

The history of nylon

Prof. L. Trossarelli

Dipartimento di Chimica IFM dell'Università di Torino, Via P. Giuria 7 Torino, Italy

1. Introduction.

Ever since it first came on the market, nylon's many uses have greatly influenced most facets of our daily lives, including mountaineering. The story of how it came into being, however, must be preceded by a few words about its place in the chemical world.

Nylon is a polymer obtained by the condensation of diamines with bicarboxylic organic acids, or from omega-amino acids. In more specific terms, it is a polyamide, i.e. one of a class of polymers whose molecular chains are formed by regularly spaced -CONH- amide groups. Like all polyamides, nylon is produced by step polymerisation in (the molecular mass increases as a function of reaction time). The characteristic features of each nylon are its structural unit or units (a unit being the residue of the monomers bonded during polymerisation to form the macromolecule), and the average number of units per molecule namely the degree of polymerisation. Since Carothers and his group invented nylon, a nylon or a polyamide has been conventionally accompanied by some figures indicating the number of carbon atoms in the structural unit(s). The first figure shows the carbon atoms of the diamine, the second those of the bicarboxylic acid. The nylon invented by Carothers and known as nylon 66 or polyamide 66, or poly(hexamethylenedipamide), therefore, is read as six-six, not sixtysix, which means that it is composed of two structural units, each with six carbon atoms, namely the residues of hexamethylenediamine ($\text{H}_2\text{N}(\text{CH}_2)_6\text{NH}_2$) and adipic acid ($\text{HOOC}(\text{CH}_2)_4\text{COOH}$). Nylon 6 or poly(6-caprolactam), another important polymer, is composed of a single structural unit, namely the apparent residue of 6-aminocaproic acid ($\text{H}_2\text{N}(\text{CH}_2)_4\text{COOH}$).

The story of the birth of nylon is inevitably intermingled with the duPont de Nemours family and the E. I. DuPont de Nemours Company and its inventor, Wallace Hume Carothers.

2. The duPont de Nemours family and the E. I. DuPont Company.

In the period known as the Terror during the French Revolution, when noble heads were ready fodder for the guillotine, Viscount duPont de Nemours, a banker, fled to the United States with his capital. His family turned their hands to the manufacture of explosives, particularly black powder. In 1903 Pierre Samuel duPont de Nemours took over the business and when smokeless powder was invented, he promptly stopped producing black powder and dynamite and switched to nitrocellulose explosives. The first world war was obviously a goldmine for both the

When the war came to an end in 1918, Pierre Samuel gained control of William Crapo Durant's General Motors and became its president. Under his guidance, GM made giant strides and was soon turning out more cars than its rival Ford.

Irénée, Pierre's brother, took over the presidency of DuPont in 1919. His admirable far-sightedness told him it was time for the company to add another string to its bow by entering the field of what we now call fine chemistry, namely the production of chemicals with a high added value. Explosives of all kinds were to be joined by dyes, drugs and textile fibres.

In 1916, DuPont had acquired Levinstein's dye technologies in England. Even so, it was unable to compete with Germany's big firms when they were once again permitted to export their products to the United State after the war. A short, sharp remedy was sought and found. Lured by very high salaries, five of Bayer's top-level technicians crossed the Atlantic together with their wives, children and servants.

In 1920, DuPont moved into textiles in a joint venture with the French manufacturer *Comptoir des Textiles Artificiels* and set up a rayon factory at Buffalo in the State of New York. Here, too, the profits were enormous because rayon was so much cheaper than natural silk. Nitration of cellulose was not abandoned, however. Explosives were still produced, along with paints, cellophane and photographic films.

It was also in 1920 that DuPont's researchers discovered, quite by chance, that a small quantity of sodium acetate transformed a nitrocellulose gel with a high solid content into a smooth flowing syrupy liquid. This was the beginning of the *nitro* paints, usually called *Duco* (an abbreviation of DuPont Company), employed for car bodies until some twenty years ago when they were superseded by the *acrylics*.

