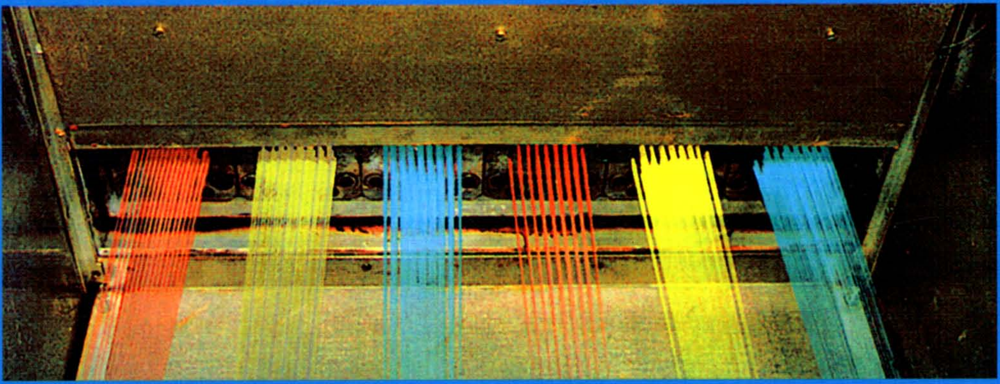
Fourné

Synthetic Fibers

Machines and Equipment
Manufacture, Properties



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Fourné

Synthetic Fibers

Franz Fourné

Synthetic Fibers

Machines and Equipment, Manufacture, Properties

Handbook for Plant Engineering, Machine Design, and Operation

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With many thanks to my wife, Ursula Fourné,
for her support and love

Preface

One hundred years of chemical fibers, and of these more than fifty years of synthetic fibers, do demand an inventory of the required technologies. While there is literature for the chemistry of the chemical and synthetic fibers, as well as for the processes and the textile testing technology, it is hardly possible to find comprehensive descriptions from installation, equipment and machinery manufacture through production of synthetic fibers and filaments and the manipulation of their properties.

The first book "Synthetic Fibers" was published in 1954 with about 160 pages and a world production of about 200,000 t/year at that time. The revised second edition from 1964 with 950 pages covered the total area of production through processing. The annual production of synthetic fibers had increased to 1.7 million t/year by then. Today, approximately 20 million t/year are produced accounting for about 45% of the world fiber production. The technical progress connected to this also requires a new edition which addresses only the first third of the topics covered in the 1964 book on 900 pages.

Further reasons for the new edition are: At the European universities only Chemnitz and Zurich maintain a department for the design of machines and equipment for the production of synthetic fibers. Textiles taught within the framework of mechanical engineering departments of other universities focuses primarily on textile engineering, while the training of the engineers is left to the specific industries. Thus this becomes an issue for about 1200 fiber production companies and over 1000 machinery makers, without having a comprehensive overview available. Many of the design elements are also unknown in the general mechanical engineering. Drive problems, auxiliaries preparation and conditions for auxiliary plants, as well as mathematical–physical and process technological items are explained in many examples.

The corresponding electro and micro-processing technology, automation and computer-integrated manufacturing are not covered in this book, as this would exceed the given frame.

This book is separated into a part on material specific processes, the corresponding installations, machines, and process data. In a further part the designs and calculations are introduced, also for different materials and varying function parameters.

The second to last chapter on fiber properties and their manipulation by Mr. Peter M. Latzke reflects a change in thought over the last 20 years: While the fiber user back then used to receive data sheets on the specific properties of a shipment, today's fiber producers have to keep all agreed upon properties constant for all future shipments and influence their production accordingly to stay within given tolerances. Production control thus has been replaced by process control that simply supervises the production parameters. Accordingly, quality systems have been specified in DIN, ISO, etc. Finally, the numerous conversion factors are shown and the fiber property ranges demonstrated according to a fiber table by Kleinhansl. Following the wish of practitioners to show most connections in measurable sizes, the author uses numerous drawings, diagrams, tables, and formulas and only a limited number of photos. He does want to point out though, that the installations, machines, and parts in the drawings have been built and installed in praxis.

This book provides a large number of diagrams, data, and companies names, but it does not expect to be complete or exclusive. There are certainly more companies producing similar or equal products; they should not feel neglected. Very often production is done according to individual ideas and guidelines, which can also result in optimum products.

The author does not want to forget to thank all those friends and companies that personally or through information, documents, figures, etc. contributed to the success of this work. Representing this group, also mentioned in the references, he would like to thank H. J. Koslowski (Chemiefasern/Textilindustrie), Dr. D. Ahrendt (Neumag), H. Enneking (Fleissner), W. Erdmann, Dr. B. Von Falkai, Dr. L. Gehrking (Fischer Industrieanlagen) J. Hartig and E. Endrun (John Brown Deutsche Engineering), Dr. E. Lenk, Dr. M. Mayer (Barmag), H. Michel (Heberlein), I. Ruzek (Corovin), Dr. K. Schäfer (Veba), Dr. H. Lückert (Ems AG), H. Wunderlich and Dr. H. D. Schumann (Zimmer AG), B. Matovinovic and A. Schweitzer (Automatik), F. A. Graf (Rieter AG), Prof. Dr. Wulfhorst (Textilinstitut of the RWTH Aachen). With drafts J. Keilert (Automatik, Granulation) and R. Wagener (Berges, frequency drives) contributed. The author also would like to thank the Central European raw material and fiber producers for numerous documents and references.

His particular thanks go to his wife Ursula for her support and love, to Dr. Wolfgang Glenz, Ms Martha Kürzl, and—last but not least—to Carl Hanser Publishers and all employees who worked on this book.

Franz Fourné

Contents

1 Introduction

1.1 General Remarks [1–3]

Natural fibers, especially wool and natural silk, have existed for several thousand years, soon to be followed by cotton, flax and the like. Their processing and usage have continuously been developed. Within one hundred years the chemical fibers and within only fifty years the synthetic fibers have improved their standard from originally being "substitute products" to recently providing about 50% of the total fibers consumed. It was a long way from the first ideas by *Hook* (1664) and *Réaumur* (1734) to the first chemical fibers [4] that were produced by *Nicolaus de Chardonnet* (1884). In 1898 in Oberbruch near Aachen, *Paul Fremery*, *Bromert* and *Urban* produced the first cooper silk filaments that after carbonization were used as incandescent filaments in light bulbs. The first fully synthetic fiber would be produced based on an idea by *Klatte* (1913) from polyvinyl chloride. *Staudinger* [6] succeeded first in 1927 under laboratory conditions to spin a fully synthetic fiber from polyoxymethylene and later from polyethylenoxide from the melt [7]. 1938 *Carothers* developed the first polycondensation fiber that was produced as Nylon by the company DuPont de Nemours & Co. Just one year later *Schlack* [10] proved that lactam can be polymerized, what resulted 1939 in Berlin-Lichtenberg in the first Perlon® fiber production. Soon IG-Farben-Industrie obtained a license for the melt spinning process for Nylon and transferred it to Perlon. After 1934 research was conducted in Germany that allowed the first semi-technical production of polyacrylonitrile fibers (PAN) during 1940 to 1943 [12, 13]. Almost simultaneously and independently of the German developments similar work was done at DuPont, so that the patent registrations almost have the same dates. Already 1950 DuPont started in the Candem plant full scale production of polyacrylonitrile fibers, what was not possible in Germany until much later. The commercial production of polyester follows around 1950 after an invention by *Whinefield* [52], and so does polypropylene around 1958 as developed by *Natta* [15]. These are the fibers that today are produced worldwide in tremendous quantities.

The development of specialty fibers began 1937 with polyurethane by *O. Bayer* et al. [14], followed by a wide range of fibers. Only Nomex® [16] and Kevlar® [17], both by DuPont, will be mentioned here. The development of high-grade carbon fibers did not begin until 1966 with the oxidation and carbonization of PAN filaments. More on this topic can be found with *Klare* [18] and *Elias* and *Vohwinkel* [19].

Many of the developed fibers could not be commercialized, e.g., fibers from polyaminotriazoles, where the pilot production was discontinued around 1965. The production of PA 7 in the USSR was discontinued due to the insufficient supply of oenanthe acid. PA 4 was too difficult to spin. Quiana® was commercialized in 1968, but in view of investments in the range of DM 600 million and the significant funds of DuPont it was discontinued in 1977, because the fiber was too expensive [20].

1.2 Conditions for the Production of Textile Fibers

Textile yarns or technical yarns and fibers have to fulfill certain characteristics that are primarily determined by the end use, and in the case of textile products also by climatic conditions. They need to be inexpensive, and it must be possible to produce them in sufficient quantities and consistent quality. In the fiber state it must be possible to blend them with other fibers.

The properties of textile fibers are primarily determined by their chemical structure, their degree of polymerization, the orientation of the chain molecules, their crystallinity, the packing density, and the cross links between individual chain molecules. In general they consist of threadlike long chains of mixed cells or stretched macromolecules etc. that are arranged more or less parallel to the fiber axis and pass through crystalline and amorphous areas. Figure 1.1 shows three models:

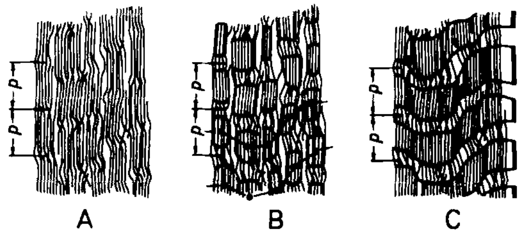


Figure 1.1
Schematic diagram of a super molecular fiber structure (according to *Hess* and *Kiessig* [21, 22]
A) Five fibrils with neighboring amorphous and crystalline regions of period *P*
B) Developed from A) to a para-crystalline macro grid (according to *R. Hosemann*)
C) Change to a para-crystalline layer grid with chain refolds

(A) amorphous and crystalline areas are arranged along the length of the fiber with the period P; (B) shows the same model in a further development towards the para-crystalline macro grid and (C) the transformation to the para-crystalline layer grid with chain refolds [21, 22]. These stages can be shown by X-ray or by differential thermo-analysis (DTA) or similar methods [23]. Cotton for example has about 60% crystallinity, viscose rayon only about 40%. The degree of crystallinity is also dependent on the temperature. PA 66 has about 75% crystallinity at 20 °C, about 52% at 85 °C, about 40% at 100 °C, and about 0% at 120 °C.

In the melt, the chain molecules have almost no orientation. When they cool during the spinning process they become a little pre-oriented. For solution spun fibers, e.g., hydrate cellulose, this pre-orientation can already be increased during the coagulation in the spin bath. Melt spun fibers, however, require a specific draw process—either in a continuous process after cooling under the glass transition temperature, or in a second separate process at a suited temperature. This drawing and orienting change the tenacity and elongation of the fibers considerably: For viscose rayon for example the tenacity increases from 1.5 to about 6.3 g/dtex (Super-Tyrex®) with a reduction in breaking elongation from about 30% to about 10%. The tenacity of PA can be arranged by drawing between values of 3 and 10 g/dtex with an elongation between 40% and 10%. Likewise this can be done with other synthetic fibers. Only filaments from liquid crystals are wound during melt spinning in a fully oriented state. Thus the fiber producer can vary orientation, tenacity and elongation depending on the material and process.

Fiber tenacity also depends on the degree of polymerization of the chain molecules. *Staudinger* [24] found that for native cellulose there is no change in tenacity with $P \geq 500$; between 500 and 200 the tenacity drops significantly with the degree of polymerization, and for $P \approx 200$ disappears. *Marsh* [25] found that high polymer fibers need a degree of polymerization of $P > 80$ to have any tenacity at all; it then increases significantly until $P \approx 250$, and increases insignificantly to $P < 600$ and not at all beyond that point. For this the distribution of chain length is important [26] as well as for many other properties. The distribution of density is also relevant for the properties: Viscose rayon has a significantly denser packed zone near the shell; the packing density of PA 6 increases with increasing draw ratios [27].

The average degree of polymerization (= average molecular weight/molecular weight of the base molecule) for cotton is around 3000, for normal cellulose 600–800, high quality cellulose and cotton linters 800–1300, viscose fibers 250–700, cupro fibers 500–600, acetate 220–300, polyamide 100–180, polyester 130–220, acrylic fibers 1000–2000, PVC fibers 1300–1800 [51], and can reach for high molecular PE for gel spinning about 160,000.

The formula schematics in Fig. 1.2 for PA 66 and in Fig. 1.3 for natural silk are an example for how much specific synthetic fibers look like natural fibers. For more examples see [30]. The main valences respond to the links along the length of the fiber. They contribute the majority of the fiber tenacity; this was already expressed by the dependence on the degree of polymerization. But the side valence links across the fiber direction provide the stability of the network. When these links are missing or loosened by heat and/or swelling a shifting of the chains can happen [27]. These cross links influence the hand and drape of textile materials. When comparing the schematics of PA 66 and natural silk it can be noticed that the cross links always appear between the oxygen atoms of the carboxyl groups and the NH-groups of the neighboring chain. For PA 66 every 100 chain atoms only have 14 amid groups and thus 14 hydrogen bridges = side valence links, whereas for natural silk each 100 chain atoms have 50 hydrogen bridges. PAN also has for each 100 chain atoms 50 hydrogen bridges. For PET the cross links are of a different nature due to the rings included in the chains: The ester group is linked through side valences to the neighboring CH_2-groups [28]. Due to the spherolites formed during the spinning of polymers the relation is more complex than shown here in the most simplistic idealization. Details can be found in [23].

Consequently and according to the studies of *Ulrich* [29] the following conditions make a fiber useful for production and industrial use as a textile material:

1. Raw materials must be available or produceable in sufficient quantities and for reasonable prices.
2. Existing methods must allow processing of these raw materials to polymers and then to filaments or fibers without high cost or damage to the environment.
3. The intermediate and final products must have sufficient continuity in terms of quality and quantity.
4. The final price of the yarn made from the fibers or filaments must be bearable for the market.
5. The fiber has to be either endless and possibly capable of being textured or must be capable of being processed in a mechanical spinning process, and must fulfill the following requirements:
   a) The resulting yarn has to show sufficient tenacity and elasticity, and the inital elastic modulus may not be too low.
   b) For textile applications the staple length should not be too low and somewhat uniform or within a desired distribution. For paper like products, reinforcements, and flock fibers, uniform staple lengths are required.
   c) The fibers have to provide a certain degree of friction among each other.
   d) Flexibility and elasticity are relevant for the mechanical spinning and subsequent processes.
   e) The fiber (dpf) determines the lowest titer of the yarn as well as the hand, breathability, comfort etc.

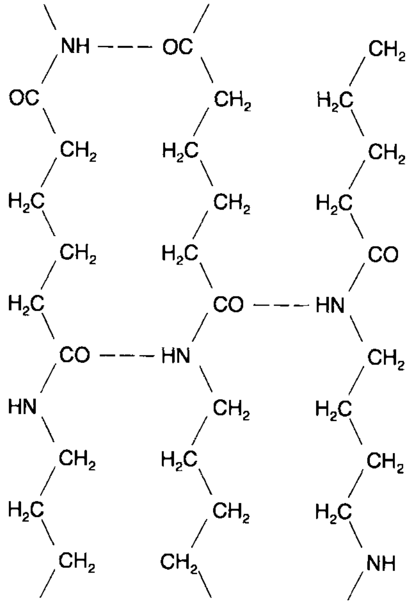


Figure 1.2 Schematic diagram of the structure of polyamide 66 (according to *Brill*)

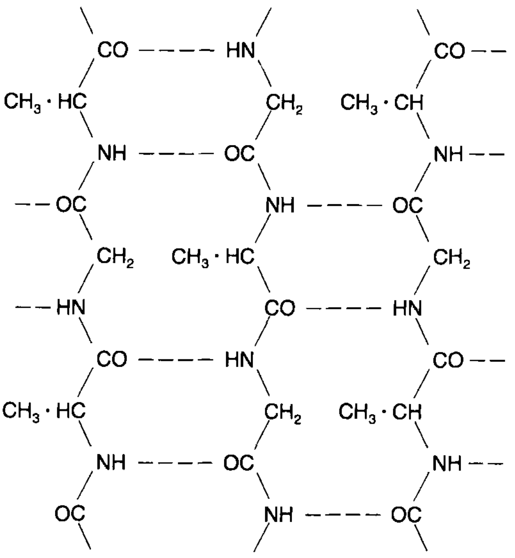


Figure 1.3 Schematic diagram of natural fiber structure: Silk (according to *Brill*) with polypeptide chains in the crystalline regions

f) The fiber should be easily dyeable; if textile dyeing is not possible, it must be able to be spun dyed.
g) Also relevant are luster, durability, insulation properties, recovery and many more properties that are difficult to measure or measure sufficiently.

These conditions can be fulfilled more or less satisfactory by chemical and synthetic fibers; with some fibers, difficulties in some of the issues cannot be avoided. Therefore they are only used in special applications, where the not fulfilled properties are unimportant; this is also true for cotton, wool and silk etc. This means that each textile fiber has certain optimal applications and may be less suited or inappropriate for other applications.

This is even more true for technical yarns, where the range of properties needed for the applications can be much more clearly defined. Carbon fibers for example combine highest tenacity at the lowest possible weight with an extremely high elastic modulus and high temperature resistance under air exclusion. Therefore it is particularly suited for tension short reinforcements in airplanes as well as for fastening Teflon reinforcements on airspace re-entry capsules. PA and PET yarns combine high tenacity and elastic modulus and optimal resistance to fatigue—all between −25 °C and +130 °C—which makes them especially suited for tirecords in high speed and heavy load vehicles and airplanes. PA-66 hollow fiber walls have high pressure resistance of up to 30 bar and pore sizes that allow water molecules to pass and salt molecules and contaminants to be retained.

As fiber fineness is a very important characteristic, Fig. 1.4 shows cross-sections of some natural and synthetic fibers between 1 and 30 den [30]. For a number of years additionally some synthetic fibers of a fineness of less than 0.01 den and coarser than 300 den are being produced. The very fine fibers have a very soft hand and good breathability while being water resistant. Technical multifilaments today usually have around 2 or 6 dpf (denier per filament), carpet yarns mostly 15...20 den, and wig hair about 28 den. Microfibers have a titer range between 0.4 and 1.0 dpf.

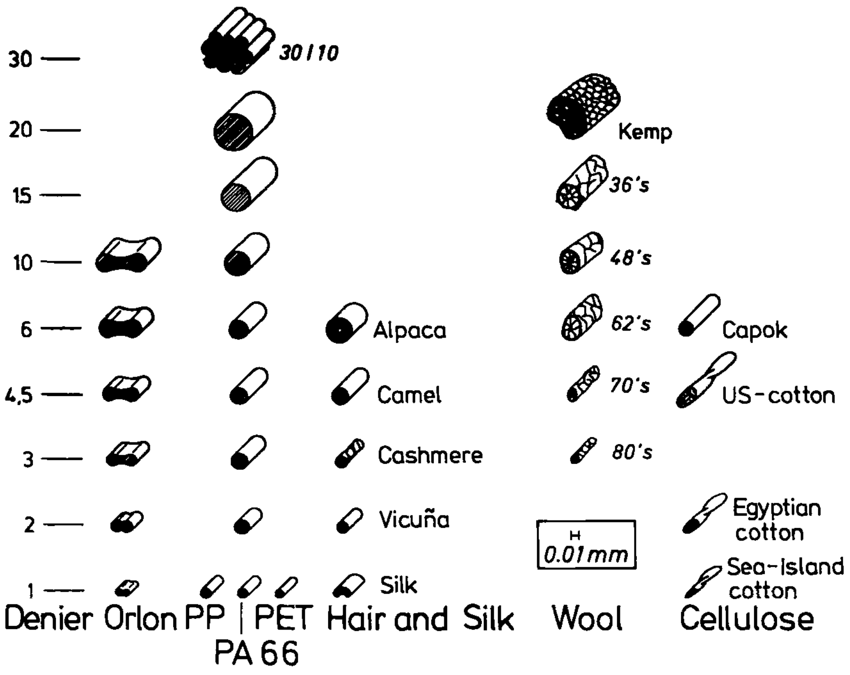


Figure 1.4 Comparison of fiber cross-sections [30]

1.3 The Most Important Fiber Raw Materials

Table 1.1 shows most of the presently used fiber materials that can be categorized by:

- Synthetic Fibers:
  - Polymerization Fibers
  - Polycondensation Fibers
  - Polyaddition Fibers
- Chemical Fibers (from natural polymers)
- Inorganic Fibers
- Natural Fibers
  - Animal Fibers
  - Vegetable Fibers

The selection and terminology reflect mostly to the Textile Identification Act and the respective regulations in the European Community.

Table 1.1 The Most Important Synthetic, Chemical, and Natural Fibers, Their Raw Materials and Production Methods

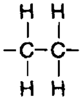
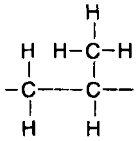
1. *Fibers from synthetic polymers* a) polymerization fibers b) polycondensation fibers c) polyaddition fibers 2. *Chemical fibers (from natural polymers)* 3. *Inorganic fibers* 4. *Natural fibers* a) animal fibers b) vegetable fibers c) mineral fibers		P = production M = modification S = specific characteristics T = end-uses, trade names
1a) Polymerization fibers		
Polyethylene (PE)  $-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{H}{C}}-$ $K = 2$ $M = 42$; $DP > 62{,}500$ $T_M = 107 \ldots 138°C$ $T_G \approx -100°C$ $(-20\% - 30°C)$	– LLDPE and HDPE are well spinnable and drawable (figure 5.6) due to short and few side chains (figure 2.89)	Chapter 2.4, see fiber table Chapter 11
Polypropylene (PP)  $K = 2$ $M = 42$; $DP > 45{,}000$ $T_M = 160 \ldots 165°C$ $T_G \leqslant 5°C$	– P: only well spinnable and hot drawable with >97% isotactic parts (Chapter 2.4.1.3)	CH 2.4.1; see fiber table Chapter 11

Table 1.1 The Most Important Synthetic, Chemical, and Natural Fibers *(Continued)*

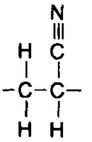
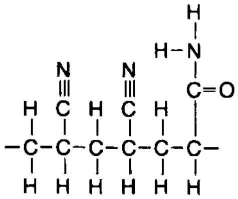
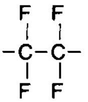
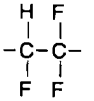
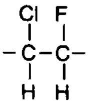
Polyacrylonitrile (PAN)  $-CH_2-CH(C{\equiv}N)-$ $K = 2$ $M = 53$; $DP > 1070 \ldots 2500$ $T_M > T$ (decomposition) $T_G = 0°C$ ($\approx 95°C$, dry)	– P: polymerization of $\geq 85\%$ ACN + comonomers, precipitation, drying, solving dry or wet spinning and aftertreatment, especially for staple fibers. Also continuous polymerization in solution for direct wet spinning possible (e.g., in $ZnCl_2$/water)	Chapter 2.5, see fiber table Chapter 11
Modacrylic (PAM)	– P: ACN-portion 50…84% (According to ISO), rest comonomers, e.g.:  $-CH_2-CH(C{\equiv}N)-CH_2-CH(C{\equiv}N)-CH_2-CH(CONH_2)-$	Chapter 2.7; see fiber table chapter 11
Polyvinylchloride (PVC) $-(CH_2 \cdot CCl_2)-$ $K = 2$ $M = 97$; $DP \approx 800 \ldots 1000$ $T_G = 75°C$ $T_M = 160 \div 200°C$ and *Polyvinylidene chloride (PVDC)*	– P: Acetone + Chlorhydroxide → vinylchloride → polymerization to polyvinylchloride: possible post chlorinating with tetrachlorcarbon – P: Ethylene or vinylchloride → vinylidene chloride etc. – M: e.g., "Saran"	Chapter 2.6; see fiber table chapter 11
Polyfluoride (FL) e.g.,  $-CF_2-CF_2-$ $M = 100$; DP: $10^3 \ldots 10^5$ $T_G = 127 \div 140$ $T_M = 327 \div 342$ (decomposed: 399°C) $K = 2$ *aliphatic fluorocarbon fibers*	Polytetrafluoroethylene (PTFE)  $-CHF-CF_2-$ Polytrifluoroethylene (PTFE, e.g., "Hostaflon")  $-CHCl-CHF-$ $M = 82$ Polyvinylfluoride $M = 80.5$ – P: e.g., polymerization of tetrafluoroethylene; special spinning processes	Chapter 2.9, see fiber table chapter 11
Vinylal	Paraffin polymers with OH-groups on every second C-atom of the main chain, partially acetyled; e.g., polymerization of vinyl alcohol and solving in water – wet spinning.	

