

J. E. MCINTYRE

Formerly University of Leeds, UK

1.1 Introduction

This chapter reviews the early development of synthetic fibres, which are defined¹ by the International Organization for Standardization (ISO) as fibres manufactured from polymers built up from chemical elements or compounds, in contrast to fibres made from naturally occurring fibre-forming polymers. The definition excludes fibres made from regenerated cellulose, such as viscose rayon and cuprammonium rayon, and from cellulose esters, such as secondary cellulose acetate and cellulose triacetate. These fibres manufactured from cellulose became established commercially many years before the first synthetic fibres were discovered and developed. There was therefore quite a considerable amount of information already available to the developers of fibres from new polymeric materials about the production of fibres from solutions of high polymers by extrusion into non-solvents, i.e. by wet-spinning, and into evaporative atmospheres, i.e. by dry-spinning, and also about filament orientation by stretching and about subsequent downstream handling. There was, however, only a very limited understanding of the nature of polymers and of their macromolecular structure and synthesis.

A major step forward in developing this understanding was taken in the 1920s, when it was convincingly demonstrated, notably by Hermann Staudinger at the Technische Hochschule in Zürich, that polymers were not colloidal assemblies of molecules of low molecular weight, as many believed, but consisted of molecules of high molecular weight. Staudinger was awarded the Nobel Prize for chemistry in 1953 for his work on this subject. A major factor in convincing the chemical community was work on polymer synthesis directed by W. H. Carothers in the early 1930s at the Experimental Station of the DuPont company in Wilmington, Delaware.

The terms *addition polymerisation* and *condensation polymerisation* were introduced by Carothers.² Addition polymerisation was defined as the chemical union of many similar molecules without the elimination of simpler molecules, and condensation polymerisation as the chemical union of many similar molecules

with the elimination of simpler molecules. Carothers recognised and stated that some polymer structures could be made by either polyaddition or polycondensation processes. Consequently the terms *addition polymer* and *condensation polymer* should strictly be applied only to samples of known polymerisation history.

An alternative method of classification that depends on the nature of the mechanism of growth of the polymer divides polymerisation reactions into those exhibiting either chain-growth or step-growth mechanisms. Most chain-growth polymerisations are addition polymerisations, and most step-growth polymerisations are condensation polymerisations, but not all. For example, stepwise polymerisations without elimination of a simple molecule, such as the formation of a polyurethane, $(-\text{OROOCNHR}'\text{NHCO}-)_n$, from a diol, HOROH, and a di-isocyanate, $\text{OCNR}'\text{NCO}$, cannot be classed as condensation polymerisations. In the ensuing discussion of the early historical development of synthetic fibre-forming polymers, polymers normally formed by chain-growth polymerisation will be considered before those formed by step-growth polymerisation.

1.2 Fibres from chain-growth polymers

1.2.1 Chlorofibres

1.2.1.1 *European development*³

Research in Germany during the period 1911–1913 by Klätte at Chemische Fabrik Griesheim Elektron led to the definition of conditions for reacting acetylene with acids to form vinyl compounds, particularly vinyl chloride and vinyl acetate. Klätte's work on the polymerisation of these products formed the basis of an application on 4 July 1913 for a patent⁴ covering the formation of fibres from poly(vinyl chloride) (PVC). Subsequent workers, such as Rein,⁵ describe Klätte's work and the filing of this patent as the beginning of the story of synthetic fibres. The polymer is shown to be soluble in hot chlorobenzene, and useful (*künstliche*) fibres are said to be obtained directly by extrusion of the solution into a precipitating bath.⁴ A US patent,⁶ filed just under a year later and evidently a considerably amplified equivalent of the patent originally filed in Germany, claims the production of polymers from vinyl acetate, vinyl chloroacetate or vinyl chloride. The formation of fibres from solutions of poly(vinyl chloride) by spinning a solution in hot chlorobenzene into a precipitating bath is described, and the spinning of fibres from poly(vinyl chloroacetate) and poly(vinyl acetate) from solvents such as acetone is also included. Despite the examples, there are no specific claims to fibre formation, and no industrial development of fibres ensued.

According to Bode,⁷ the first synthetic fibre was produced by Hubert at the laboratories of IG Farben at Wolfen, north of Leipzig, from PVC. Work on this topic had begun in the rayon laboratories at Wolfen in about 1928, and all the high

polymers made within IG Farben, other than cross-linked products such as phenol–formaldehyde and urea–formaldehyde resins, were tested. In 1931 Hubert, Pabst and Hecht filed a patent⁸ in which they described the production of fibres by wet-spinning PVC, dissolved in cyclohexanone at room temperature, into 30 % acetic acid. The claims are directed specifically towards a multistage drawing process at a draw ratio of 3 : 1 or above. Tenacities up to 2.5 grams per denier (gpd) are obtained in examples.