In 1922, Pierre Samuel told his brother Irénée that Thomas Midgley, one of GM's researchers, had invented *tetraethyl lead*, the antiknock agent added to petrol for better combustion and used in premium grade fuel until a few months ago. DuPont's researchers were given the task of working up the process and a production plant.

From what has been said so far, one can readily imagine it was not all that difficult for Dr. Stine, head of DuPont's chemical Department since 1924, to convince the company's President and the Executive Committee in 1927 to put twenty thousand dollars into a project for research in pure science.

At Wilmington, Delaware, this new venture took shape as the company's *Pure Science Section* (jokingly referred to as *Purity Hall*). It was easy enough to find the heads for colloid chemistry researches (Prof. E.O. Kraemer, University of Wisconsin) and for the catalysis group (Dr. G. Taylor, DuPont). As the head of organic research, many voices were raised in favour of Dr. Wallace Hume Carothers, instructor in organic chemistry at Harvard since 1926. And so it was that the path of Carothers, the inventor of nylon, crossed that of DuPont when, on 1 February 1928 and after much anxious heart searching, he finally entered the company's employ.

3. Wallace Hume Carothers.

But who was this Carothers ? Born at Burlington, Iowa, on 27 April 1896, he was a prey to periods of deep depression that in the end led to alcoholism and suicide in a room at the Philadelphia Hotel in Philadelphia on 29 April 1937.

In July 1915, Carothers qualified as an accountant at the Des Moines Capital City Commercial College in Iowa and in the following September entered Tarkio College at Tarkio, Missouri, to follow its courses in science (chemistry, physics, mathematics, etc.). Initially an assistant in the Commercial Department and then in English for the first two years, he moved to the Chemistry Department and in 1920 took his B.Sc. In September of the same year, he joined the Chemistry Department of the University of Illinois and took his M.A. the following summer. During the academic year 1921-22, he lectured on analytical chemistry and physical chemistry at the University of South Dakota. In 1922, he returned to the University of Illinois and started work on his doctoral thesis on the catalytic reduction of aldehydes with osmium oxide under the supervision

of Prof. Roger Adams. He took his Ph.D. in 1924 and joined the university's staff as an instructor in organic chemistry. Two years later, he was offered a similar post at Harvard and quickly stood out as a brilliant organic chemist.

4. Carothers and his research group.

Carothers and his researchers at DuPont had their first success in 1930 when they synthesized polychloroprene. It made its debut on the market as Duprene, and in 1936 it became the familiar neoprene, the world's first synthetic rubber and still unrivalled for many applications, such as O-rings and wetsuits.

Carothers's research team had discovered the tricks needed to produce macromolecules (superpolyesters) with molecular weights of more than 4000, which had once seemed an insuperable limit. They were removal of the small molecule (usually water) formed as a by-product of the polyesterification reaction; need to have a ratio as close as possible to 1 between the reacting carboxyl and hydroxyl groups throughout the polyesterification; the intervention of reactions, which Carothers and his colleagues called transesterification, and. These, however, were laboratory achievements whose practical applications were confined to fibres on which was observed for the first time the orientation produced by what the researchers called *cold drawing*.

By the end of 1931, DuPont had not very much to show as the outcome of its basic research programme. As we have said, its superpolyester fibres were seen as oddities with no hope of a commercial future, while Duprene's full range of uses was still unknown and its chances of competing with natural rubber were hamstrung by the latter's nose-diving prices during the Great Depression in 1929. To make matters worse, Carothers was wont to keep the scientific community informed of all the results of his research in papers published or read at congresses. As events were to show, some things should have been kept under wraps or in the bottom drawer, since their over-hasty revelation enabled others to steal a march on Carothers and his group. Two examples can be cited.

The first concerns nylon 6 or poly(6-caprolactam). In 1930, Gérard Berchet together with Carothers investigated the polymerisation of 6-aminocaproic acid and obtained a low molecular weight polymer together with a cyclic compound they called lactam.

They considered that their line of research had come to an end and announced that lactam did not polymerise under polyamide-forming conditions in either the presence or the absence of a catalyst. When I.G.Farben Industrie's technicians in Germany knew about Carothers' nylon 66, they dug out his paper on 6-caprolactam and very soon (in 1941) managed to synthesise nylon 6, which was sold as Perlon.