Table 1.1 The Most Important Synthetic, Chemical, and Natural Fibers *(Continued)*

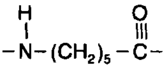
Trivinyl	Paraffin polymers with nitril groups or one or two Cl-atoms at every second C-atom; e.g., mixed polymerization of acrylonitrile and two other vinyl components, e.g., vinylchloride and vinylidenchloride with 50%; solving in acetone and wet spinning.	
Elastodien	Paraffin polymers with methyl branches and sulfur bridges to neighboring chains; e.g., polymerization of isoprene and dienes with or without vinyl monomers; or starting with natural latex; cutting vulcanized thin rubber plates into narrow stripes or extrusion of latex emulsion (Latex) respectively benzene-rubber solution through spinnerets; wet spinning; vulcanization of the coagulated and dried filaments.	
1b) Polycondensation fibers		
Polyamide 3 (PA3) $-CH_2{=}CH(OC \cdot NH-$ $-CH_2 \cdot CH_2)_n-NH_2$ $K = 4$ $M = 71$ $T_M = 165°C$	– P: Head-tail polymerization from acryloamide with alkaline catalysts or from chlorcyan and N-carbosulfamide acid chloride + olefins → sulphochloride groups → β-lactam (III) for polymerization. – T: thus far no technical production and application	
Polyamide 4 (PA4) $-NH-(CH_2)_3-C{:}O-$ $K = 5$ $M = 85$ $T_M = 200 - 265°C$ $T_G = 76°C$	– P: Polycondensation at 265°C → vacuum drying → melt spinning drawing; very difficult, because $t_{spin} = t_{decomposition} - 2°C$ – S: good textile properties, but to date not commercial due to P; $\gamma = 1.25$ g/cm^3	Chapter 2.2.2
Polyamide 5 (PA5) $-N \cdot H-(CH_2)_4-C \cdot O-$ $K = 6$ $M = 99$ $T_{M,\ theoretical} = 300°C$ $T_{M,\ in\ praxis} = 259°C$ for n $\frac{30°C}{m - cresol} = 0.25$	– P: only successful in laboratory scale. – T: none – S: $\gamma = 1.2$	
Polyamide 6 (PA6)  $-\overset{H}{\overset{\vert}{N}}-(CH_2)_5-\overset{O}{\overset{\vert\vert\vert}{C}}-$ $K = 7$ $M = 113$; $DP > 100–200$ $T_M = 215°C$ $T_G = 40 \ldots 42°C$	– P: Crude oil → benzene → cyclohexanon → ε-aminocaprolactam → pressure free polycondensation at 275°C...260°C during about 18 h with an approximate yield of 88%; past condensation possible; possible to melt spinning; up to about 40 dtex final denier with air quench, for ≥65 dtex spinning titer (≥0.08 mm diameter) with water quench; can be drawn	
Polyamide 7 (PA7) $N \cdot H-(CH_2)_6-C{:}O-$ $M = 113$; $DP > 100$ $T_M = 233°C$	– P: Ethylene (at 100 bar with radical formers) → tetrachloralkane → ω-chloroethane acid → ω-amino oenathe acid → pressure free polycondensation → PA7; can be melt spun and drawn; almost no monomers or oligomers – S: good properties for textile and technical applications, $\gamma = 1.10$ g/cm^3 – T: very short production around 1960 discontinued due to high raw material cost	Chapter 2.2.3, see fiber table chapter 11

Table 1.1 The Most Important Synthetic, Chemical, and Natural Fibers *(Continued)*

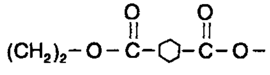
Polyamide 8 (PA8) $T_M = 209°C$; $\gamma = 1.08$ g/cm^3 *Polyamide 9 (PA9)* $T_M = 200°C$; $\gamma = 1.06$ g/cm^3 *Polyamide 10 (PA10)* $T_M = 188°C$; $\gamma = 1.04$ g/cm^3	No applications	
Polyamide 11 (PA11) $N \cdot H-(CH_2)_{10}-C \cdot O-$ $M = 169$, $DP \cdot 100$ $T_M = 190°C$	– P: Castor oil (over 5 steps) → aminoundecan acid → polycondensation from aqueous suspension over 3 steps in a tube, then evaporation, polycondensation, then reaching the condensation equilibrium: $\eta_{265°C \approx 600...100 \text{ P}; \gamma-1.04}$ kg/cm^3; can be spun and drawn like PA6 – S: Similar to PA6 and PA66, but only minimum moisture absorption, dimensionally stable – T: Zippers, ropes; too expensive for textiles	
Polyamide 12 (PA12) $N \cdot H-(CH_2)_{11}-C:O-$ $M = 183$; $DP > 100$ $T_M = 179°C$	– P: Butadiene-trimerization → 11-aminoundecan acid → Laurinlactam → almost 100% polymerization; direct spinning possible – T: especially for coarse deniers and wires; no textile applications yet; $\gamma = 1.01$ g/cm^3	Chapter 2.2.5.5
Polyamide 46 (PA46)	– P: from 1,4 diaminobutane (DAB from ACN and watercyanid) and adipic acid	Chapter 2.2.5.1
Polyamide 66 (PA66) $NH-(CH_2)_6-NH-CO-$ $-(CH_2)_4-CO-$ $K = 14$ $M = 226$; $DP > 80...200$ $T_M = 250...252°C$ $T_G = 42°C$	– P: hexamethylendiamin adipate in aqueous solution is polycondensated at approx. 285°C and spun continuously or via chips and then drawn – S: well dyeable similar to PA6; partially better properties than PA6 $\gamma = 1.14$ g/cm^3	Chapter 2.24; see fiber table chapter 11
Polyamide 610 (PA610) $NH-(CH_2)_6-NH-$ $K = 18$ $M = 254$; $DP > 100$ $T_M = 215°C$	– P: with Sebacic acid (from castor oil), rest similar to PA66; polycondensation at 245...260°C – S: best wet tenacity PA	Chapter 2.2.5.2
Quiana $T_M = 260...275°C$ $T_G = 135°C$	– P: polycondensation from Bis-(4-amino-cyclohexyl-)-methane (from Anilin and formaldehyde) and dicarbonic acid with 9...14 C-atoms – S: excellent textile material: best crease recovery – T: Production (DuPont) discontinued due to high cost $\gamma = 1.03...1.04$ g/cm^3	
Polyester (PES)	– Common name for polymers from dicarbonic acid or dicarbonic esters and glycoles	
Polyethylene terephthalate (PET)  $K = 10$ $M = 192$; $DP > 100...200$ $T_M = 257...264°C$ $T_G = 70...75°C$	– P: from DMT + EG via transesterfication or from TPA + EG via direct esterification to diethylene glycol (DEG) and polycondensation at ≥285°C to PET; spinning via continuous melt processing or via chips dried to ≤0.004% H_2O; hot drawable – S: excellent for technical use and textile yarn, staple fiber	

Table 1.1 The Most Important Synthetic, Chemical, and Natural Fibers *(Continued)*

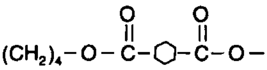
Polybutylene terephthalate (PBT)  $(CH_2)_4-O-\overset{O}{\overset{\|}{C}}-C_6H_4-\overset{O}{\overset{\|}{C}}-O-$ $K = 12$ $M = 284$; $DP \geq 100 \ldots 200$ $T_M = 225°C$ $T_G = 440°C$	– P: similar to PET but from butylene glycol + DMT or –TPA; polycondensation temperature about 250°C – S: good textile properties; can be dyed carrier free – T: higher cost than PET	Chapter 2.3.7
Polyurea	– linear macromolecule with repeating functional groups (–NH–CO–NH–) – P: polycondensation of urea with aliphatic diamines; melt spinning	Chapter 2.8.7
Aromatic polyamides (Polyaramides) with meta structure (molecules in ring arrangement) $T_{(Decomposition)} = 371°C$ $T_G = 280 \ldots 290°C$ M = 192; DP = 220...260	– P: m-phenylene diamine and isophthalic acid chloride is solution polymerized in DMAC, neutralized and directly dry spun. – S: $\gamma = 1.38$ – T: Nomex (DuPont), Conex (Teijin)	Chapter 2.11.2, Fiber table chapter 11
Aromatic PA with parastructure $M = 278$; $DP = 550$	– P: phenylene diamine and terephthalic acid chloride are polycondensated and disolved in concentrated sulfuric acid and wet spun – S: $\rho = 1.44$ – T: Kevlar (DuPont), Twaron (Akzo)	
Super absorbent products (SAP)	– P: from hydrogen-aryl and -alkal and/or hydrolyzed polyacrylo amides – S: moister absorbency of up to 230g/g fiber, salt water absorbency of up to 50g/g fiber – T: disposable diapers	see chapter 2.12.5
Polyaryletherketones $M = 288$ (PEEK)	– P: condensation of acid chlorides under Friedel–Kraft conditions produces low molecular –(R)–O–(R)–COCl; with HF as a solvent and BF_3 as a catalyst high molecular compounds are formed for extrusion processing – S: see figure 2.124 – T: Victrex (ICI)	
1c) Polyaddition fibers		
Polyurethane (PUR)	– linear macromolecule from paraffin chains that are connected by the urethane group –NH–CO–NH– – P: polyaddition of diisocyanates and dioles, e.g. hexamethylene diisocyanate and 1,4 butandiol; melt spinning	
Elastan (EL) (also "Spandex") ≥85% segmented PUR	– P: polyaddition of a linear dihydroxy polyester (e.g. polyethylene glycol adipate) or a dihydroxy polyether (e.g. polytetramethylene etherdiol) with excessive diisosyanate and chain lengthening or cross linking with diamino compounds (e.g. diamines) in solvents (e.g. DMAC or DMF) for direct dry or wet spinning; also reactive spinning possible with a reaction of the prepolymer in the coagulating bath with diamin. Melt spinning in development, possible with similar yarn properties.	

Table 1.1 The Most Important Synthetic, Chemical, and Natural Fibers *(Continued)*

1.2 Chemical fibers (from natural polymers)		
Viscose rayon (CV) Hydrate cellulose $DP = 300-500$ (High tenacity: 400–500)	– P: Cellulose with a high o-portion is changed with soda lye to alkali cellulose and then with carbon disulfide to cellulose xanthogenate; Dissolving in diluted soda lye, maturing, and spinning into a sulfuric acid/water bath for coagulation; washed repeatedly and de-sulfured (if possible), dried. Continuous process and winding process produce Rayon filament, cut wet into staple and drying produces staple fiber.	See fiber table chapter 11
Cupro (CUP) Hydrate cellulose $DP = 300-400$	– P: Dissolving cellulose in cupperoxide ammoniac → wet spinning (funnel spinning process), washing, drying and winding or cutting – T: Only produced in four location around the world because more expensive than CV	See fiber table chapter 11
Modal (CMD) Hydrate cellulose $DP \Rightarrow 300$	– P: Modified viscose process with wet spinning	
Acetate $2\frac{1}{2}$ cellulose acetate $P_m = 250–400$	– P: Acetylizing of cellulose with acetic acid, partial saponification; dissolving in acetone; primarily dry spinning; endless winding or cutting to staple fiber	See fiber table chapter 11
Triacetate (CTA) Cellulose-3-acetate $P_m = 300–400$	– P: Acetylizing of cellulose with acetic acid → dissolving in dichloromethane → dry or wet spinning, drying and winding	
Protein fibers (casein) *Zein or other vegetable proteins* *PROT (Protein)*	– P: Casein precipitated with acid or lab ferment from milk and dissolved in soda lye → wet spinning → stabilizing → drying – P: Extraction of Zein (e.g., from corn flour) → precipitation and dissolving in soda lye or extraction of peanut press cake with diluted lye → dissolving and wet spinning etc. – T: For some time was wool substitute and blending fiber; not stabilized used as release yarn in knitting	
Alginate fibers metal alginates (ALG)	– P: Extracts from (sea) alga → alginic acid → dissolving in diluted soda lye → wet spinning and stabilizing in metal salt baths, e.g., NaCl	
1.3 Inorganic fibers		
Glass fibers (GF) primarily low alkali Bor silicate glass, e.g., about 52% SiO_2 about 11% B_2O_3 about 14% Al_3O_3 and about 17% CaO	– P: Melting of ground mixture of quartz sand and additives at 1400…1600°C; spinning by jet draw or jet blow or centrifugal process (all gravimetric or by rod draw process – T: Endless glass filament or staple (glass wool)	See fiber table chapter 11
Basalt fibers	– P: Clean whinstone by melting twice and pouring into cold water → cast into crucible from PtRh, melt and draw gravimetric to filaments at over 3000 m/min and wind; "rock wool" spun directly from first melt by jet blow or centrifugal process	Chapter 2.13.4

Table 1.1 The Most Important Synthetic, Chemical, and Natural Fibers *(Continued)*

Metal fibers *(MTF or MT)*	– P: Coarse rolled wire from metals or alloys are drawn in several steps through draw plates or draw stones with thermal treatment between steps until the desired fineness has been reached; e.g., for 1.4571 drawing up to a diameter of 1 μm is possible.	See fiber table chapter 11
Carbon fibers *CF* > 90% pure C	– P: Primarily from post drawn PAN fibers, but also CV or PVAL fibers 3-step process: Stabilizing (= oxidation) → carbonization → graphitization	Chapter 5.7; see fiber table chapter 11
1.4 Natural fibers **1.4a) Animal fibers**		
Wool (WO) *keratin*	– fineness: 2–50 dtex see figure 1.4	See fiber table chapter 11
Alpaca (keratin) Hair (wool) of the alpaca (type of camel)	– P: Shearing Earlier also re-used wool from rags, that contained vegetable fibers, which were removed by carbonization	
Lama (keratin) Hair (wool) of the lama (type of camel)	– P: shearing	
Camel (keratin) Base hairs of camels and dromedaries more than 10 cm in length, lightly curled, light red to yellow brown, or the beard hair dark brown to black	– P: Hairs fall out in bundles in spring – T: Best qualities for yarns for underwear, lower grades for "press cloth"; weather proof coat fabrics	
Cashmere (keratin) Hair of the cashmere goat, off white, low crimp, silky shine, very fine, beard hair coarser	– P: Combing out or pulling in spring – S: Very soft hand, appreciated as wool, also in blends with wool – T: Fine yarn ladies' dress cloth 3-ply filling yarn (Nm 50 to 60 worsted yarn, 40 ... 80 ppcm), knitting yarn	
Mohair (keratin) Up to 150 mm in length, strong, simple hair of the true angora goat	– P: Shearing (once or twice per year)	
Angora (rabbit) *(keratin)* Primarily pure white, fine and soft hairs; beard hairs coarser	– P: Several shears per year, or combing and pulling in spring and fall – T: Felts, very shiny mohair yarns, etc.	
Vicuña (keratin) Hair (wool) of the Latin American mountain lama (type of camel)	– P: Shearing after corralling	
Yak (keratin) Hair of the Tibetan ox	– P: Shearing	
Guanaco (keratin) Hair of the Latin American guanaco (mountain lama, type of camel)	– P: Shearing after corralling	

Table 1.1 The Most Important Synthetic, Chemical, and Natural Fibers *(Continued)*

Hair (keratin) Other animals (especially horse hair)	– P: Shearing or cutting of tail hair – T: Upholstery, filling materials, etc.	
Silk (SE) *(Natural or Mulberry silk)* $P_m \approx 2500$	– S: Fibroin (silk substance 70 ... 80%) → Sericin (silk bast, 3 layers, 19 ... 28% → fat substance (0.5 ... 1%) → mineral components (0.5 ... 1%)	See fiber table chapter 11; schematic in figure 1.3
1.4b) Vegetable fibers		
Cotton *(CO, also Bw)* Native cellulose $M = 162.14$ P_m (raw) ≈ 7000 $P_m \approx 6500$	– Fineness depending on origin 1 ... ≈4 dtex; figure 1.4	See fiber table chapter 11
Flax, linen (LI) Bast layer of the up to 1 m long flax plant fiber length 600 ... 700 mm yield 45 ... 55% cellulose $P_m \approx 8000$	– P: Pulling of the plant (linum usitatissimum) when starting to yellow; after drying and removing the seed bolls, retting removes the bast fibers from the wood, breaking and hackling → tow → line	See fiber table chapter 11
Hemp (cellulose) Bast fiber of the hemp plant (cannabis sativa) of up to 3 m height Color: off white, silver or pearl gray, greenish or yellowish, lighter is usually better	– P: Similar to flax, but also pulled when green between breaking and hackling usually some scutching or cutting – M: Bast hemp is broken hemp; pure hemp after removing impurities; strand hemp is broken and scutched, stone or spin hemp is ready to be spun, ground hemp is made by peeling the bast from the stem – S: Much higher tenacity than LI (and LI higher tenacity than cotton) – T: Coarse yarns, twisted or plied or braided ropes, tars depending on origin, Galician, Polish, French etc. split hemp is particularly fine	
Abacá (cellulose) Leaf stalk fiber (from the leaf stem) of the fiber banana, musa textilis, also Manila) fibers are yellow-white or brown, shiny, stiff, and weatherproof	– P: Manual or mechanical pulling of the fiber bundles (possibly after rotting) from the leaf flesh, drying and hackling; or by use of a defibreur – M: Long hemp yarns $Ne \geq 0.65 = Nm \geq 0.39$ spun, hemp tow yarns $Ne = 0.39 \ldots 10$; finest fibers by stamping in a mortar for fine fabrics – T: Ropes, netting, cable wrap, saddle thread, twine	
Alfa (cellulose) Leafs (stalks of the esparto grass (stipa tenacissima)	– P: Two year old stock dried after harvest, boiled to destroy the chlorophyll, retting in running water, separate from other matter with wooden clubs	
Coco (cellulose) Fruit fiber between the shell and the core of the coconut	– P: After braking the outer layer solving of the fibers from the inner nut, months of retting in a mixture of fresh and salt water, removing of the fiber coat by beating, scutching and pressing; drying, hackling. The combings are pulled by gear teeth and are cleaned, bleached, dried and mechanically spun. – S: Highly resistant to weather and mechanical wear – T: Rope, twine, mats, runners, foot mats, etc.	

Table 1.1 The Most Important Synthetic, Chemical, and Natural Fibers *(Continued)*

Sisal (cellulose) Leaf fiber of the agave sisalana (Mexico) fiber yellow white, shiny, resistant against humidity	– P: Mainly mechanical pressing to separate the flesh from fibers and rinsing, centrifuging, and drying – T: Twine, rope, coarse fabrics, crimped for upholstery
Jute (cellulose) Bast fiber of the East Indian jute plant (corchorus capsularis and oliotorius) fibers of 2–3 m length lighter color: better brands	– P: Harvest by cutting above the water level, water retting, removal of the bast coat by hand, washing and drying – M: Best type: Serajgunge (fine fiber, good color), Narajgunge (slightly lower quality), Daisee (very fine, but undesirable dark), Dacca (hard, brittle, but pure color), Dowrah (coarse, hard, short, wood like and dark brown); cuttings are mechanically separated roots, lowest grade jute – S: Yarns of 0.06...4.2 Nm – T: Woven fabrics (burlap, carpet backing, wall coverings, etc.) ropes, cable
Kenaf (cellulose) Stalk bast fiber of the kenaf plant (hibiscus cannabinus)	– P: Cold water retting, similar to hemp
Ramie (cellulose) stalk bast fiber of the ramie plant (bohemia nivea, member of the nettle family $P_m \approx 6500$	– P: The 1.2...2 m stalks are separated from wooden portions (no retting possible) → stiff gummed bast → degumming by soaking in caustic soda, then washing, bleaching, drying – M: Chinese type white, Indian type greenish – S: Softer and more flexible hand than flax, very fine, elastic, shiny, high tenacity – T: Rare, in linen, lace, etc.
Broom (cellulose) From the South European broom (spartium coparius)	– P: Chemical retting from the stalks of the plant – S: Fine, brownish, soft, but high tenacity – T: in blends with flax and hemp tow for ropes and coarse fabrics, with reed fibers can be blended for coarse woollen yarns
Asbestos Magnesium or iron silicates weathered minerals serpentine (chrysotile) and hornblende (amphibole) Processing illegal due to risk of cancer. Only natural mineral fiber	– P: Mining (surface or underground); gentle separation of the fibers from stone – M: Depending on mining site: Canada (Thedford and Black Lake) Siberia (Perm and Irkutsk) and type: Crocidolite or blue asbestos, Chrysolite or white asbestos, Amosite and Tremolite asbestos – S: High resistance to heat and acids, low heat and electric conductivity high splittable and splits by itself until floating in air and hazardous to lungs and breathing. – T: Past: Insulation material, in blends with cement for construction felts. – Due to cancer risks the production and use in no longer allowed

Further detailed properties of selected fibers can be found in chapter 11 “Fiber Table” at the end of this book.

1.4 Economic Development

Between 1900 and 1960 the production of chemical fibers increased from practically zero to about 3 million tons p.a. (i.e. an annual increase of about 50,000 tons. Then it increased to about 21 million tons p.a. until 1990 (i.e. an annual increase of about 600,000 tons p.a.). In 1946 the activities of the synthetic fiber industry were limited to three corporations with a total production of 21,000 tons p.a. on a semi industrialized scale and remained tied to the chemical fiber industry until 1960. In 1960 its worldwide production was 700,000 tons p.a. After that the fast growing production was partially independent of the chemical fiber industry and reached about 18 million tons p.a. in 1990, an average annual increase of about 580,000 tons. Figure 1.5 (graphs d–e) shows that the increase from 1960 on was almost exclusively due to synthetic fibers, while the production of chemical fibers and natural fibers remained almost constant—see also Table 1.2 [30, 33]. Also the number of production facilities for synthetic filaments and fibers increased from 511 in 1965 to about 1300 in 1985 (Table 1.3), while there were only 166 chemical fiber plants left.

The expansion of the synthetic fiber industry did not happen continuously. It was interrupted by several recessions around 1973 and 1981 as well as in 1991/93 (Fig. 1.6), where in some cases the production capacities even had to be reduced.

This overall development was caused by:

- the tremendous increase in the world population from about $3 \cdot 10^9$ in 1960 to about $5.3 \cdot 10^9$ people in 1990, or an increase around 1990 of 1.8% p.a.;
- the continuously increasing demand for textiles by individuals from about 5 kg/year and person in 1960 to about 8.0 kg/year and person in 1990 (Fig. 1.7). There are however significant regional differences from about 1 kg/year and person in Central Africa to about 24 kg/year and person in the USA;
- since 1980 the increased demand in home furnishings and technical textiles;
- the limits in agriculturally useable area that limits the increase of natural fiber production.

Figure 1.7 also shows that the per capita consumption since 1960 could only increase because of the synthetic fiber production (curve c).

This allows some conclusions with respect to the annual investment volume of the synthetic fiber industry. If the average lifetime of an existing production facility is assumed to be 20 years, 5% need to be re-invested annually, i.e. today for about 1.1 million tons p.a. Investment for expansion needs to be added, and according to Fig. 1.8 these additional capacities range from 0 to 1.6 million tons p.a. This

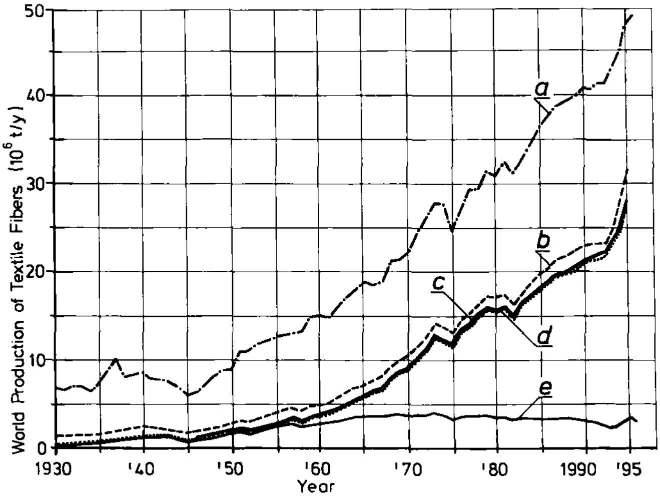


Figure 1.5
World production of textile fibers
a) Total
a)–b) Cotton
b)–c) Wool
c)–d) Silk
d)–e) Synthetic filaments and fibers
e) Chemical filaments and fibers (mainly hydrocellulose and acetate)

Table 1.2 Global Production of Different Textile Fibers (1000 t/a)

Year	World population	Rayon and acetate			Synthetic							Natural fibers									Synthetic total[7] %a[6]
		filaments	fibers	total	PET- fibers and filaments	PA- fibers and filaments	PAN	Olefins	others	total	%[5]	Cotton	%	Wool	%	Raw	Silk	%	Total	%[5]	
1890	–	–	–	–	–	–	–	–	–	–	–	2720	79	726	21	12	0.3	32458	100	3458	
1900	1.550	0.9	–	0.9	–	–	–	–	–	–	–	2165	81	730	19	17	0.4	3912	100	3913	
1910	1.686	5.4	–	5.4	–	–	–	–	–	–	–	4320	84	810	15.7	23	0.4	5153	99.9	5158	
1920	1.811	14.5	–	14.5	–	–	–	–	–	–	–	4470	84	808	15.2	27	0.5	5305	99.7	5320	
1930	2.070	205	3.2	208	–	–	–	–	–	–	–	5480	81	1000	15.3	52	0.8	6532	96.9	6740	
1940	2.295	541	585	1126	–	5	–	–	–	5	0.1	6230	73	1135	13	59	0.7	7424	86.8	8555	
1945		402	200	602	–	17	–	–	–	17	0.3	4320	72	1040	17	11	0.2	5371	89.7	5999	
1950	2.516	872	739	1611	≈ 10	70	–	–	~2	82	0.9	6220	69.3	1060	11.8	19	0.2	7299	81.2	8992	
1955	2.757	1043	1252	2295	≈ 82	266	30	–	~10	388	3.1	8740	69.4	1263	10.0	29	0.2	10032	79.7	12715	−12.6
1960	3.019	1142	1465	2607	≈ 119	407	105	–	~70	701	4.7	10250	69	1440	10	30	0.2	11690	78.1	14998	−24.3
1965	3.324	1372	2074	3446	≈ 469	~1040	388	≈80	≈100	2077	11.0	11884	62.9	1484	7.8	32	0.17	13400	70.8	18923	−19.4
1970	3.693	1391	2194	3585	1635	1924	1010	338	140	5047	22.8	11784	53.0	1659	7.5	40.8	0.18	13484	61	22116	−10.0
1975	4.076	1148	2068	3216	3357	2462	1418	716	165	8118	32.9	11343	46.1	1578	6.4	45	0.18	13346	54.1	24680	−7.4
1980	4.453	1130	2392	3522	5066	3234	2048	1048	210	11606	37.9	13872	44.9	1599	5.2	53	0.17	15524	50.6	30652	−1.4
1982	4.586	967	2227	3194	5097	2913	1977	1048	260	11295	36.5	14738	47.4	1624	5.2	55	0.18	16417	53.4	30906	−9.0
1984	4.763	959	2428	3387	6065	3342	2352	1312	340	13411	39.4	15528	45.2	1672	4.9	55	0.16	17255	50.2	34053	−5.5
1986	4.917	934	2307	3241	6959	3411	2456	1723	380	14929	40.2	17181	45.6	1684	4.5	56	0.15	18921	51.0	37091	−7.7
1987	5.024	915	2371	3286	7581	3645	2478	1909	460	16073	41.6	17494	44.7	1731	4.4	56	0.14	19281	49.9	38640	−4.4
1988	5.112	950	2421	3371	8041	3793	2428	1994	520	16776	42.4	17552	43.9	1764	4.4	57	0.144	19373	49.0	39520	−3.6
1989	5.201	927	2415	3342	8425	3901	2340	2141	580	17387	41.9	18733	44.7	1933	4.6	66	0.16	20732	50.0	41461	−0.5
1990	5.292	864	2351	3251	8578	3812	2224	2227	640	17481	42.2	18714	49.2	1964	4.6	66	0.16	20744	50.0	41440	−3.0
1991	5.384	793	2068	2861	9208[1]	3617[2]	2466[3]	2300[4]	720	18311	443.4	18650	44.2	1934	4.6	67	0.16	20651	49.0	42162	−3.0
1992	5.477	676	2039	2715	9803	3612	2408	2280	760	18863	44.7	18758	44.5	1793	4.2	67	0.16	20618	48.9	42196	−3.0
1993	5.572	656	2029	2685	10209	3696	2388	2160	790	19341											−2.5

Remarks:
Filament (%): [1] 46 [2] 83 [3] 0.2 [4] [5]
Staple Fibers (%): [1] 54 [2] 17 [3] 99.8 [4] 98[5]
[5] including about 65,000 t foil yarns and fibers
[6] of total[7]

The numbers vary in the literature by about 5%, because the basis on production, demand, sales, or end-use are usually not defined; foil yarns and fibers are based on estimates.

Table 1.3 Number of Producing Firms by Production and Region

Year	Region	Acetate	Rayon	PAN	PA	PET	Others	Σ	PP*
1965	Western Europe	15	80	21	61	28	27	232	18
	Eastern Europe	9	47	13	30	13	6	118	3
	North America	11	20	9	42	22	19	121	38
	South America	8	14	2	23	15	1	63	1
	Asia	11	37	15	33	21	26	143	21
	Africa	–	3	–	3	1	–	7	1
	Total	54	201	60	192	100	79	684	82
1975	Western Europe	12	50	26	76	57	16	237	121
	Eastern Europe	–	26	7	12	10	3	58	10
	North America	9	10	10	50	55	18	152	74
	South America	8	13	4	39	33	2	99	45
	Asia	6	34	16	63	67	22	208	45
	Africa	–	2	–	2	3	–	7	1
	Total	35	135	63	242	225	61	761	296
1985	Western Europe	12	25	30	91	66	19	206	117
	Eastern Europe	–	33	10	19	20	3	52	18
	North America	8	7	12	44	44	10	125	104
	South America	8	9	6	60	50	4	137	52
	Asia Oceania	6	56	21	85	131	19	318	61
	Africa	–	2	–	3	7	–	12	3
	Total	34	132	79	302	318	55	920	355
1990	Western Europe	7	21	18	71	56	14		118
	Eastern Europe	4	41	8	24	21	4		20
	North America	5	5	8	48	48	12		99
	South America	6	4	4	37	36	3		48
	Asia Oceania	9	58	28	75	124	3		65
	Africa	–	3	1	8	15	–		4
	Total	31	132	67	263	300	36	829	354

*) Polypropylene spinning facilities, usually smaller capacities of about 10... 100 t/24 h.

means that equipment manufacturers for the chemical and synthetic fiber industries have to adjust to deliveries between 1.1 and 3.7 million tons p.a. within an 8 to 9 years cycle. These numbers closely match those of engineering firms and equipment manufacturers [34]. In 1990 engineering firms built 39 installations worldwide with a combined capacity of 0.8...0.9 million tons p.a. Using average capacities of production units these capacities for 1990 equal 14 large staple fiber units with about 100 tons p.d. and 50 to 100 filament units with 20...10 tons p.d. and 36 compact spinning units of each 14 tons p.d. These numbers also allow the conclusion that there are approximately 280 staple fiber units and between 2200 and 1100 filament units currently producing.

