Synthetic Fibres

合成纤维

[英] J.E.麦金太尔 编著

付中玉 译

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内 容 提 要

本书是配合高等院校高分子材料及相关专业实施双语教学而引进的英文原版著作。本书简述了合成纤维的发展历史，具体介绍了聚酰胺纤维、聚酯纤维、丙烯腈系纤维、聚烯烃纤维及其改性纤维的共聚、纺丝工艺、物理性能、染色性能、应用及发展前景。本书可供高等院校高分子材料及相关专业师生使用，也可供化纤工业的科技人员参考。

出版前言

进入 21 世纪，各高校纷纷在提高素质教育、与国际接轨方面进行了积极的探索。其中"双语教学"成为推进素质教育的又一着陆点。教育部于 2001 年 8 月发布文件，针对本科教学工作提出 12 项措施，其中明确要求各高校在三年内开设 5% ~ 10% 的双语课程，并引进原版教材和提高师资水平。这使得高校双语教学势在必行。双语教学既是教育自身对课程设置的调整，也是社会发展对教育改革的必然要求。实施双语教学不仅可提高学生的英语水平，适应未来的发展，更重要的是提高我国综合国力和国际竞争力的需要。

通过问卷调查、座谈等方式，我们了解到双语教材的缺乏是高校实施双语教学的一大难点。作为科技出版社，我们拥有纺织、染化、服装、工美等专业人才，并和英、美等国家的专业出版社、院校、协会保持着良好的合作，因此，我们希望利用自身专业优势，与高校合作出版双语教材，使之成为高校实施双语教学的先行兵。

经过广泛的调研、深入的讨论，我们在双语教材的内容、出版形式等方面形成了较完整的思路。目前，我社出版的双语教材按专业分为四个系列：纺织工程专业双语教材、轻化工程专业双语教材、高分子材料专业双语教材、服装专业双语教材。所选图书均为国外的经典教材，其内容与国内相关专业课程相近，便于学生在掌握专业基础知识的同时，开阔视野，提高语言应用能力。我们将力求出版形式多样化，既有原汁原味的影印本，又有中译本和中文注释版本。部分教材将配有多媒体光盘，更加丰富了教材的表现手段，有助于提高学生的英语听说能力。

可以说，这是我们在双语教材出版方面所进行的一次有意义的尝试，希望能对高校的双语教学的开展起到抛砖引玉之用，也希望读者对双语教材的出版提出建议、意见，以便我们在今后的工作中逐步改进、完善。

出版者

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Historical background 历史背景

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1.1   Introduction

引言

This chapter reviews the early development of synthetic fibres, which are defined[1] 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.

合成纤维
国际标准化织织

成纤聚合物
再生纤维素／粘胶丝
铜氨丝／酯
醋酸酯／三醋酸酯

挤压／非溶剂／湿法纺丝
干法纺丝／长丝／取向／
拉伸
大分子结构

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

加成聚合／缩合聚合

1

加聚物／缩聚物

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.

机理
链增长／逐步增长

逐步聚合
聚氨酯／二醇
二异氰酸酯

成纤聚合物

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, $(-OROOCNHR'NHCO-)_n$, from a diol, HOROH, and a di-isocyanate, OCNR'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.

基于链增长型聚合物的纤维

1.2   Fibres from chain-growth polymers

含氯纤维

1.2.1   Chlorofibres

在欧洲的发展

1.2.1.1   *European development*[3]

乙炔
酸／乙烯基／氯乙烯／醋酸乙烯酯

聚氯乙烯

氯苯

凝固浴

氯化醋酸乙烯

丙酮

Research in Germany during the period 1911–1913 by Klatte 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. Klatte's work on the polymerisation of these products formed the basis of an application on 4 July 1913 for a patent[4] covering the formation of fibres from poly(vinyl chloride) (PVC). Subsequent workers, such as Rein,[5] describe Klatte'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 Huhert 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 patent[8] 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.

交联
酚甲醛和脲甲醛树脂

环己酮
醋酸／多级拉伸
拉伸比／强度／旦（纤度单
位）

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]

后氯化

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 produc-
tion there continued under the name *Piviacid*. A similar product was manufactured
in the USSR under the tradename *Chlorin*.[10]

收缩
过氯乙烯纤维

纺织品／过滤织物／不朽／
耐酸

In France, it was found by Rhône-Poulenc that mixed solvents (acetone plus
carbon disulphide or acetone plus perchloroethylene[11]) 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]

二硫化碳／四氯乙烯

苯

1.2.1.2   US development

在美国的发展

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 application[13] 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

共聚物／脂肪族酸

长丝

纱线／湿强度
伸长／弹性

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 单丝
also entered the monofilament market using Dow's polymer and their *Saran*
tradename. PVDC, unlike PVC, is crystallisable – a consequence of the symmetric 可结晶的／对称的
nature of the $-CH_2-CCl_2-$ repeating unit – with a melting temperature of about 重复单元
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 tempera-
ture. Fabrics made from the monofilaments, which are tough, readily cleaned and 坚韧的
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)　　　　　　　　　　　　　　　　　　聚乙烯醇

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 外科缝线
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 aldebyde, such as formalde- 醛
hyde or acetaldehyde. It includes formation of fibres by hydrolysing poly(vinyl 乙醛／水解
acetate) in hydrochloric acid, reacting the product with trioxymethylene (a source 盐酸／三聚甲醛
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 碳酸钠
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 乙酸甲酯／乙醇
not commercialised.

In the USA, early research on poly(vinyl alcohol) fibres at DuPont led to two
patents, USP 2 169 250[26] 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 无机盐／硫酸铵
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 甲基丙烯酸
polymerisation catalyst) or dimethylolurea in the solution. The product is then 催化剂／二羟甲基脲

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 甲醛 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 乙烯醇系纤维 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.

丙烯腈系纤维 ## 1.2.5   Acrylic fibres

聚丙烯腈 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 ammo-季铵 nium compounds, such as benzylpyridinium chloride. In the second,[30] they are 苄基吡啶镓氯化物 concentrated solutions of metal salts in water, such as 67 % lithium bromide, 80 % 溴化锂 zinc chloride and 77 % sodium thiocyanate. Although Rein later reported[31] that 锌/硫氰酸盐 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 氯化锌 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 acryloni-trile 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 identify-有机溶剂 ing 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 二甲基甲酰胺 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)

聚乙烯纤维

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.

抗张强度
抗张回复

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-spinning[39] and by solid-state extrusion.[40]

模量
凝胶纺丝 / 固态挤出

1.2.7   Polypropylene (PP)

聚丙烯纤维

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 co-ordination 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]

络合物 / 烷基 / 钛

支化

烯烃
丙烯

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 patent[44] 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.

聚酯

流变的

浓色体
单体
塑料

"短纺"或"紧凑"工艺
卷绕

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.

基于逐步增长型聚
合物的纤维

1.3   Fibres from step-growth polymers

尼龙;聚酰胺

1.3.1   Nylon; polyamide

脂肪族的

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 Berchet[45] 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 review[46] 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, $H_2N(CH_2)_8COOC_2H_5$. Fibre-forming polyamides of this nylon x type were claimed in a DuPont patent[48] 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

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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 patent[49] 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 patent[51] 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

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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 previously[49] 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

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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 first[53] granted 'by mesne assignments' to DuPont and later[54] to the Alien Property Custodian. The present position of nylon fibres is dealt with in Chapter 2.