If Carothers and Berchet had kept their results to themselves instead of rushing into print, they and DuPont would certainly have managed to produce nylon 6.

The second story runs as follows. One of the earliest polyesters studied by Carothers in conjunction with J. Arvin (1929) was that obtained when phthalic acid is condensed with ethylene glycol. The results were not entirely disappointing, but by no means encouraging. What was produced, in fact, was simply a low molecular weight (about 4000) vitreous resin and the research was abandoned.

Even today, one fails to understand why Carothers and Arvin did not try replacing phthalic acid,

whose two carboxyls are in the *ortho* position, with terephthalic acid, whose two carboxyls are in the *para* position. Had they done so, they would have been the earlier discoverers of poly(ethylene terephthalate), otherwise known as Terylene, the strong polyester fibre perhaps even more widely used than nylon.

Despite the crisis of the early 1930s, rayon continued to sell well. One disadvantage of this artificial silk, however, was that, like its natural silk, its filaments reflect the light, whereas wool, cotton and linen fabrics have a duller look and never dazzle. There was no particular reason for preferring an opaque to a shiny material. The dictates of fashion, however, determined the preferences of the late 1920s and rayon fibres were duly made opaque by the addition of very fine titanium oxide. DuPont was not the first to develop this technique and had to manufacture through licensing agreements with its competitors.

The fact that rayon, whether shiny or dull, had made such gigantic strides over the course of the years led Dr. E. J. Bolton, head of the Company's Chemical Department, to stress the importance of devising an entirely new textile fibre in his end-year report for 1933.

At the beginning of 1934, therefore, Carothers in response to the suggestions of Dr. Bolton took a second look at the polyamides that had given so little satisfaction a few years earlier. A polyamide can be synthesised in the same way as a polyester by intermolecular condensation with either an organic dicarboxylic acid and a diamine or by intramolecular condensation of an omega-amino acid. A water molecule is always eliminated in each condensation step. The degree of polymerisation depends on how the experimenter manages to shift the reaction equilibrium towards the formation of the polymer, which can only be done by removing the water formed by condensation of the functional groups involved in the reaction. The first problem to be solved was how to get over the experimental difficulties this involves.

In their previous work on the derivation of polyamides from 6-caprolactam, Carothers and Hill were unable to obtain fibres from the small amount of polymer they obtained because its melting point was so high that it decomposed before the melting temperature could be reached. Carothers' first objective, therefore, was to produce polymers whose melting point was high enough (obviously higher than that of his polyesters) to enable them to be used as fibres, but low enough to allow them to be processed without decomposing. This in turn posed a second problem. The way to lower the melting point of a polyamide would be to use an amino acid with a large number of methylene groups, since Carothers and Hill had already shown that a very long chain paraffin melts at about 100°C.

There was also the possibility that intramolecular condensations might lead to the formation of cyclic compounds competing with the intermolecular condensations forming the polymer chain. Carothers' work on such compounds had shown that rings with more than 10 atoms are rarely formed. This, too, pointed to the employment of an omega-amino acid whose amine and carboxyl groups were separated by an appropriate number of methylene groups.

Carothers therefore asked one of his coworkers, Dr. Donald Coffman, to prepare 9-aminononanoic acid ($\text{H}_2\text{N}(\text{CH}_2)_8\text{COOH}$), in which eight methylene groups separate the amine and carboxyl functional groups involved in the condensation reaction. He expected that this would give a polyamide whose melting point was low enough to provide fibres without decomposing. In addition, there was very little likelihood that 10-atom cyclic compounds would be formed.

A way for removing as much water as possible, in order to obtain a polymer with polymerisation degree high enough for the formation of fibres, remained to be found. Carothers decided to replace 9-aminononanoic acid with its ethyl ester since this would result in formation of much more easily

removable ethyl alcohol during polycondensation. On 23 March 1934, Carothers asked Coffman to prepare this ester. Between 4 April and 21 May 1934, Coffman was able to obtain some sufficiently pure ester. When he polymerised it two days later, he obtained polyamide 9, a polymer that at first sight had all the features of a high molecular weight product and was therefore a superpolyamide. On 24 May, Coffman heated it in a bath at 200°C, a little higher than its melting point, dipped in a cold glass rod and drew out a strong, not brittle filament that produced shiny fibres when cold drawn.