Figure 1.8 demonstrates the production development from 1970 to 1990 by the three major polymers and for 1990 also by regions. Table 1.4 also shows the production development by regions, and Table 1.2

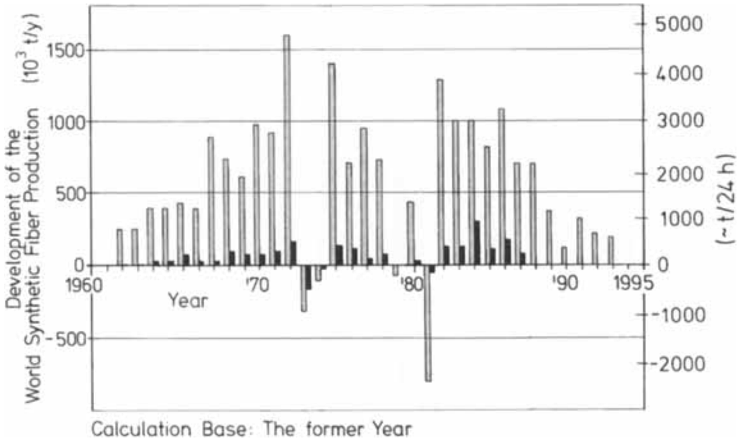


Figure 1.6 Annual increase or decrease of synthetic fiber production as an indicator for the annual investment rate

the breakdown by filament and staple fiber for the most important polymers. Not mentioned in Table 1.2 are polyolefines, where staple fibers and BCF make about 90% of the production.

The stagnation of synthetic fiber production in the highly industrialized countries does not mean that the industry is being reduced in those regions. Only the production of commodity items is being moved to the low cost countries, while in Western Europe, the USA and Japan more high tech fibers are being produced—low quantities relative to the total production, but with a high production value.

At the same time one tries to reduce production cost by using ever bigger units and more automation. This is only possible as long as companies in the rest of the world, e.g., Taiwan and South Korea, do not

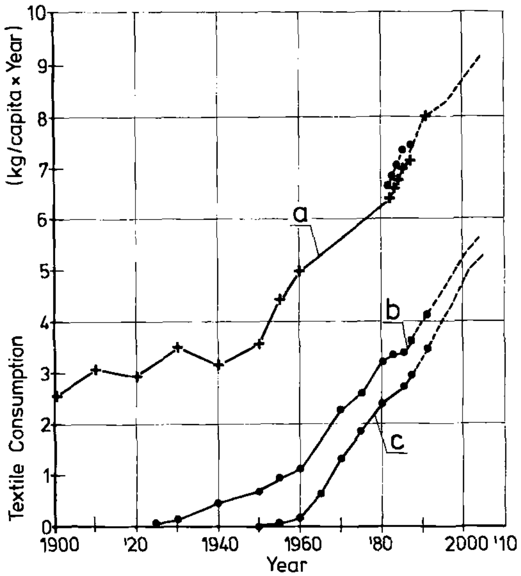


Figure 1.7
Average textile consumption in the world per person and year (since 1900 [38])
a) Total consumption
b) Chemical fibers (mainly cellulosic)
c) Synthetic fibers

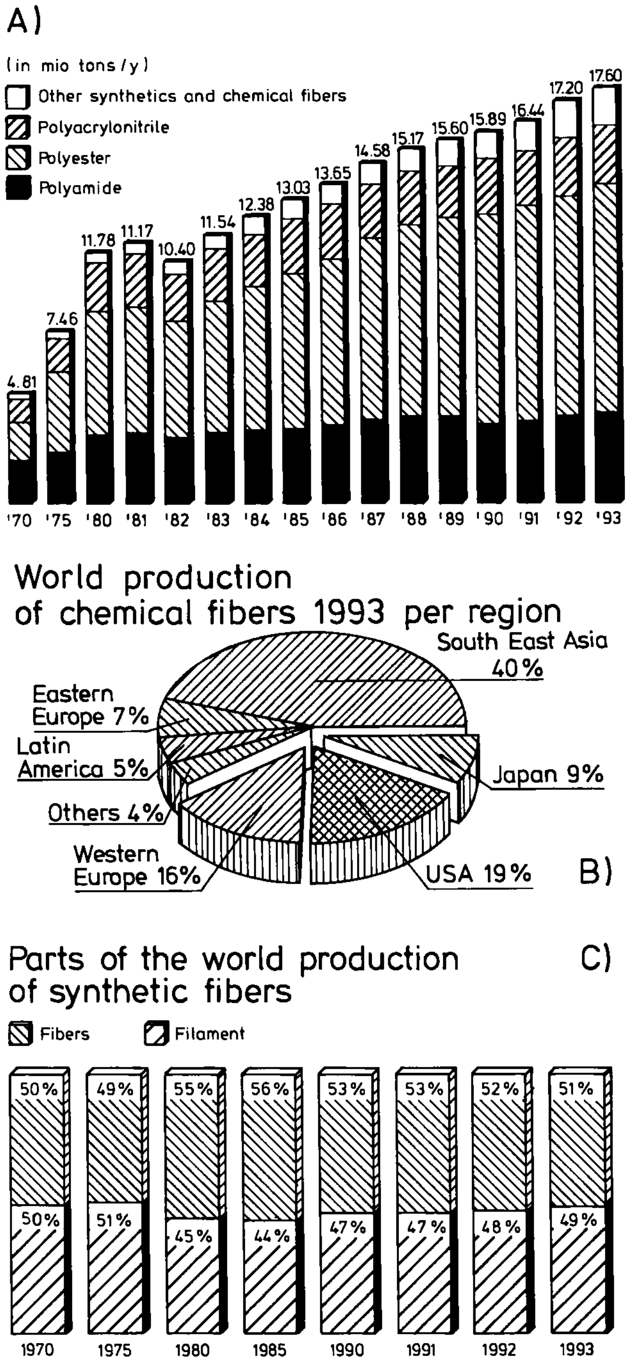


Figure 1.8 Break down of the global production of synthetic fibers and filaments

A) By fiber type

B) By region: USA 23%, Western Europe 18%, Japan 9%, all others 50%

Table 1.4 Global Synthetic Fiber Production by Region or Country

	1960	1970	1980	1986	1988	1990	Filament % (1990)
Western Europe		984.2		1893	1972.9	1822.7	38.3
w/o FRG	246	490.8		745	751.1	778.8	47.1
Eastern Europe		4152.9		660	695.2	821.1	49.4
w/o GDR	?	40.0		158.8	163.5	131.4	45.6
w/o USSR		1665.5		757.8	868.8	913.5	49.4
East Asia	–	6.1		219.5	281.0	400.3	
w/o Japan	129	968.7		1382	1381.0	1425.0	49.3
w/o South Korea	–	42.9		862.4	1115.0	1189.9	52.9
w/o Taiwan	–	40.8		1232.1	1430.2	1621.5	53.5
w/o India	–	15.6		220.7	321.6	430.9	60.1
w/o Indonesia	–	0		164.2	194.8	270.0	58.6
w/o PR China	–	11.1		747.4	1074.3	1309.4	38.6
Mid East, Oceania, Africa		26.5		207.1	232.7	219.7	50.8
America		120.2		193.7	197.5	212.1	
w/o USA, Canada	288	1571.5		3058.4	3244.2	3002.3	45.3
Mexico	–	46.7		296.3	345.9	323.3	40.8
Brazil	–	41.1		237.0	239.7	206.1	58.2
Others		156.8		1022.8	1141.1	1628.2	
Total	701	4876.3	10779	14058.2	15650.5	16497.4	46.4
For comparison (world total)							
Cigarette (acetate) tow production				362	422	462	
Glass fiber production				1449	1845	1826	

do the same. When increasing a plan production unit the production costs can be approximated from those of a smaller unit as follows:

$$K_2 = C_2 \cdot (\text{raw material costs}) + (C_2/C_1)^{0.6} \cdot K_1 \tag{1.1}$$

K total cost	Index 1 smaller unit
C capacity	Index 2 larger unit

This means that the raw material costs increase proportionally with the capacity (neglecting improved terms in purchasing and transportation), but all other costs increase only with the 0.6 exponent to the capacity. If for example $K_2 = 2 \cdot K_1$, these costs will only increase by 52%. The fiber production in a 240 tons p/d. unit with 2000.-DM per ton raw material cost and 1000.-DM per ton other cost will reduce the cost per ton to 2760.-DM/t instead of 3000.-DM/t when doubling the capacity.

The useful size of a unit can only be determined when knowing all the facts about the regional conditions and the market. This is also true for the integration of such a unit into a larger corporate complex. Thus today unit sizes range from about 10 tons p.a. to $2 \cdot 70{,}000$ tons p.a. in the USA to a polyester plant in the PR China with $9 \cdot 70{,}000$ tons p.a. [36, 37] (now going to $18 \cdot 70{,}000$ t/a). The following overview may prove useful:

Unit size		Type of unit	Usage	Preferred countries for investment
kg/24 h	tons p.a.			
50...500	15...150	Filament unit	R&D speciality yarns	USA, Western Europe, Japan, PR China
200...2000	50...600	Speciality filament	Production	as above
7000	2200	Filament unit	Production	everywhere
4000...40,000	1300...13,000	Compact unit Small (preferred autoclave) Polycondensation and spinning unit	Fiber production Production	everywhere India, Indonesia South Asia, East Asia
80,000...160,000	27,000...54,000	Large (continuous) Polycondensation units and others	Large scale production	PR China, Taiwan, former USSR
400,000	130,000	as above	as above	USA

As continuous polycondensation units with 200...400 tons p.d. and a directly connected fiber spinning unit can only produce one standard product for a long time period, the problems shift from the technical production to the marketing side of this standard product. In the above mentioned example of the polyester facility in the PR China, however, the production represents only 0.5 kg per year and person.

Chip production and synthetic fiber production are part of the chemical sector, and the question needs to be asked, what percentage of the production of a chemical company or group of chemical companies should be for fiber production. If the production starts from the polymer chips it is practically independent and can be almost 100%, but usually those productions are connected with a specific textile corporation. For larger polymerization units, byproducts have to be used. Part of the polymer production can be sold in form of chips to the plastic industry or other spinning plants. For these combinations a fiber part of 30...50% of total sales proves to be useful. If on the other hand filaments and fibers are produced in large chemical corporations, the recessions of 1973 and 1981 showed that large corporations with more or less exclusive fiber production could not survive and had to merge with chemical corporations of similar sizes (e.g., Enka (AKU) b.v. with Zoon b.v. to become Akzo b.v.). Others were already part of a chemical corporation (e.g., Hoechst AG, Bayer AG, Rhône-Poulenc S.A. and others) and could cover the sometime losses from their fiber production that way. Also vertically integrated groups (like Beaulieux S.A. as a carpet producer) had better survival chances. This experience showed that synthetic fiber production should only amount to no more than 20% or even better less than 10% of the total corporate sales, so that losses from fiber production could be covered more easily. The large number of small production sites mainly survived by producing specialties that cannot be produced efficiently by the large producers either because the production quantity is too limited or the required flexibility is too high.

1981 *Falkai* [23] published a graph showing the relation between the sizes of the production units and the sizes of the factories for PAN fiber production (Fig. 1.9). The smallest economical wet spinning unit he sees at 5000...7000 tons p.a. (= about 24 tons p.d.), the smallest economical dry spinning unit at 10,000 tons p.a. (= 30 tons p.d.), what should equal about 64 dry spinning chambers per machine. The smallest PAN fiber units must have considerably larger capacities than comparable melt spinning units, because they can only produce economically when recycling the solvents, spin baths, etc. Generally one counts on the use of about 75% solution and 25% dry substance. One also has to account for about 3...7% losses when recycling the solvents.

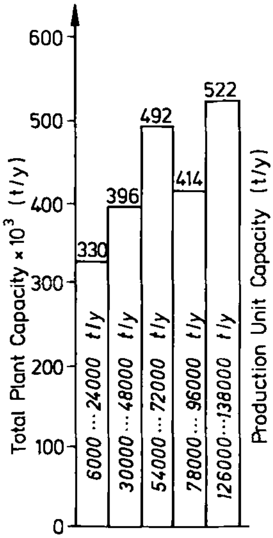


Figure 1.9
Production plant and production line sizes of a PAN plant (approximately 1980) [23]

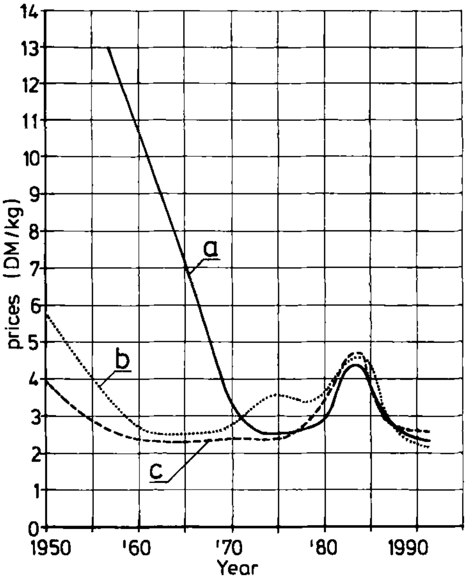


Figure 1.10
Approximate price development from 1950 to 1990 for
c) Viscose staple fiber
b) Cotton
a) Polyester staple fiber (cotton type)

1.5 Price Developments

Other than many commodities synthetic filaments and fibers have dropped in price since about 1950 except for a price increase during the oil crisis. This reduction in price is due to the considerable increases in capacity of the units without requiring significantly more labor. Labor intensive production has been moved to the low wage countries. An other factor is the fast worldwide communication that leads to

Table 1.5 Price Development of Monomers and Auxiliary Materials (DM/kg)

Year	Caprolactam	AH-salt	DMT	TPA	Ethylene glycol	ACN	Toluolene	Benzene	Dowtherm	Spin oil	$TiOP_2$ (AN atas)
1948	8.40	8.00									
1958	5.40	5.50	5.60		1.50	3.15			2.64...3.47	2.80...4.70	3.20
1964	3.60	4.00	3.00			1.20	0.21	0.258			
1968				3.00			0.193	0.246			
1978							0.321	0.402			
1988					0.76		0.472	0.664			
1989		3.00	1.23			1.25					6.00
1990	3.10...3.30 1) 2.94 2)		1.20	1.23 1) 0.91...1.04 2)	1.17	1.50		0.80	3.60...6.80		

AH SAlt = Monomers for PA66
DMT = Dimethylterephthalate

ACN = Acrylonitrile
TiO_2 = Dulling Agent

1) Germany
2) USA and Far East

Table 1.6 Development of Polymer Prices between 1958 and 1990 (DM/kg)

Chips, etc.	PAN powder	PA 6	PA 66	PET[1]) FGR	PET[1]) USA	PET[1]) lowest	PET $[\eta]=1.0$	PP
1958	3.80...4.00	7.00	7.40	7.60	7.00			
1988					2.38			≤2.40
1989				2.30...2.45	2.00	1.90		2.04...2.29[2])
1990	≈3.60	3.90...4.1	4.20	2.18...2.3	2.20	1.70	2.45	1.50...1.80

1) $[\eta]\approx 0.63\ldots0.67$
2) cheapest: 1.30 DM/kg from Far East

Table 1.7 Development of Yarn and Fiber Prices from 1936 to 1988

	1936	1948	1954	1958	1968	1978	1988	Region
Natural fibers								
Cotton, Egypt. cat.g	1.46	7.30	4.60	4.46				D
USA, middle	0.80	3.13	3.15	3.43	2.55	3.32	2.70	D
Wool, merc., 64 s	2.77	10.99	13.84	10.69				D
64 s	1.39	3.26	7.95	8.32				D
Japanese raw silk	5.51	13.51	49.91	46.24	–	–	–	GB
Flax, water-roasted	1.29	3.41	3.72	3.63	–	–	–	GB
Regenerated fibers								
Viscose fibers								
1.5 denity $\frac{17}{16}''$	1.10	.1.02	2.59	2.59	–	–	–	GB
–	–	–			4.08...4.95			Japan
–	–	3.24	2.96	2.35	2.78	2.86		USA
–	–	2.95	2.95	–	–		–	D
Acetate fibers	–	–	4.70	3.91	–	–	–	D
Regenerated filaments								
Viscose 150/27 den pirn	3.46	5.46	6.35	5.98	–	–	–	GB
Acetate filaments	–	–	–	6.11	–	–	–	USA
Cupro 150/112 den	–	–	–	6.70	–	–	–	USA
Synthetic fibers								
PAN, dry spun	–	22.40	14.82	11.90	–	– }	2.91...3.96	USA
wet spun	–	21.10	12.96	10.70	10.40	– }		
	–	–	–	–	–	–	3.00...3.30	Western Europe
	–	–	–	–	–	–	4.16	Japan
	–	–	–	–	–	–	3.16	Korea, Taiwan
PET 3 den	–	–	14.82...15.56	11.67...13.10	4.75	2.67	2.75	USA, GB
1.5 den	–	–	–	–	–	–	3.12...3.21	USA
	–	–	–	–	–	–	3.50...3.90	Western Europe
	–	–	–	–	–	–	3.08	Japan
	–	–	–	–	–	–	2.98	Taiwan
	–	–	–	–	–	–	2.73	Korea
PA 6	–	21.20	14.75	12.90	9.40	–	3.58...4.37	
PA 66	–	–	13.80	11.90	9.50	–	–	
PP 3.3 dtex	–/–	–	–		7.80	–	~6.00	
6.7...7 dtex	–	–	–	–	–	–	2.60...2.30	

Table 1.7 *(Continued)*

	1936	1948	1954	1958	1968	1978	1988	Region
Synthetic filaments								
PA 6 15/1	–	114.00	64.50	48.50	30.10	–	–	
30/13...21	–	54.00	32.50	22.14	19.20	–	8.30...8.90	
840/140	–	–	13.70	11.10	8.10	–		
22/7 textured	–	–	–	–	–	–	12.40...12.90	Western Europe
BCF	–	–	–	–	–	–	~6.00	
PA 66 33...44 dtex	–	–	–	22.50	19.20	–	8.50...9.000	Western Europe
840/ den	–	–	14.20	11.10	8.10		6.30	
22/7 textured	–	–	–	–	–	–	8.50–9.45	Western Europe
BCF	–	–	–	–	–	–	~6.00	
PP BCF, spun dyed	–	–	–	–	–	–	5.00	
PET pirn/bobbin	–	–	–	18.60	–	–	3.72–4.40	
70 den								
100 den	–	–	–	–	–	–	–	
150 den	–	–	–	–	–	–	–	
1100 den	–	–	–	13.90	13.00	–	–	
POY 150 den	–	–	–	–	–	–	4.00...4.20	Western Europe
75 den	–	–	–	–	5.40	–	3.33...3.49	USA, Korea, Taiwan
Textured 70 den						7.35	6.31	Western Europe
100 den						5.88	5.05	
150 den						5.58	4.77	

underbidding of prices of intermediate and final products, especially from Far East countries. These low price materials are often of good quality because the companies work with the most modern production equipment.

Table 1.5 shows that prices of the most important monomers (Caprolactam, AH-salt, DMT, and TPA) have dropped from 8 DM/kg in 1950 to about 3 DM/kg in 1988, for acrylonitrile from 3.50 DM/kg to about 1 DM/kg. The same is true for the prices of polymer chips (PA and PET), according to Table 1.6 from about 8 DM/kg to 2.50...4.00 DM/kg. PP chips by now have reached prices of only 2.00...1.50 DM/kg or lower.

This price development of course influences the prices of the final products as can be seen in Table 1.7. Most of the commodity synthetic fibers today have prices between 3.50 and 5.00 DM/kg for standard titers. Non-textured filament yarns with more than 30 den are available for 8.50...10.00 DM/kg.

Table 1.8 Price Indices for Chemical and Natural Fibers in Germany [33]

Number	Year	1973	1978	1983	1986	1988	1990
581	Synth. filament yarns	101.0	84.5	95.5	100.4	889.7	96.8
580	Synth. staple fibers	77.8	73.4	90.5	100.6	91.7	90.7
579	Synth. filament yarns and staple fibers	90.3	79.4	92.9	100.5	90.6	93.8
578	Cellul. filament yarns and staple fibers	57.9	73.4	93.7	103.0	105.7	109.1
577	Chemical fibers, total	92.3	78.2	93.1	101.0	93.6	96.9
793	Textured yarns	110.8	87.2	97.2	104.1	93.9	102.3
118	Sheep wool	139.6	85.7	118.3	94.9	145.2	
116	Cotton	93.4	89.3	119.5	72.8	73.5	

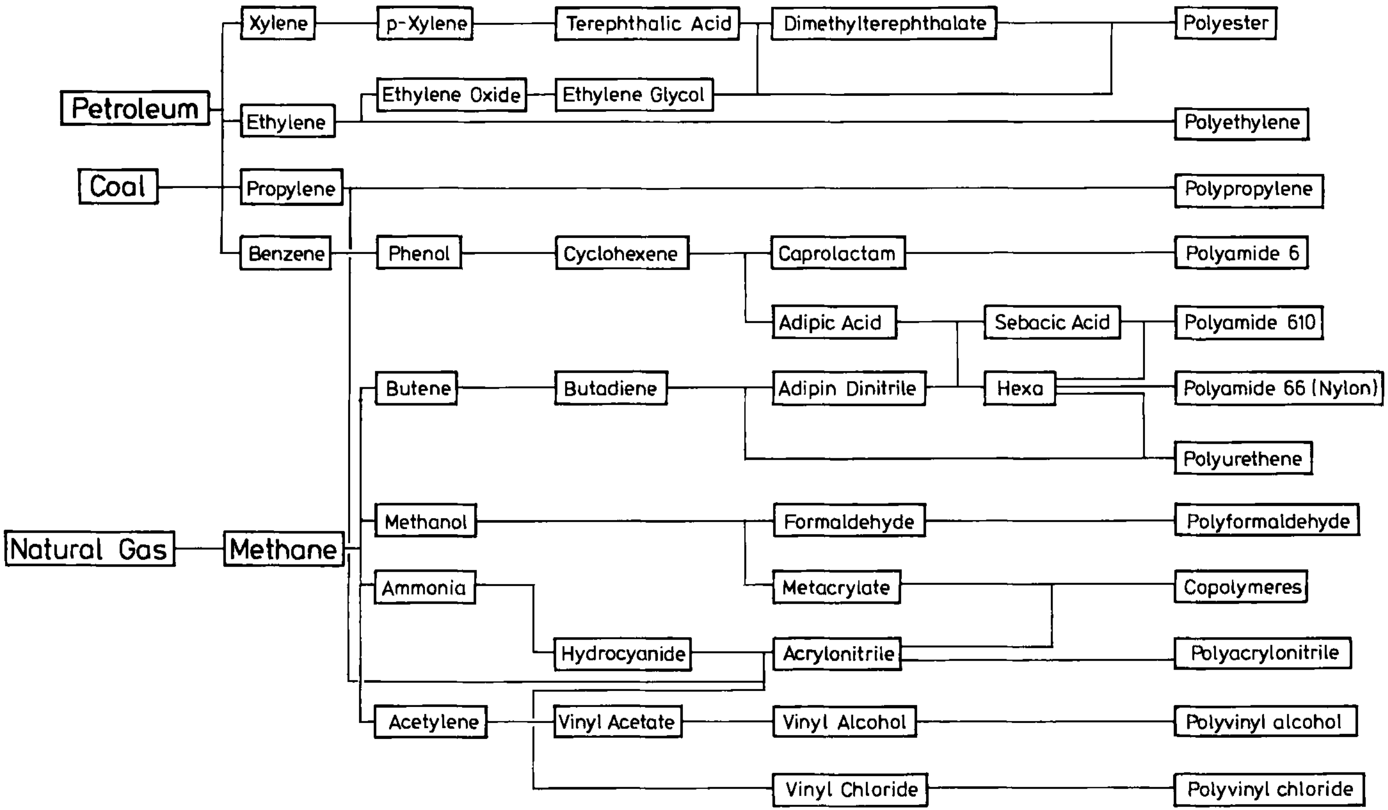


Figure 1.11 Raw materials and their intermediate steps to the polymer.

Textured PET multifilaments of 70 den are around 6.50 DM/kg and of 150 den only about 5.00 DM/kg if a good deal is available. PP staple fibers of 6 den can be purchased as low as 2.60 DM/kg and of 10 or 15 den as low as 2.30 DM/kg in large order quantities. Flat PP filament yarn den 1000 f 72 is offered for 4.10 DM/kg; BCF texturing is 0.50 DM/kg, and spin dyeing is depending on the dyestuff 0.40...0.80 DM/kg more expensive.

This price development can be seen in the comparison of polyester staple fibers, cotton, and rayon staple fibers in Fig. 1.10 and in Table 1.8 with the German price index for different fibers and yarns between 1973 and 1990.

