starch that he observed through his microscope as molecules or micelles and this led to the proposition that organic materials with colloidal properties such as albumin and cellulose, so common in living organisms, were aggregates of these micelles held together by some unstated force. Progress in this field was hampered by the difficulty of dissolving, crystallizing and determining the molecular weight of colloidal substances. The renowned German chemist Emil Fischer, for example, was highly skeptical of the claim that the blood protein hemoglobin had more than the minimum molecular weight (as indicated by multiplying each of the ratios of individual elements by their atomic weights and then summing them, which for one specific type of hemoglobin equals 16,709).

Routine methods of determining the molecular weight of small molecules, derived from the osmotic pressure or the depression of freezing point of solutions of the molecules, become difficult because the larger the molecule the smaller are these effects. Nevertheless, by 1900 there could be found at least eight papers describing estimations of the molecular weight of organic substances ranging from 5,700 to 32,400. Even the evidence from the powerful new technique of analyzing the patterns made by diffraction of X-rays when passed through crystals was failing to resolve this conflict. Studies done by the Austrian researcher, Herman F. Mark who was then working on polymer production for the German chemical firm I.G. Farben, had led to the conclusion that the molecules could not be larger than the crystalline unit cell determined by the X-ray technique. Mark summarized the situation many years later, after completing a career in polymer chemistry at the Polytechnic Institute of Brooklyn, in New York. He contrasted Staudinger's concept of organic molecules that were extremely large, relative to the concepts of proper size and behavior of organic molecules that were promoted by famous chemists.

The conventional thinking was simply that this idea of the macromolecule was unnecessary. Evidence from studies by Michael Polanyi in 1921 and R. Brill in 1923 for example, on the crystalline structure of the common organic molecule cellulose, indicated strongly that the elementary crystalline component, the unit cell, defined the limit of the size of individual molecules of cellulose.

Give credit to the skeptics for their pragmatism. Their disdain for grease chemistry, for slimy biological colloids, is entirely understandable in its historical context. There were no laboratory methods and instruments developed specifically for studying these materials; in contrast to a wide range of well tried means of increasing knowledge about how simple, orderly, molecules work. Why struggle with questions unless simple enough to be formulated as a hypothesis which can then be tested with existing techniques?

However, the question of that colloids actually were, if not representing a special state of matter, had been tackled by various workers since the turn of the century. In Britain, Gilbert Adair obtained from measurements of the osmotic pressure

exerted by hemoglobin, the red protein of blood, a molecular weight four times larger than the usual estimate. In Sweden, Theodor Svedberg and Herman Rhinde took these proteins so seriously that they became engineers, inventing a large and complex machine to study them. This was an ultracentrifuge; it subjected substances to extremely high gravitational forces, from 5,000 times the force of gravity then, now up to hundreds of thousands. Their paper on this and an improved version, replete with detailed engineering drawings of their handiwork, are thought-provoking reads for most modern scientists, used to ordering everything ready made from catalogues. They showed that hemoglobin settled out as a distinct zone in the liquid preparation, indicating it had a uniform particle size and not a range of sizes that an aggregate would show. The Swedish workers calculated in 1926 a value for hemoglobin using equations that balanced the rate at which the hemoglobin was driven away from the centrifuge spindle with the rate at which it diffused back toward the spindle: a molecular weight 68,000. Now, Max F. Perutz and fellow workers have confirmed the hunch of Adair through decades of intense study using the technique of X-ray crystallography. Hemoglobin is a tetramer, comprised of four repeats of the basic unit indicated by the empirical formula, hence this higher molecular weight.



As soon as Charles Stine received agreement of the Executive Committee for his program of science research at DuPont he set about hiring chemists with established reputations. He failed. They did not want to work in industry; not even for the higher salaries, better resources and promise of freedom of enquiry in academic style. Stine asked Roger Adams of the University of Illinois to join; he asked James B. Conant of Harvard University. Gradually it dawned on Stine that prejudice of academics against mere industry was a strong emotion in those days and that the higher the status of the academic the more prejudiced they were likely to be. This even applied to those scientists with strong links to the industrial applications of their research findings; links that have always been common in the development of chemical science and technology. Stine tried to hire Louis B. Fieser, an associate professor of organic chemistry at Bryn Mawr College. He tried to recruit Reynold C. Fuson from the University of Illinois. By 1928 Stine and Tanberg had recruited only one of the scientists of the 15 that they had budgeted for.