So far no product suitable for commercial use had emerged, but it was then found that post-chlorination of PVC to the point where it contained about 1.5 chlorine atoms per vinyl residue in the chain gave a polymer that was readily soluble in acetone. Although, according to Bode,⁷ the suggestion for post-chlorination may have originated with Hubert, the patent covering this process was filed in 1932 with Schönburg named as the sole inventor.⁹

This post-chlorinated PVC fibre had a softening point 25–30 °C higher than the unmodified PVC, but fabrics still had to be washed at a temperature no higher than 40 °C in order to avoid shrinkage. Solutions in acetone could easily be spun into water, and commercial production of the resulting perchlorovinyl fibre, named *PeCe*, began on a small scale at Wolfen in 1934. A larger plant commenced production in 1938.⁷ The areas of use were, and remained, principally technical textiles such as filter fabrics, rot-free fishing nets, and acid-resistant industrial clothing. After World War II, this plant lay in East Germany (DDR) and production there continued under the name *Piviacid*. A similar product was manufactured in the USSR under the tradename *Chlorin*.¹⁰

In France, it was found by Rhône-Poulenc that mixed solvents (acetone plus carbon disulphide or acetone plus perchloroethylene¹¹) would dissolve PVC. A dry-spinning process based on such mixed solvents was introduced in 1949, the product being sold under various trade names such as *Rhovyl*. In Japan, a mixture of acetone and benzene (40 : 60) was used in a similar way by Teijin to produce *Teviron*.¹²

1.2.1.2 US development

Development of chlorofibres in the USA occurred later than in Germany. In September 1937, Rugeley, Feild and Conlon of Carbide and Carbon Chemicals filed a patent application¹³ that described the formation of synthetic fibres from copolymers of vinyl halides with vinyl esters of aliphatic acids, the average molecular weight being at least about 15 000. Typically the polymer was a 90 : 10 molar copolymer of vinyl chloride with vinyl acetate. It was dry-spun into air at 80 °C from a solution in acetone containing 23 % of the polymer. The filaments were stretched in two stages by about 140 % and set at constant length by immersion in water at 65 °C for 2 to 3 hours, to give a yarn with a wet tenacity of 2.75 gpd, an elongation to break of 15 %, and elasticity ‘similar to silk’.

This was the basic patent covering *Vinyon*, one of the first synthetic fibres made

commercially available in the USA. Production and sale of *Vinyon* by the American Viscose Corporation began in 1938, using *Vinylite* copolymer supplied by Carbide and Carbon.¹⁴ An elastomeric version of this product, Vinyon E, was introduced in 1943. It contained a plasticiser that permitted the production of yarns with reversible elongation approaching 400 %. Its use was confined to products for military purposes, and its production ceased after the end of World War II. Neoprene (polychloroprene), which had been discovered by Collins, a member of Carothers's research group, in April 1930 and commercialised as an elastomeric polymer by DuPont, was also used to make elastic threads during the war.¹⁵

1.2.2 Modacrylic fibres

The prospects for fibres manufactured from copolymers of vinyl chloride with vinyl acetate were limited by their low softening points and poor dyeing properties. Carbide and Carbon Chemicals therefore went on to develop a fibre based upon a copolymer of about 60 % vinyl chloride and 40 % acrylonitrile, which was dry-spun from acetone.¹⁶ Despite containing over 50 % of vinyl chloride, this type of product is now classed generically as a modacrylic fibre because it contains more than 35 % (but less than 85 %) by mass of groups derived from acrylonitrile.

An early patent for this type of product, filed in May 1943,¹⁷ describes a process for making a VC/VN, i.e. vinyl chloride/acrylonitrile, VC/AN (VN, or vinyl nitrile, is an old name for acrylonitrile) copolymer containing typically about 60 % of vinyl chloride by weight, which is soluble in acetone and resists deformation at temperatures above 100 °C. It is made by operating an emulsion copolymerisation at high VC/AN ratio with maintenance of that ratio by adding AN at intervals. Neither homopolymer is soluble in acetone.