1.6 Raw Materials

In 1964 *Fourné* [30] published a schematic graph on the natural raw materials leading to monomers and polymers that is still valid today. Certain quantitative shifts between petroleum, coal, and natural gas due to price increases of individual raw materials might repeat or reverse themselves today, e.g., from petroleum to coal, if mineral oil experiences a shortage or a price increase. Speculative thoughts about starting from sand, limestone, water, mineral salt, air, as it is theoretically possible, are not realistic at this

Table 1.9 Monomer Capacities 1988/90 (in 1000 t/a)[4] [39]

	Caprolactam	DMT	TPA	Acrylonitrile
EC	875[1)]	1000[2)]	935[3)]	1275
Eastern Europe	950	631	60	550
USA, Mexico	600	2065	1845	1140
Latin America		80	100	150
Japan	475	335	1060	580
Taiwan			660	
South Korea			500	
India		145		
PR China		245	260	
Africa	130			
Others	270	123	?	305
Total	3300	4624 (4960)	530 (6550)	4000

Table 1.10 Global Monomer Capacities and Fiber Production

Monomer	Year	Capacity (1000 t/a)	Fiber production (100 t/a)
Caprolactam	1988	3129	3793
AH-salt		>3000	
DMT	1988	4715	8041
TPA	1988	7355	
ACN	1987	4000	2478
PP, PE	1988	≫2000	1994
		???	470
Total			16776

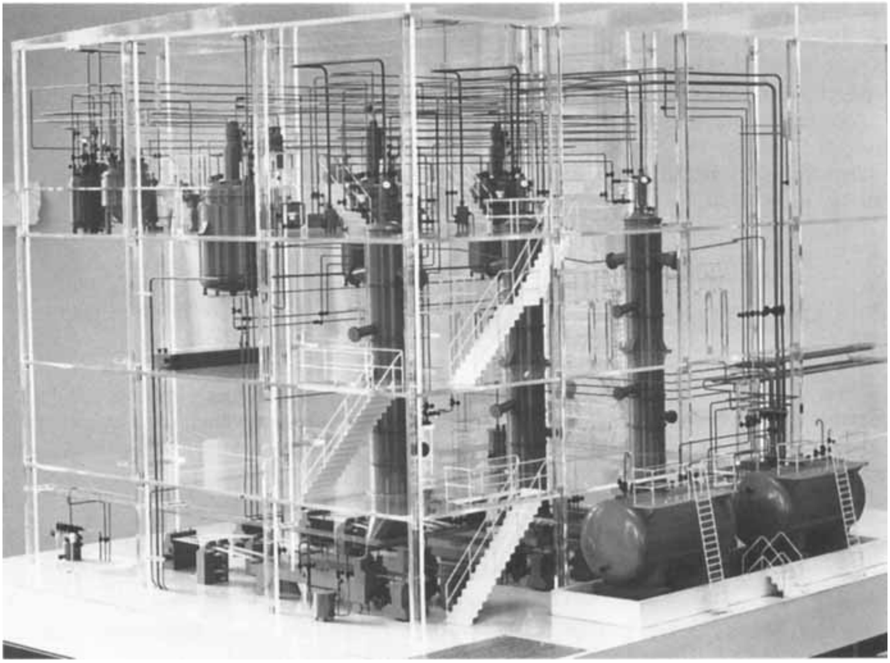


Figure 1.12 Model of a polyamide 6 polycondensation plant for approximately 40 tons/24 h chips [50]
Lower right: Storage bins for molten caprolactam;
Upper left: The preparation and mixing vessel; vertically: three VK tubes, each with approximately 10 m^3 volume; underneath: stringth quenching troughs (water quenches) with take-up and chip cutters

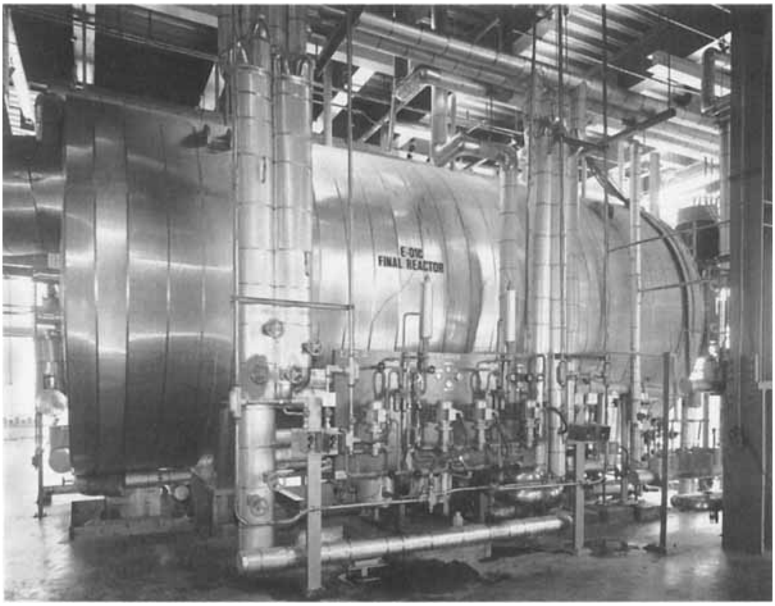


Figure 1.13 Polyester finisher for approximately 130 t/24 h [42]; inner volume approximately 40 m^3 corresponding to about 3 m diameter · 7 m length

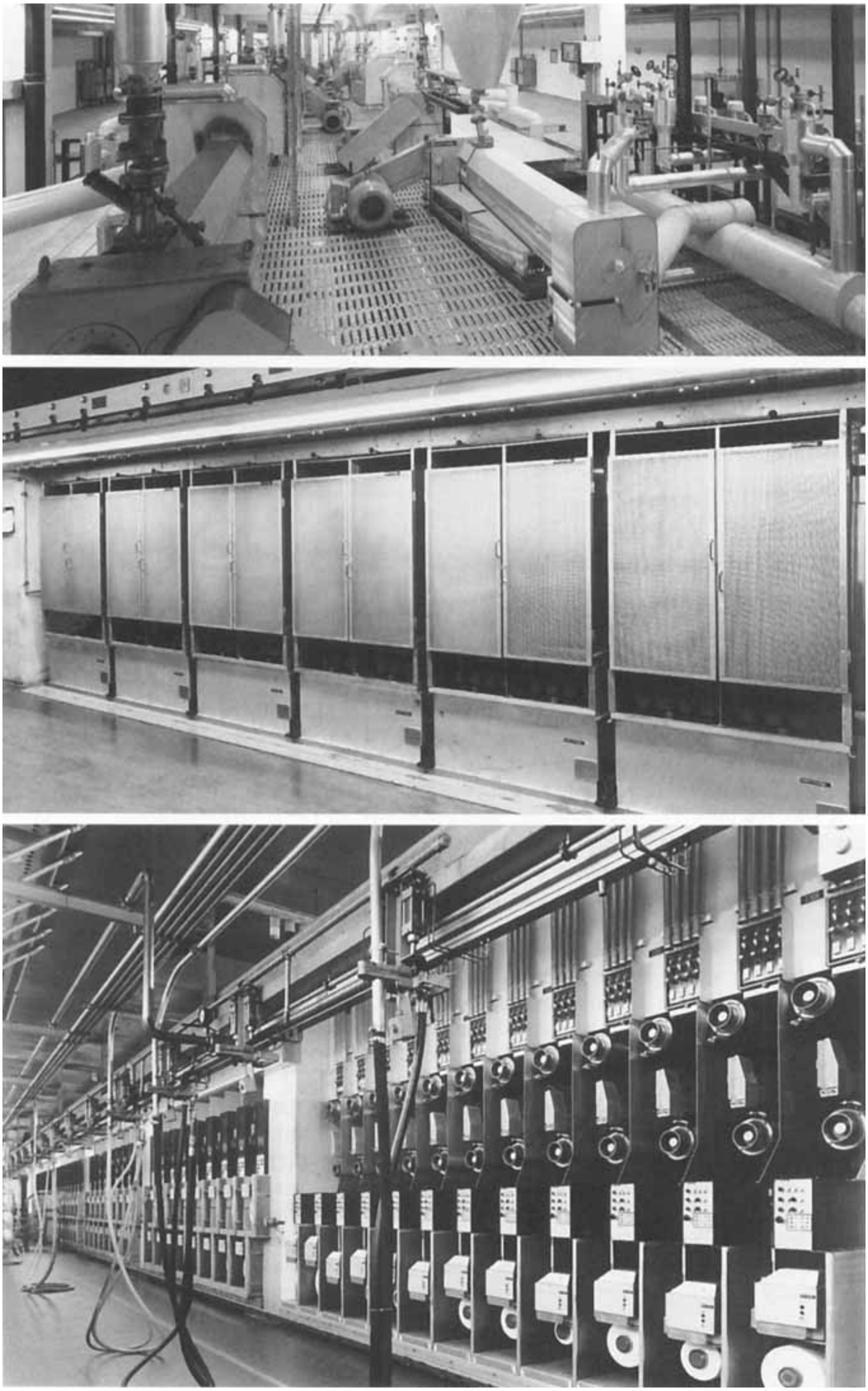


Figure 1.14 Three floor polyester filament spinning plant [44]; upper: Spinning extruder deck with insulated melt distribution piping; middle: Spinning heads with air quench chambers; lower: Ground floor with POY take-up machines (with godets)

Figure 1.15 Draw texturing plant with FK6 false twist draw texturing machines [44]

point of time due to the tremendous amount of energy required [23]. In 1979 only 6% of the mineral oil were used for the petrochemical industry and only 0.33% for the synthetic fiber industry. Within the scope of this book major shifts in the raw material supply are thus unlikely.

The required amount of raw petroleum (naphtha) for each one ton of PA is 2.7 tons, PAN is 2.3 tons, and PET is only 1.6 tons. Thus the synthetic fiber production in 1987 consumed about 30 million tons of naphtha with an annual rate of increase of about 5 million tons. One ton of mineral oil only contains about 20% of naphtha, which results in an annual increase in consumption of 25 million tons crude oil. This total consumption of crude oil might result in a return to more coal, which would result in a significant price increase.

Chemical fibers enjoy the advantage of natural raw materials that grow again, wood cellulose or cotton lint and rather simple auxiliary materials (NaOH, H_2SO_4, CS_2, CH_3COOH, $(CH_3)_2CO$, etc.) and are generally available, so that there should not develop any problems other than environmentally.

The world production of the most important monomers is shown in Table 1.9, where the increase of the TPA capacities is particularly striking [39]. Table 1.10 also compares the monomer capacities to the fiber productions.

Another important source of raw materials can be provided in the recycling of used textile materials. Waste generated during the production (3...10%) is recycled in some form already today. Recycling of used textile materials at today's state of technology is still a major problem—partially due to the lack of classification, partially due to the contamination, finishes, and dyestuffs etc.

Figures 1.12 to 1.19 shall provide a first impression of equipment used for the production and finishing of synthetic filaments and fibers, as described in more detail in the following chapters with the help of drawings. The texts under the figures should be self-explanatory.

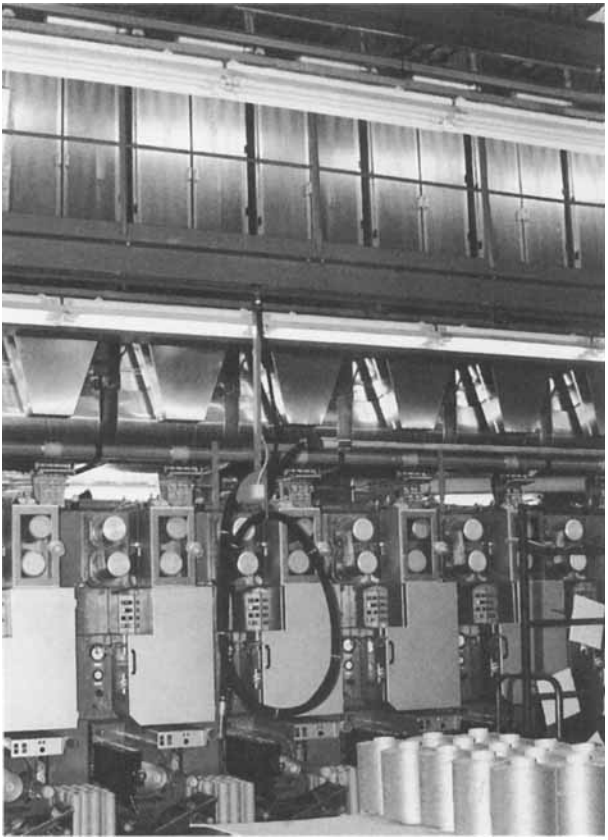


Figure 1.16
Carpet yarn spin-draw-texturing plant for BCF [45]

Figure 1.17 Two-staple fiber aftertreatment lines for approximately 200 tons/d capacity [43]

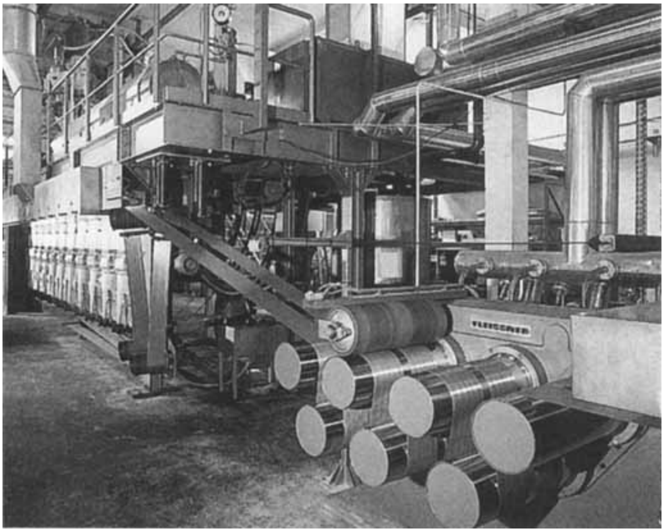


Figure 1.18
Compact spinning plant (one floor) for polypropylene or polyester or polyamide 6 staple fiber [49, 43]

Figure 1.19 Areal view of a complete production plant for polyester and polyamide 6 filaments, staple fibers, chips, synthetic thermo bonders and other specialties. Start of construction around 1950 from a wood saccharisation plant; extended and reconstructed in phases; photo of 1992 [48]

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2 Polymer Specific Processes

2.1 Polymerization, Polycondensation, and Polyaddition

Polymers suitable for the production of synthetic fibers are all created by linking atoms or atomic groups. This can be done by three reactions differing in their chemo-physical process [1, 6]. This chapter primarily deals with the engineering problems of the necessary equipment and machines in the process sequences. There are far more polymers that are suited for fiber formation; they are not covered here, because they can be produced on very similar equipment but are not relevant from a market or quantity point of view today. The production of the monomers from the raw materials is also briefly addressed. Figure 2.1 shows the formation mechanism of synthetic polymers [411].

2.1.1 Polymerization

This is the linking of low molecular monomers to long chain molecules with uniform links (e.g., Polyamide, PA). If different links are combined (e.g. Dynel®) the process is called co-polymerization. Monomers have to be activated to polymerize, e.g., by heat and/or catalysts or simply by light (e.g., vinyl chloride).

Only chemical compounds with double bonds ($-CH_2{=}CH_2-$ or $-CH_2{=}CH-Cl$) can produce chain molecules in this sense, e.g., polyvinyl chloride is produced from vinyl chloride:

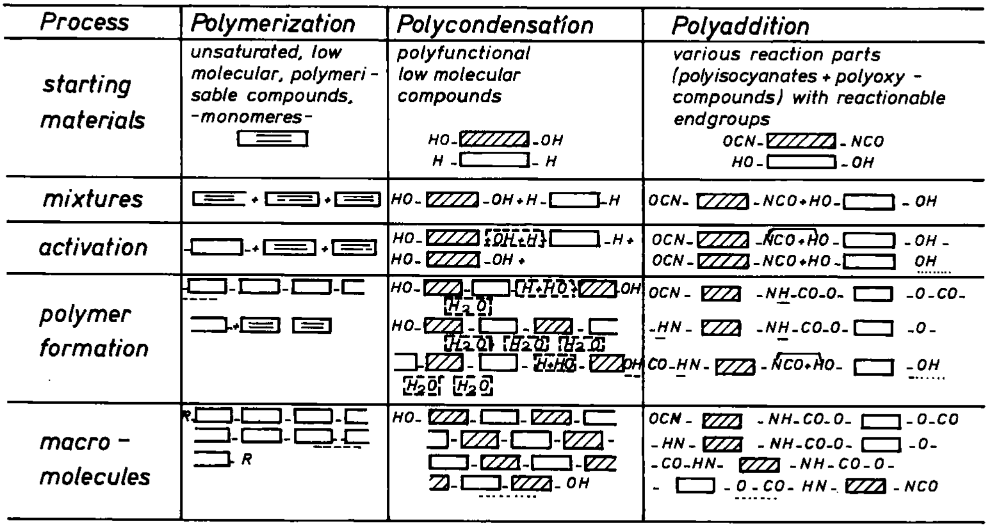
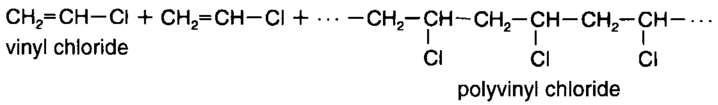


Figure 2.1 Formation mechanism for synthetic polymers [411]

Also included in the polymers are polyacrylonitrile (PAN), the polyolefines, polyvinyl alcohol and the like. With respect to polyamide 6 the opinions are split whether the production is polymerization or polycondensation; both descriptions are used. Polyamide 66, however, is certainly created through polycondensation.



$$\underset{\text{vinyl chloride}}{CH_2{=}CH{-}Cl} + CH_2{=}CH{-}Cl + \cdots \underset{\text{polyvinyl chloride}}{-CH_2-\underset{Cl}{\underset{|}{C}H}-CH_2-\underset{Cl}{\underset{|}{C}H}-CH_2-\underset{Cl}{\underset{|}{C}H}-\cdots} \tag{2.1}$$

2.1.2 Polycondensation

This is a linking of low molecular compounds while simultaneously splitting off byproducts, e.g. water, alcohols etc. The relation of the raw materials to each other determines the average molecular weight. Upon completion of the polycondensation all byproducts have to be removed, because they will influence the polycondensation equilibrium. Polycondensation happens according to the following scheme:

Within this book the most important polycondensation products are the polyamides (PA66, PA610, PA11 etc.) and polyester.

$$\underset{\omega\text{-amino acid}}{H_2N-R-COOH} + H_2N-R-COOH + \cdots \underset{\text{polyamide}}{-NH-R-CO-NH-R-CO-} \cdots + \underset{\text{water}}{H_2O} \tag{2.2}$$

2.1.3 Polyaddition

Polyaddition is the linking of low molecular polyfunctional compounds. The stoichiometric relation of the reaction elements and the chemo-physical mass equilibrium determines the chain length. Polyurethane is produced this way:

$$\begin{aligned} &\underset{\text{glycol}}{HO-R-OH} + \underset{\text{diisocyanate}}{OCN-R_1-NCO} + HO-R-OH + OCN-R_1-NCO + \cdots \longrightarrow \\ &\longrightarrow \cdots \underset{\text{polyurethane}}{-R-O\cdot OC\cdot NH-R_1-NH\cdot CO\cdot O-R-O\cdot OC\cdot NH-R_1-\cdots} \end{aligned} \tag{2.3}$$

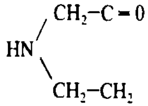
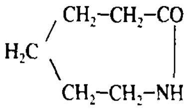
2.2 Polyamides (PA)

2.2.1 Introduction

Only a few of the many known polyamides [1] have reached large scale significance for spinning. Of the few in Table 2.1 only polyamide 6 (PA6) and polyamide 66 (PA66) came to large scale production.

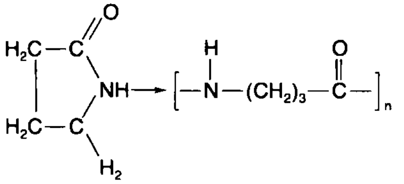
The naming follows the number of C-atoms in the basic molecule: PA6 contains 6 C-atoms, PA66 has 6 + (4 + 2), with the latter one for the combination of a diamine with a dicarbon acid. As the number of C-atoms increases, the melting point decreases; with the combination of diamines it is also lower for an even number of C-atoms than for an odd number [1]. Copolyamides, e.g. from PA6 and PA66 or PA 610 also have lower melting points below the connecting line of the two individual melting points [1]. Copolyamides from three components (see Chapter 2.12.6) [3, 4] are used as thermo bonders or thermo fibers. Quiana® [5] has excellent textile properties, but production discontinued due to its high cost.

Table 2.1 Important Polyamides for the Production of Textile and Industrial Yarns

PA	from/and	T_P (°C)	T_G (°C)	ξ(%) at a relative humidity of 65%	100%	γg/cm^4	σ_B g/dtex	E_{max} g/dtex · %	σ_{wet}/σ_B (%)	ε_B (%)	Examples	Monomers
4	γ-butyrolactam	260…265		9	28	1.25			70…80			
6	ε-aminocaprolactam or -caproic acid	215	35…44	4.5	9.5	1.13…1.14	4…11	41	85…90	24…40	Perlon®	
7	ω-aminoheptane acid (oenanth acid)	225…233		2.8	5	1.10	8.1…8.5	46…49	92	14…16	Enant	$H_2N-(CH_2)_5-COOH$
11	ε-aminoundecane acid	185		1.5.		1.08		48		14…22	Rilsan®	$H_2N-(CH_2)_{10}-COOH$
12	laurin lactam	175										
	diamin + dicarbonic acid											
46	1.4 diaminbutane + adipic acid	290	82 ($\zeta=0\%$) − 5($\zeta=65\%$)	4.5…5		1.18	8	30…32		14	Stanyl®	$H_2N-(CH_2)_4-NH$ + $HOOC-(CH_2)_4-COOH$
66	hexandiamine (1.6) + adipic acid	255…260	42	3.5	9…10	1.14	8.2…8.7	54	85	18	Nylon	$H_2N+(CH_2)_6-NH_2$ + $HOOC-(CH_2)_4-COOH$
610	hexandiamine (1.6) + sebacic acid	209…223		2		1.09	5…6			15…20		$H_2N+(CH_2)_6-NH_2$ + $HOOC-(CH_2)_8-COOH$

2.2.2 Polyamide 4 (PA4)

Mentioned frequently since 1955, but never entering industrial production, PA4 is produced from butyrolactam, 2-pyrrodilinon or α-2-pyrrolydone [7]:



(2.4)

The monomers are obtained by pressing acetylene through a dehydrated solution of calcium pyrolidonate in 2-pyrolidone. The addition of butyrolactam improves the yield, just as a carboxylate salt as a catalyst. According to *Baeskai* [8] it is possible to reduce the polymerization time from 2...3 days to 2...3 h with 70% turnover for the required molecular weight with a quaternary ammonium compound [9].

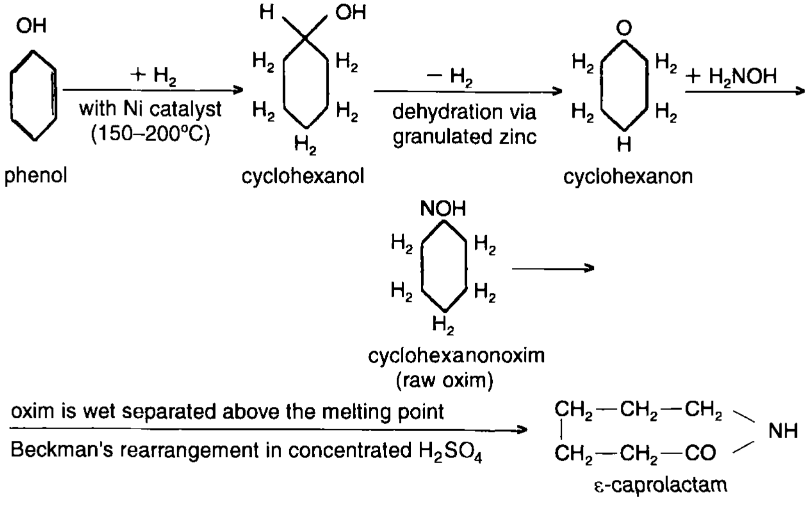
Melt spinning is quite difficult, because the melting point is only about 2...3 K under the decomposition temperature. The production is also too expensive; the yarn has a very low elastic modulus; it fibrillates during washing and texturing does not provide sufficient stability.

2.2.3 Polyamide 6 (PA6)

After *Carothers* assumed that caprolactam could not be polymerized [10], *Schlack* managed to polycondensate caprolactam to PA6 in 1938 [11]. In the countries east of the German border the production of PA6 was quickly established after that, especially for parachute silk. West of this border PA66 was produced as "Nylon". After 1945/47 the production of stocking silk 15 den f1 and 60 den f13 started: The first West German installation was at Vereinigte Glanzstoff-Fabriken AG in Obernburg/Main with 16 spinning heads for a production of about 200 kg/24 h. In 1951 *Fourné* built the first Perlon® fiber installations with 2 × 3 t/24 h for *Schlack* in the plant Kunstseidefabrik Bobingen. These capacities today reach 70 t fibers/24 h per installation respectively 330 kg/24 h per spinning position with dtex 44 f8.

2.2.3.1 Production Process for Caprolactam

The originally mostly used process started with phenol gained from the carbonization of pitcoal.

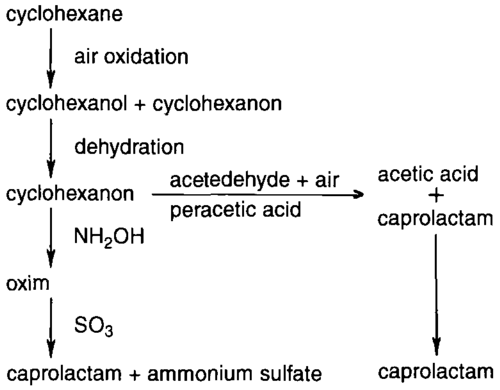


(2.5)

The partial dehydration of cyclohexanol to cyclohexanon ($S_P = 88$ °C) is done catalytically via granulated zinc. It is also possible to work oxidatively in the liquid state with chromic acid or in the gas state with air and fine dispersed silver as a catalyst [13].

To change cyclohexanon with a solution of hydroxylamindisulfo acidic sodium (directly gained from sodium nitrite and sulfur dioxide), the acid is gently weakened with alkalic lye or ammoniac. Beckmann's rearrangement [14] of the oxime with n-H_2SO_4 is so severely exothermic that it is useful to let both run into the stirring vessel under good cooling, and drawing out consistent amounts of caprolactam. Neutralization of the sulfur-acidic lactam solution is done with ammoniac or ammonium bisulfite. Lactam will split off as an oily layer on top of the sulfate solution. Purification is achieved by two vacuum destillations, first via phosphoric acid and then via soda lye ($S_P = 120$ °C at 10 mm Hg). The lactam is flaked out and packed air and water tight. The yield in the phenol, the cyclohexanol and the cyclohexanon phase is each around 95%, but it is considerably lower for cyclohexanonoxime and lactam. For each 1 kg caprolactam approximately 2.8 . . . 3 kg ammonium sulfate are produced, that in limited quantities can be used as fertilizer.

According to *Schwartz* [15] since the 1970s cyclohexane can be transferred through air oxidation into a mixture of cyclohexanol (anol) and cyclohexanon (anon) and other oxidation products. Cyclohexanol and cyclohexanon are separated from each other and the remaining byproducts. The latter produces also cyclohexanon by dehydration, that can be changed to caprolactam and ammonium sulfate or only to caprolactam according to the following scheme:



(2.6)

Cyclohexane is gained from petroleum or by hydration of benzene; it is available in vast quantities.

2.2.3.2 Polymerization of Caprolactam to Polyamide 6

The final polymer product of this reaction is

$$H_2N-\left[HN-(CH_2)_5-CO\right]_n-COOH \tag{2.7}$$

The degree of polymerization n for spinnable products is between about 130 and 250 (lower values for textile fibers, high values for tire yarn).

Polymerization can take place hydrated or dehydrated. With water (i.e., hydrolytic polymerization) three reactions happen parallel to each other:

- With water or water repellent materials [16–21] the first reaction is a hydrolysis of caprolactam while opening the rings to the free acid and then the polycondensation while splitting off the water.
- Parallel there is a direct addition of caprolactam to the opened lactam radicals [17].
- In addition to this there is a possible imide change that promotes the establishment of a distribution equilibrium. This imide change moves the equilibrium of degrees of polymerization with lower water contents [H_2O] to higher values (see Fig. 2.2) [22], and the same is true for lower temperatures T.

Appropriate catalysts increase the rate of polymerization [23]. The equilibrium can be calculated from

$$\left[H_2O\right] = K(T, [H_2O]) \cdot \left[-COOH\right] \cdot \left[-NH_2\right] \tag{2.8}$$

K follows Table 2.2 for not stabilized PA. When stabilizing for example with 0.35 mol-% butylamine + 0.35 mol-% acetic acid the result for $\bar{P}_n = 100$ is a water content (not stabilized) of 0.66% and stabilized of 0.28%, respectively for $\bar{P}_n = 200$ of 0.17 and 0.015% [12].

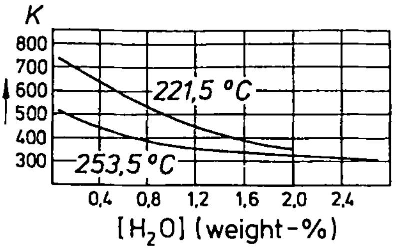


Figure 2.2
Equilibrium *K* as a function of the water (H_2O) content (in mol/mol caprolactam)

Table 2.2 Dependency on Temperature of the Equilibrium Constant with the Lactam Rings at C 6, C 7, and C 8

	K at *T* [°C] 220	230	240	250	260	265
for CL 6	C6					
	800					
	740					
	770···775	672	603	507···510	447	415
	C7					450
	C8					
e.g., $H_2O = 415 \cdot [-COOH] \cdot [NH_2]$ at 265°C Thus follows: Equilibrium water contents for different degrees of polymerization P_n not stabilized and with mono-functional compounds stabilized, $T = 265°C$						
	$\bar{P}_n$	H_2O Weight %	$\bar{P}_n$	H_2O Weight %	$\bar{P}_n$	H_2O Weight %
not stabilized	100	0.66	150	0.29	200	0.17
stabilized	100	0.28	150	0.067	200	0.015
*with each $3.5 \cdot 10^{-2}$ mol acetic acid and butylamine per mol caprolactam						

The cationic polymerization in the dehydrated phase can for example be performed with amino salts of strong acids (e.g. butylamino hydrochloride) at a similar rate as the hydrolytic polymerization with built in catalysts (e.g. amino caproic acid), and will also result in similar monomer contents in the equilibrium (Fig. 2.3a and b).

For comparison Fig. 2.3a also shows the alkalic polymerization (graph Na) that is about 50 to 100 times faster [30], but cannot produce a sufficiently stable polymer for spinning (Fig. 2.4). The average degree of polymerization increases within 10...15 min to $P_n \approx 400$ to 450, only to then drop rapidly (after 2 h to < 200 and after 5 h to < 100 [31–35]).

