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:

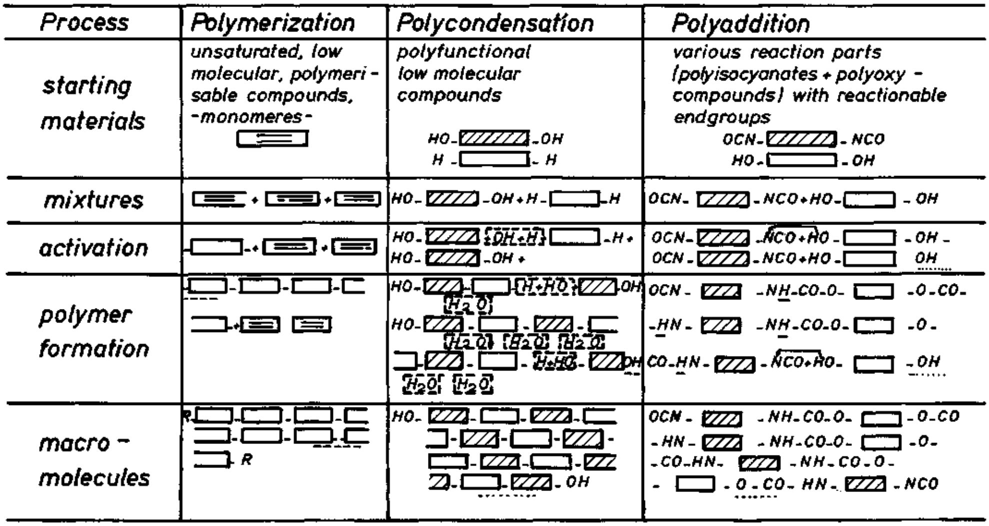
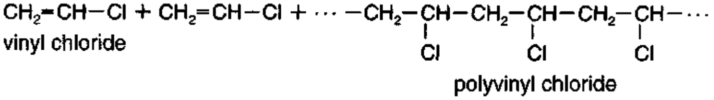


Figure 2.1 Formation mechanism for synthetic polymers [411]

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



$$\underset{\text{vinyl chloride}}{CH_2{=}CH{-}Cl} + CH_2{=}CH{-}Cl + \cdots \; \underset{\text{polyvinyl chloride}}{-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-CH_2-\underset{Cl}{CH}-\cdots} \qquad (2.1)$$

or polycondensation; both descriptions are used. Polyamide 66, however, is certainly created through polycondensation.

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.

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

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:

$$\underset{\text{glycol}}{HO-R-OH} + \underset{\text{diisocyanate}}{OCN-R_1-NCO} + HO-R-OH + OCN-R_1-NCO + \cdots \longrightarrow \qquad (2.3)$$

$$\longrightarrow \cdots \; \underset{\text{polyurethane}}{-R-O \cdot OC \cdot NH-R_1-NH \cdot CO \cdot O-R-O \cdot OC \cdot NH-R_1-\cdots}$$

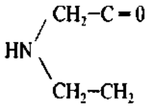
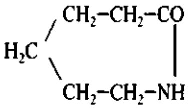
2.2 Polyamides (PA)

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.

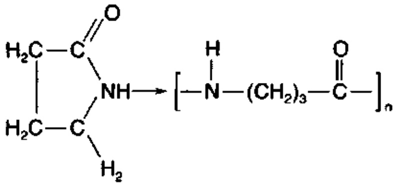
The naming follows the number of C-atoms in the basic molecule: PA6 contains 6 C-atoms, PA66 has 6 + (4 + 2), with the latter one for the combination of a diamine with a dicarbon acid. As the number of C-atoms increases, the melting point decreases; with the combination of diamines it is also lower for 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		γg/cm^4	σ_B g/dtex	E_{max} g/dtex · %	σ_{wet}/σ_B (%)	ε_B (%)	Examples	Monomers
				65%	100%							
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].

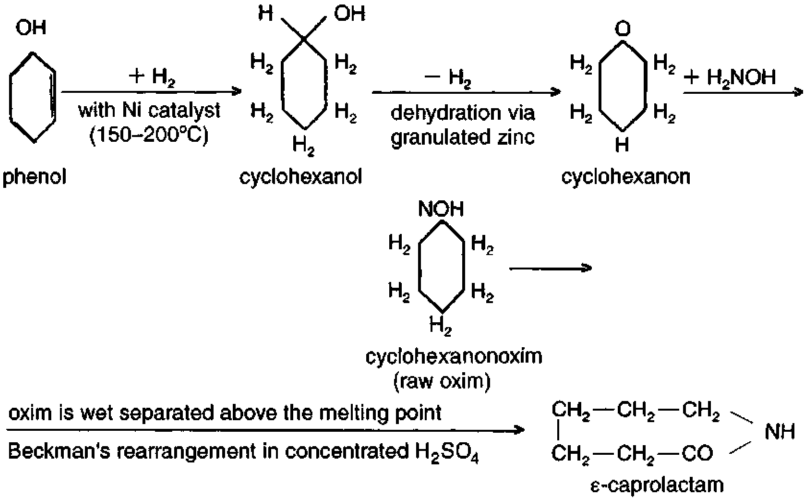
Melt spinning is quite difficult, because the melting point is only about 2…3 K under the decomposition temperature. The production is also too expensive; the yarn has a very low elastic modulus; it fibrillates during washing and texturing does not provide sufficient stability.

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.