A continuous-filament yarn, *Vinyon N*, based on this polymer was introduced in 1948, but the main commercial potential of the product was in staple fibre.^{18,19} *Dynel* staple fibre was introduced in 1949; and the continuous-filament product was withdrawn in 1954. Several other modacrylic fibres were commercialised, notably *Verel* (1956, Tennessee Eastman) and *Teklan* (1962, Courtaulds), both AN/VDC copolymers.²⁰

The inherently flame-retardant nature of modacrylic fibres has been the chief property leading to their use, which has been largely in furnishing fabrics and in pile fabrics. Subjecting them to very high temperatures, however, can lead to the evolution of toxic gases.

1.2.3 Poly(vinylidene chloride) (*Saran*) (PVDC)

The most widely recognised tradename for poly(vinylidene chloride), *Saran*, was introduced by the Dow Chemical Company. Patents covering the production of PVDC fibres were filed by Dow, initially in 1937.²¹ Commercial production began in 1940. The Firestone company employed Dow's *Saran* polymer to manufacture

monofilaments, using the tradename *Velon*, and several other extruding companies also entered the monofilament market using Dow's polymer and their *Saran* tradename. PVDC, unlike PVC, is crystallisable – a consequence of the symmetric nature of the $-\text{CH}_2-\text{CCl}_2-$ repeating unit – with a melting temperature of about 220 °C. The molten homopolymer is not sufficiently stable for sustained melt spinning, so in practice small amounts of other monomers, usually vinyl chloride or acrylonitrile, are copolymerised into the PVDC to lower the melting temperature. Fabrics made from the monofilaments, which are tough, readily cleaned and resistant to combustion, have been widely used in, for example, deck chairs.

PVDC fibres are classed as chlorofibres in the list of generic terms for fibres approved by the ISO, which does not recognise *Saran* as a generic term. In the USA, however, *Saran* is approved by the Federal Trade Commission as a generic name for fibres made from PVDC containing more than 80 % by weight of units derived from vinylidene chloride (VDC).

1.2.4 Poly(vinyl alcohol)

A patent filed in Germany in March 1931 by Herrmann and Haehnel, from the laboratories of the Association for Electrochemical Industry in Munich, and succeeding patents in other countries, including the USA, claim the use of poly(vinyl alcohol) fibres as surgical sutures.²²⁻²⁴ These products made for use as sutures were probably the first commercial synthetic fibres, but fibres made from unmodified poly(vinyl alcohol) were not suitable for normal textile use because of their sensitivity to water.

An early patent, first filed in France by Belloc in April 1932 and assigned to Société Nobel,²⁵ describes the manufacture of an artificial textile fibre spun from a condensation product of polyvinyl alcohol and an aldehyde, such as formaldehyde or acetaldehyde. It includes formation of fibres by hydrolysing poly(vinyl acetate) in hydrochloric acid, reacting the product with trioxymethylene (a source of formaldehyde), and wet-spinning this reaction product from the aqueous acidic solution in which it is formed into dilute aqueous sodium carbonate. The polymer can alternatively be isolated and dry-spun from solutions in various volatile solvents, for example a mixture of methyl acetate and ethanol. This process was not commercialised.

In the USA, early research on poly(vinyl alcohol) fibres at DuPont led to two patents, USP 2 169 250²⁶ and 2 236 061,²⁷ both applied for in May 1937 and issued respectively in 1939 and 1941. The patent with the later issue date describes the formation of films and fibres from poly(vinyl alcohol) by extruding an aqueous solution of the polymer, typically 16.7 % concentration, into a concentrated solution of an inorganic salt, such as 18 % ammonium sulphate. The fibres made in this way were of course still soluble in water. The other patent overcomes this deficiency by including a polymerisable material such as methacrylic acid (plus a polymerisation catalyst) or dimethylolurea in the solution. The product is then

heated at a temperature sufficient to cause this second component to polymerise and also to react with the poly(vinyl alcohol), which is thus insolubilised. This product and process were not developed further by DuPont.

Sakurada and his co-workers found that poly(vinyl alcohol) wet-spun into concentrated aqueous sodium sulphate could be made insoluble in water by heat treatment at temperatures in the order of 210 °C followed by reaction with formaldehyde.²⁸ This procedure, reported and patented in Japan in 1939, became the most commonly used basis for production of the class of fibres known generically as Vinylal fibres (but in the USA as Vinal fibres). Although a pilot plant was built in Kyoto in 1942, commercial production of *Kuralon* by Kurashiki Rayon (Kuraray) did not begin until 1950. Production of poly(vinyl alcohol) fibres is still mainly located in Japan, where most of the further process development has taken place, and in other Far Eastern countries such as China and North Korea.