They changed tactics, asking around for chemists with recently completed PhDs who were recommended by their supervisors as showing exceptional promise. Wallace Carothers disliked lecturing at Harvard and was unproductive there as a researcher, but by then he had made a name for himself with his two seminal papers. Enticed along to DuPont, he enthused about the fundamental work being done by Staudinger on rubber. This was a simple example of a substance that Staudinger had demonstrated as an almost endless chain held together as a flexible whole by ordinary valence forces between its constituent atoms. Carothers tentatively proposed to tackle this problem of the nature of polymers by synthesis experiments. He would build very large molecules by well defined reactions between known simple starting blocks, so that there could be no doubts about the

resulting structure. Charles Stine understood that fundamental work on polymers could contribute to DuPont's need for an improved synthetic silk. He must have been relieved to hire a scientist in tune with his own ideas. Carothers arrived at the headquarters of DuPont in Wilmington, Delaware, early in 1928. Within a year he was joined by 20 or so scientists, most of them with recent PhDs.

Carothers was galvanized when he found himself with brand new laboratories, new staff, a generous budget for equipment and reagents, and a good library. How could he prove Staudinger's hypotheses on the structure of polymers? He anticipated a reaction from mixing simple well understood carbon containing substances. Molecule A with two reactive groups on it, as xAx . Molecule B, having two different reactive groups, yBy , to be mixed with xAx . Would he get $xABx$ as a new compound? If so, it would probably form a small ring as the x and y groups at the ends of a short chain like this reacted together. Carothers also knew, however, that large rings, anything much more than six carbon atoms, are unstable. If he started with other substances D and E that contained more carbon atoms, when they joined the reactive groups x and y at the ends would be far enough apart to not fuse into a ring but to undergo the energetically more conservative linear reaction of $xDEDEDEy$. Would this lead to $xDEDEDEDE . . . DEy$ and so on for a very long way? Ideal substances for this experiment Carothers knew to be alcohols reacting with acids to form esters; or more specifically, glycols and dicarboxylic acids mixed to polymerize as polyesters. He set his team of chemists the challenge of synthesizing a polymer of molecular weight higher than the 4021 that Emil Fischer had achieved in Germany. Fischer knew this precise weight because he had synthesized the polymer from measured quantities of small molecules of known composition and thus the molecular weight of the polymer could be calculated directly from the constituent atomic weights.

This was a research opportunity that most can only ever dream of and Carothers and his workers, in the laboratory that soon was nicknamed Purity Hall by others on the site, proceeded to astound the world of chemistry with a chain of papers describing such experiments in a way to vindicate the hypotheses of Staudinger. '*Studies on polymerization and ring formation. I. An introduction to the general theory of condensation polymers*' was published in 1929, through to number VIII in 1930. Charles Stine had carefully created an environment that was as conducive to science research as possible within a private manufacturing company. Stine had little difficulty in finding support for this way of improving business and the general managerial ethos at that time was conducive to cultivation of research freedom.

DuPont deliberately maintained a strong and decentralized departmental structure to encourage initiative. This inevitably resulted in competition between departments, which the top executives tolerated or even encouraged. This tension between centralization and decentralization has been analyzed as being greater in the research and development departments of DuPont than in any other area. The driver of this conflict was considered to be the autonomy that the researchers always sought for their work and the situation was compounded by the disparity between the semi-private objectives of the researchers with often unclear or

conflicting objectives of the managers at DuPont. Probably as a result of the departmental autonomy, there were incentives to do good research and development: 10% of individual budgets could be spent on projects that were essentially private and not part of main supervised projects; pay was substantially better than at universities and better than most competing commercial companies; there were bonuses in form of company shares for both exceptional work and for outstanding service.



During the first world war, Germany desperately needed rubber for the tires of its strategic transports, but supplies of natural rubber were blockaded. However, the vast German chemical industry was capable of several methods to synthesize rubber from simpler chemicals such as isoprene. Alternatively, they could use a process, invented in Russia in 1901 by Ivan Kondakov, which started from the similar building block called dimethyl butadiene to polymerize into polybutadiene. These early synthetic rubbers were adequate for some uses but poor substitutes for robust tires. Wallace Carothers knew about isoprene rubber from his studies of the German research papers, and DuPont's technical managers knew there was a potentially vast market for tough synthetic rubbers.

Elmer K. Bolton was one of these managers, he became the new head of the Chemical Department when Stine was promoted in 1930, and thus the boss of Carothers and his team at the Experimental Station. Bolton's previous remit at DuPont had been to direct research on synthetic rubber. A pragmatic industrial chemist at the best of times, now Bolton, along with DuPont and their customers, faced tough times indeed with impending economic depression in America. He made it clear to the science researchers, the Virgins of Purity Hall, that they were expected to be inventing profitable products more urgently than seeking understanding of how the natural world works.