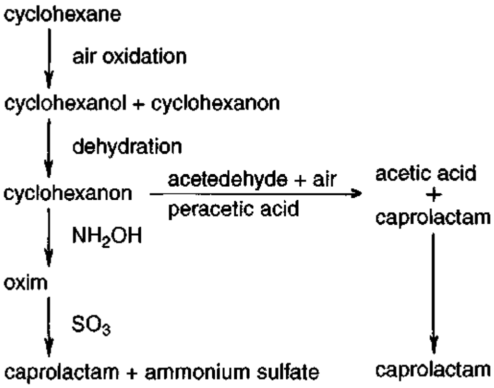


(2.5)

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].

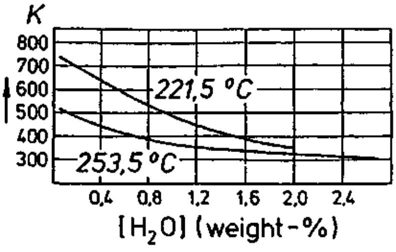


Figure 2.2
Equilibrium *K* as a function of the water (H_2O) content (in mol/mol caprolactam)

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

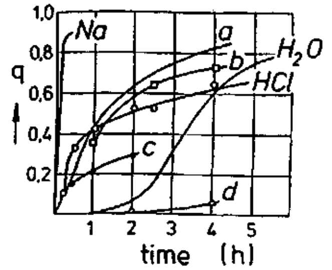


Figure 2.3a
Polymerization of caprolactam without water, with initiators (0.025 mol/mol caprolactam, q = not more extractable part of the initial caprolactam, T = 254 °C)
a: $NH_2(CH_2)COOH$, b: NH_4Cl,
c: $CH_3C_6H_4SO_3H$, d: CF_3COOH

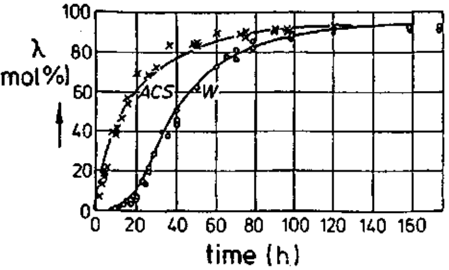


Figure 2.3b
Comparison of the polymerization of lactam with 0.01 mol water (o, W) and with the same molar part of amino caproic acid (x, ACS) (—— calculated curves)

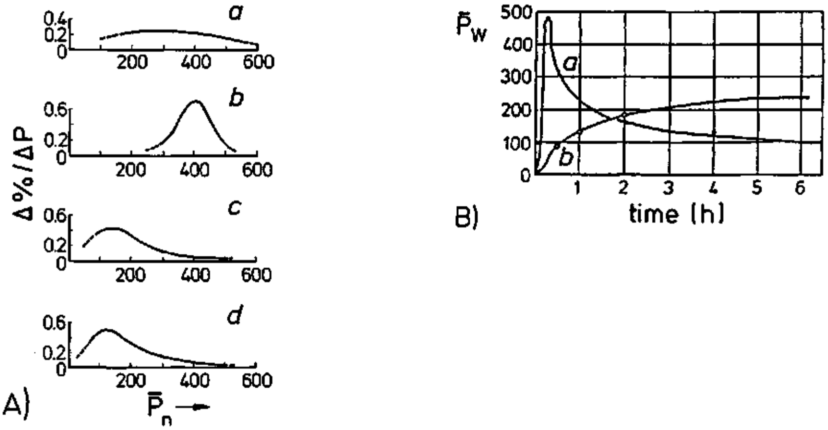


Figure 2.4 *A*) Distribution of the degree of polymerization P of the rapid polymerization after different times of heating: $a = 5$, $b = 15$, $c = 240$, $d = 360$ min.
B) Degree of polymerization as a function of time with different levels of concentration or temperatures

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:

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

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 $\eta_{rel.} = 1$ (measured in n-H_2SO_4), for each 100 mol caprolactam about 2.0, and for each 150 mol a $\eta_{rel.} \approx 2.5$.

The approximation for the degree of polymerization for PA6

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

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 $\eta_{rel.} = 2.6$. Without the water $\eta_{rel.} = 3.0\ldots3.1$ is reached. If the water is removed by vacuum from the melt, a higher molecular weight is also obtained.

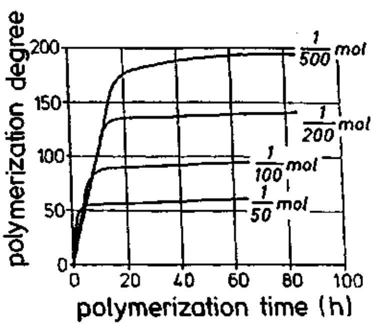


Figure 2.5
Influence of a catalyst quantity on the degree of polymerization of a caprolactam polymer P_n (according to *A. Matthes*)
($DP \approx 124(\eta_{rel.} - 1)$)

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

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

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

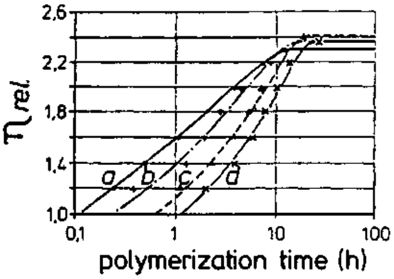


Figure 2.6
Polymerization of caprolactam with (a, b, c) and without (d) water at 260 °C without pressure (AH salt in % of weight: a = 5, b = 2, c = 0.5, d = 0)

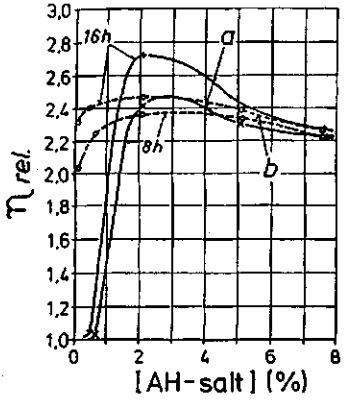


Figure 2.7
Influence of AH-salt and water on the relative viscosity $\eta_{rel.}$ of a caprolactam polymer after 8 respectively 16 h at 260 °C (a = without, b = with water) polymerization time

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.