1.2.5 Acrylic fibres

The earliest descriptions of potentially useful solvents for spinning polyacrylonitrile are in two patents due to Rein, of I G Farbenindustrie, that were originally filed in Germany in 1934. In the first,²⁹ the solvents are low-melting quaternary ammonium compounds, such as benzylpyridinium chloride. In the second,³⁰ they are concentrated solutions of metal salts in water, such as 67 % lithium bromide, 80 % zinc chloride and 77 % sodium thiocyanate. Although Rein later reported³¹ that these early German procedures had proved impractical, concentrated aqueous sodium thiocyanate was to become one of the most important solvents for wet-spinning acrylic fibres (e.g. *Courtelle* from Courtaulds, *Creslan* from American Cyanamid) and concentrated aqueous zinc chloride has also been used by at least two producers (*Beslon* from Toho, *Zefran* from Dow-Badische).³² A patent filed by American Cyanamid in the USA in April 1940 covers polymerisation of acrylonitrile in concentrated aqueous zinc chloride and formation of fibres by wet-spinning the resulting solutions,³³ although Cyanamid's commercial product, *Creslan*, was ultimately wet-spun from aqueous sodium thiocyanate. Concentrated metal salt solutions were also shown by Rein to dissolve some other vinyl polymers, such as the reaction product of poly(vinyl alcohol) with formaldehyde.

In a paper published in 1950, R. C. Houtz of DuPont described the results of a research programme carried out in that company's laboratories aimed at identifying suitable organic solvents for spinning polyacrylonitrile fibres.³⁴ The programme, stimulated by the fundamental work of C. S. Marvel on the solvation of polymers, led to the filing by DuPont of 15 patent applications, in the names of six different inventors. They were issued as US patents 2 404 713 to 2 404 727 on one day, 23 July 1946, but generated from applications some of which dated back to June 1942. Of these, the most significant for DuPont's development of *Orlon* was due to Latham.³⁵ It included spinning from dimethyl formamide (DMF), the solvent chosen for commercial production of *Orlon*, and is cited in other patents in the

series as representing ‘the first successful dissolution of polyacrylonitrile in a solvent suitable for solvent spinning’.

Although DuPont supplied experimental acrylic fibres for military applications as early as 1942,¹⁸ it did not announce plans for commercial production of *Orlon* until 1949. Production of *Orlon* continuous-filament yarn began in 1950, and of staple fibre in 1952. Production of *Acrilan* staple fibre by Chemstrand also began in 1952, and staple fibre was to prove much the more important product for acrylic fibre producers in general.

1.2.6 Polyethylene (PE)

Fibre-forming polyethylene is reported to have been discovered by ICI early in 1933,³⁶ although the basic patent was not filed until 1936.³⁷ A further ICI patent,³⁸ also filed in 1936, describes its melt-spinning and orientational drawing to form fibres with tensile strength as high as 25 kg mm⁻². Despite its low cost, its low melting point, lack of dye sites and relatively poor tensile recovery made it unsuitable for major development in textile end-uses.

Polyethylene monofilaments were produced commercially on a small scale by conventional melt extrusion and drawing of polymers made by the high-pressure type of polymerisation process, starting during World War II. A typical product of this type was *Courlene*, first produced in 1950 by Courtaulds and used, for example, in fusible interlinings. Solution spinning processes were patented at an early stage by both ICI and DuPont, particularly for making fine filaments, but did not prove commercially viable. More recently, processes for manufacturing polyethylene with a very low degree of branching and very high molecular weight have been discovered and developed. Polyethylene fibres with outstandingly high tensile strength and modulus have been produced from such polymers by novel processes, notably by gel-spinning³⁹ and by solid-state extrusion.⁴⁰

1.2.7 Polypropylene (PP)

Polypropylene was the last of the four major synthetic fibres of the title to be commercialised. As discussed above, ethylene, the lower homologue of propylene, can be converted into a useful crystallisable polymer that consists of slightly branched polyethylene by free radical polymerisation under very high pressure. Propylene, however, only forms non-crystallisable gums of low molecular weight under analogous conditions. In 1953 Karl Ziegler, director of the Max Planck Institute for Coal Research at Mülheim in Germany, discovered inorganic coordination catalyst systems based on complexes of aluminium alkyls and titanium chloride that permitted polymerisation of ethylene to give a product of high molecular weight with little or no chain branching, using pressures typically of 1 to 10 bar. Ziegler licensed this process to the Italian firm Montecatini, for whom Giulio Natta was a consultant.⁴¹

Early in 1954 Natta and his co-workers at Milan Polytechnic began to study the application to other olefins of catalysts of the type discovered by Ziegler and found that their use for polymerisation of propylene led to crystalline polymers of high molecular weight. Natta's first patent on this subject was filed in Italy on 8 June, 1954. This date was incorrectly given in the corresponding US patents^{42,43} as 1955, and the error was not corrected until 14 months after the grant and publication of the patents in the USA. The assignment of the corresponding British patent⁴⁴ to Montecatini and Karl Ziegler is interesting in that it seems to give Ziegler, who was not an inventor, a beneficial interest in the invention.