In DuPont's Rubber Laboratory, researchers knew how to make butadiene building blocks into polybutadiene synthetic rubber, but butadiene itself was difficult. They looked for alternatives and in a series of outside collaborations with Julius Nieuwland, a researcher at the University of Notre Dame, Indiana, they developed vinylacetylene as an intermediary; this they easily hydrogenated to form butadiene. By chance Gerard Berchet, a Frenchman whom Carothers had persuaded to come to the Experimental Station several years previously, left a sample of vinylacetylene in a flask together with hydrochloric acid. Berchet, it seems, forgot the sample in the flask and his assistant Arnold M. Collins later found it. Meanwhile the mixture had transformed into a white mass of rubbery consistency. With difficulty, Collins extracted it from the flask to find he could bounce this amazing stuff along the bench. The mixture had polymerized into polychloroprene.

Without delay, DuPont patented the process to produce a completely new type of synthetic rubber. They gave it the trademark Neoprene, which remains now a well known specialty rubber with a high resistance to dissolution by oils and petrol that natural rubber does not possess. The workers at the Experimental Station had a

patentable, newsworthy and profitable product to show to the world. However, the scientists, especially Carothers, were less impressed. The discovery had been an accident, pure serendipity. In essence, this new rubber could just as well have resulted from a mass screening program. In stark contrast was their ambition to cut through as much of the laborious empiricism of mass screening as possible by rationally designing new materials from first principles.

Meanwhile the more intellectually challenging study of polyesters continued. Could they beat the record molecular weight synthesized by Emil Fischer? Could they exploit the limited knowledge available to predict what sort of polymer would result from a calculated combination of starting acid and alcohol? Julian W. Hill and James Arvin belonged to the group working through a large number of experimental combinations; empirical screening still had its uses. A complication of the condensation reactions was that they produced water as a by-product. This inhibited further polymerization so the molecule could not elongate and its weight remained low. How could they dispose of this contaminating water?

Hill adapted an age-old technique. He assembled a complex glass apparatus in which the polymerization reaction occurring in a small open dish heated by electricity. Above this dish was a glass vessel with its flat base just above the reaction mixture and the glass was cooled by water circulating within the vessel. Everything was contained within a sealed glass sphere, about the size of a melon. From the hot reaction mixture water easily evaporated off, and when condensed on the cooled glass was removed from further inhibition of the reaction. They called the construction a molecular still.

Hill tried this apparatus with a new combination of alcohol and acid: he mixed propylene glycol with hexadecamethylene dicarboxylic acid and heated them. They called the resulting polymeric material polyester 3,16 using a naming system they had devised, based on that particular glycol having 3 carbon atoms and that acid having 16 carbon atoms. Soon they measured its molecular weight at 12,000; three times the previous record! Furthermore, they detected glycol and dicarboxylic acid groups in the polymer, proving that chains had been formed, not rings. This was more like the rational design of their ambitions.

Carothers described this in the first of his series of papers on polymerization; leading to not only a convincing corroboration of Staudinger's hypotheses but to increasing the predictive power of the understanding of these reactions. His method was strikingly simple compared to Staudinger's indirect approaches. The combination of normal small molecules using well known reactions of organic chemistry was very likely to produce polymers of great chain length that had known structure and constitution. He could predict the structure, and then examine the new molecule to test if it confirmed prediction. Demonstrating the presence or absence of the end groups of the chains was usually sufficient. Carothers also was able to predict that condensation polymers were much better candidates for fiber production because they tended to form linear chains and thus much more likely to be crystalline than the amorphous addition polymers.

There was more to come: the type of unexpected observation that comes only to the prepared, to the dedicated researcher at the bench either tinkering with a new variation, or in this case simply doing a routine manipulation that resulted in something new. The secret is to realize its significance. Julian Hill needed to remove a sample of polyester 3,16 from a reaction vessel. He used a glass rod, and on withdrawing the rod the polyester pulled out as a strong thread. The thread would keep on coming as long as the researchers pulled on the remaining polyester and they soon noticed that if they pulled harder on the fiber the slightly dull and cloudy substance would thin out at a specific point, a neck, to form a thinner and lustrously transparent thread that was even stronger.

The fiber looked like silk, but it was stronger and more durable than silk. They had synthesized it from ordinary chemical stock. No silkworms munching on mulberry leaves, no wood pulp dissolved in acid or alkali. This was what their paymasters were hoping for: pure and controllable fibers of high value that could be synthesized in huge quantities from cheap chemical feedstock. DuPont soon had Carothers and their patent experts working to file for broad protection of their intellectual property. They filed a pair of applications in 1931, eventually granted in 1937.