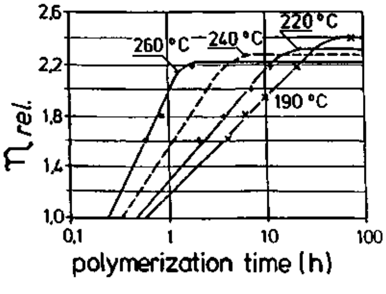


Figure 2.8
Polymerization of caprolactam as a function of time with temperature as parameter

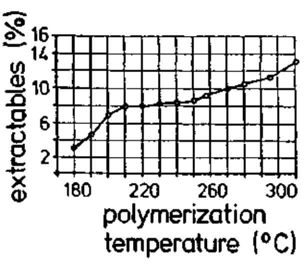
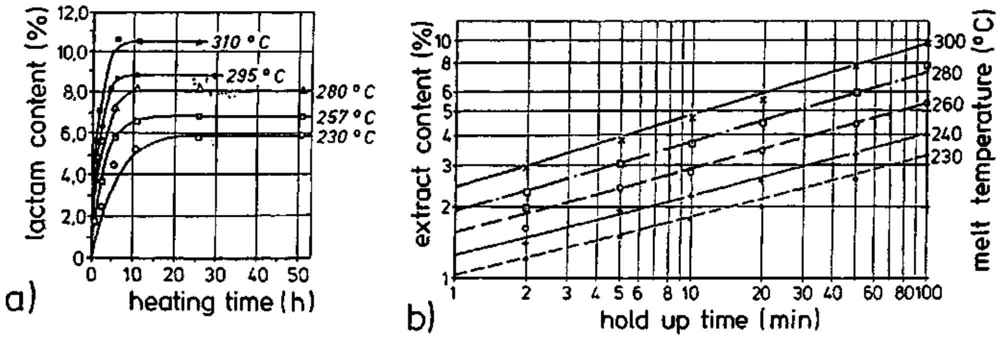


Figure 2.9
Low molecular parts (lactam and oligomers) of polycaproamide as a function of temperature [39]



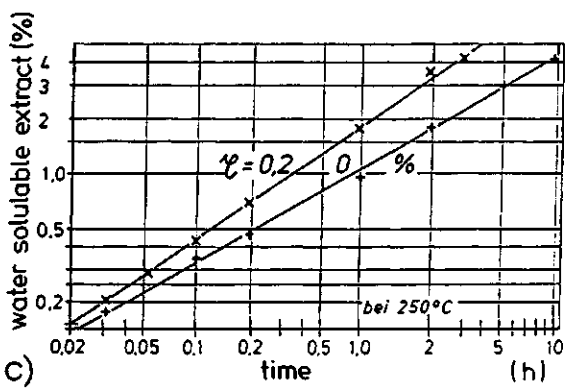


Figure 2.10
a), b) Lactam and oligomers reformation in fully extracted polycaproamide as a function of temperature and time [40];
c) with water content as parameter

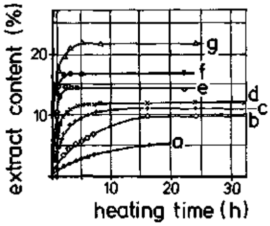


Figure 2.11
Equilibrium reformation of lactam and oligomers in prior fully extracted molten polycaproamide in the presence of water at 250°C [41]:
(a = dry polycaproamide, b = with 0.2% water, c = 1, d = 2, e = 10, and f = 20%, g = 30% water in the polycaproamide)

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			
Cyclical dimers and trimers	1.3			
Cyclical tetramers	0.6	2.5...3	3...3.5	3.2...4
Cyclical pentamers	0.5	lower values at 221.5°C		
Cyclical hexamers and higher rings	0.7	higher values at 253.5°C		

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.

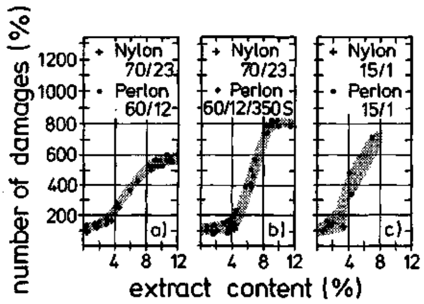


Figure 2.12
Influence of the remaining extractables in PA6 on the processing properties relative to those of the fully extracted PA6 and PA 66 yarn:
a) Flaws on a false twist texturing machine
b) on a pineapple coning machine
c) on a hosiery knitting machine

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 $\eta_{\mathrm{rel.}} = 2.7\ldots2.8$, two step polymerization a $\eta_{\mathrm{rel.}} = 3.0\ldots3.1$, and with two intermediate surfaces (the first one after about 15% and the second one after 50…70% of the total time) a $\eta_{\mathrm{rel.}} = 3.2\ldots3.3$ can be achieved.

If a vacuum is arranged at the evaporation surface, $\eta_{\mathrm{rel.}}$ also increases considerably (see Fig. 2.13 with $\Delta\eta_{\mathrm{rel.}} \approx 0.7$ 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.