According to *Rothe* [26] also the polymerization of caprolactam initiated by ammonium salts is cationic. Also hydrochloric or phosphoric acids are quite successful; the latter, however, does not provide

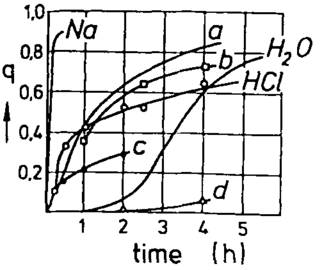


Figure 2.3a
Polymerization of caprolactam without water, with initiators (0.025 mol/mol caprolactam, q = not more extractable part of the initial caprolactam, T=254 °C)
a: $NH_2(CH_2)COOH$, b: NH_4Cl,
c: $CH_3C_6H_4SO_3H$, d: CF_3COOH

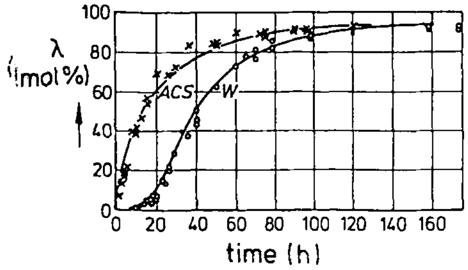


Figure 2.3b
Comparison of the polymerization of lactam with 0.01 mol water (o, W) and with the same molar part of amino caproic acid (x, ACS) (—— calculated curves)

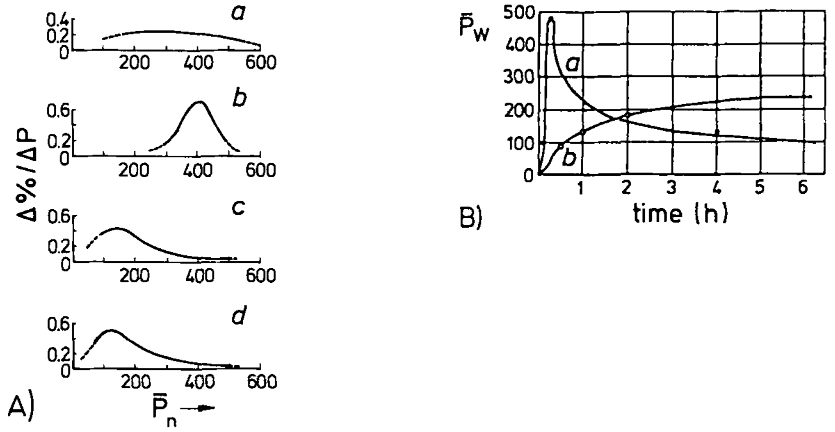


Figure 2.4 *A*) Distribution of the degree of polymerization P of the rapid polymerization after different times of heating: $a=5$, $b=15$, $c=240$, $d=360$ min.
B) Degree of polymerization as a function of time with different levels of concentration or temperatures

uniform results, because phosphoric acid polymerizes by itself and thus splits off water into the system [27–29].

It is also possible to polymerize below the melting temperature: At 75 °C caprolactam turns into a PA with $\bar{P}_n \approx 10$. Caprolactam at a temperature of 85...90 °C can be mixed with catalysts and poured into a form for reaction and hardening. The heat of polymerization of only 3.2 kcal/mol will increase the temperature by 50...60 K.

Stabilizing the Chain Lengths

It is useful to add a compound to the caprolactam in the case of the hydrolytic as well as the cationic polymerization that will enter a thermo-stable bond with the end groups in order to avoid further addition of chain links; this way a uniform polymer will be made. Such compounds are mostly acetic acid, formic acid or adipic acid, less often stearic acid [36] or more general aliphatic or aromatic dicarbon acid or similar amines, e.g. H_2SO_4, HCl, NaOH or hydrochlorid salts from aminocarbon acids etc. Acetic acid for example will form rather stable acetamide end groups:

$$\left[-OC(CH_2)_5NH-\right]_n + CH_2COOH \longrightarrow HO\left[-OC(CH_2)_5NH-\right]_{n-1} + \left[-OC(CH_2)_5NH-\right]OCCH_3 \tag{2.9}$$

According to *Ludewig* [37] 1 mol of acetic acid for each 50 mol of caprolactam will result in an extracted dried PA with a viscosity of $\eta_{\mathrm{rel.}} = 1$ (measured in n-H_2SO_4), for each 100 mol caprolactam about 2.0, and for each 150 mol a $\eta_{\mathrm{rel.}} \approx 2.5$.

The approximation for the degree of polymerization for PA6

$$P_n \approx 100 \cdot (\eta_{\mathrm{rel.}} - 1) \tag{2.10}$$

shows that the chain length is defined by $n =$ mol of caprolactam per mol of chain stopper. Figure 2.5 confirms this with a deviation of less than 10%. Traces of water have a similar result: The addition of 2% AH-salt with water to caprolactam results in a $\eta_{\mathrm{rel.}} = 2.6$. Without the water $\eta_{\mathrm{rel.}} = 3.0\ldots3.1$ is reached. If the water is removed by vacuum from the melt, a higher molecular weight is also obtained.

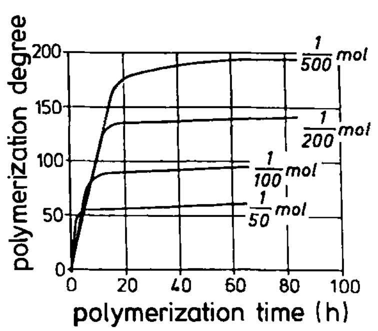


Figure 2.5
Influence of a catalyst quantity on the degree of polymerization of a caprolactam polymer P_n (according to *A. Matthes*) ($DP \approx 124(\eta_{\mathrm{rel.}} - 1)$)

The content of acetic acid in the melted caprolactam can be determined by titration with $n/10$ NaOH as follows:

$$\frac{100 \cdot 0.0060}{25\ \text{g caprolactam (from melt)}} \cdot (n/10\ \text{NaOH}) = x\%\ \text{acetic acid} \tag{2.11}$$

x is usually 1/50...1/100 mol acetic acid/mol caprolactam, i.e. 0.1...0.05% of weight.

With AH-salt and water the beginning rate of reaction increases considerably with the salt concentration, but reaches a similar final viscosity after about 10...16 h of polymerization time (Fig. 2.6). The maximum is reached with or without water with about 2...3% AH-salt (Fig. 2.7). With the continuous precondensation and VK tube polymerization at temperatures of 250...265 °C acceptable short polymerization times can be obtained. The resulting water vapor is withdrawn by a condenser above the VK-tube head, but it also eliminates the entrance of oxygen from the air. It is difficult to completely

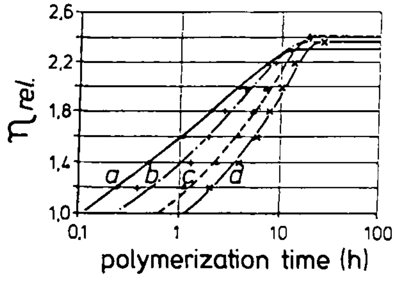


Figure 2.6
Polymerization of caprolactam with (a, b, c) and without (d) water at 260 °C without pressure (AH salt in % of weight: a = 5, b = 2, c = 0.5, d = 0)

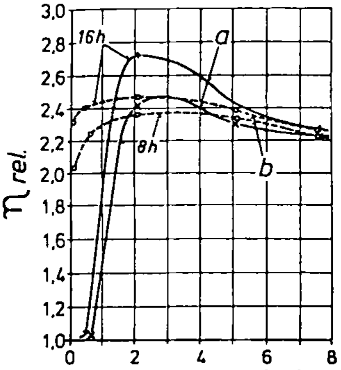


Figure 2.7
Influence of AH-salt and water on the relative viscosity $\eta_{\text{rel.}}$ of a caprolactam polymer after 8 respectively 16 h at 260 °C (a = without, b = with water) polymerization time

remove this water vapor from the viscous melt, resulting in the risk of foam formation. However, the remaining water in the melt acts as a non-controllable chain stopper and can result in inconsistent viscosities.

The addition of larger quantities of AH-salt produces copolyamides with a lower melting point (−2.5 °C per 1% AH-salt). It is better to add ε-amino caproic acid with a similar function, that will polymerize into the chain like a caprolactam molecule.

Influence of Polycondensation Temperature

With an increase in temperature and all other conditions constant the rate of reaction will increase (Fig. 2.8); at the same time the final viscosity will be a little lower, mainly because of residual contents of low molecular parts (Fig. 2.9). This contents of extract will always reform; i.e. if the extract is removed by extraction and drying, and the polymer heated to the same temperature or molten, after sufficient time the appropriate content of extract for this temperature will return (Fig. 2.10). For the transport of melt in tubes the reforming after relatively short times is important (Fig. 2.10b). It also increases with increasing water content, so that melting should be done in a dry state if possible (Fig. 2.11).

The technical polymerization of caprolactam, however, is not finished upon reaching constant viscosity (Figs. 2.6 or 2.8), i.e. at 260...240 °C after 2...10 h, but several hours later that are needed for homogenizing; this results in practically 16...20 h.

The water soluble extract does not only consist from monomers but according to Table 2.3 also from various oligomers, i.e. higher caprolactam compounds (di-mers, tri-mers etc.); this is important for vacuum extraction. The boiling point of these oligomers even in the low vacuum range (<0.1 mbar) is too high for them to be evaporated.

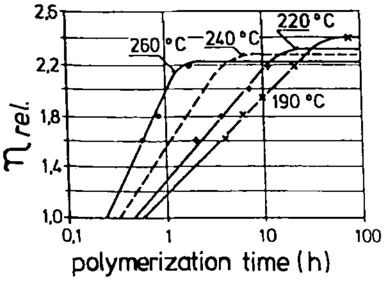


Figure 2.8
Polymerization of caprolactam as a function of time with temperature as parameter

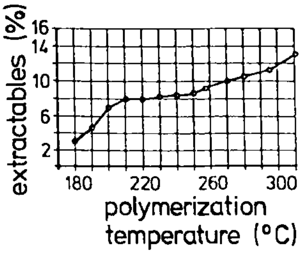


Figure 2.9
Low molecular parts (lactam and oligomers) of polycaproamide as a function of temperature [39]

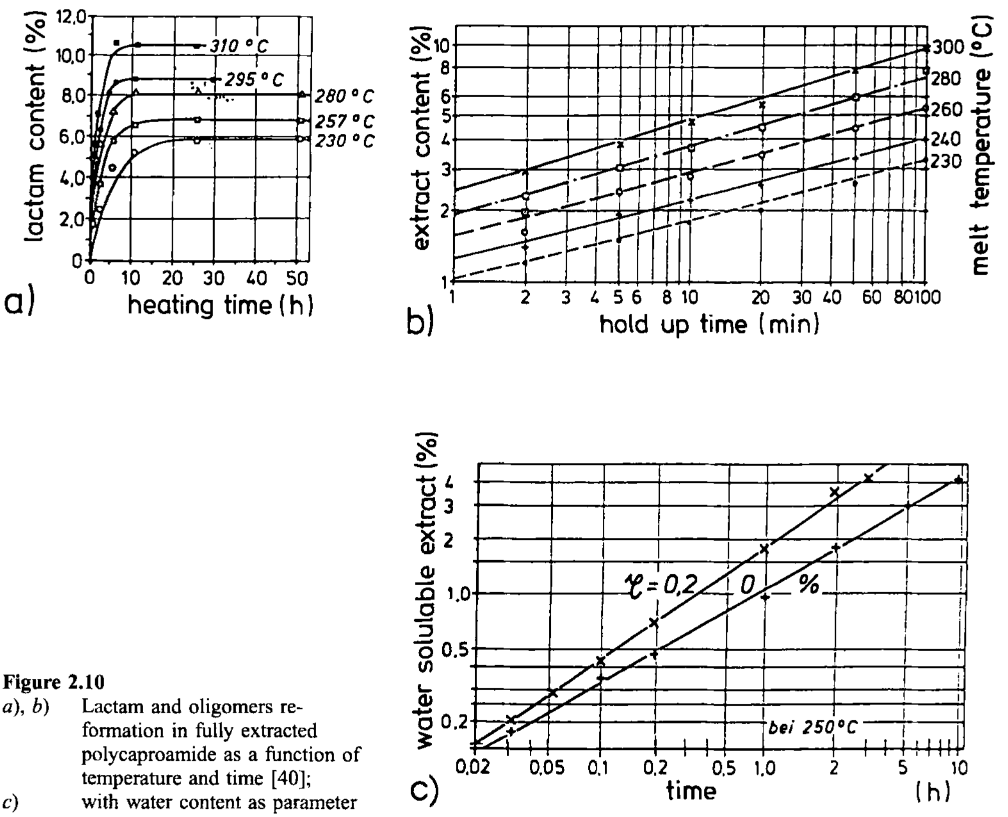


Figure 2.10

a), *b*) Lactam and oligomers reformation in fully extracted polycaproamide as a function of temperature and time [40];

c) with water content as parameter

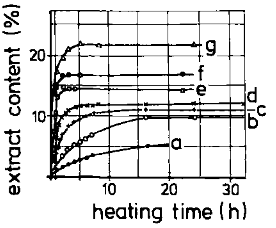


Figure 2.11

Equilibrium reformation of lactam and oligomers in prior fully extracted molten polycaproamide in the presence of water at 250°C [41]:
(a = dry polycaproamide, b = with 0.2% water, c = 1, d = 2, e = 10, and f = 20%, g = 30% water in the polycaproamide)

Table 2.3 Extract Content of Polyamide 6 in the Polymerization Equilibrium

	Extract content (%)	Extract content (%)		
Types of bonds	according to [4]	according to [22] water content mol H_2O/mol caprolactam		
		0.2	0.5	1.0
Caprolactam	8.4	2.5...3 lower values at 221.5°C higher values at 253.5°C	3...3.5	3.2...4
Cyclical dimers and trimers	1.3			
Cyclical tetramers	0.6			
Cyclical pentamers	0.5			
Cyclical hexamers and higher rings	0.7			

On the other hand it is important for the processability of the yarns to have a content of extracts of $\leq 2.5\%$ as shown in Fig. 2.12 [43]: A higher content of extracts increases the number of machineability problems considerably. PA66 (Nylon) with less than 3% (usually $< 1.5\%$) content of extracts shows much better processability.

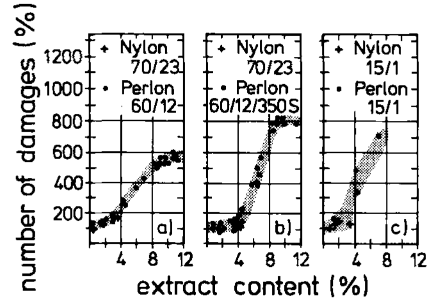


Figure 2.12
Influence of the remaining extractables in PA6 on the processing properties relative to those of the fully extracted PA6 and PA 66 yarn:

a) Flaws on a false twist texturing machine
b) on a pineapple coning machine
c) on a hosiery knitting machine

Influence of Vacuum on PA6 Melts

With the appropriate selection of catalysts or chain stoppers at only one or several intermediate surfaces the degree of polymerization of PA6 can be increased. One step polymerization achieves a $\eta_{rel.} = 2.7 \ldots 2.8$, two step polymerization a $\eta_{rel.} = 3.0 \ldots 3.1$, and with two intermediate surfaces (the first one after about 15% and the second one after 50…70% of the total time) a $\eta_{rel.} = 3.2 \ldots 3.3$ can be achieved.

If a vacuum is arranged at the evaporation surface, $\eta_{rel.}$ also increases considerably (see Fig. 2.13 with $\Delta\eta_{rel.} \approx 0.7$ within about 1 h). The reasons for this are the reduction of water content and the reduction in extract content [37]. *Fourné* [43] found the evaporation throughput (Fig. 2.14) of mostly monomers and part of the di-mers and achieved at around 0.1 mbar a final monomer content of about 0.7% at 200 g/ min · m^2 evaporation. The remaining extract content from dimers and oligomers was still around 2.8%. This melt, however, is very stable: The reversing time of the water soluble extract is about two to three times as long as with 0.2% water in the melt (after 0.5 h without water in the melt to about 0.5…0.7%, with 0.2% water to 1.4…1.5%). If one assumes 0.6% maximum extract content in the yarn, it will be reached starting from 0% with 0% H_2O after 17.4 min, with 0.2% H_2O already after 8 min.

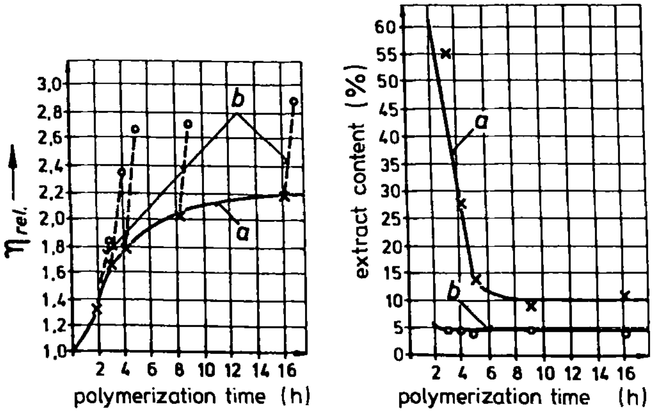


Figure 2.13
Left: Caprolactam polycondensation with following extraction
(———— viscosity increase without vacuum (a),
– – – – with vacuum (b): initiator 5% aminocaproic acid + H_2O)
Right: As a function of time [42]

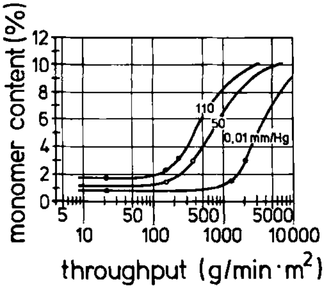


Figure 2.14
Continuous vacuum demonomerization of PA6 melt;
Monomer content as a function of the throughput Q and of the vacuum

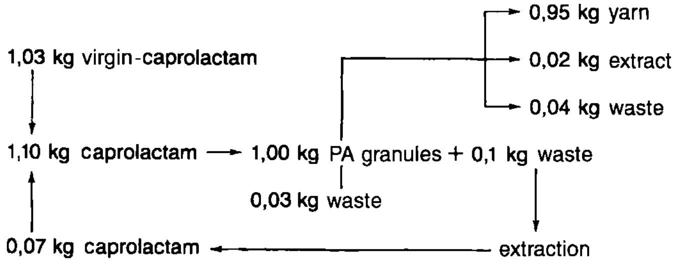
2.2.3.3 Extrusion, Pelletizing, and Drying

Filaments and fibers for textile and technical applications today are almost exclusively produced from chips that are extruded, water cooled, and wet extracted. To achieve higher viscosities it is possible to combine drying with a solid phase polycondensation (see Fig. 4.49a). Stringth casting and pelletizing are described in detail in Chapter 4.3, drying, etc. in Chapter 4.5. Crystallization is not necessary. The optimal stringth temperature for stringth pelletizing is around 68...70 °C. Ribbon casting is outdated.

Stringth extrusion produces uniform chips, preferably with 2...2.5 mm diameter · 3 mm length with a throughput of 20...30 kg/h · stringth. For dry pelletizing the strands are taken up at 60...90 m/min, for under water pelletizing at 45...100 m/min. The wet chips are temporary stored to drain. For the under water pelletizing a centrifuge dehydration step is useful (see Chapter 4.3). In the continuous extraction process the chips can be fed directly into the head of the continuous extractor (see Fig. 2.25).

2.2.3.4 Remarks on Polycondensation and Important Process Characteristics of PA6

The structural and sum formulas, molecular weight, and properties of caprolactam can be found in Table 10.7.1.2. The yield of polycondensation or polymerization can be seen in the following schematic:



(2.12)

This means that a larger PA6 polymerization installation requires a lactam recycling unit for economic reasons. Assuming 13...15% lactam and polymer waste in a vertically integrated installation between spinning, winding, and drawing, and additionally up to 5% waste in the conventional production between the chips to the finished filaments or fibers, this allows for 16...20% of the production quantity to be re-used through regeneration. When spinning POY with revolver winders or in the staple fiber production with can take-up this waste can be reduced by 2...3% (see Fig. 2.15 [54]).

The typical chip properties of some final products can be seen in Table 2.4 [54]. Approximate relations between $\eta_{\mathrm{rel.}}$—measured in n-H_2SO_4 as well as in formic acid—and the average melt viscosity in dependence of the temperature is shown in Fig. 2.16. For further polymer and chip properties see [45] and Chapter 10.

For cooling during the stringth extrusion as well as for extraction only desalted (or destilled) water must be used, that is pumped directly to the lactam recycling installation after it is enriched with to 5 or 8...10% monomers respectively oligomers.

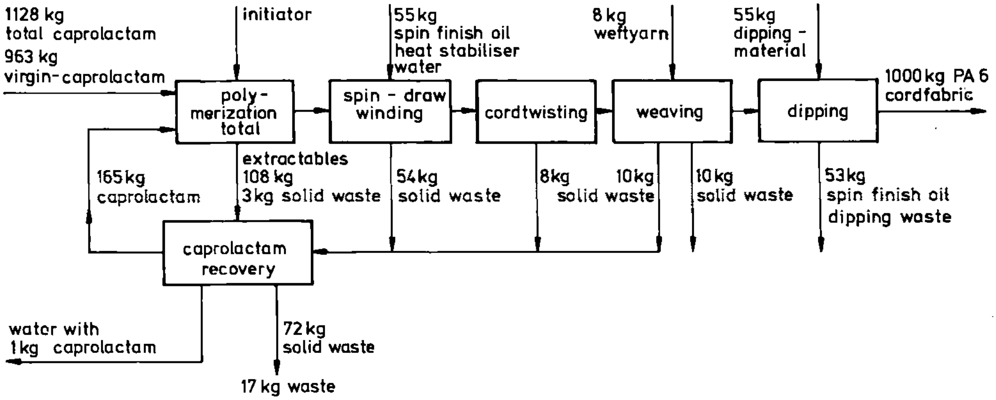


Figure 2.15 Material flow of a PA6 polymerization for the production of tire cord with lactam recovery (Zimmer AG [44])

Table 2.4 Important PA6 Chip Properties for some Final Products (according to Zimmer [44])

	$\eta_{rel.}$ (H_2SO_4)	H_2O content %	TiO_2 %	Extract %	Product
	2.4...2.6	0.08	0...1.5	0.6	Textile Filaments
Caprolactam ↓	2.5...2.7	0.08	0...0.3	0.6	Staple Fibers
	2.7...2.9	0.08	0.15	0.6	Carpet yarn
Polyamide 6 Chips →	2.8...3.0	0.08	0...0.05	0.6	Fish net Yarn
	3.2...3.4	0.08	0...0.05	0.6	Tire yarn
	2.7...3.3	0.12	0...0.15	0.6...1.5	Technical, Plastics Films, foils

Klare [39] indicates 24 h processing time for the autoclave extraction with the rotary agitator. An intermittent installation after 4 · 2 h at 90 °C water will reach $\leq 0.6\%$ extract and at 120 °C water at 2 bar $\leq 0.2\%$ final extract.

The final water content (about 1% or 6...20% depending on the type of mechanical dewatering) only has a limited effect on the drying time. In a rotating vacuum drum dryer or (more advantageous because it runs empty automatically) in a vacuum biconus dryer traditionally with a 95 °C water heater drying was done in 32 h/lot to $\leq 0.08\%$ remaining humidity, today at 120...125 °C water in 20 h/lot. In a vacuum dryer that will achieve about 0.1 mbar empty, after 3 h drying about 2 mbar, and at the end of the drying process about 0.5 mbar can be achieved. The drum can be filled to about 70% of the volume at a weight level of 0.65 kg/l. During the final 2...3 h of the drying process it is useful to lower the temperatures to under 80 °C or even better to 60 °C. Emptying or transport has to be done under vacuum or pure nitrogen because of the risk of electrostatic attraction of dust particles. Further transportation should include some dust removal for abrasion dust and chip particles that were created during drying.

Higher drying temperatures bear the risk of yellowing. Beginning, intermediate, and final rinses may only be done with pure nitrogen.

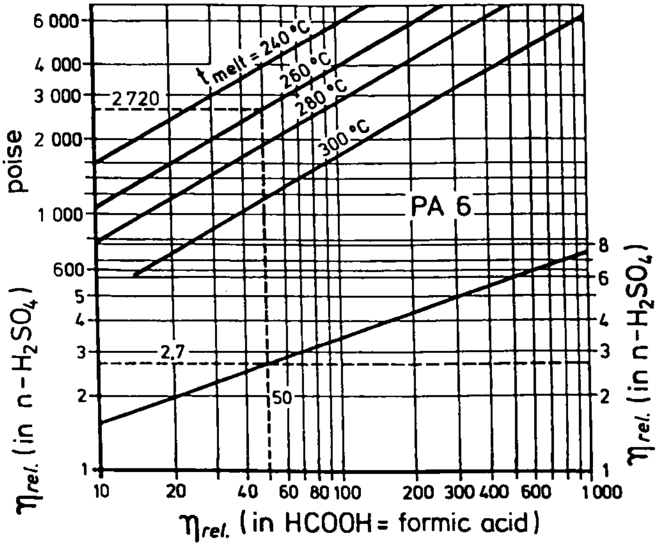


Figure 2.16
Relation between the relative solution viscosity $\eta_{\text{rel.}}$ in n-H_2SO_4 and formic acid and of the melt viscosity with the melt temperature as parameter

Continuous drying is done in a tower in which at the bottom pure nitrogen with $\leq 0.005\%$ O_2 and a dew point of about −40 °C blows against the dropping chips. The entering N_2 has a temperature of about 125 °C, transfers its heat along the way to the chips and extracts the moisture; briefly before exiting it is re-heated to avoid condensation. Such continuous dryers can also be placed directly onto the entrance of the spin extruder. (Fig. 4.55 [531]).

Recipes for the Production of PA6

Simple possibilities to produce spinnable chips are as follows:

Process I: (2.13)

Caprolactam is melted under pure N_2 at 80...90 °C in a water heating jacket melter.

Catalyst:	40% AH-salt dissolved in destilled water
Dulling agent:	TiO_2 as 20 to 40% suspension in molten caprolactam started under pure N_2
Ratios:	For each 110 kg caprolactam 3.3 kg AH-salt (i.e. 8.25 kg or 8.01 l catalyst solution; $\gamma = 1.03$) and the TiO_2 in the desired degree of dulling (see Table 2.4); mix homogeneously.
Process:	Polymerize for 24 h at a starting temperature of 190 °C increasing over two hours to 275 °C for 22 h (possibly at 265 °C) and then extrude at 260 °C by the extruder head into completely desalted water of about 30...40 °C and form chips.

Process II: (2.14)

Prepare caprolactam and dulling agent as under I.

Catalyst:	According to the ratio 0.23 mol-% per mol of caprolactam solve 0.1222 acetic acid in 1 kg of destilled water.
Ratios:	Add 1.1222 kg H_2O and acetic acid plus dulling agent to each 110 kg of caprolactam and mix homogeneously.
Process:	Polymerize at 245 °C (or with a brief starting phase from about 190 °C) for 30 h, then extrude at 257 °C as under I and cool in water and form chips.

Process II produces a somewhat more homogenous polymer. Both products contain about 10...11% parts that can be water extracted.

2.2.3.5 Polymerization of Caprolactam in an Autoclave

Today this process is only used for small quantities, frequently changing qualities, and specialty products. An old scheme of such an installation is found in [46]. To produce 1000 kg/lot of extracted PA6 chips, the reactor autoclave needs a volume of about 1700 l. Installed autoclaves range up to 6...8 m^3. Figure 4.10c shows a practical construction of an autoclave, the conceptual installation is shown in Fig. 2.17.