Synthetic fiber

Euphoria of discovery and invention was short lived for Carothers and his team. They demonstrated superbly the necessary chemical principles but their fiber was doomed commercially. Its melting point was less than heat from a domestic iron and it dissolved easily in dry cleaning liquids. Elmer Bolton increased the pressure on Carothers now that commercial synthetic fibers were seen to be feasible. Obviously, what they needed was a polymer of higher melting point and lower solubility. It is one of the great ironies of this story that Carothers and his workers had come extremely close to that goal already, but discarded the crucial initial findings in the rush to achieve predictable and controllable high molecular weight polymerizations.

Early on in the work at the Experimental Station, Edgar W. Spanagel had performed one of the many alcohol-acid esterification reactions. He used ethylene glycol as the alcohol and phthalic acid as the diacid and obtained a glassy resin of molecular weight 4,000; too low to be of much interest. In the resulting polymer, the diacid groups formed a sharp kink aligned at 60° to each other. This prevented the formation of a polymer suitable for fibers. Carothers wrote up the reaction, along with 18 other polyester reactions in a purely descriptive paper. Then in 1940, two researchers in the laboratories of the Calico Printers Association in Britain, J.R. Winfield and J.T. Dickson, took a closer look at this reaction. They found a way to make a closely similar polyester, without the kinks in the chain, by using terephthalic acid, which is an isomer of phthalic acid. They had invented polyethylene terephthalate. Soon people throughout the world knew it as Terylene; manufactured by Imperial Chemical Industries in Britain and then under license by DuPont, who promoted it as Dacron. This polymer, as fiber and moldings, remains

the most successful of them all in terms of the bulk manufactured and numbers of different firms now producing it.

The other irony was an error of commission in one of the series of papers on polymerization. Carothers, Berchet and others during early days of the Experimental Station had tried the polymerization of an amino acid, 6-aminocaproic acid. They obtained a polymer of low molecular weight as a grey waxy mass. In addition, they obtained a second product that consisted of a cyclic molecule: caprolactam. Carothers concluded, for chemists of the world to read, that there is not a reversible relationship between the lactam and the polyamide.

At the time chemists in competing companies might have been surprised at such an admission; a naive mistake from an employee of DuPont, unnoticed by the patent experts checking the draft papers of the company's researchers before granting permission to publish. In 1930 the context of knowledge was insufficient to raise any further interest in this reaction. A reputable scientist from a major company claims that a particular polymerization is impossible – strange thing to do – but so what?

However, the context was to change radically. In 1937, during the preparations for the public fanfare about the invention of nylon, DuPont had been in other negotiations with I.G. Farben and told them about their new invention, fully confident of the protection from their very broad patent. Patent lawyers and chemists in the German company quickly found the statement, now astonishing, about the lactam that could not polymerize. Within a year, chemists at I.G. Farben successfully rose to the challenge. They exploited the gap left in the patent protection for polyamide that DuPont had so jealously tried to guard all for themselves. The I.G. Farben chemists found a way to open up the cyclic lactam so it polymerized as a linear polyamide that was equal in every practical respect to DuPont's nylon. The German company had no problem patenting their polyamide because Carothers had declared the reaction impossible, thus patent examiners deemed it not to be covered by DuPont's patent. They gave the name Perlon to the new polyamide.

Profits from the original polyamide were permanently reduced for DuPont, although they remained large enough by any standards. The culprit for this impending loss was seen to be the liberal publication policy of the Chemical Department. Senior managers soon changed the policy by reasserting commercial pragmatism more suitable for an environment of increasing economic and political fears. Records reveal the story: from 1924-28 there were 7 papers produced at 0.12 per researcher; for 1929-33 (after Carothers joined) there were 114 papers at 1.2 per researcher; by 1939-43 this had dropped to 13 papers at 0.12 per researcher and it took until the 1950's and 1960's for these two measures to equal the original spurt of productivity from the Experimental Station.

Despite Carothers's growing success at DuPont it seems he still hankered after academic life and fitted poorly into the commercial atmosphere of DuPont, the more so when the utilitarian Elmer Bolton became his boss and persuaded him to

turn from discovery to invention. Carothers had been operating substantially as if in different economic and social system, free to admit to his international peer group of organic chemists that he thought a particular reaction impossible.



Silk is a natural polyamide: a protein produced by the caterpillars of silk-moths who spin enormous lengths of it to form a fibrous cocoon around themselves for protection during their transformation into adults. Proteins are polymers with their constituent molecular groups joined by amide bonds. Chemists knew then that polyamides could be synthesized by reacting a diacid with a diamine, and that amide groups are chemically similar to ester groups. The prospects for making a polyamide suitable for forming into fibers were promising. Carothers predicted the team could synthesize such polymers to have a suitably high melting point by adjusting the number of carbon atoms between the amide groups in the macromolecular chain. Carothers, Berchet and Hill had made experimental polyamides in their first year at the Experimental Station but the product they obtained, starting with aminocaproic acid, had a melting point that was too high for practical use; they could not draw fibers from the charring hot mass.