Since their introduction, production of polypropylene fibres has steadily grown in volume to become second among synthetic fibres only to polyester, in spite of their manifest limitations. They melt at a temperature (about 165 °C) that was deemed too low for commercial development during DuPont's early choice of a nylon structure for commercial exploitation. Using the catalyst systems of the original Natta type, the polymer has a very wide molecular weight distribution, which leads to rheological problems during extrusion, such as melt fracture. The fibres are virtually undyeable using established classes of dyestuff, so coloration depends almost entirely on melt pigmentation using master-batch techniques. On the other hand, the monomer and polymer are among the cheapest available, and are the basis of a very large plastics industry, of which polypropylene for fibres forms a relatively minor part. There are many large-scale producers of the polymer, which is widely available on a commodity basis. Although this has sometimes led to a situation where the price and availability of the polymer have been controlled by the current needs of the plastics outlets, it has also encouraged a situation where there are very many relatively small-scale fibre-producing units, often concentrating upon particular sectors of the fibre market. This contrasts sharply with the structure of the market for the other major synthetic fibres, where production of the polymer and the fibre are commonly linked within a single company. It is easy, for example, for small-scale producers to spin polypropylene fibres competitively using the 'short-spin' or 'compact' process, which employs a slow extrusion rate and a take-up speed of only 200–500 m min⁻¹ and thus allows the filaments to solidify in the threadline very soon after extrusion. Such processes require much less space than processes operating at higher speeds, and consequently incur significantly lower capital cost.

The present position of polypropylene fibres is dealt with in Chapter 5.

1.3 Fibres from step-growth polymers

1.3.1 Nylon; polyamide

The word *nylon* was coined by the American chemical company E I duPont de Nemours (DuPont) as a name for its aliphatic polyamide fibre, which was launched commercially in 1938. It was deliberately not registered as a trade-

mark, and *nylon fibre* became an internationally accepted generic name for fibres based upon linear polyamides. The generic name *polyamide fibre* has the same meaning as nylon fibre, but *nylon fibre* is used principally in countries that derive their fibre technology directly or indirectly from the USA, and *polyamide fibre* in countries that derive their fibre technology from Germany. These two generic names continued to retain identical meanings when they were jointly redefined by ISO in 1977 as 'having in the chain recurring amide groups at least 85 % of which are attached to aliphatic or cyclo-aliphatic groups'. This change was made in order to exclude the new aromatic polyamide (aramid) fibres such as *Nomex* and *Kevlar* that had very different properties and uses. Nomenclature in this field, and in some other fields of synthetic fibre production such as polyester, remains rather confusing since the definitions of the generic names often exclude products that would be included when using the same term for standard chemical nomenclature.

In February 1928, Wallace H. Carothers joined DuPont from a position as an Instructor in organic chemistry at Harvard University, and set up a major research programme to elucidate the nature of polymers. In 1930, Carothers and Berchet⁴⁵ studied the thermal polymerisation of ϵ -aminocaproic acid and found that it produced a mixture of a polyamide and the cyclic monomer ϵ -caprolactam. Fibres were not obtained from the polymer, probably because it was of too low a molecular weight. Moreover, the authors stated that the lactam does not polymerise under the conditions of formation of the polyamide either in the presence or in the absence of catalysts. This statement was later used by Schlack to justify the novelty of his invention of fibres from polymerised caprolactam.

In a review⁴⁶ written early in 1931, Carothers reported that a number of polyamides had been prepared by J. E. Kirby in Carothers's laboratory at DuPont by the action of aliphatic dibasic acids on aliphatic diamines. These materials were all much less soluble than the analogous polyesters, which had already been synthesised in the same laboratory. The polyamides also had much higher melting temperatures than the corresponding polyesters. No indication of their molecular weight or of any fibre formation was provided.