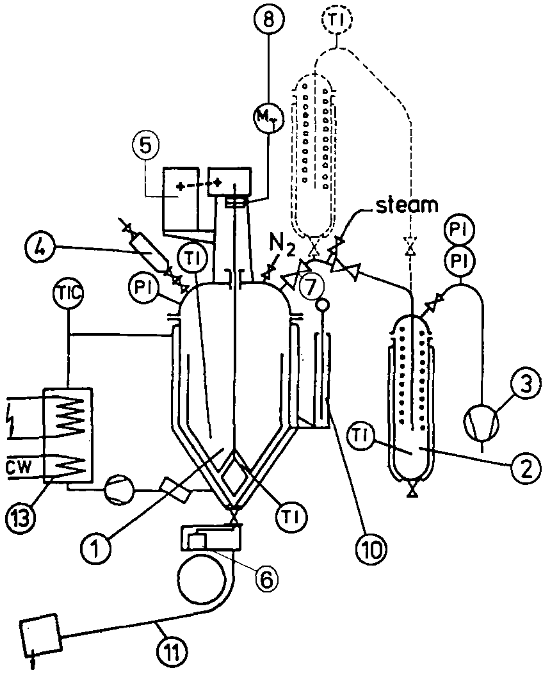


Figure 2.17
One-autoclave polymerization installation for caprolactam to PA6, pressure free, including a vacuum stage

1	Polycondensation autoclave
2	Vacuum condenser
3	Vacuum pump
4	Additive injection vessel
5	Agitator drive, speed adjustable
6	Casting head with die

For polymerization with water or for PA66:

7	Pressure reduction station (from approximately 10 bar for PA6 or 25 bar for PA66 to normal pressure, numerically controlled. Extension for PET is possible with an additional reflux condenser.
8	Torque moment measuring device
10	Hydraulic for autoclave opening (by feed pump, vessel can be lowered)
11	Casting wheel with water quench stringth cooling and cutter
13	Electric heater/cooler for heat transfer oil

The process has been described above. Melting of the caprolactam, mixing with the additives, and the polymerization can be done in the same autoclave. Adding the additives during the process can be done through an additive injection vessel (*4*) even under pressure. To achieve uniform chips, the extrusion time should not exceed 60 min: This requires a stringth granulator for about 30 stringths, that then is not being used for the next 23 h, unless it is mobile under many autoclaves. If water is used during the polymerization, the pressure can be controlled by the steam relief pressure valve. For the overall process the autoclave must be heated by liquid in order to cover the temperature range from about 80...270 °C, if possible following a program. The extrusion of the melt is done either with 10 bar N_2 pressure in the autoclave or with a lower pressure by using an extrusion pump between the autoclave outlet valve and the casting head (*6*).

All parts that are in contact with monomers and the polymer should be made from materials following ASTM 316 and the contact surfaces should have industrial polish (300 grain) or electric polish to $R_t \leq 0.4$ µm.

2.2.3.6 Continuous VK-Tube Polymerization

This can be done without pressure for caprolactam with $\leq 5\%$ H_2O as well as with a prepressure stage. The water prepressure stage aids the opening of the caprolactam rings.

A simple schematic in Fig. 2.18 shows the melter and mixer (*1*), the mixer and storage tank (*3*), the prepolymerization tube (*6*), the VK tube (*7*), the extrusion head (*10*) with extrusion pump (*8*) and casting trough (*11*). To avoid "drift through", the VK tube is equipped with hole plates as in Fig. 2.18a that help to homogenize the flow time across the cross-section of the tube. The process temperatures in the melter and the storage tank are 80...85 °C (with water heater), in the prepolymerizer about 220 °C (with liquid Dowtherm) and in the VK tube 260...275 °C depending on the final product. The highest achievable solution viscosity (in n-H_2SO_4) is about 2.8. If the VK tube heating jacket is separated into three zones, it is useful to choose 230 °C for the upper zone, 260...270 °C for the middle zone, and 257...260 °C for the lower zone. For heat transfer reasons within the melt such VK tubes can only have inner diameters of up to about 400 mm.

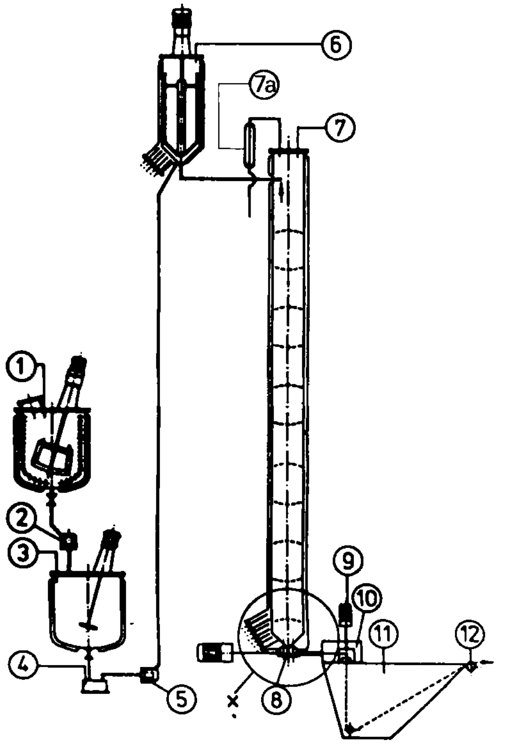


Figure 2.18
Schematic drawing of a PA6 VK tube polymerization
1 Lactam melter and mixer
2 Filter
3 Lactam mixer and storage tank
4 Dosing pump (piston type)
5 Filter
6 Prepolymerization tube
7 VK tube
7a Evaporation condenser
8 Extrusion gear pump with adjustable drive
9 Stringth die in
10 Extrusion head
11 Casting trough
12 Water stripper

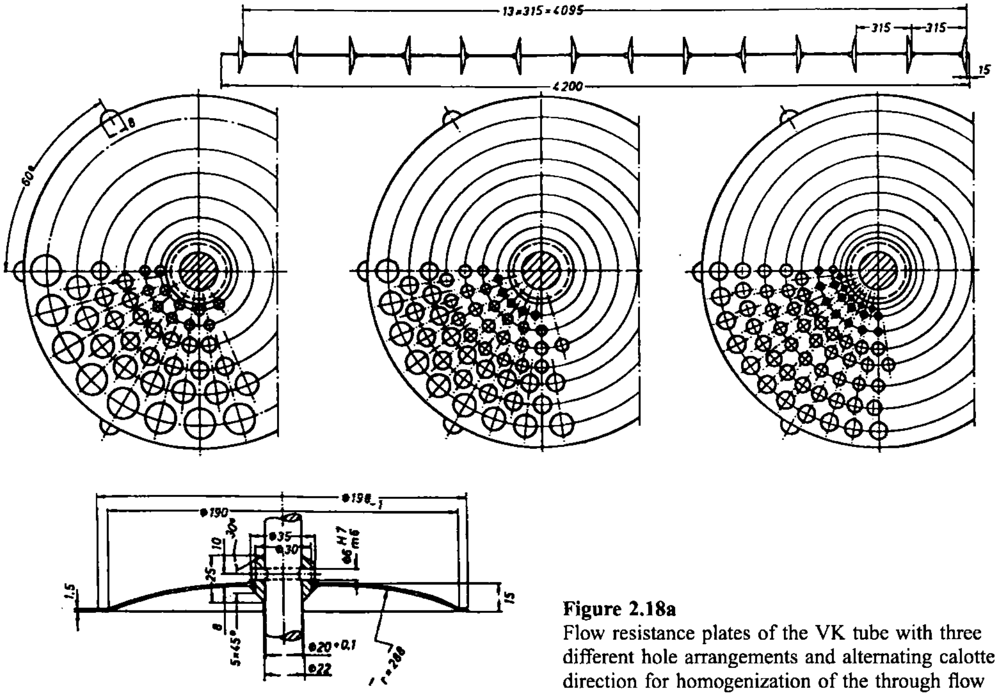


Figure 2.18a
Flow resistance plates of the VK tube with three different hole arrangements and alternating calotte direction for homogenization of the through flow

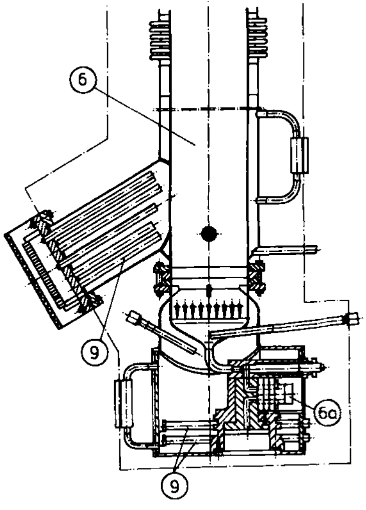


Figure 2.18b
Details in Fig. 2.18
6 Lower end of the VK tube
6a Extrusion gear pump
9 Electric heating rods

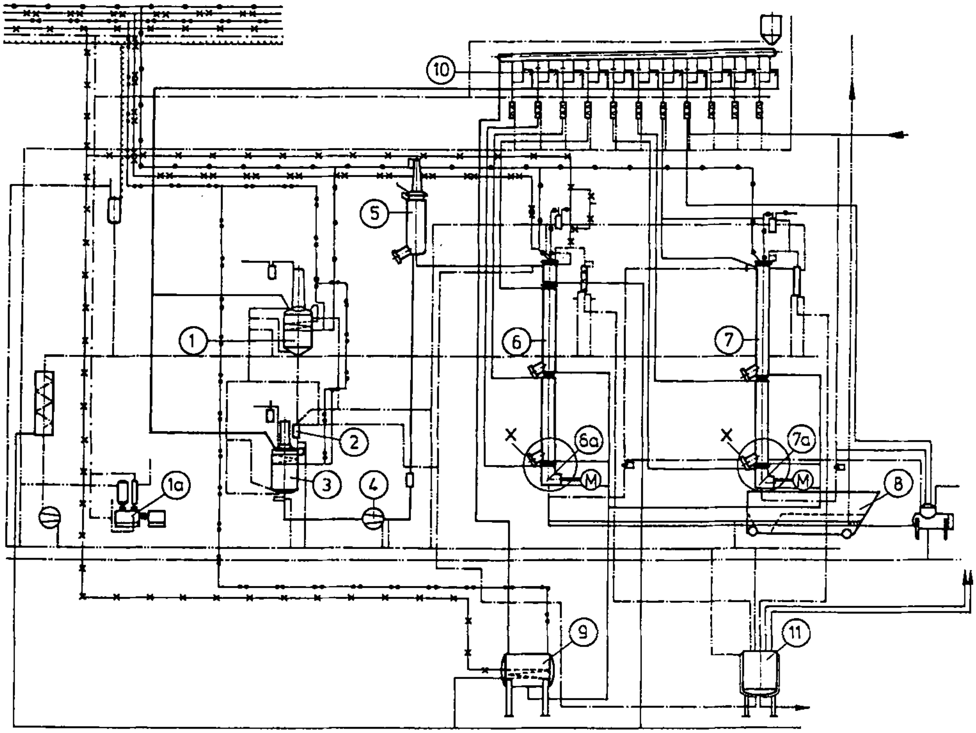


Figure 2.19 Flow sheet of a PA6 VK tube polymerization
1 Lactam melter and mixer
1a Vacuum installation for *1* (dehydrating)
2 Filter
3 Lactam storage and mixing vessel
4 Dosing pump (piston type)
5 Prepolymerization tube
6 First VK tube
6a Melt gear pump
7 Second VK tube
7a Extrusion gear pump with casting head
8 Casting trough (water quench)
9 Electric Dow heating system
10 Dow loss condensers
11 Dow condensate receiving tank

Figure 2.19 shows the process scheme of a three zone VK tube installation for a throughput of about 3500 kg/24 h respectively 3000 kg/24 h PA6 chips extracted. Considering the specific devices for temperature homogenization, the tube (*6*) can be increased in diameter to allow for more capacity. The extrusion head (detail X) can be designed similar to Fig. 2.18b with a throughput of 3500 kg/24 h and with an extrusion pump of 100 cm^3/revolution.

Larger installations which engineering firms today [44, 53, 526] deliver with capacities up to 70 t/24 h need to consider the exothermic process of the polymerization of caprolactam. This is done by installing temperature homogenization plates across the VK tube in distances of no more than 2 m along the direction of the material flow. Today, up to 1600 mm cross-section is common. Temperature

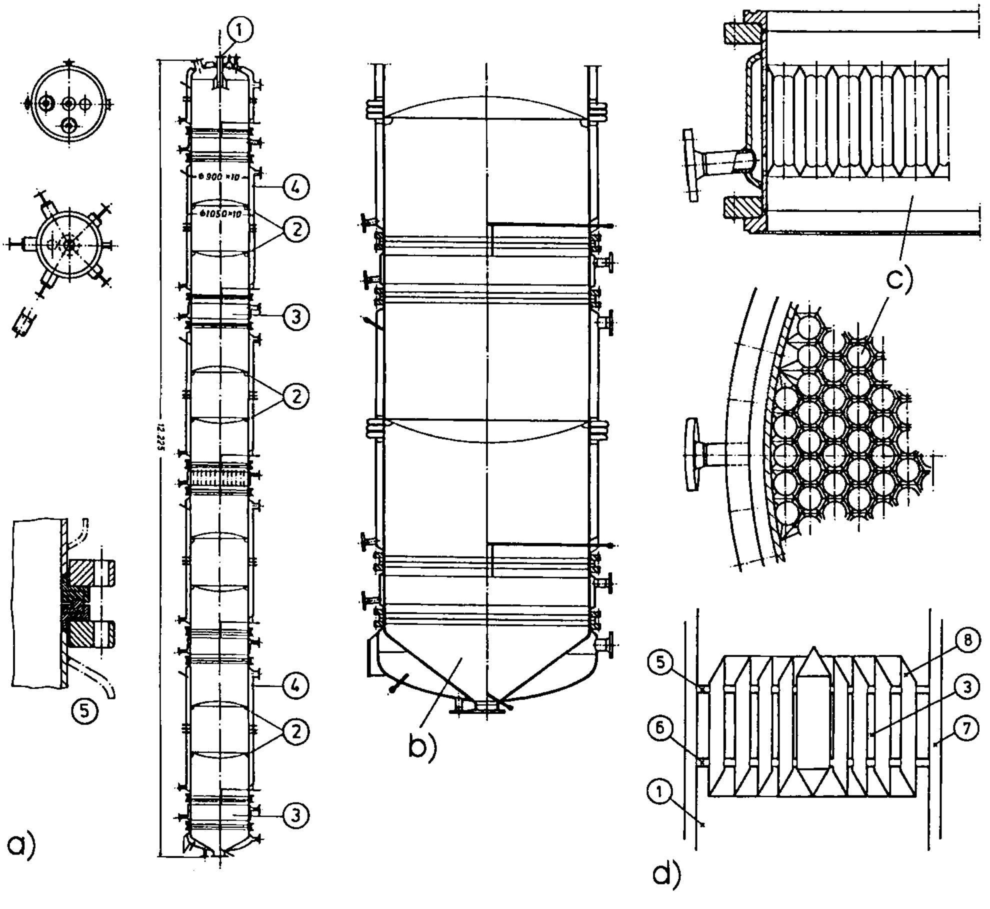


Figure 2.20 Principles of a large (commercial) VK tube (about 22 m^3 volume)

a) Cross-section of a complete VK tube with (*1*) melt supply, (*2*) perforated resistance plates, (*3*) temperature homogenization plates, (*4*) heating jacket with length compensation, (*5*) flanges;

b) Lower end of the VK tube

c) Design details of a temperature homogenization plate: The melt flows downwards through the round openings, the ribs are surrounded by liquid or Dow vapor

d) Ring temperature homogenization plate [626]

1 Melt room
3 Melt room between the ribs
5 Connection pipes for Dowtherm
6 Dow condensate flow to the
7 Dow heating jacket
8 Ring ribs, hollow

homogenization in the VK tube either works like in Fig. 2.20a by heat exchanger (see Fig. 2.20c [47]) or according to Fig. 2.20d [524, 526]. The ribs are touched on one side by the polymer melt, on the other by Dowtherm.

For the transport of the caprolactam membrane pumps or piston type pumps are used. The flow of the melt from prepolymerization to the first VK tube is done at the entrance of the caprolactam in the prepolymerizer from underneath leveled through an overflow. Further transportation of the melt from the lower first VK tube to the next VK tube head can be achieved by gear pumps that are controlled by the level of the second VK tube, e.g. by γ-radiation. Two condensers must be installed above each VK tube head, one to run, the other as standby for example for cleaning, to condensate and discharge the gas products. Each heating zone needs a separate Dowtherm loss condenser.

Table 2.5 gives recommendations for the size of the reactors. Many more suggestions for continuous polycondensation of caprolactam are discussed in [49] as well as for vacuum demonomerization in [49, 50].

Table 2.5 Recommended Reactor Sizes for PA6 VK Tube Polycondensation

Capacity kg/24h	Melter l	Mixer l	Caprolactam l	Prepolymerization l	1st VK tube l	2nd VK tube l	η_{ref} max.
300	100	—	180	—	280	—	2.7
1000	400	—	600	—	1 150	—	2.7
3000	1000	1000	1500	400	1 700	1300	3.0
10 000	2000	2000	4000	1500	6 500	3500	3.1
20 000	4000	4000	8000	2500	12 600	7 500	3.1
50 000	8000	8000	15 000	6000	35 000	15 500	3.1

2.2.3.7 Vacuum Demonomerization

This process can lower the extract content of the melt to 2.5...3.5% and that of the monomers to $\approx 0.5\%$. At the same time the viscosity of the solution can be increased to $\eta_{rel.} \approx 3.6 \ldots 3.8$. There are two different designs;

- melt film flowing down a vertical tube wall [50, 51], probably outside heated by dow,
- multi disc or spiral disc finisher.

The evaporation surface of the first is considerably smaller than that of the disc finisher: At 6 m effective height 300 mm inner diameter the first has an evaporation surface of 5.5 m^2. At 1 mbar and 7%

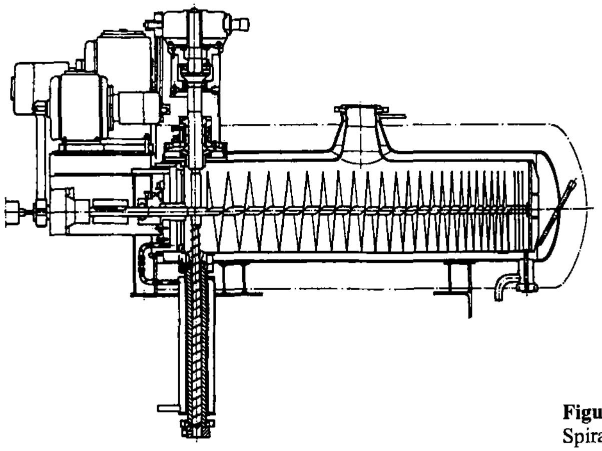


Figure 2.21
Spiral disc vacuum demonomerizer for PA6 melt

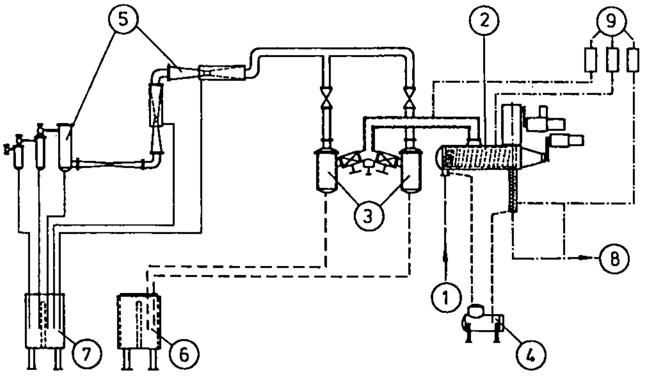


Figure 2.22
Flow sheet of a vacuum demonomerizer in a PA6 VK tube polymerization with
1 PA melt from the VK tube
2 Vacuum demonomerizer (finisher)
3 Vacuum condensers
4 Dow evaporator
5 5-stage steam vacuum jet
6 Lactam receiver
7 Barometric condensate receiver
8 Demonomerized PA6 melt to spinning
9 Dow loss condensers

evaporation of the throughput this represents about 1600 kg/24 h melt. A disc finisher as in Fig. 2.21 with a diameter of 1 m and 30 discs has a length of about 4.20 m with an evaporation surface of 42 m^2; then, all other items the same, a throughput of about 12 t melt/24 h results.

Even though vacuum demonomerization in the case of PA6 yields a too high final extract content for spinning and was replaced by wet extraction, Fig. 2.22 shows it within the overall system, because there are similar applications for PET (see Chapter 2.3).

2.2.3.8 Extraction of PA6 Chips

Today wet extraction is generally used, and the remaining extract content in the chips is usually between 0.2 and 0.6%. Figure 2.23 shows the flow diagram of an extraction installation working in lots. The PA6 stringths from the polycondensation unit (Fig. 2.19) are length reduced in the chip cutter (*2*) with 18

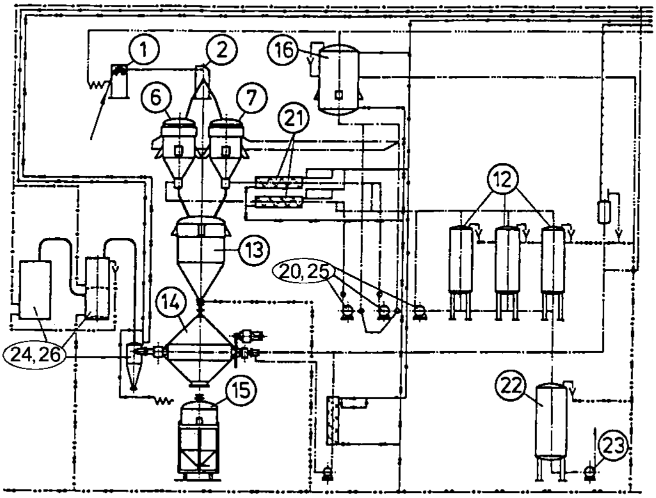


Figure 2.23 Flow diagram of a batch chip extraction as a continuation to Fig. 2.19 with
1 Stringth take-up from the casting trough
2 Dry chip cutter
6, *7* Extractors
12 Extract water containers for 4-step process
13 Wet chip receiver
14 Biconical vacuum dryer
15 Transport trolley for dried chips
16 Pure water storage
20 Centrifugal pumps
21 Steam or hot water heat exchangers
22 Lactam water container
23 Supply pump to the lactam water recovery
24 Steam or hot water heat exchanger for *14*
25 Circulation pumps
26 Dust separator, condenser, and vacuum pump for *14*

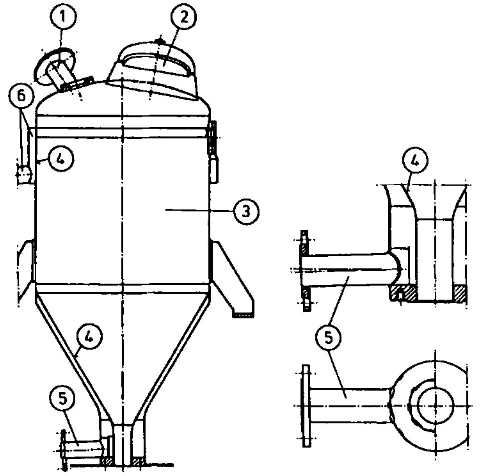


Figure 2.23a Chip extractor (items *6* and *7* in Fig. 2.23) with

1 Filling stud
2 Man hole
3 Extraction room
4 Sieve bottom respectively wall
5 Extract water entrance (from pumps *20* through the heat exchangers *21* in 2.23)
6 Extract water overflow ring and return to one of the intermediate containers (*17*, *18*, *19*)

The extract water circulation should be (60...100) times extractor volume

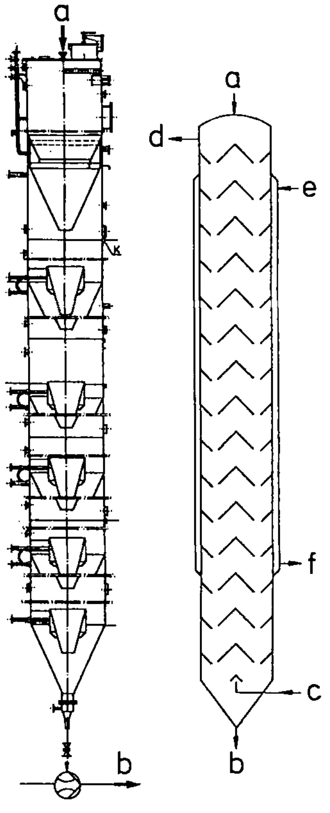


Figure 2.24 Schematic drawing of a continuous PA6 chips extraction (left: according to [524], right according to [54])

a = Feeding; *b* = Emptying or discharging; *c* = Nitrogen feeding; *d* = Drying gas overflow; *e* = Heating water outlet; *f* = Heating water supply

stringths of 10 t/24 h and then lead into one of the two extractors (*6*, *7*); each of these has a filling time of 8 h. They are designed according to Fig. 2.23a with a conical sieve bottom (*4*), through which the extraction water flows upwards. The flow speed is generated by a circulation pump (*20* and others) with a capacity of two times the extractor volume per minute, so that the chips whirl around in the extraction water. This water is withdrawn through the upper sieve (*4*), lead back to the circulation pumps (*20*), heated in the heat exchanger (*21*), and then flows back to the ring extractor bottom. During the first 2 h of an extraction cycle very concentrated water is used (e.g. from the extract water vessel (*12.3*)) that after 2 h exits into (*22*) to be moved via pump (*23*) to the lactam recovery. During the next 2 h less concentrated water from (*12.2*) is used and towards the end pumped into (*12.3*) and so on. For the last 2 h of each lot fresh water from (*16*) is used and pumped within 2 h into (*12.1*). The wet chips fall into the wet chip receiver (*13*), collected to the correct amount, weighed, and then passed on to the dryer (*14*) (Fig. 2.23).

An easier installation is the continuous extraction according to Fig. 2.24. At the bottom hot water of 110...120 °C is pumped in depending on the height of the column that flows opposite (upwards) to the extracted chips and arrives at the top with about 90...95 °C. This will result in an extract concentration of 8...10% in the water, which is then pumped to the lactam recovery, whilst the chips, when discharged at the bottom, will only contain ≈0.4% extract. Discharging is done via a rotary valve.

Klare [49] showed that efficient recovery for the extract water will result in economic yields: Of 1 t extracted dried chips during dissolving etc. 1.8 kg, from polymerization to chip cutting 9.3 kg, and during drying 1.7 kg are lost. On the other hand it is possible to recover 75.2 kg of the 81.4 kg extract; i.e. the total loss is only 1.9%.

2.2.3.9 Large PA6 Polymerization and Chip Production Installations

Modern large scale installations for the production of 40...70 t/24 h PA6 chips for spinning are only available with the necessary know-how from three to five manufacturers [53, 54, 524]. Their principle is quite similar, so that it is sufficient to describe one (Fig. 2.25): From the lactam entrance (*8*) [53] to the VK tube (*9*) [54]—possibly with a pressure step and a second normal pressure step—the product flows to the stringth casting (*12*) and the under water pelletizing to the wet extraction (*14*) and the continuous drying (*17*) to the intermediate storage tanks with chip cooling (*19*). The only differences in the three installations are in the details that were described in the previous chapters. The chip types from the installation [54] are specified in Table 2.4 and are equivalent to those of other installations. Most

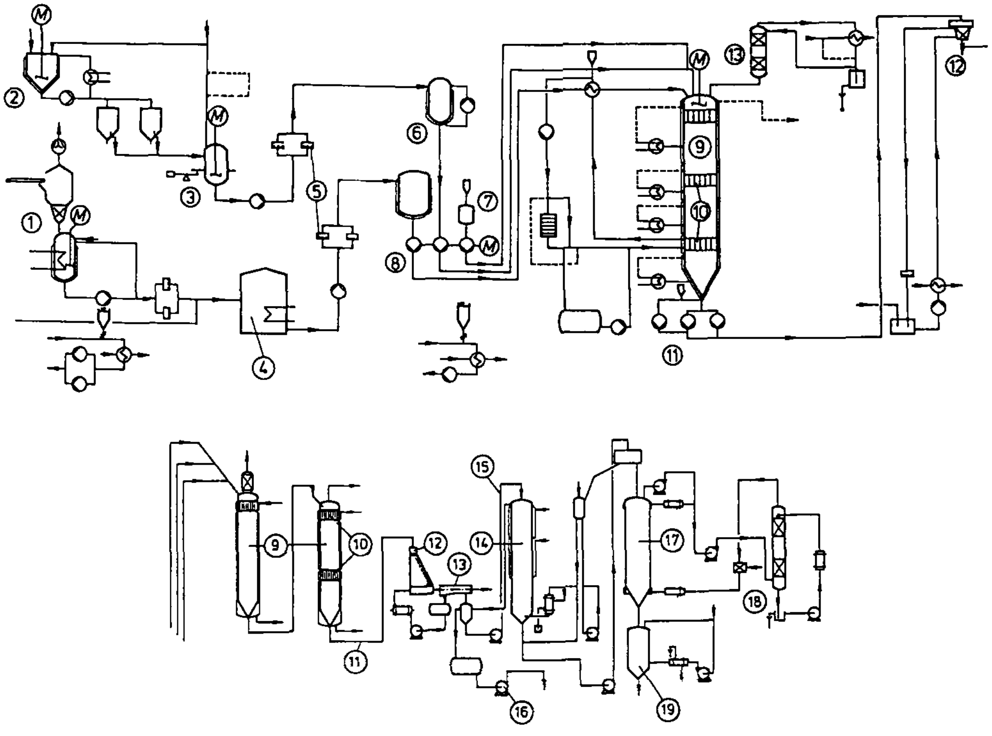


Figure 2.25 Flow diagram of a commercial size continuous PA6 chip polymerization plant according to [54]

1 Lactam supply and melter
2 Lactam melter with additive supply
3 Lactam mixer and additive mixer
4 Lactam melt storage
5 Exchange filter
6 Lactam additive supply tank
7 Additional additive tank
8 Lactam storage with dosing pumps (piston type)
9 VK tube (pressure stage)
10 Second VK tube (pressure free stage) with temperature homogenization plates
11 Melt pipe, jacketed
12 Under water pelletizer
13 Chip dehydrating
14 Continuous chip extractor
15 Wet chip supply
16 Lactam water pump to recovery
17 Continuous chip dryer
18 Dryer hot gas system
19 Chip storage with circulation gas cooling

installations were probably built by [54], most of them in the former COMECON [524]. The range of the relative solution viscosity variation (measured in n-H_2SO_4) is consistently given $\leq \pm 0.015$.