Their goal was to synthesize a polyamide with lower melting point whilst retaining a molecular weight of at least 10,000 for good properties of fiber formation. The polyester 3,16 had many carbon atoms between its functional end groups and it had a melting point too low. Carothers predicted that starting with molecules with more carbon atoms than the five found between the functional groups of aminocaproic acid, in their first attempt at a useful polyamide, should lower the melting point. Aminononanoic acid, with eight carbons in the right place was the subject of their first experiment. Carothers directed Donald D. Coffman to try this, but additionally with a trick of starting with the ester of aminononanoic acid so that instead of the troublesome water molecules being produced as a harmful waste product, ethanol would be produced as an inconsequential by-product. They would have no need of the molecular still; a difficult thing to scale up for mass production. Coffman took more than a month just to prepare the starting materials. Thereafter he promptly synthesized a new polymer that melted at 200°C and was resistant to dry cleaning liquids. Moreover, they could spin it into fibers and then stretch or cold-draw them to form a strong, flexible, durable and lustrous artificial silk. According to their naming system this was polyamide 9.

This new polyamide showed tremendous promise: the basic chemistry was robust and open to many rational manipulations. They soon found, however, that improvements were necessary because the starting amino acid was too expensive and the polymerization process was difficult to control for a consistent range of molecular weights. In 1934, Wesley R. Peterson joined Don Coffman to work on new pathways for synthesis of polyamides. Peterson insisted, against the advice of Carothers, that instead of the diester pathway used for polyamide 9, it would be best to use the diamine plus diacid reaction because it would be easier to control the reaction by starting with a precise proportion of 1:1 of these two monomers. This was more difficult than it sounds if done by mixing then heating them together

to polymerize. Small residues of unreacted monomer in the polymerizing mass spoiled the required properties. Peterson invented the alternative of simply mixing cold the acid and base monomers and leaving them to neutralize each other to form their chemical salt. Automatically the product was in the exact proportion required. By a purification step, they removed excess of either monomer from the salt, which was then heated to stimulate polymerization. The process was so effective that the chains grew long enough to raise the viscosity of the resulting polymer too high for processing into fiber. Again Peterson used a procedure disapproved of by Carothers, a deliberate contamination with acetic acid to terminate the growing chains to give a molecular weight of about 10,000 with a suitable viscosity when molten.

Soon they produced polyamide 5,10 from the reaction of the 5 carbon pentamethylene diamine the 10 carbon diacid known as sebacic acid. This new polymer had nearly all the properties they were looking for in early experimental batches. Larger batches provided material to melt for spinning into a fiber that seemed good for textile manufacture, although the melting point was still too low for ironing of fabrics. Carothers and his team were pleased and possibly too content with this; prepared to let the chemical engineers get to work with expanding the process and for textile experts to improve its manufacture into fiber. Elmer Bolton, however, was more skeptical; he was paid to understand and operate within the wider commercial constraints. Castor oil was the source of the sebacic acid monomer for reacting with the diamine to make polyamide 5,10. Agricultural crops of castor seed plants were not his idea of a source of cheap and readily available feedstock for a chemical factory. Bolton insisted that Carothers look for an alternative reaction.

Tension grew between these men, of very different temperament and approach to the chemical industry. Could it have been, nevertheless, crucial to the process of invention? Carothers was by this time already finding himself drawn away from the impending phase of product development by his obsession with how atoms and molecules join to make macromolecules. He knew that satisfying Bolton's demands would involve a long and tedious plod through a series of combinations of diamine and diacid each with from 2 to 10 carbon atoms; a total of 81 combinations from the plausible monomers available. For this task, the predictive power of their understanding was insufficient to narrow down these many variations any further. They were back to the heuristic approach: try it and see, then try again, and again. The job was delegated to Gerard Berchet, who was keen to make something work after missing the crucial observation that led to Neoprene rubber and the failure with the caprolactam pathway to polyamide 6.

On the 28 February 1935, Berchet wrote in his laboratory notebook, an essential document to support claims for patenting: 'Adipate of hexamethylene diamine. 7 g. diamine, 8.8 g. acid and 20 cc. m-cresol heated 215° for 3 hours. Water came off during the first half hour. The temp. was then raised to 255-260° and the cresol distilled off in vacuum. The residue solidified at one time but then melted again at 265°. It was heated under 1 mm at 265° for 3 hours. On cooling (overnight) the polymer broke the flask by contracting and showed a tenacious adherence to glass.'