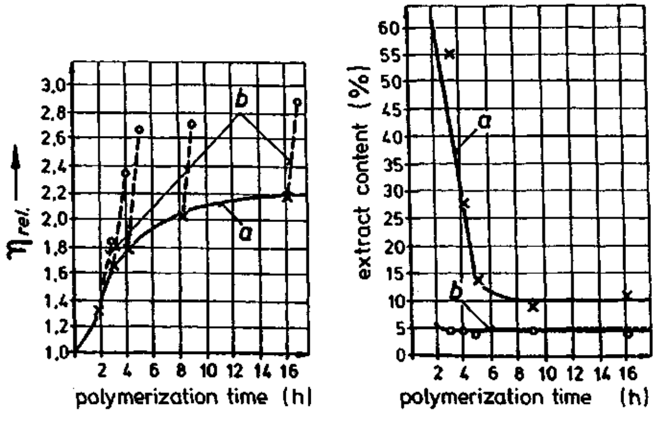


Figure 2.13
Left: Caprolactam polycondensation with following extraction (——— viscosity increase without vacuum (a), – – – – with vacuum (b): initiator 5% aminocaproic acid + H_2O)
Right: As a function of time [42]

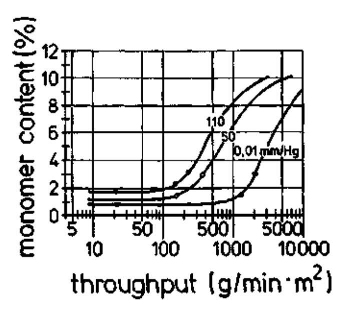


Figure 2.14
Continuous vacuum demonomerization of PA6 melt;
Monomer content as a function of the throughput Q and of the vacuum

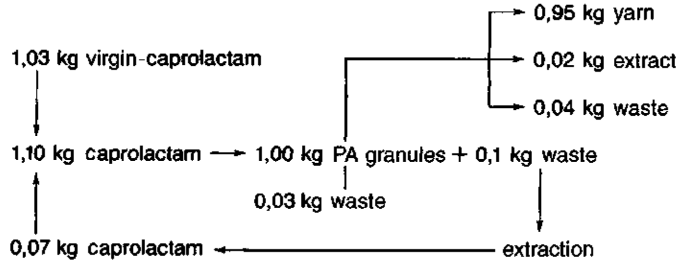
2.2.3.3 Extrusion, Pelletizing, and Drying

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.

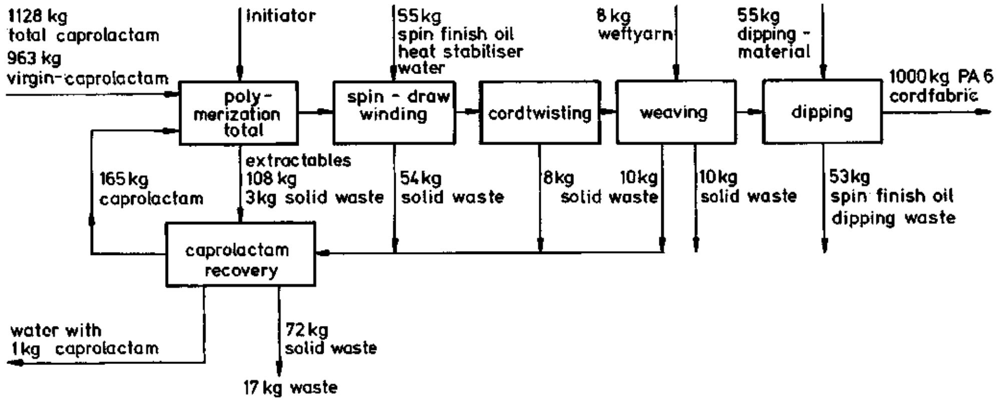


Figure 2.15 Material flow of a PA6 polymerization for the production of tire cord with lactam recovery (Zimmer AG [44])

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.

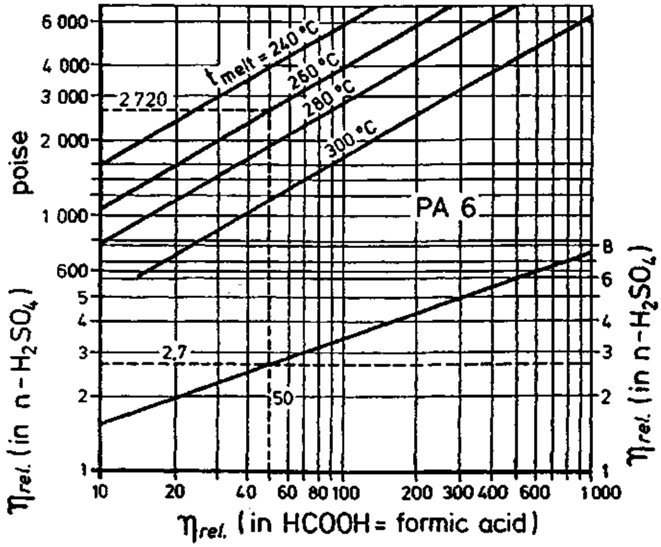


Figure 2.16
Relation between the relative solution viscosity $\eta_{\text{rel.}}$ in n-H_2SO_4 and formic acid and of the melt viscosity with the melt temperature as parameter

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.

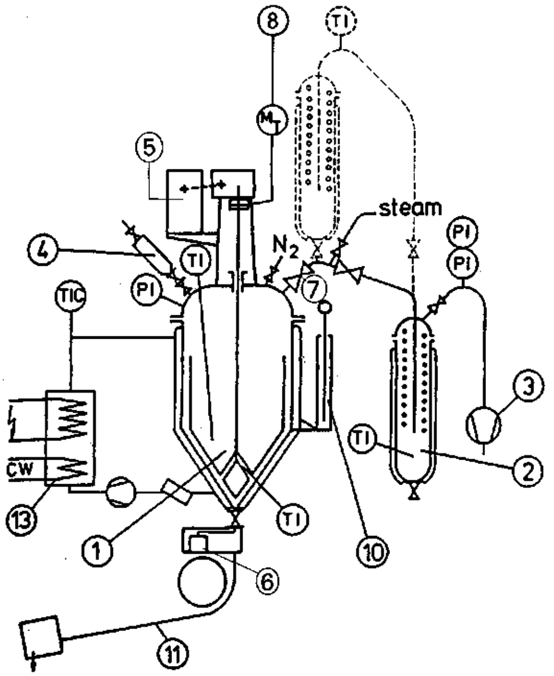


Figure 2.17
One-autoclave polymerization installation for caprolactam to PA6, pressure free, including a vacuum stage

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 $R_t \leq 0.4\ \mu m$.