The first polyamide fibre was not prepared until 24 May 1934,⁴⁷ when D. D. Coffman, a member of the Carothers team, made fibres by melt-spinning nylon 9 that had been synthesised by polymerising ethyl 9-aminononanoate, $\text{H}_2\text{N}(\text{CH}_2)_8\text{COOC}_2\text{H}_5$. Fibre-forming polyamides of this nylon x type were claimed in a DuPont patent⁴⁸ filed in the USA on 2 January 1935. The examples included formation of fibres not only from nylon 9 but also from nylon 6 made by polymerisation from both 6-aminocaproic acid and ethyl 6-aminocaproate, but not from caprolactam, which the Carothers team seems still to have regarded as unpolymerisable.

The success with nylon 9 was rapidly followed by the synthesis of fibre-forming polyamides of the nylon x,y type from a wide range of diamines and dicarboxylic acids. Initially, the favoured candidate for commercial development was nylon

5,10, made from 1,5-diaminopentane and sebacic acid, but it was displaced on grounds of its low melting temperature (about 190 °C) and higher cost by nylon 6,6, which was first made by G. J. Berchet on 28 February 1935.⁴⁷ A decision in favour of commercial exploitation of 6,6 was taken by E. K. Bolton in July 1935.⁴⁷ A patent⁴⁹ claiming fibres from polymers of this nylon x,y type was filed on 9 April 1937, just 20 days before Carothers died. The first large-scale production plant was constructed at Seaford, Delaware, and started operation early in 1940.⁵⁰

In January 1938, Paul Schlack found that, contrary to statements by Carothers, caprolactam could be polymerised and the polymer could be melt-spun and drawn to form strong fibres.⁷ In June of that year I G Farbenindustrie filed a patent⁵¹ based on Schlack's work that claimed a process of polymerising a monomeric lactam containing no fewer than five aliphatic carbon atoms in the ring other than the carbonyl group at a temperature above the melting point of the lactam to a stage where the resulting product can be continuously spun from the melt into continuous threads, without removal of volatile products. One of the 31 examples in Schlack's patent describes the polymerisation of ϵ -caprolactam using the corresponding amino acid hydrochloride as a catalyst, followed by melt-spinning and orientational drawing of the product to form acid-dyeable fibres with a tenacity of 6 gpd. Polymerisation of the amino acids, particularly 6-aminohexanoic acid, had previously⁴⁹ been shown by DuPont to lead to melt-spinnable products, but further progress along that route was inhibited by lack of availability of the amino acids and by the difficulty of purifying them, neither of which was a problem with caprolactam.

I G Farbenindustrie immediately began to develop an industrial process for caprolactam production, polymerisation and melt-spinning. The polymerisation unit, developed by Ludewig,⁵² was based upon a continuous process using a tubular polymerisation unit called a VK tube (*Vereinfacht Kontinuerlich* = simplified continuous). In spring 1938, DuPont offered I G Farben a licence to produce nylon 6,6. The Americans were surprised when I G Farben told them of their own development and offered them a licence for nylon 6. The following year, DuPont's nylon 6,6 melt-spinning technology, based on a grid-melting process rather than rod spinning as used initially by the Germans, was made available to I G Farben, and thereafter production of nylon 6 fibres in Germany was implemented using melt-spinning units imported from the USA. The first industrial production unit for the lactam, based on phenol and using the Beckmann rearrangement process for converting cyclohexanone oxime to caprolactam, started up in 1940. A larger plant at Ludwigshafen the following year was devoted mainly to nylon 6 moulding plastic, but a plant dedicated to production of the fibre, by now known as *Perlon*, started up at Landsberg in April 1943.

It is interesting to note that further patents filed by Schlack in this field that were issued in the USA after its entry into World War II were at first⁵³ granted 'by mesne assignments' to DuPont and later⁵⁴ to the Alien Property Custodian. The present position of nylon fibres is dealt with in Chapter 2.

1.3.2 Polyesters

Among the earliest commercial synthetic polyesters were the alkyd resins or glyptals, based typically upon reaction of glycerol and phthalic anhydride to form a highly branched and ultimately cross-linked polymer and used, for example, in paints and varnishes. In 1928 a patent⁵⁵ was filed, initially by Allgemeine Elektrizitäts-Gesellschaft in Germany, that claimed processes for making fibres by melt extrusion of incompletely cross-linked polymers of this type and then baking them at a temperature sufficient to cause further cross-linking. Solution spinning from solvents such as acetone was also claimed. These fibres did not become commercial products.