It was a very hard, horny solid melting at 252-254°. It was very readily spinnable. Sample turned over to D.D.Coffman. There was obtained 12.5 g. of polymer, yield 90%. 3/1/35 GJB . . . ' Harry Dykstra witnessed and signed this entry on 21 March.

They had made hexamethylenediamine adipate, or polyamide 6,6 to use its common chemical name. It had properties almost as good as polyamide 5,10 although the melting point was now disappointingly high. How were they to handle a polymer that required such high temperatures to keep it molten? Since it had such low solubility in all feasible industrial solvents, the method used for viscose of making a solution for spinning was not an option. The only option seemed to be forcing it through the spinning machine whilst molten. Bolton kept faith in his commercial judgments: both monomers were easily synthesized from the organic solvent benzene, a very common industrial chemical readily distilled from petroleum oil or even made from coal. He insisted that all future development concentrate on this polymer. By 1937 DuPont were able to file for a patent titled 'Synthetic fiber' and this was granted in 1938.

This rapid development from invention to product in the market place was due to the efforts of at least half the team in the Experimental Station and others in the Chemical Department in a full assault on the practical details of manufacture. The hexamethylene diamine, although it could be synthesized from benzene stock, was only available as a research reagent; to make it in bulk required much work on new catalysts. Edgar W. Spanagel made a crucial contribution. He found the diamine evaporated off the hot reaction mixture and spoiled the balance of the reaction. Instead of using the traditional glass reaction vessel, they had to use one of metal, in other words an autoclave, which allowed high pressure as well as high temperature. This in turn required a solution to the problem of heat transfer. If they heated the reaction vessel from outside then polymer would form nearest the walls and delay the polymerization of the monomers in the center, leading to inconsistent product.

They devised a radical answer by dissolving the salt formed from the two monomers in water, then heating this solution within the autoclave sufficiently for polymerization. At this temperature, the water would violently boil and so keep the material thoroughly mixed during polymerization. On release of the pressure, the unwanted water steamed off. The necessities of chemistry at manufacturing scale had taken the scientists a long way from the molecular still on Julian Hill's laboratory bench. When the polymerization reaction was complete, the nylon was produced as chips, ready for melting at 285°C, followed by spinning. They had to design new machinery to handle the molten nylon and then they found that as the nylon was forced through the tiny holes, called spinnerets, bubbles formed in the melt and these led to breaks in the forming fibers. They solved that problem by keeping the molten nylon at high pressure to compress the bubbles back into the liquid. The entire spinning machinery occupied three floors of the factory: from chip hopper at the top, down to the melt oven and spinnerets, pulled through rollers at high speed, cold-drawn along the way through rollers at different speeds, finally to the wind-up bobbin. From the start of the research on polymers at the Experimental Station to the invention of polyamide 6,6 took eight years; to develop

nylon to the point where it could be commercially launched locally in 1939 took another five years.



With the invention of polyamide 6,6 DuPont knew they were unlikely to face competition immediately. They spent large sums providing their researchers with access to the latest literature; the bills for sending technical managers and senior researchers to chemical industry meetings and academic conferences were probably higher. They had all manner of collaborations with their competitors; by word of mouth they knew better than from searching the literature that their polyamide developments were probably five years ahead of anyone else. Furthermore, protected by a comprehensive and strong patent, they could devise simple manufacturing methods that would suffice economically as long as they could produce sufficient material to meet anticipated high demand. This was especially true because the demand was for an improved version of a highly desired domestic product of high value. A better silk, possibly a cheaper silk. Or failing that a type of silk that could be woven into clothes that would resist creasing and dirt, or knitted stockings that would not unravel into ladder-like runs. Something durable in those cost-cutting days.

The strategy of the marketing experts at DuPont was simple. First, discretely test it in the market – disguised as a new type of toothbrush bristle. Hopefully that would satisfy a hidden demand from customers who had little alternative but clean their teeth with brushes made from animal bristles – soggy unhygienic items. Meanwhile, DuPont involved hosiery manufacturers with the troublesome business of adapting existing silk spinning and knitting procedures to use the new material. Then they had to dream up a name for what the chemists called ‘fiber 66’. No-run was offered but rejected because it was not strictly true; the new material did run although not nearly as readily as silk. Nuron, after rayon, was offered but sounded too much like a nerve tonic. Nilon sounded better, except it could be pronounced three ways. Nylon: that was it, simple and unequivocal. So confident were DuPont of the sweeping success of their invention that they expected the commercial name to become a common household name, so ignored registration for trademark. Nylon rapidly gained the status of a generic name, used routinely in chemistry textbooks.