2.2.3.10 Spinning and Drawing of PA6 Filaments

Many details of this are described in Chapter 4, so that here only the primary items will be covered. PA6 filaments provide an excellent material for many end uses, e.g. tire cord for extreme weight trucks or airplane tires or carpet yarns etc. On the other side it cannot compete with PA66 in many uses [55], mainly because of the lower elastic modulus, e.g. for ladies' stockings filaments or for high volume effect yarns. It is also more difficult to dry heatset the fabrics at 190 ± 2 °C than for PA66 at 225 ± 6 °C. On the other hand PA6 can be died more evenly than PA66.

Typical spinning temperatures are mentioned in Table 2.6 as a function of $\eta_{rel.}$ (see also Table 2.4) together with the resulting melt viscosities. They are adjusted with the spinning temperatures to almost always the same values.

Sucking of the evaporates right under the extrusion spinneret is necessary, because this is where in the first 10...15 cm about 0.5...1% of the spun weight are evaporated as extract and/or decompositioned products.

For the length of the necessary cross-air cooling zone see Fig. 3.18 and Table 2.7.

Table 2.6 Typical Melt Temperatures for Spinning PA6

$\eta_{rel.}$		T °C	Melt viscosity[1] P
2.3	Melt grid	257...265	1200
2.6	Extruder for textile fibers, carpet yarn	260...285	1200
2.8	Technical yarn	280...290	1200
3.0			
3.4	Tire Cord	285...300	1200

1) according to Fig. 2.118

Table 2.7 Spinneret Take-up Speeds for PA6 Spinning

	Final titer dtex	Spinning titer dtex	Air quench cooling length m	Take-up speed m/min
LOY	33	100	1.35	250...350
	28	84	1.35	300...400
	22	66	1.35	400...500
	16.5	50	1.35	500...650
	6.6	22	1.20	1000...1200
	3.3	12	1.10	1200...1400
POY	5.5	6.8	1.80	5200...5400
	3.3	4.1	1.40	
	2.0	2.4	0.90	5600...5700
	1.0	1.4	0.60	3300
	0.7	1.0	(0.4)...0.5	3200

In spinning LOY, even for the continuous direct drawing to FDY or BCF, the take-up speed is depending on the individual filament titer (dpf) as seen in Table 2.7. Here the take-up tension between the spinneret and the first godet is relatively low.

The possible residual draw decreases with increasing take-up speed; this is shown in Fig. 2.26. The double logarithmic graph shows clearly that up to about 800 m/min and beyond 5000 m/min there is no significant influence of spinning speed on the draw, while it does drop from about 3.5 to 1.1 between these speeds; this is not as clear in the linear graph. If the filaments can have a remaining draw of 40%, they can be spun according to the 4 HS process with a POY spinneret take-up (Fig. 2.27 [61]); if they can additionally keep an irreversible 10% remaining stretch, they can be taken up and wound directly from the spinneret at ≥ 6000 m/min. This way a self texturing carpet yarn can be produced through the cross-section (-•) and very asymmetrical cooling.

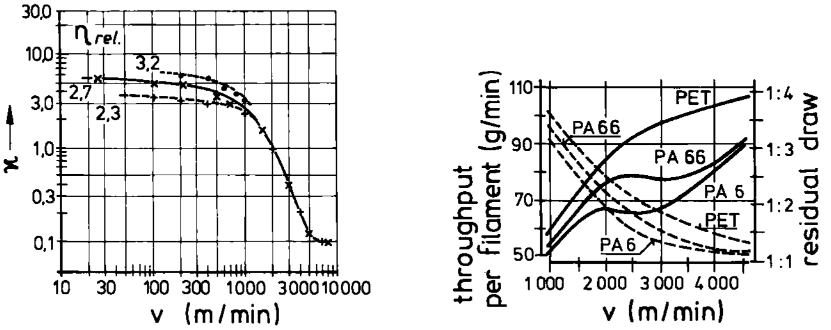


Figure 2.26 Residual draw of PA6 filaments $1:(1+x)$ as a function of the spin take-up speed with the parameter relative solution viscosity; left: in double logarithmic, right: in a linear diagram with comparison curves for PA66 and PET

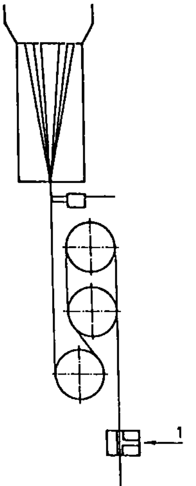


Figure 2.27
Diagram of the PA6-4HS spinning system [61] with POY take-up from the spinneret, one step draw to about 6000 m/min, steaming (*1*) and winding

Today generally the following is used for the spinning of PA6:

- for textile yarns: Spin take-up for LOY monofilaments 10...22 dtex at 800 m/min and multifilaments with 3...6 dtex at 1000...1300 m/min; spin take-up for POY multifilaments with 3...6 dtex per filament finished titer at about 5400 to possibly > 6000 m/min;
- for straight fine yarns: Drawing on a one step cold draw twister between the delivery roll and the godet with an idler roll with at least four wraps without a draw pin with speeds of about 800 m/min for 230 dtex and about 1000 m/min for 22 dtex;
- for high bulk yarns: On draw texturing machines (one heater) with friction discs (PUR) with 400...700 m/min take-up speed on soft bobbins; starting material preferably POY;
- for carpet yarns, two steps: Spin take-up about 600...800 m/min over two godets onto a friction winder, if possible with a changing revolver; then on a carpet yarn draw texturing machine at 700...1500 m/min draw speed, texture and wind. Stufferbox machines in this process only work with 400...500 m/min; one step: Spin take-up 500...800 m/min over the finishing roll and the pre-take-up godet; one step hot drawing at 110...130 °C on the first godet duo to ≈190 °C on the second godet duo with about 1800 m/min for 25 dtex per filament respectively up to 2200 m/min for 17 dtex per filament; air texturing with hot compressed air of 2.5 bar and 190...210 °C, cooling on a cooling drum, opening of the loops and tensioning on a step godet and soft winding on a revolver winder, preferably with two packages per head and two or four filaments, i.e. on one or two winding heads per winding position; four packages per winding head are possible but not usually done, because the yarn length per package becomes too short; 2 packages are preferred;
- technical yarns: Spin take-up 700...1000 m/min, especially for 5 to 7 dtex per filament, over a pre-take-up duo ($v = -0.5...1\%$), then two step hot drawing with 90...110 °C/130...150 °C/185...195 °C to 4200/4300 m/min, winding on a revolver winder for ≤600 dtex four filaments, up to 3000 dtex two filaments;
- tire yarn: Spin take-up at 700...800 m/min, for 6.6 dtex per filament pre-take-up duo as above, then over four godet duos with 70...110 °C/130...150 °C/185...195 °C/cold (<40 °C, possibly water cooled), to 3600/3750/3500...3600 m/min, for 840 dtex four filaments, up to 1680 dtex two filaments per winder;
- staple fibers: For fine titers about 3000 holes per spinneret are used; other than that the hole distance is given by (0.7...1) × finished dtex, but at least 3 mm; spin take-up speeds depend on the dtex per filament as in Table 2.7. Filaments of up to 24 spinning positions are cabled to a tow, very wet finished and coiled into cans. In the fiber line almost boiling wet drawing is recommended.

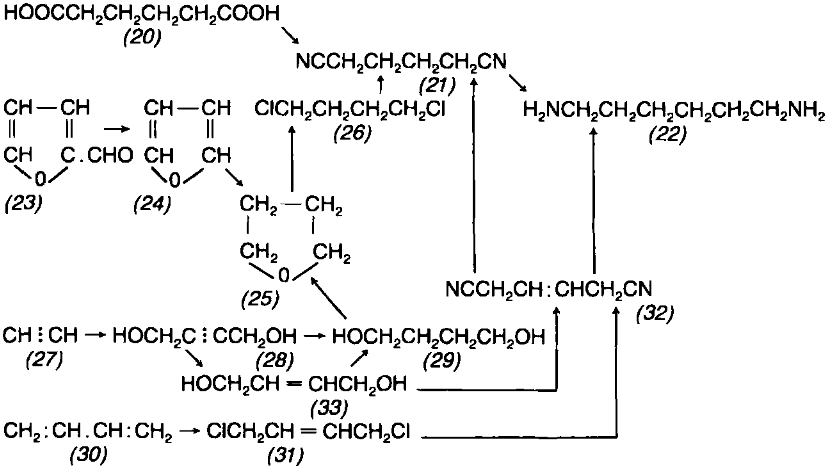
2.2.4 Polyamide 66 (PA66)

The first polymers and filaments produced originally by *Carothers* and associates in 1938 were based on hexamethylenediaminadipate. The melt spin process for this polymer was licensed already in 1939 to IG-Farbenindustrie for the production of PA6 filaments [63, 64]. Not until these patents expired, PA66 made a global break through, especially because it provided some textile technological advantages for some end uses (see Chapter 2.2.3.10).

2.2.4.1 Production of the Monomers

Older processes to produce adipic acid from phenol [65–67] go via cyclohexanol (anol) and cyclohexanon (anon) with oxidation in air using manganese nitrate as a catalyst [68, 69] with a theoretical yield of 95...97%. According to other patents it is also possible to work with acetic acid [70, 71].

Hexamethylene diamine is gained from adipic acid dinitril [55] according to one of the following processes:



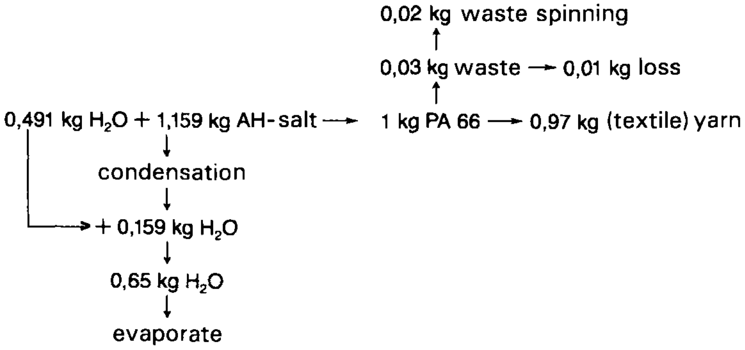
(2.13)

For a more detailed description see [74–78]. 60...80% hexamethylene diamine and 20% hot adipic acid form a well crystallizing salt that will precipitate. The vapors created by the reflux from a reflux condensator. The product, the AH-salt, must contain very exact equimolar quantities of both components. Testing can be done by checking the pH value in an aqueous solution (10%: 7.6...7.7 is equivalent to the turning point of the potentiometric titration curve [79]). Crystallization also functions as a purification, which is important for the polycondensation, especially if the material is for spinning.

2.2.4.2 Polycondensation of AH-Salts to PA66 in Autoclaves

This is still today the mostly used process. According to *Graves* [80, 81] 100 kg AH-salt (adipic acid hexamethylene diamine) should be dissolved in 42.4 kg water and mixed with 0.0067 kg acetic acid as a stabilizer—according to *Spunagel* [82] $\frac{1}{50}$ mol acetic acid per each mol AH-salt—then the autoclave should be rinsed with pure nitrogen and heated over 1...1.5 h to 220 °C with a vapor pressure of 24 bar. The pressure is then reduced by a pressure release valve to 17 bar and kept constant for about 1...2 h. Over the next 2 h the mass is heated under constant pressure to 275 °C. After a slow pressure reduction to 2 bar it is again kept constant for 0.5 h, and then the content is extruded rapidly (< 10 min) with 8...10 bar pure nitrogen in stringths of 3...4 mm diameter into the cooling water bath. With an under water chip cutter the stringths are cut at 150 m/min (about 100 kg/h x stringth), i.e. 60 stringths result in 1000 kg chips in 10 min extrusion time. This time should not be exceeded, because the product is not thermostable, and the adipic acid decarboxylizes during the decomposition.

For the material flow of the polycondensation the following scheme is valid:



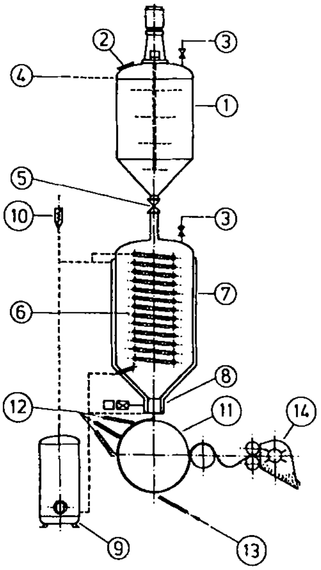


Figure 2.28 Flow Diagram of a PA66 batch type polycondensation

1 Dissolver for AH-salt
2 Man hole and filling
3 Connection for vacuum and nitrogen
4 Connection for destilled water
5 Discharge valve
6 Polycondensation autoclave
7 Jacket for Dow vapor
8 Extrusion pump with drive (not needed for extrusion with nitrogen pressure).
9 Dow evaporator
10 Extruded PA66 ribbon or stringths
11 Cooling drum
12 Cooling water spray
13 Drying air
14 Chip cutter

Process description:

1. Filling the salt-water solution into the autoclave against a pressure of about 18 bar over 15...45 min; then adding stabilizer and dulling agent.
2. Raise temperature to 240 °C under constant pressure of 18 bar over 175 min.
3. Raise temperature to 270 °C while reducing the pressure from 19 bar to normal pressure over 120 min.
4. Extrusion of the polymer through a slit of 12" × $\frac{1}{4}$"; cooling with cold pure water and cutting, approximately 14 kg/min. Total cycle time about 7 h

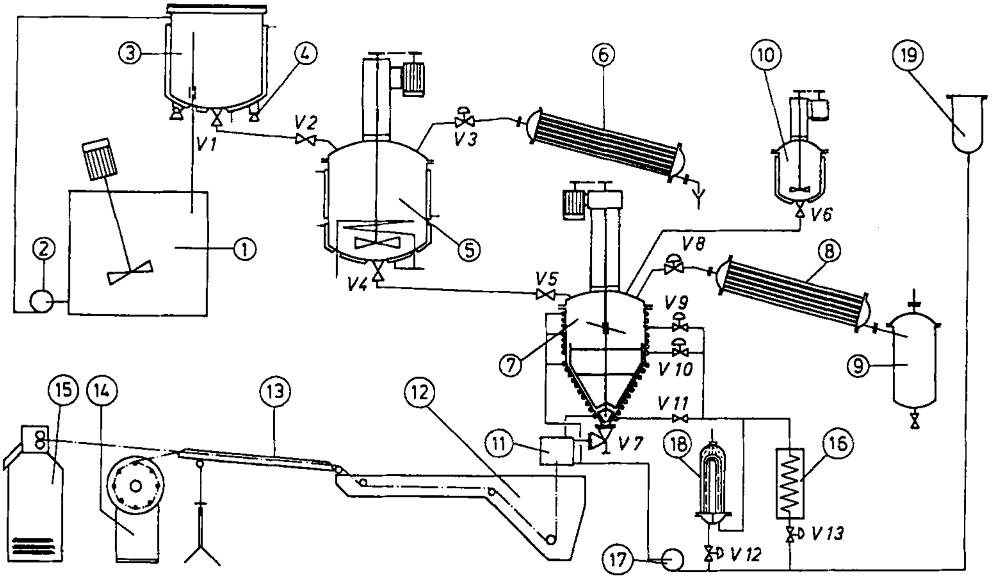


Figure 2.29 Flow sheet of a two-stage autoclave polycondensation for PA66

1 AH-salt dissolver and storage bin
2 Supply pump
3 Measuring vessel
4 Weighing scale
5 Pre-polycondensation autoclave ($\leq$25 bar)
6 Decompression control valve (V3) and condenser
V4, *V5* discharge valve combination
7 Finish polycondensation autoclave
V8 Relief valve
8 Condenser
9 Water receiver
10 Additive supply tank
11 Casting head
12, *13* Cooling trough and groove
14 Take-up for PA66 stringths
15 Chip cutter and chips
16, *17*, *18* Dowtherm circulation
19 Dow expansion vessel

Figure 2.28 shows the principle of a one-autoclave installation and describes the process.

Splitting the polycondensation process into two subsequent autoclaves [84] (see Fig. 2.29) results in significant advantages: The prepolycondensation autoclave (*5*), designed for 20 bar, is heated with its content to about 260 °C at 18...20 bar, held like that for 1 h, and then over 1 h via (V3) reduced to 1.5...2 bar. The material is then pressed into the finisher autoclave (*7*) and finished within 2 h with a final pressure of 1 bar. Stringth extrusion and chip cutting should take place within 10 min. To produce 1000 kg of chips per batch, the first autoclave (*5*) needs a volume of 2300 l and the second (*7*) a volume of 1800 l. This is equivalent to a capacity of 8...9 t/24 h. To fully use an under water chip cutter, it should be installed mobile under 3...4 parallel working installations. The stringth cooling line and/or the centrifuging of the water from the chips should be set, so that the chips only contain $\leq 0.5\%$ humidity: Then it is not necessary to apply further drying for the vapor spinning process [86]. For the extrusion spinning process, however, the PA66 chips have to be very evenly dried and possibly also be conditioned, so that they enter the extruder with a humidity of about $0.08 \pm 0.01\%$. The necessary drying is achieved with a 95 °C hot water jacket dryer in low vacuum (empty ≤ 0.1 mbar) over 30 h, cooling to ≤ 60 °C over the last 4 h. A continuous drying like for PA6 in pure nitrogen (see Fig. 2.25) is also possible, but PA66 tends to yellow much more easily. Here, too, there should be some conditioning in the lower part of the drying tower.

2.2.4.3 Continuous Polycondensation of PA66

The continuous polycondensation of PA66 has already been done by DuPont about 30 years ago; not until now do some other large corporations follow with similar processes, because the continuous process delivers a more uniform product if time ranges and delays are short between the end of the polycondensation and the filament extrusion or stringth casting.

The presently known industrial continuous PA66 polycondensation installations [87–89] are mainly working at DuPont. According to the process scheme in Fig. 2.30, the entering AH-salt solution is processed in such a way that it is pressed by a double piston type pump (*2*) with a 60% AH-salt content against a pressure of 20...28 bar through a tube preheater (*3*) that is heated by the exhaust steam of the polycondensation vessel. This hot salt solution is then lead into the stage polycondensation reactor (*4*) that is jacket heated in three stages from 204 to 270 °C, with the solution temperature increasing to 230 °C with a pressure of 18.5 bar. To avoid run through the reactor (*4*) is sectioned by a number of bulkheads: every other compartment has a separate steam outlet. The precondensate is removed from the sump of the reactor end by an extrusion pump (*6*) and pressed onto a decompressor (= flasher, *10*) that has been heated to 290 °C, with a final pressure of only 1 bar. This is where the in (*8*) prepared dulling agent is added through a dosing pump. The prepolymerisate then flows through pipes (*7*) into the disc evaporator or the spiral layer evaporator, so that the last remaining traces of water evaporate and the polycondensate takes the temperature of 275...280 °C. The extrusion pump (*15*) presses the material through the polymer pipe (*16*) to the individual extrusion heads. Installation details are described in [90–92] and another process in [93].

2.2.4.4 Spinning and Drawing of PA66 Filaments

Other than the general conditions mentioned in Chapter 4.6 for melt spinning installations, specifically for PA66 the following needs to be observed:

- The thermo instability of the melt requires very short and consistent delays, i.e. short and low volume melt pipes that are smooth and free of corners and easy to clean. According to Fig. 2.31 already 10% depolymerization occur at an average duration time of the melt [86] between 70 and 150 s; at an average flow speed of 2 cm/sec this responds to a maximum pipe length of 0.40 to 1.20 m, because the melt content of the sump or the screw metering zone and the measuring head, the extrusion pump and the extrusion head also require some delay time. It is also not admissible for the pipe wall temperature to exceed 40 K above the melting point of 258 °C. This condition of short pipes with low volumes is difficult to fulfill for fine titers, e.g. 22 dtex f7 (pipe length ≈14.2 cm), but 8 filament

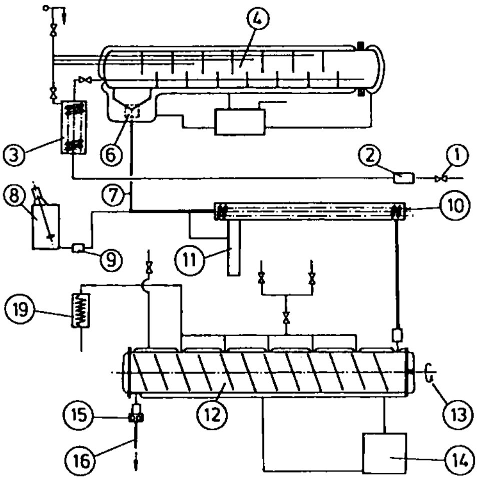


Figure 2.30
Flow diagram of a continuous PA66 polycondensation installation [74]

Item no.	Item name	Material flow
1	From dissolver	48% AH-salt solution, 608 kg/h, equivalent to 2430 kg/batch
	Weighing tank	9.2 l/min $\gamma = 1.09$, $\eta = 17$ cP
	Supply pump	
	Pre-evaporator	↓
	105,000 kcal/h	evaporation of 75 kg/h
	≅ 200 kg steam/h	↓
		60% salt solution ≅ 7.58 l/min; 105 °C; $\eta = 15.7$ cP
2	Supply pump to reactor	0.4...9 kg/min
3	Preheater	106 °C
		↓
	47,000 kcal/h	208 °C
	≅ 88.5 kg/h steam	21.2 bar
4	Reactor	↓
	3 stages of 204–247–270 °C	235 °C
	182,000 kcal/H ≅ 192 kW	
	Exhaust steam	239 kg/h
6	Extrusion pump	315 l/h ≅ 291 kg/h 85% polymer and 15% water $\gamma = 0.95$; $\eta = 150$ cP
8	TiO_2 tank, 750 l, stirrer, 1 kW	
9	Mixer for 0.7% TiO_2; 7 kg/h = 7.2 l/h ≅ 0.002 kg TiO_2/kg polymer	
10	Flasher (decompressor) for items 6 and 9: 300 °C to 0 bar at 290 °C	
11	Dow condensate	
12	Finisher, normal pressure (1 bar), 275 °C, 10 rpm; evaporation 52.25 kg/h	
13	Finisher screw drive	
14	Dow condensate	
15	Extrusion pump: 14.1 kg/cm^2, 275 °C; 247 kg/h polymer; $\gamma = 0.98$; $\eta = 800$ P	
16	To extrusion or spinning	

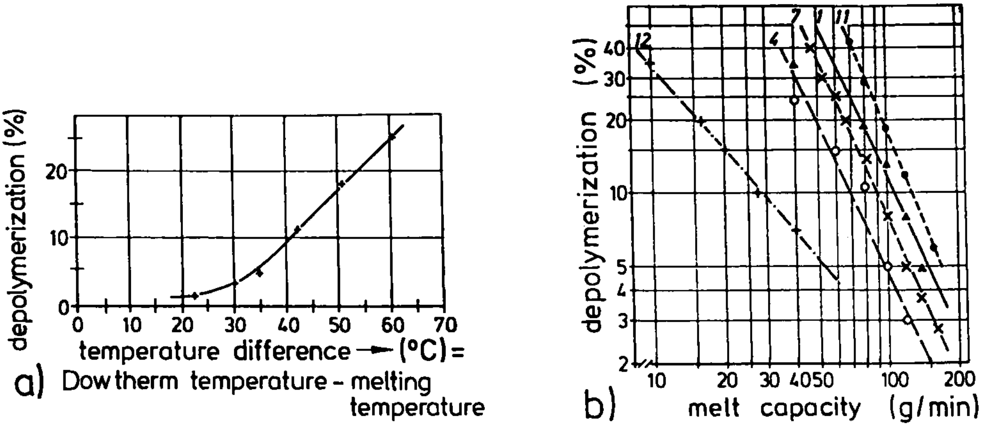


Figure 2.31 Influence of the difference between the Dow temperature and the melting point on the depolymerization (*a*) and the melt capacity *Q* (*b*) for different melt grid systems [86]

1 Pipe melt grids
4 Vertical rib melt grids
7 Solid silver perforated plate
11 Pin grid (hollow finger)
12 Solid aluminum star grid, electrically heated

spinning of 77 dtex POY does not provide problems, and carpet yarn allows pipe lengths of 290 cm with an inside diameter of 20 mm without difficulties.

- The vapor melt grid spinning so far has only been successful in spinning PA66: The chips drop with a residual humidity of 0.3 . . . 1% according to Fig. 2.32 onto the grid (*2*) with a Dow vapor temperature of about 280 °C (respectively 1.71 bar); the water evaporates, and the chips (*1*) melt. This increases the sump level (*3*) until the melt covers the grid and thus isolates the heat transfer to the chips. Then the sump surface drops again, and the contact surface for the heat transfer is increased for further melting. Thus exactly the amount of chips melt that is removed from the sump for spinning. Due to the evaporation the melt also approximates the optimal water content [94]. The water vapor also acts as a protective gas, so that no pure nitrogen is required.

The melt capacity of a grid spinning head *G* can be increased by the pressure on the chips [86] according to the following

$$G\,[\mathrm{g/min}] \approx 10^{-4}\{270 + 25 \times p\,[\mathrm{bar}]\} \times F\,[\mathrm{cm}^2] \qquad (2.15)$$

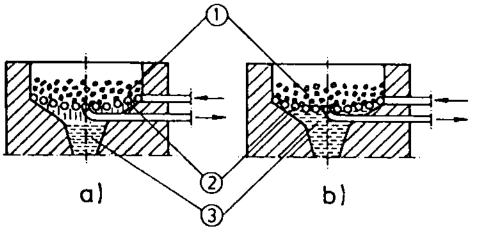


Figure 2.32
Operating scheme of the Dow vapor melt grid
a) Polymer melts by contact with the grid and fills the sump below
b) Sump is filled to the grid and thus reduces the contact area and simultaneously decreases the melt capacity
1 Chips
2 Dow vapor condenser pipe grid
3 Melt in sump

F is the melt surface area and p the pneumatic pressure on the relatively short chip screw (Fig. 2.33); this is also true for the pressure in the extruder. However, the melt capacity (here equal to the throughput capacity) through the grid is limited by the melt viscosity. If only the own weight is loaded onto the chips, the melt capacity drops above 500 P, and yields only 20% at 1000 P. With a one thread pressure screw the capacity drop starts around 1000 P, so that the capacity does not drop to 20% until 5000 P [86].

Similar melt grid spinning heads as in Fig. 2.33 are still used today in large numbers for example for POY-PA66 fine titer multifilaments and monofilaments [95, 96].