These fibres were similar to and in some respects better than natural silk and could thus have entirely replaced it. Carothers, however, immediately realised that they would make no headway on the market because the monomer endowed with the degree purity needed to obtain high molecular weights was hard to prepare and handle. He therefore turned his attention to other monomers and combinations of diamines and dicarboxylic acids. By the end of July, Dr. W.R. Peterson had prepared polyamide 5-10, another superpolyamide, by reacting pentamethylenediamine $\text{H}_2\text{N}(\text{CH}_2)_5\text{NH}_2$ (5 carbon atoms) with the ethyl diester of sebacic acid $\text{C}_2\text{H}_5\text{CO}(\text{CH}_2)_8\text{COOC}_2\text{H}_5$ (10 carbon atoms), with the elimination of ethyl alcohol.

Bolton, however, did not really believe that polyamide 5-10 could be turned into a marketable product and continued to urge Carothers to carry out a systematic investigation of potential polyamides. At the beginning of 1935, this task was entrusted to Gérard Berchet, whose preparation, purification and polymerisation of diamines and dicarboxylic acids soon produced a number of potentially interesting polyamides. One of these, poly(hexamethylenedipamide) or polyamide 66, was obtained from hexamethylenediamine and adipic acid on 28 February - 1 March 1935.

This was a solid, horny mass that melted at 252-254°C and an easy source of fibres, though such a high melting point indicated that it would probably decompose during hot drawing. Luckily for DuPont, however, this fear proved groundless and what we now know as nylon was born.

In the summer of 1935, Dr. Bolton virtually ordered Carothers to concentrate on polyamide 66 as a likely candidate for production on an industrial scale and abandon polyamide 5-10. Its very attractive qualities, in fact, were offset by the fact that sebacic acid had to be made from castor oil, a raw material whose production would never be able to keep up with the demand for the new fibre, whereas adipic acid could be and indeed was prepared from benzene, a petroleum derivative and hence available ad lib.

Industrialisation of polyamide 66 proceeded at full speed, but naturally required the involvement of dozens of chemists and engineers. By this time, however, it was becoming increasingly clear that Carothers was no longer mentally fit to supervise and take part in their work. Bolton thus required him to share his responsibility for the research with Dr. Graves. Carothers has always been given all the credit for the invention of the new synthetic polyamidic fibre. Whereas in other patent applications Carothers's name was accompanied by the one of the coworker who had materialised the invention in practical terms, those relating to nylon, its preparation and uses (all lodged after his death) bear his name only. In truth, of course, he never took any substantial part in the development of nylon.

5. Announcing of nylon.

By comparison with the broadcasting of the past, on this occasion silence was the order of the day. Not a word leaked out to the rest of the scientific world from the day when Berchet completed

the synthesis of polyamide 66 on 1 March 1935 and its industrialisation got under way until 20 September 1938, when three patents were granted in the name of W.H. Carothers to E.I. DuPont de Nemours and Company, Willmington, Delaware, as U.S. Patent 2,130,523 *Linear polyamides suitable for spinning into strong pliable fibers*, U.S. Patent 2,130,947 *Diamine dicarboxylic acid salt (suitable for forming spun fibers, etc.)*, which describes the purification of hexamethyldiamine adipate crystals, subsequently known as nylon salt, and U.S. Patent 2,130,948 *Synthetic fibers*, which describes the polymerisation of hexamethylenediamine adipate acid to form poly(hexamethyleneadipamide).