At about the same time, in February 1928, Carothers joined DuPont and set up a major research programme to elucidate the nature of polymers. He chose as one of his main topics the reaction between diols and dicarboxylic acids, which could confidently be expected to produce polyesters in a structurally unequivocal way. By using a 5 % excess of the diols over that theoretically required, Carothers and Arvin⁵⁶ obtained polyesters with molecular weights up to about 4000. These products were not fibre-forming, but J. W. Hill⁵⁷ devised a polymerisation unit in which a mercury diffusion pump was used to reduce the pressure to 10^{-5} mm of mercury. Hill reacted octadecandioic acid with an excess of propane-1,3-diol and used his molecular still to reduce the amount of propanediol present in the vapour space. He thus obtained a product with a molecular weight of about 12 000. On 30 April 1930, he found that he could pull fibres from the molten polymer, and that when these fibres were subjected to an extensional force they extended irreversibly at a neck to form an oriented fibre of greatly increased tensile strength and modulus.^{58,59} Carothers's research team went on to make many such fibre-forming polyesters, but they were nearly all made from aliphatic reactants and melted at temperatures that were too low to permit their use in textiles. Internal DuPont documents show⁶⁰ that the possibility of forming a polyester from ethylene glycol and dimethyl terephthalate was examined in October 1934 by a member of the team, E. W. Spanagel, but the conditions used did not lead to a useful product.

An aliphatic polyester with a relatively high melting temperature (223 °C) which had much earlier been made by polymerisation of glycolide, which is the cyclic dimer of hydroxyacetic acid,⁶¹ was known to Carothers but not further evaluated. It is in fact too readily hydrolysed to be commercialised for general fibre use. This very simple polyester was nevertheless used some 30 years later by American Cyanamid⁶² to make absorbable surgical sutures (*Dexon*), whose efficacy depended upon their gradual hydrolysis within the body.

The publications of Carothers were read with keen interest by J. R. Whinfield, who had previously worked with C. F. Cross, one of the inventors of viscose rayon. Whinfield initiated a programme of research in his laboratory at the Calico Printers Association (CPA) in Accrington, UK, and early in 1941 his junior colleague, J. T. Dickson, synthesised a high-melting, fibre-forming polyester from ethylene

glycol and terephthalic acid.⁶³ A patent application was filed on 29 July 1941.⁶⁴ Its potential importance led the UK Ministry of Supply, applying war-time regulations, to place an embargo on its publication. The patent, which was not published until 1946, covers poly(alkylene terephthalate)s in general. In addition to poly(ethylene terephthalate) it exemplifies other members of the series, notably poly(trimethylene terephthalate), which has more recently also become of commercial importance due to the development of improved syntheses of propane-1,3-diol, as discussed in Chapter 3.

An initial evaluation was carried out in UK government laboratories.⁶⁵ The results were very encouraging, and in December 1943 ICI was told about the discovery. ICI then took over further development. In July 1944 ICI told DuPont about the new polyester fibre under the terms of an existing long-term agreement to exchange research results and DuPont began its own evaluation and development. DuPont acquired the US patent rights directly from CPA. The US patent⁶⁶ was not filed until September 1945 and was completed by and assigned to DuPont. ICI acquired the rights for the rest of the world, built production plants in the UK and Canada, and licensed producers elsewhere, initially seven companies in five other countries. ICI and its subsidiary companies used the name *Terylene*, which had been given to the fibre by Whinfield. DuPont initially gave it the temporary name *Fiber V*, and in early 1951 named the product *Dacron*.

Polyester fibre production grew rapidly. Polyester displaced nylon as the leading class of synthetic fibre in 1972. The present position of polyester fibres is dealt with in Chapter 3.

1.4 Elastomeric fibres

The generic name ‘elastane fibre’, approved by the ISO, defines ‘a manufactured fibre composed of synthetic linear macromolecules having in the chain at least 85 % (by mass) of segmented polyurethane groups that rapidly reverts substantially to its unstretched length after extension to three times that length’. This definition is unusual among the ISO generic descriptions of fibres in containing a physical property as well as specifying a chemical structure. In the USA another generic name, ‘spandex’, is approved by the Federal Trade Commission (FTC) and generally used. It differs from the ISO definition in omitting the physical property, and also in omitting the restriction to linear polymers. The development of elastomeric fibres of this type has largely been based on the concept of using polymers containing alternating hard segments and soft segments. The former provide long-term stability of the initial unstressed dimensions of the fibre through association between polymer chains, and the latter provide recoverable stretchability through their relatively low polymer chain modulus, coupled with relatively athermal extension and recovery behaviour.