- For extrusion spinning of fine titer PA66 filaments the chips need to be dried thoroughly to 0.05 ± 0.01% or more even humidity; the constancy is improved by 2 to 5 h conditioning (e.g. in nitrogen at 20 °C with 10% remaining humidity etc.). It is also necessary that the spinning heads and their pipes follow the stability conditions in Fig. 2.31, and the melt may not be delayed beyond the calculated times. Final titers of 70 dtex x 8 ends and 150 dtex x 4 ends etc. can be spun from extrusion spinning heads after thorough drying.
- Double screw extruders with synchronized screws create a similar vapor melt surface as the grid spinning head due to only partially filled screw spiral depths.
- PA66 melt pipes must be easy to clean, i.e. either straight with no dead space at the plugs and/or easily removable.
- PA66 spinnerets may not contain any dead spaces or corners that can stagnate the flow. This is also necessary for the channels in the extrusion pumps.
- Filtration before the extrusion spinneret is done (in the direction of flow) by a plate filter—(stainless steel filter)—sand filter, 25...32 mm high—fine woven filter with a fineness of 20 μm for textile titers and 10 μm for micro fibers.
- The spinneret bores for LOY textile filaments have a diameter of 0.2 mm x 2 *D* length; trilobal spinnerets will then only have a slit of 0.1 mm. For the textile filament spinning of POY the bore diameter is only 0.15 mm.
- Steam blanketing of the spinnerets is advantageous. The spinneret bottoms will stay clean and usable for about 2 to 4 times the length of time. The necessary quantity of the steam overheated to the extrusion temperature is about equal to the extrusion mass.
- For highly viscous materials, e.g. tire yarn, a hot shroud of 200...300 mm length is often placed under the spinneret.

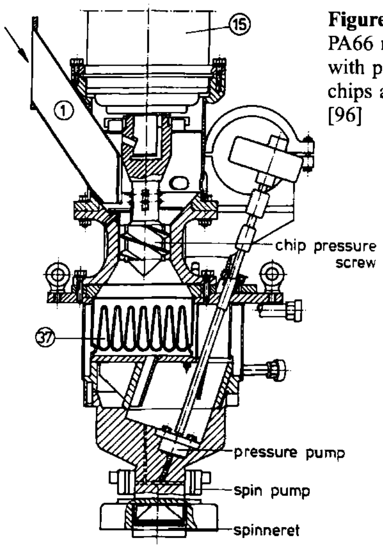


Figure 2.33
PA66 melt grid spinning head with pressure screw onto the chips and a booster pump [96]

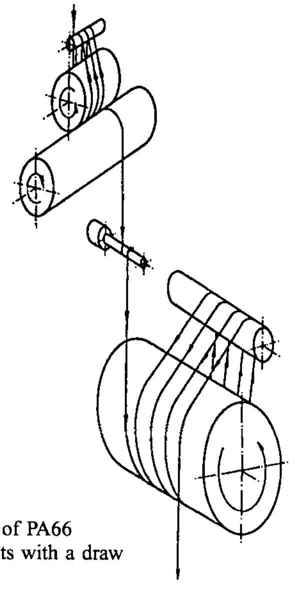


Figure 2.34
Cold drawing of PA66 textile filaments with a draw pin

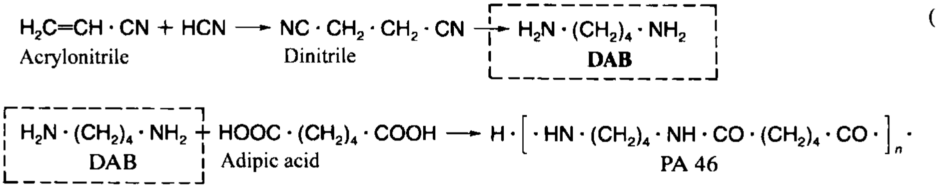
- The cooling air should meet the filaments as closely under the spinneret or the hot shroud as possible [97]. For fine textile titers a bosom shaped airflow profile is useful and for staple fibers, BCF and industrial filaments a constant airflow profile. The air temperature should be ≤ 14 °C.
- For spinning LOY it is beneficial to use vaporized spin tubes (see Chapter 4.7.5.5) between the lower end of the quench chamber and the upper end of the take-up machine, that are filled with saturated vapor and may not show any condensation on the inside.
- Take-up speeds: for LOY 10...27 dtex fl around 800...600 m/min; for textile multifilaments around 1000...1300 m/min; tire yarn and carpet yarn are taken up at 500...700 m/min and are then directly drawn, carpet yarn ($\eta \approx 2.7$) at a ratio around 3.5, cord ($\eta \approx 3.6...3.8$) at a ratio around 5. In POY spinning of textile filaments take-up speeds of 6000 m/min or more achieve better intermediate and final products than take-up speeds of 5400 m/min or less.
- Spin bobbins with yarn, especially POY bobbins, are very sensitive towards friction drives and changes in temperature or relative humidity over time or place. For a take-up speed of more than 5500 m/min it is recommended to use a spindle drive in order to avoid heating up the yarn by friction. Depending on the winding position of the outer guide, the friction heat from a friction drive can cause irregular heating of the bobbins and climatic variations near the bobbins.
- Filament preparation should be located in the air quench for POY spinning and in the yarn entrance of the take-up machine for LOY spinning or heavy denier yarn.
- It is useful to condition POYand LOY bobbins prior to draw twisting or draw texturing at 20...22 °C and 60...65% relative humidity for 16...20 h.
- Draw twisting is similar to the PA6 process, but for textile filaments in one zone over a cold draw pin made from agate or sintered aluminum oxide (Fig. 2.34) and at least 4 wraps each from the delivery roll and the polished godet with a dull hard chromed idler roll.
- Tire yarn spin draw winding is done over a kiss roll or pin preparation in the entrance of the draw winder, filament tension roll with idler, four heated godet duos and a revolver winding head for 2800...3800 m/min, usually two filaments per position, but also four filaments per position.
- Draw texturing for fine titers should be done with a smallest angled filament path.

2.2.5 Other Polyamides

These are presently used only in limited quantities or have just been introduced to the market, e.g. Stanyl® = PA46 [100, 101].

2.2.5.1 Polyamide 46 (PA46)

Polyamide 46 is produced from 1,4 diamine butane (DAB) and adipic acid [98]. DAB is gained from acrylonitrile (ACN) and cyan hydroxide. DAB and adipic acid make a salt that polymerizes in a watery solution to a low molecular product, that then polycondensates at 225 °C to the desired molecular weight:



(2.15)

$$\underset{\text{Acrylonitrile}}{H_2C{=}CH\cdot CN} + HCN \longrightarrow \underset{\text{Dinitrile}}{NC\cdot CH_2\cdot CH_2\cdot CN} \longrightarrow \boxed{\underset{\textbf{DAB}}{H_2N\cdot(CH_2)_4\cdot NH_2}}$$

$$\boxed{\underset{\text{DAB}}{H_2N\cdot(CH_2)_4\cdot NH_2}} + \underset{\text{Adipic acid}}{HOOC\cdot(CH_2)_4\cdot COOH} \longrightarrow H\cdot\underset{\text{PA 46}}{\left[\cdot HN\cdot(CH_2)_4\cdot NH\cdot CO\cdot(CH_2)_4\cdot CO\cdot\right]_n}\cdot$$

PA46 differs from PA6 and PA66 only in the number or methyl groups and their distribution. It contains more amide groups than the comparable polyamides [99] and therefore more hydrogen bonds, more symmetry and crystallizes faster and to a higher level.

A comparison of the respective properties is shown in Table 2.8 and Fig. 2.35. These properties cause specific expectations towards tire cord, sewing thread, filters and felts. As of 1990/91 only pilot installation quantities were available, and further developments are expected.

Table 2.8 Representative Properties of PA Yarns in Comparison

	PA6	PA66	PA46	PA610	PA11
Melting point [°C]	216...222	255...262	290	215	185
Crystallization temperature [°C]	173	218	265	166	
Glass transition temperature [°C]					
at 0% relative humidity	60	74	82		
normal	40	42	46		
at 65% relative humidity	5	8	5		
Density					
(at 20°C)	1.14	1.14	1.18	1.075	1.04
(at spinning temperature)	098...1..00	0..98...1..0	1.02	0.933	0.91
Specific heat					
(at 20°C, kcal/kg°C)	0.4	0.4		0.37	0.58
(melt, kcal/kg°C)	0.66	0.75		0.63	0.61
Melt heat (kcal/kg)	46	47		46...48	
Textile filaments:					
Tenacity (cN/dtex)	3...4	3.5...4..5			4.5...6.8
Breaking elongation (%)	30...70	30...60			15...40
Shrinkage (%)					
in boiling water	0.5...1.5	0.5...1.5			
in hot air (165°C)	33...5	2...4			
Shrinkage tension (g/tex)					
in hot air (165°C)	0.2	0.2			

2.2.5.2 Polyamide 610 (PA610)

Polyamide 610 is produced from hexamethylene diamine and sebacic acid; the acid was originally produced from castor oil. It is alkalized at 250 °C with a strong soda solution to castor acid, that is split into sebacic acid and octanol with a yield of 50...55% [102]. Sebacic acid can also be produced via the Kolbe synthesis [103]. Equimolar quantities of hexamethylene diamine and sebacic acid in water or methanol form the PA610 salt, a white crystalline powder with $S_p = 170$ °C. Polycondensation occurs similar to PA66 under pressure, subsequent pressure drop and extrusion at 245...260 °C in water; this will produce a high tenacity transparent polymer.

PA610 is primarily used for the production of monofilaments by extrusion or mixed into PA6 or PA66 (4%) or co-polymerized into these as sebacic acid to increase the wet knot tenacity and transparency in water, especially for fishing nets and fishing lines.

2.2.5.3 Polyamide 7 (PA7)

Even though *Falkai* [104] and *Schwartz* [105] consider PA7 to have the most suited properties for textile and technical applications ($S_P = 223$ °C, $x_{65\%} = 2.8\%$; $x_{100\%} = 5\%$; relative wet tenacity about 90%; tenacity approximately equal to PA6 or PA66; breaking elongation $\approx 14...16\%$; $E = 46...49$ cN/dtex; $E_{wet}/E_{dry} \approx 62\%$; shrinkage at boiling $\approx 8...10\%$, specific density 1.1 g/cm^3; almost no monomers in the polymer; good thermal stability), it completely disappeared from the market, because there is no sufficiently economic synthesis of raw material. ε-amino oenanth acid was produced in 1950 in the USSR [107]. Raw materials are either carbon tetrachloride and ethylene that are run over 7-chlorheptanic acid. It is also possible to start with caprolactam [107, 108].

Polycondensation can be done in an autoclave as well as in installations similar to the VK tube with an introductory pressure step and a second normal pressure VK tube. The product can be extruded in water and then cut into chips and dried like PA6. Aside from directly spinning the melt from the VK tube it is also possible to extrude the chips into filaments, but at some 10 K higher temperatures than PA6. The usual drawing follows; the chips or filaments only contain 1.5% extractable parts (in methanol; monomers and oligomers).

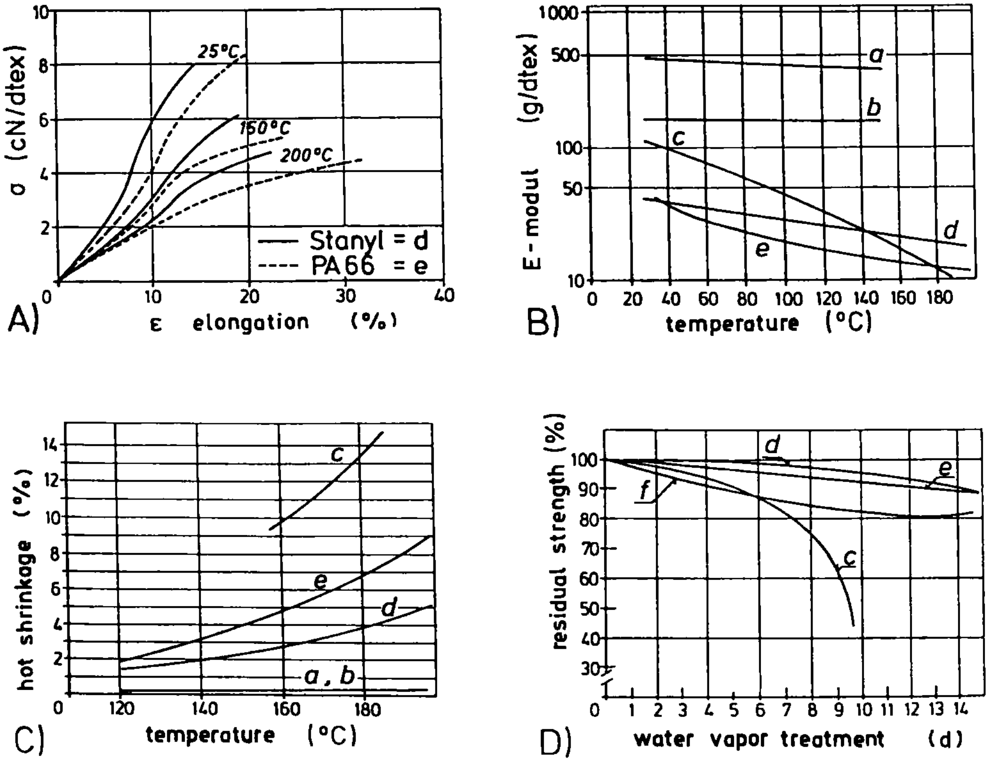


Figure 2.35 *A*) Stress (σ)/Strain (ε) diagram of "Stanyl" PA46 and PA66 multifilaments at different temperatures [101]

B) Elastic modulus as a function of temperature [101]
a) Kevlar, *b*) rayon, *c*) PET, *d*) PA46 "Stanyl", *e*) PA66, *f*) PA6

C) Hot shrinkage *β* as a function of temperature
a, *b*) rayon, Kevlar, *c*) PET, *d*) PA46, *e*) PA66

D) Residual strength $\sigma_{res.}$ as a function of steaming time at 140 °C
f, *e*) PA6, *d*) PA46, *c*) PET

2.2.5.4 Polyamide 11 (PA11, Rilsan®)

Starting material is castor oil [109], that by splitting via methanolysis turns mainly into castor methylester acid. Cracking in water vapor at 550...600 °C produces heptanal and ester, that is lead through a pipe with water vapor at 575 °C and then chilled. This ester is alkalized, treated to bromoundecanic acid that crystallizes as ε-aminoundecanic acid in watery ammonia solution.

Polycondensation happens in a watery suspension with all the necessary additives in a vertical tube, where on top water evaporates, and towards the bottom with increasing temperature polycondensation progresses. The homogenized melt can be lead towards the spinnerets directly and produces textile filaments at 265 °C with a melt viscosity of 600...1000 P. These filaments have a very silk like hand. However, Rilsan® has lost its significance as a fiber raw material.

2.2.5.5 Polyamide 12 (PA12®)

According to *Wilke* [110] butadiene can catalytically be changed to cyclododecatrien-(1,5,9), i.e. into a C_{12}-ring. The remaining cyclododecantrien is destilled with a yield of 95% [111]. The change to 12-lactam can be done via air oxidation and oxime.

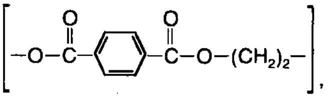
This laurinlactam can be polyadded as free amino acids to a polymer. This process can be accelerated significantly by adding acids similar to the end group stabilizers. The polymer is very thermo-stable, so that the polymerization can be done at temperatures up to 300 °C [112].

2.3 Polyester (PES)

2.3.1 Introduction

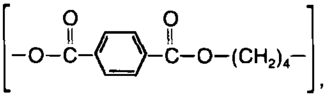
Even though a great number of polyesters [114] has been evaluated by now, only a few of them are around that can create good fibers and are crystalline with a melting point between 220 and 280 °C, and only three of them gained significance in fiber production:

Polyethylene Terephthalate
$T_G \approx 70\cdots80$°C; $T_S \approx 260$°C



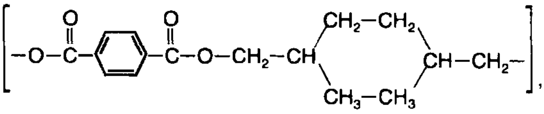
(PET) (2.17)

Polybutylene Terephthalate
$T_G \approx 40$°C; $T_S \approx 225$°C



(PBT) (2.18)

Polyester from 1,4-Dihydroxy-
methylcyclohexane
and terephthalic (Kodel®)
$T_G \approx 60\cdots90$°C; $T_S \approx 250\cdots300$°C;
both depending on the content
of trans isomers



(2.19)

Today polyester (2.19) is no longer being produced.

Polyethyleneterephthalate (PET) was developed by *Whinfield* and *Dickson* in 1939 [115], and the patent was sold to ICI [116] respectively licensed to DuPont [117], who then sub-licensed [118], e.g. to Farbwerke Hoechst AG (Trevira®) and to Vereinigte Glanzstoff-Fabriken^{AG} (Diolen®). The basic patents expired in 1966. About the distribution of filament yarns, staple fibers, technical yarns etc. in the world refer to Chapter 1.4. The most important products today are textured POY-set yarns, technical yarns and cotton type fibers.

Until 1976 dimethyl terephthalate (DMT) was the most important raw material; since then terephtalic acid (TPA) [119] has gained in significance and today accounts for about 54%.

Advantages of the use of TPA are shown as follows:

Raw material	TPA	DMT
Consumption per kg PET	0.87 kg TPA 0.50 kg Glycol	1.01 kg DMT 0.645 kg Glycol
Catalysts	antimony acetate no ester changing catalyst	Sb_2O_3 + metal acetate
Byproducts	no methanol, but H_2O	contaminated glycol and methanol (0.323 kg/kg + 0.333 kg/kg)
Rate of polycondensation	higher	lower
COOH groups	smaller	possibly larger
Price advantage	about DM 0.15/kg	—
Installation involvement	somewhat more	somewhat less

Table 2.9 Sizes of Polyester Installations and Consumption of Glycol

Year	Installation size t/24 h		Glycol Consumption	
	Esterification/transesterification and precondensation	Installation size t/24 h polycondensation	DMT Glycol/mol	TPA Glycol/mol
1968	15...20	15...20	1.8	1.7
1980	250	125	1.53	1.2
1990	360	175	1.53	1.2

Table 2.9 shows the development of installation sizes according to [120] with their specific consumption of glycol. Today's low consumption of glycol especially for TPA is possible to condense of the evaporated glycol and then re-entering it into the process until the stoichiometric quantity has been reached. Then the surplus glycol evaporates and is removed as condensate. In a separate process this glycol condensate is entered into the beginning step [54].

In addition to the mentioned polyesters, aromatic polyesters gained some significance as "liquid crystals", however so far only in small quantities and only for high temperature applications (see Chapter 2.4.5).

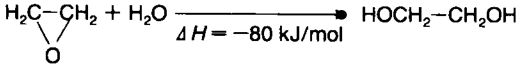
2.3.2 Production of Dimethyl Terephthalate (DMT), Terephthalic Acid (TPA) and Ethylene Glycol (EG)

To a large portion DMT is produced by a process of the Hüls-Troisdorf AG [123], also known as the Imhausen or Witten process:

The carefully cleaned p-xylene is oxidized with air over Co- or Mn-salts of organic acids as a catalyst at 150 °C under pressure to produce p-toluic acid. This toluic acid is changed at 240 °C at 30...40 bar without catalysts to p-toluic acid methyl ester and in a second step oxidized to terephthalic acid monomethyl ester. Then the semi-ester is estered with methanol over zinc chloride or phosphoric acid to DMT.

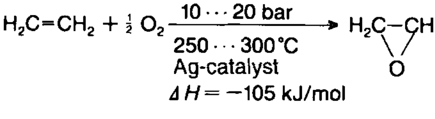
The best known process for the production of terephthalic acid is from Amoco [125]: p-xylene is changed directly to raw terephthalic acid by a radically catalyzed liquid filament oxidation at 200 °C and 15...30 bar in acetic acid with Co-Mn catalysts and Br bonds [126–129]. For example 48.8 parts of p-xylene (95% purity), 100 parts of pure acetic acid, 0.6 parts mangan acetate and 0.5 parts ammonium bromide are heated in an autoclave to 195 °C, and 400 l air are passed at 31 bar while stirring. After 4 h of oxidation the yield is 75% of the theoretical yield for TPA [129]. Further increases in the yield see in [130]. For a long time it was not possible to produce sufficiently pure TPA for PET production. However, by now pure TPA (MP-TPA = Medium Purified Terephthalic Acid [132–134]) and even highly purified TPA (HP-TPA = High Purified Terephthalic Acid) are available, with the main difference being in the p-carboxybenzaldehyde (PCB) content. For fiber quality it should be no more than 50 ppm, better <25...30 ppm. The removal of the contamination is done by a simple washing process [135, 136].

Ethylene glycol is primarily produced by the ethylene oxide process [137]:



$$H_2C{-}CH_2(O) + H_2O \xrightarrow[\Delta H = -80\ \text{kJ/mol}]{} HOCH_2{-}CH_2OH \qquad (2.20)$$

Technically one works in a 0.1% (sulfuric or oxalic) acid at 60...70 °C [138] or in a neutral medium at 160...200 °C and 10...20 bar [139]. The content of byproducts (diglycoles and polyglycoles) is kept low by working in a diluted watery solution (1 part ethylene glycol to 5 parts of water). Ethylene oxide is produced by oxidation of ethylene:



(2.21)

It is important to remove the large amount of exothermic heat and to avoid the sintering of the silver by an optimal arrangement. Other processes are the *Halcon* process [140] and the synthesis gas process [141].

2.3.3 Process for the Production of Polyethylene Terephthalate (PET)

This process has two steps: First DMT or TPA is mixed with EG and transesterified or directly esterified. The resulting diglycole terephthalate (DGT) with parts of ternary and similar intermediate products) is polycondensated in a second step with the help of a catalyst and possibly a stabilizer at 270... ≈300 °C under vacuum; this will split off EG. The PET can either be produced as chips or directly to fibers.

2.3.3.1 Transesterification of Diethylene Glycolterephthalate and Ethylene Glycol to Diglycole Terephthalate

Transesterification starts above 150 °C under normal pressure with inert gas up to 197...198 °C or up to 220 °C with methanol (CH_3OH) separation under a reflux cooler for the EG. First either the DMT is melted (at about 185 °C) and added into the hot EG or it is dissolved as a salt in the hot EG. To avoid DMT sublimation the temperature can only be increased slowly. A slight EG surplus is recommended. Increased temperature results in a faster reaction (Fig. 2.36a). The process is completed upon reaching the stoichiometric transition: In praxis after 3 h at 197...200 °C over 98% CH_3OH are evaporated [142]. Very important is the selection of a catalyst and its quantity, which will not only determine the rate of the reaction but also side reactions, the thermostability and the color of the polyester (Fig. 2.36b–c and Table 2.10) [143, 144]. According to this, the most efficient catalysts for transesterification are acetates with Cd,

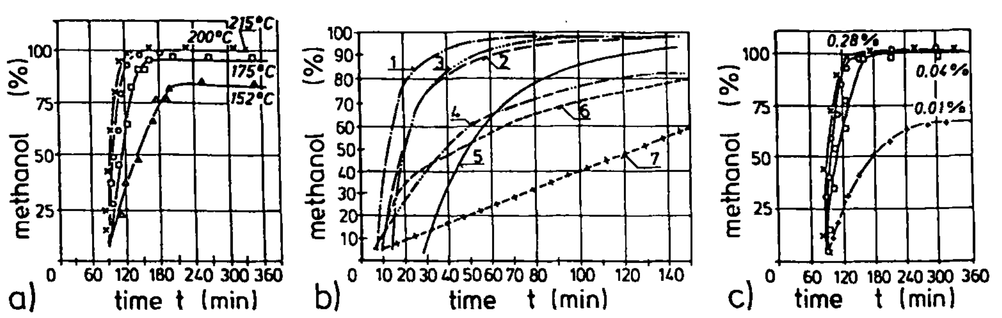


Figure 2.36 Methanol separation during the transesterification of DMT

a) With addition of 0.2% $Zn(CH_3COO)_2$ + PbO with the reaction temperature as parameter [142]

b) At 200 °C with different catalysts (0.14% metal acetate) as parameter (*1* Cd-, *2* Zn-, *3* Co-, *4* U-, *5* Pb-, *6* Na-, *7* Ni-acetate)

c) For different catalyst concentrations [$Zn(CH_3COO)_2$ + PbO in the relation 2 : 1]

Table 2.10 Influence of the Catalysts on the Properties of Polyethylene Terephthalate

	Catalyst	η_{rel}. Equ/10^6 g	COOH	Color	Thermal Decay
I	$Ti(OCH_3)_4$	1.420	33	yellow/yellow brown	very weak
	Fe(III)-acetyl acetonate	1.408	36	light brown/brown	
	$Pb(CH_3COO)_2$	1.378	34	yellow/dark yellow	
	$Sb(OCH_3)_3$	1.372	27	light gray/yellow	
	$Mn(CCH_3)COO)_2$	1.365	31	light yellow/yellow brown	
II	$Zn(CCH_3COO)_2$	1.375	75	colorless/dark yellow	weak
	$Co(CCH_3COO)_2$	1.368	43	violet/brown	
	$Cd(CCH_3COO)_2$	1.328	35	light yellow/brown	
III	Cr(III) acetyl acetonate	1.216	24	colorless/yellow	stronger
	CoO_2	1.168	15	colorless/light yellow	
	$LiCCH_3COO$	1.262	14	colorless/yellow	
	$NaCCH_3COO$	1.162	16	colorless/yellow	
	$Mg(CHCH_3COO)_2$	1.286	36	colorless/yellow	
	$Ca(CCH_3COO)_2$	1.126	12	colorless/light yellow	
	CH_3BO_3	1.138	23	colorless/light yellow	
IV	$Ni(CCH_3COO)_2$	1.255	112	light green/red brown	stronger

η_{rel}., measured in phenol/tetrachloroethane 1 : 1, 20°C, 3 h after the beginning of polycondensation

Zn, or Co. As the transesterification progresses and the temperature increases, more EG moves through the reflux condenser, and the CH_3OH composition has to be closely monitored (e.g., by measuring the density). Other factors influencing the reaction rate are the purity of the raw materials, hydrolytic or thermic damage of the DMT (e.g., by storing the DMT melt too long), or possibly water content. A large portion of not transformed methylene ester groups (10...25%) inhibit the achievement of high mol masses [145, 130]. A fast increase of the reaction temperature results in the formation of a high portion of diglycol byproducts.

2.3.3.2 Direct Esterification of Terephthalic Acid and Ethylene Glycol to Diethylene Glycolterephthalate

Whinfield [146] already did some investigations into this, but did not find any useful results due to the slow reaction and the insufficient purity of the TPA. Even after the development of HP-DPA and MP-DPA polyether was formed in a side reaction. The reaction rate is increased by temperatures above 240 °C and by pressure [147, 148]. Adding water reduces the creation of ether [149]. One process uses the addition of an amine (e.g., n-butylamine, diisopropylamine, triethylamine) [150]. In another process for each mol TPA about 1.2 mol glycol with 0.01...0.04 mol of a tertiary amine are added under nitrogen at 260 °C and 5.2 bar [151], that with catalysts (e.g., alkali- or earth alkaliphenolates, hexafluorphosphates, silicates, fluor silicates or metal-Ac) lead to esterification.

The most important process today uses the addition of glycolterephthalates to the TPA-EG paste under pressure above 240 °C [152]. Esterification of TPA with DGT, possibly with small additions of glycol, has also been described [153].

During direct esterification ether forming side reactions are possible: this side reaction is acid catalyzed and can be prevented by adding small quantities of sodium hydroxide or a quartiary organic hydroxide; otherwise the melting point of PET is lowered too much.

Direct esterification produces water, but an exact stoichiometric limitation as during transesterification is not important. With the correct design of the reactor direct esterification requires 250...260 °C and 1.5...2 bar overpressure. Stabilizers (phosphites or phosphates) can be added to the polymer melt after esterification to increase time and temperature stability. Polymers on the basis of TPA are due to the