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.

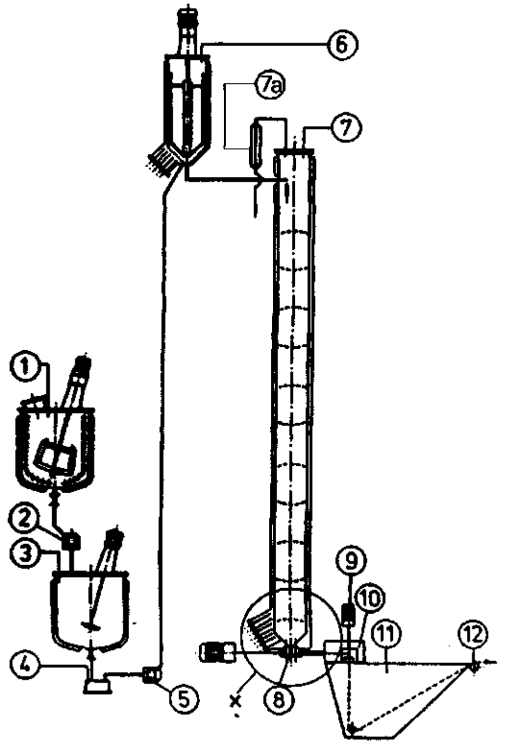


Figure 2.18
Schematic drawing of a PA6 VK tube polymerization
1 Lactam melter and mixer
2 Filter
3 Lactam mixer and storage tank
4 Dosing pump (piston type)
5 Filter
6 Prepolymerization tube
7 VK tube
7a Evaporation condenser
8 Extrusion gear pump with adjustable drive
9 Stringth die in
10 Extrusion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

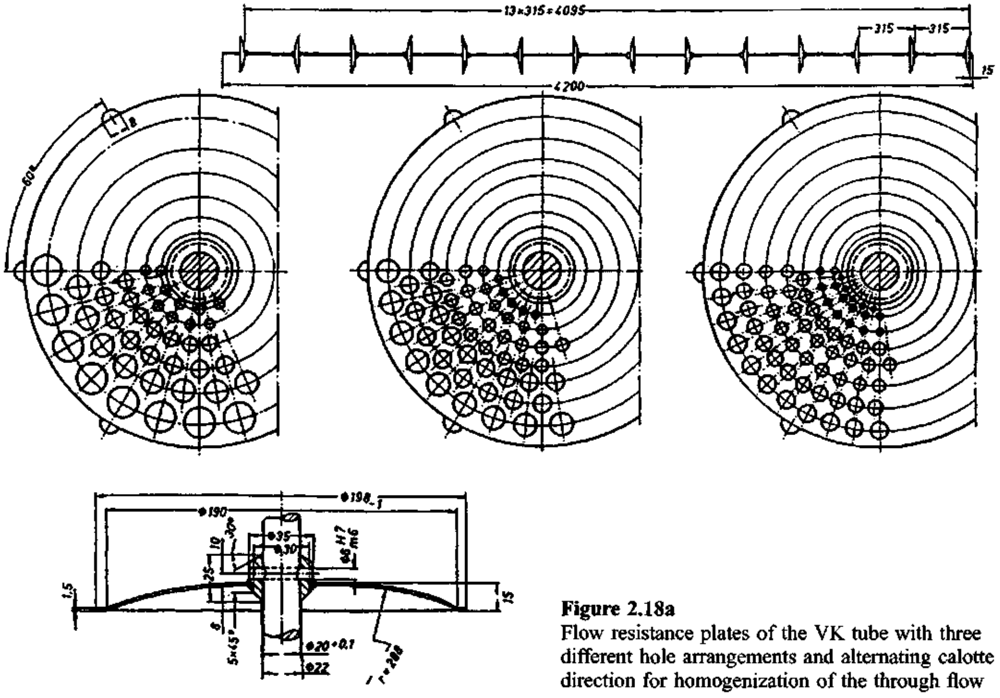


Figure 2.18a
Flow resistance plates of the VK tube with three different hole arrangements and alternating calotte direction for homogenization of the through flow

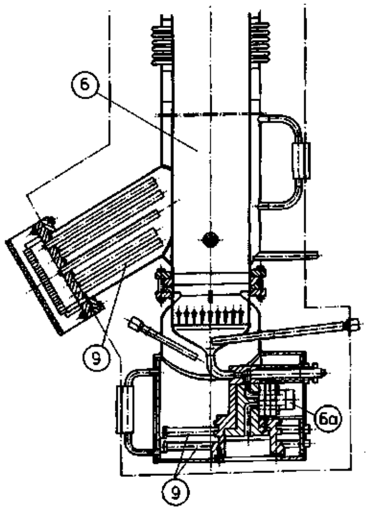


Figure 2.18b
Details in Fig. 2.18
6 Lower end of the VK tube
6a Extrusion gear pump
9 Electric heating rods