Charles Stine, by then the vice-president of DuPont, officially announced the invention of nylon at the New York World’s Fair in 1939, where an audience of 3000 members of women’s clubs gathered. White coated boffins explained the new miracle fiber invented by DuPont alongside fashion models clad in stockings and short skirts (well, knee length in those modest times), who played tug-of-war with samples of the wares to demonstrate their elastic good fit and toughness. This was in the days when scientists and engineers were national heroes, able to produce a cornucopia of new domestic goods and appliances. Those were the days long before the word plastic was stretched far enough to include a pejorative meaning. Standard policy of DuPont on marketing new products was to persuade customers to change from an accepted product of a competitor to a hopefully improved

product by stressing that their product was a fruit of science and technology. Boffins in white coats amongst the mysterious paraphernalia of the laboratory were minor heroes. Not that the ladies needed any persuasion by gentlemen in white coats of the merits of nylon stockings. Customers besieged stores selling them; newspapers reported nylon riots.

The fatal day that Japanese forces attacked Pearl Harbor signaled the end of supplies of silk, mostly from Japan, as the sea routes from the whole production area were enveloped by a huge war zone. For DuPont, America and her allies, nylon could not have been developed at a better time. DuPont directed all efforts on nylon for mass production to meet the huge and urgent demand for a wide variety of fabrics, cords and ropes, and a light, tough unreactive solid that could be machined.



The University of Chicago offered the chair of a new department of chemistry to Carothers in 1934, a potential fruit of his growing reputation. He turned it down, explaining to the principal of the university that he had exciting developments at DuPont. In 1935, he was busy with as much theoretical work on the nature of polymerization as he could manage, now that he was becoming a celebrity as the inventor of Neoprene. He had a new colleague in such studies, Paul J. Flory, a physical chemist with a newly awarded PhD and superior talent at mathematics than Carothers. DuPont hired Flory and assigned him to the Experimental Station. Flory was asking why it was not possible to give a precise molecular weight to a polymer, what was the statistical pattern of the lengths of the myriads of chains of carbon, hydrogen, nitrogen and so on? Carothers anticipated a fascinating dive into the mysteries of atomic and molecular forces defining the extraordinary behavior of these new fibers.

Furthermore, the Faraday Society, in Britain, had invited Carothers to one of their prestigious meetings, to be held in September 1935 in the University of Cambridge, on Phenomena of Polymerisation and Condensation. He knew that Staudinger, Mark, Meyer and many other peers would be there. He knew that other delegates would regard him as a star performer but he also feared his poor abilities as a lecturer and his unease in a crowd. Rather than lead the team developing fiber 66 he was content to leave the job to Bolton. Instead he made time to push his mind deeper and deeper between the interstices of his molecular chains and crystals, between the functional groups, the bunches of hydrogen atoms around a carbon, the buzz of electrons in their shells – or were they in clouds?

The proceedings of the Faraday Society covering that meeting are an evocative read. There were assembled on the one hand Hermann Staudinger and Wallace Carothers and supporting acolytes; promoters of the new hypotheses of normal valency to explain these incredible macromolecules. Whilst on the other hand were Kurt Meyer, Herman Mark and others who still clung desperately to colloids. At that late hour they still promoted what they called the New Micellar Hypothesis to explain aggregates of molecules in ordinary colloids. The papers are clear, simple

and forceful. The ample and fully transcribed discussions were vigorous, contentious, and mostly went in favor of the macromolecule men.

This was, nominally, the best moment of Carothers's public career. There he was, in that febrile pre-war atmosphere, in Europe amongst his German speaking peers, talking molecules and electrons, with the knowledge of a hugely profitable invention about to be revealed, with offers from prestigious universities to follow. He speculated in his paper about his second big idea; that proteins are the macromolecules to look at, that something about their theoretical limitless scope for variation holds a key to understanding the nature of living things. He had the idea that proteins could only work in living organisms if they related to some other physical substrate to hold them in place whilst they formed in the shape necessary for them to have precise biological function. Carothers in 1935 was starting out on a mental adventure that would take others, within two decades, to the discovery of the structure of DNA and the natural synthesis of proteins.

Yet something was awry. Wallace Carothers, the shy researcher, up there on the heights gazing out over a vista of grand and fascinating opportunity, made only one short contribution to the debates. He avoided the conference photograph, he went off by himself for a desultory holiday in Paris. Two years later he died by his own hand. Elmer Bolton was to write of him: 'Carothers read from the depths of organic chemistry such as I have never seen. I think that he is the smartest organic chemist that the DuPont company ever had.'