In 1942, DuPont began work designed to identify a synthetic replacement for cotton-wrapped rubber, based at first on the rubber-like properties of *N*-substituted

This polymer could be synthesised and spun into fibres using solvents of the type already used by DuPont to make the acrylic fibre *Orlon*, and its commercial production was based on the same solvent, dimethyl formamide. The product was supplied initially (from 1959) as *Fiber K* and then (from 1962) from a full-scale production plant as *Lycra*.

When DuPont announced its intention of producing an elastomeric fibre based on this type of chemistry, the Bayer company rapidly revived its interest in a similar product. By 1964 it had commercialised a fibre named *Dorlastan*, the initial form of which was based on aliphatic polyester soft segments connected by hard segments. These hard segments were produced by first end-capping the soft segments with MDI and then reacting the product, dissolved in dimethyl formamide, with carbodihydrazide, $\text{H}_2\text{N.NH.CO.NH.NH}_2$.⁷⁴

A new method of producing elastomeric fibres, reaction spinning, was developed by the US Rubber Company. A copolyester soft segment was capped by an aromatic diisocyanate, and the product was extruded through a spinnerette into a bath containing a diamine dissolved in water. The filaments produced in this way had a skin of segmented polyurethane but an incompletely reacted core, and were then reacted with further diamine or water to chain-extend or cross-link the polymer precursors inside them.⁷⁵ A commercial product, *Vyrene*, was introduced in about 1958, but discontinued after a few years.

Another reaction spinning process, which is described in patents filed in 1962⁷⁶ and 1964⁷⁷ by Globe Manufacturing Co, was based on extrusion of liquid, slightly branched aliphatic polyesters or polyethers, capped with diisocyanates, into a solution of a polyamine such as ethylenediamine in an inert organic solvent such as toluene. Globe's product was named *Glospan*. Wet-spinning was used in a process developed by Peters⁷⁸ and even melt-spinning has been used commercially for elastane thread production.

A feature of elastomeric fibre development and production is the large number of different chemical and fibre extrusion processes that have been described and practised industrially.⁷³ There has been continuous evolution of improved products, aimed largely at overcoming problems of oxidative and thermal instability, particularly of the products based on polyether soft segments, and hydrolytic instability, particularly of the polyester-based products. The market is, however, now dominated by the dry-spun fibres, and particularly by *Lycra*.

1.5 Brief overview

The foregoing discussion of the early evolution of synthetic fibres deals largely with the dates, locations and key individuals involved in the inventive steps leading to the various classes of synthetic fibre. The earliest published description of formation of synthetic fibres is generally acknowledged to be that in a patent filed in Germany by Klatte in 1913, describing the spinning of chlorofibres from solutions of poly(vinylchloride). The earliest commercial production of a

synthetic fibre seems to have been due to Herrmann and Haehnel, based on patents filed in Germany in 1931–33. This product, however, was a poly(vinyl alcohol) surgical suture, unsuitable for conventional textile applications. The earliest commercial development of fibres for textile use was that of partially chlorinated PVC fibres (*Pe-Ce*) by I G Farbenindustrie in Germany, based on a patent filed in 1932. Small-scale commercial production began in 1934.

Polyamides were the earliest class of fibre to become established as major commercial products. The first fibre of this class to be made on a laboratory scale, nylon 9, was synthesised by Coffman, a member of the research team at DuPont headed by Carothers, in May 1934. Nylon 6,6 fibres were first made in a laboratory in January 1935, and the first major production unit began operation in December 1939. A patent-free route to nylon 6, based on polymerisation of caprolactam, was discovered in January 1938 by Paul Schlack of I G Farbenindustrie. A plant for commercial production of this fibre (*Perlon*) began production in Germany in January 1943.

Acrylic fibres and polyester fibres were the next two major classes of synthetic fibre to be commercialised. The early development of both took place in the 1940s. In the case of the acrylics, identification of suitable solvents for spinning fibres led many companies to enter the market, the first two being DuPont (1950) and Chemstrand (1952), both in the USA. In the case of polyester, the crucial invention was due to Whinfield of Calico Printers Association in the UK, and the product was developed into commercial production by ICI in the UK and DuPont in the USA. The fourth major fibre, polypropylene, was discovered in 1954 as a result of academic research into catalysts for polymerising olefins by Ziegler in Germany and Natta in Italy. The polymer rapidly became available to a wide range of fibre producers, large and small, so that the market rapidly became highly competitive.

These four major fibre classes, nylon, acrylic, polyester and polypropylene, are the subject of the following four chapters.

1.6 References

Note: The dates given here for patents are those of grant and/or publication. Dates of filing, which may be several years earlier, are given in the text where they are of particular significance.

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