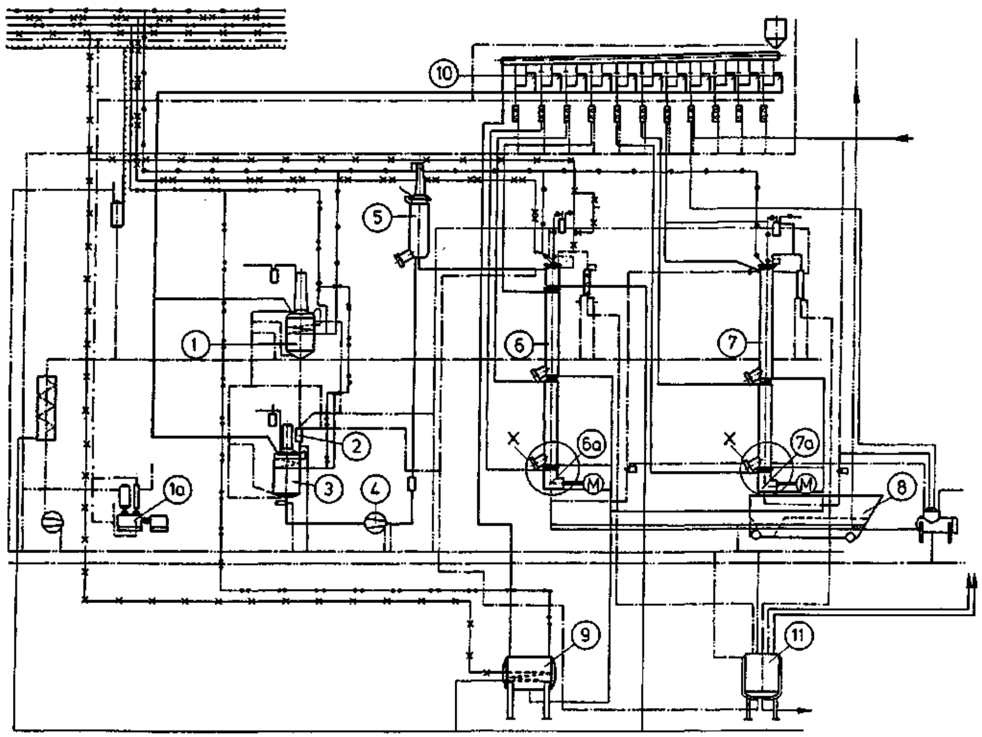


Figure 2.19 Flow sheet of a PA6 VK tube polymerization

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

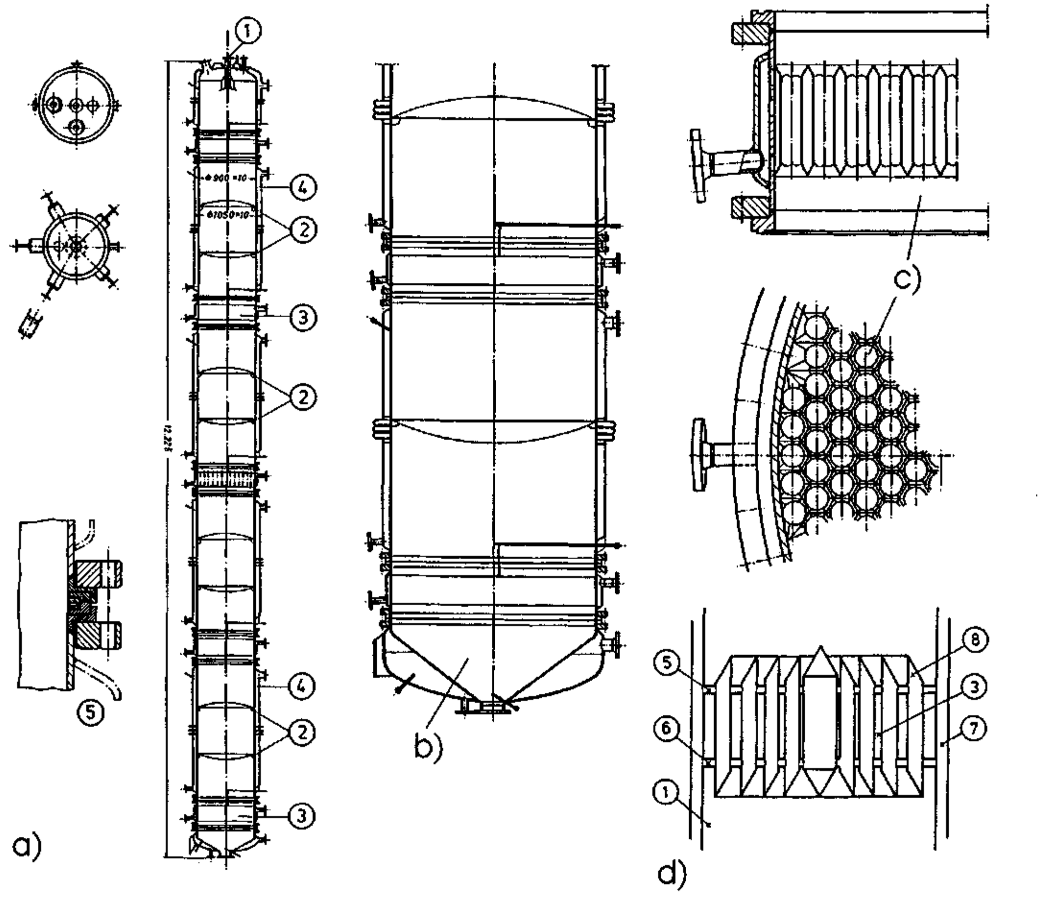


Figure 2.20 Principles of a large (commercial) VK tube (about 22 m^3 volume)

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	*6* Dow condensate flow to the
3 Melt room between the ribs	*7* Dow heating jacket
5 Connection pipes for Dowtherm	*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%