Wallace Carothers operated in two worlds. Well documented are the strains of this balancing act on his on his personal and intellectual life. Of those worlds, the one he preferred from the start and always gravitated back to, is unfamiliar to most outsiders looking in on the business of research and invention. The other world is the wider one of business, trade and profit that most people are familiar with from their work or transactions with shops and commercial services. Careful observers of science know the former world as a gift economy; certainly an indigestible concept for conventional business methods and economic theory. Gifts indeed – don't be daft! In obvious contrast, the economy of trade and commerce is for profit, or at the very least money must be made in order to keep the business going, whatever the mission statement written by the public relations department may state.

Carothers in the academic world of his early university posts in Missouri, South Dakota, Illinois and Massachusetts, operated in a gift economy. As long as his employers were prepared to provide him with an adequate salary and facilities, he could afford to operate in this parallel world. The benefit to the universities was diffuse and vague. Some teaching maybe, or do you think you would you be more effective in the laboratory? Whatever the answer, universities need staff who can meet the expectations of their students for teachers who also do the research that later appears consolidated into textbooks. Otherwise the students might as well go direct to the textbooks in the library.

What gifts did Carothers have to offer in this strange economy? Not inventions, for they are too rare and chancy a commodity for maintaining the business of being an autonomous scientist building a reputation. Moreover, it takes more than the usual stock of university laboratory equipment to make a plausible push toward the invention business. Carothers offered information. That is the basic commodity for entry into a gift economy as researcher: the potatoes and corn. In return for the gift is given recognition: the cents and pennies. Recognition from other researchers almost exclusively: unlikely from either family or friends who would only vaguely understand, or from an employer typically unaware of what had been offered.

Recognition is a scarce resource, best gained by the quality of the knowledge offered. Carothers was ambitious, so he offered more than just information, he offered knowledge in that first paper of his on the structural formula of diazobenzene-imide. That in turn contributed to growing understanding amongst other chemists of a particular way of molecules combining. That was worth more than cents and pennies; it was also worth collateral benefits, an offer of a salary, laboratory, office and library at a university of the highest prestige.

Despite his lack of immediate success at Harvard, Carothers remained a reluctant recruit to DuPont. Offers of better salary, facilities, running costs and opportunities were unattractive to him and many like minded chemists because what they sought most of all as researchers was autonomy of action coupled to the satisfaction of recognition from members of their peer-group. The primary and tangible gift of the researcher to his or her peer group is of course the research paper. They offer this freely to the publisher who makes an ordinary commercial profit whilst the researcher often has to pay for its printing and distribution from the research fund. The point for the researcher is that the details of how the work was done, the results and the conclusions to be drawn, are made internationally available to anyone else both with access to the journal and in possession of the same specialist knowledge and skills.

Usually the audience of other researchers, those who will read such a paper as a matter of necessity and routine, is counted in surprisingly low numbers. A typical research peer group consists of 100 to 150 members, about the limit for remembering their names and reading their papers. The larger the group the more fissile it is likely to be, with spontaneous splits into problem areas that are parallel but sufficiently distinct to justify a smaller group. The constraint on size seems to owe more to psychological factors that may derive from our long past – successful bands of hunter-gatherers perhaps.

A commercial publisher appears to conventional economics as winning both ways with this bizarre transaction: typescripts arrive free and unsolicited, then the scientists who wrote the papers persuade their institution to pay for the journals in which to read papers written by their competitors. The spontaneous but strict social rules of the gift economy, however, ensure that the author retains moral rights over the original data and interpretations in the paper. These are not to be confused with what are formally called intellectual property rights, which belong to the separate

realm of profit economies and whose enforcement requires lawyers. Moral rights in the gift economy are far cheaper to enforce by the unspoken threat of exclusion from the peer group.

Moreover this strange gift economy is not in such natural conflict with commercial and industrial imperatives as it might seem. Successful technological companies often operate as what are called second-movers, that is they derive their specialist knowledge and methods for manufacture from both openly available literature and the tacit information available through discussion and guessing of other's knowledge. First-movers are obviously those that innovate and invent independently. Such a business strategy requires skilled and experienced researchers to understand what is going on at the frontier with all its uncertainty.

Access to scientific knowledge is not cheap despite its appearances; to gain entry into the meaning of the information requires the same sort of ticket as to a scientific peer-group: contributions to research that can be offered in a gift economy. Thus for both the first-movers and the second-movers, science research in the firm's own laboratories has long been a successful strategy. The result is, in America for example, about 10% of research papers in the open literature coming from industry. The result is that fundamental scientific research of the highest quality is done in industry and openly published. Sometimes it results in the required innovations and inventions; usually it is likely to give the collateral advantages that Charles Stine so clearly promoted to the directors of DuPont. Sometimes it has unintended consequences, but more tales of that in later chapters.

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