On 22 September 1938, the New York Times carried an article entitled *New Silk Made on Chemical Base Rivals Quality of Natural Product*, and an editorial penned four days later reported: *a new kind of nylon has been produced ... Because of its impact on the silk trade.... Japan has reason to worry.*

Man's very first synthetic fibre, stronger than steel, fine as a spider's web, more elastic than any of the common natural fibres, splendidly shiny and due to be marketed with the commercial name of *nylon*, was presented by Dr. Stine, a DuPont vice president, at the New York World Fair on 27 October 1938. His words, according to the papers, were received with little more than polite respect until he mentioned that a factory had begun to knit nylon hosiery and these new stockings felt better than silk stockings, didn't bag or snag, and when they snagged they didn't run. At this point that passive audience come to see Katherine Hepburn, the famous actress, stood and applauded.

Nylon immediately got off to a flying start. DuPont, indeed, had to build another two plants to flank the first, itself not yet fully worked up. The very first product turned out, even before stockings, was bristles for toothbrushes.

Heavy capital expenditures were needed to industrialise nylon development as well as the production plants.

Nylon stockings quickly become known as *nylons*. They were presented to the public for the first time at the San Francisco International Exhibition in February 1939 and almost simultaneously made available to the company's Wilmington employees only. In October, the citizens of Wilmington itself were able to buy them. On 15 May 1940 came the great moment when nylons were placed on sale throughout the United States at USD 1.15 - 1.35 a pair. The shops were taken by storm and almost five million pairs were bought on that day alone.

When the United States came into the war a campaign was mounted to collect nylon and nylons for the war effort. Nylon was quickly employed for parachutes fabric, braided parachute cord, outwear and tenting and tire yarn and glider towrope, etc. The vanguard of the U.S. Army floated to earth in Normandy carried by and covered with nylon. During the war some 13,000 tonnes of nylon were produced per year. In 1945, nylons came back to the shops, though about a couple of years were needed to catch up with the stocking demand. By 1949, production had raised to 25,000 tonnes a year.

6. About the name.

The origin of the word nylon has been told in what may be called an official story. But as in all stories, there is a legend. One apocryphal versions were passed on more by word of mouth than anything else and are still better known and more widely believed than the official story.

Throughout its development and prior to its introduction on the market, polyamide 66 was

simply referred to as *fibre 66*. When the time came to launch it, a trade name obviously had to be found. One year before nylon announcement, Dr. H. Church, head of research at DuPont's rayon Department at Buffalo, suggested playfully the acronym *Duparoooh*, which stood for DuPont "DuPont ulls a Rabbit Out of hat". Names such as *novasilk* and *synthesilk* were discarded because the company wanted its new synthetic fibre to conquer the market on account of all its high qualities and not just as a substitute for silk. A committee of three formed in 1938 collected a list of 400 names but no one of them met approval. Dr. E.K. Gladding, one of the committee member, proposed *Norun* with stockings in mind, but changed it to *Nuron* since also stockings of the new fibre would run. Here, however, the question of how this should be pronounced arose. An American "noo" (= new) as in "noon" was possible, but a British "new" would have seemed like "neuron". Replacement of the "r" by an "l" to form "*nulon*" was proposed, but once again the sound of the "u" would be uncertain and an expression such as "new nulon" would also be cacophonous. At this point a vowel change was suggested: "*nilon*" instead of "*nulon*". But was this "ni" to be pronounced as in "need" or in "nine" ? In the end, the name selection committee opted for a "y". The pronunciation problem was solved and "nylon" was born.

This is the official DuPont version. The legend is much more intriguing and presumably offers one of the many examples of a tendency among English-speaking peoples to invent humorous, sarcastic or derogatory versions of familiar acronyms. It was not very difficult, therefore, for some wag to come up with "Now You Lose Old Nippon" or "Now You Lousy Old Nippon". Apart from the evident threat posed by nylon to Japan as the largest producer of natural silk and hence the end of its leadership in the manufacture of fibres and choice fabrics, the period when nylon appeared was marked by very strong anti-Japanese feelings. An American success was thus accompanied by an open desire to offend Japan. The two appealing versions probably saw the light at the same time as nylon itself in October 1938 and quickly spread from coast to coast. Such was their effect, indeed, and so much better were they known than the official version, that in February 1941 DuPont commissioned a Japanese newspaper to publish a denial that the word nylon had the meanings attributed to it. This however has never become sufficiently known to dethrone the legendary versions in the eyes of the mass of mankind, even today.