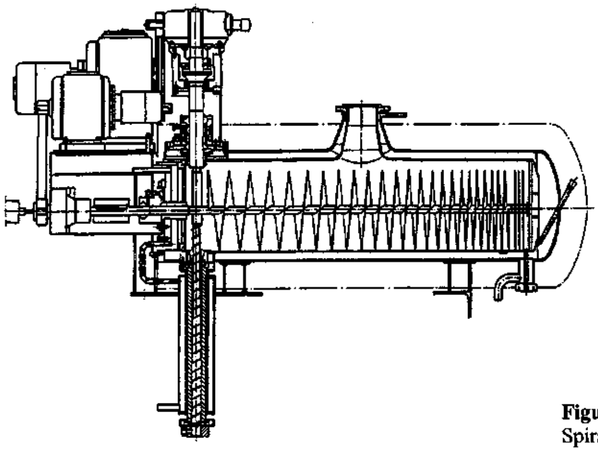


Figure 2.21
Spiral disc vacuum demonomerizer for PA6 melt

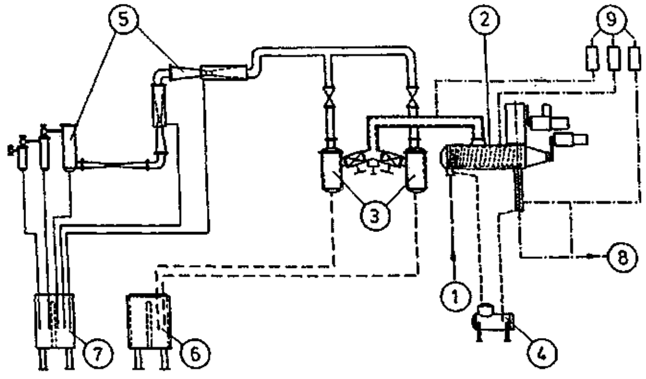


Figure 2.22
Flow sheet of a vacuum demonomerizer in a PA6 VK tube polymerization with
1 PA melt from the VK tube
2 Vacuum demonomerizer (finisher)
3 Vacuum condensers
4 Dow evaporator
5 5-stage steam vacuum jet
6 Lactam receiver
7 Barometric condensate receiver
8 Demonomerized PA6 melt to spinning
9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

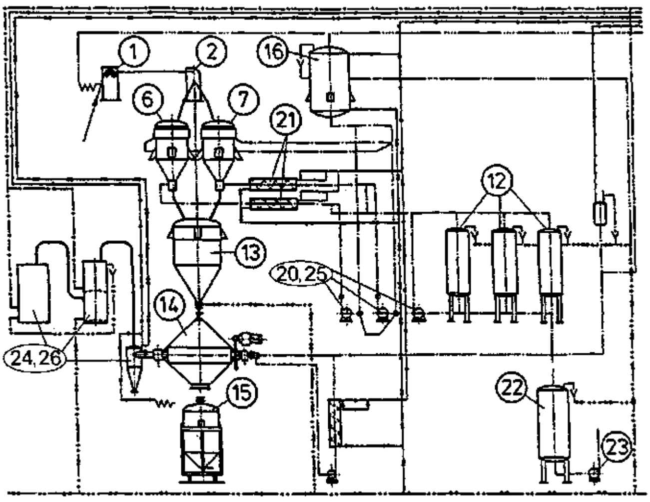


Figure 2.23 Flow diagram of a batch chip extraction as a continuation to Fig. 2.19 with
1 Stringth take-up from the casting trough
2 Dry chip cutter
6, 7 Extractors
12 Extract water containers for 4-step process
13 Wet chip receiver
14 Biconical vacuum dryer
15 Transport trolley for dried chips
16 Pure 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*

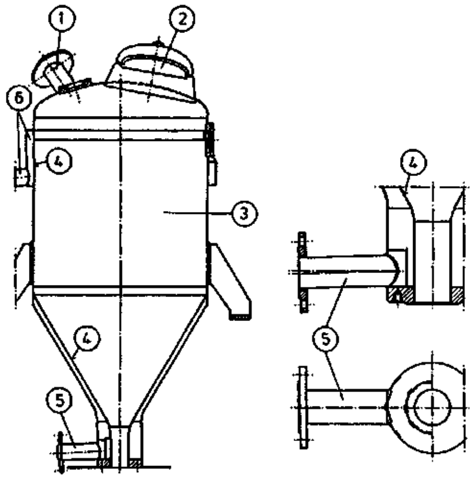


Figure 2.23a Chip extractor (items *6* and *7* in Fig. 2.23) with
1 Filling stud
2 Man hole
3 Extraction room
4 Sieve bottom respectively wall
5 Extract water entrance (from pumps *20* through the heat exchangers *21* in 2.23)
6 Extract water overflow ring and return to one of the intermediate containers (*17*, *18*, *19*)

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

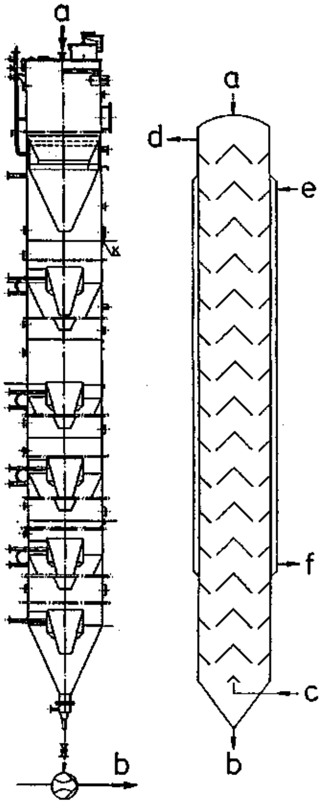


Figure 2.24 Schematic drawing of a continuous PA6 chips extraction (left: according to [524], right according to [54])

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

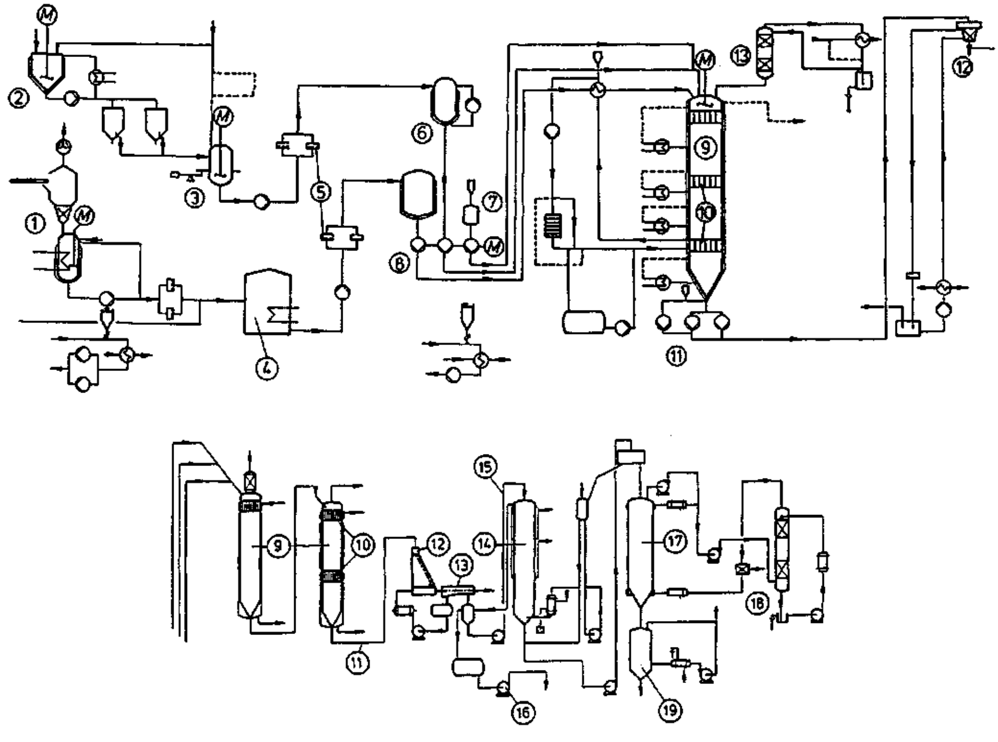


Figure 2.25 Flow diagram of a commercial size continuous PA6 chip polymerization plant according to [54]

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.

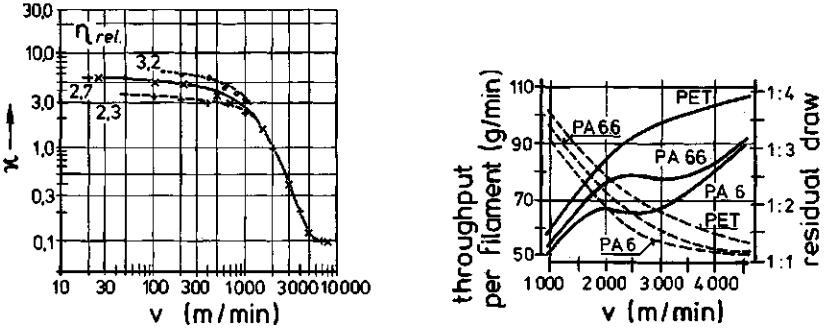


Figure 2.26 Residual draw of PA6 filaments 1 : (1 + x) as a function of the spin take-up speed with the parameter relative solution viscosity; left: in double logarithmic, right: in a linear diagram with comparison curves for PA66 and PET

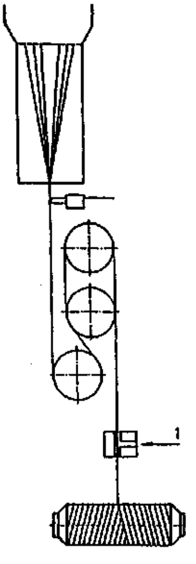


Figure 2.27
Diagram of the PA6-4HS spinning system [61] with POY take-up from the spinneret, one step draw to about 6000 m/min, steaming (*1*) and winding

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.

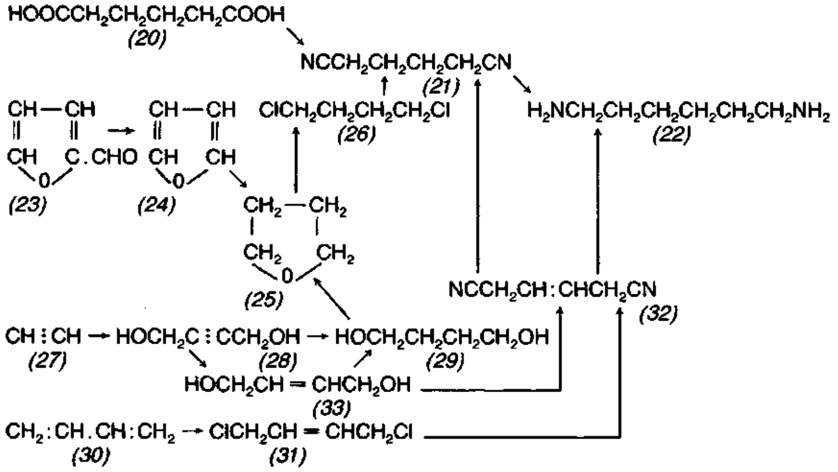
2.2.4 Polyamide 66 (PA66)

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:



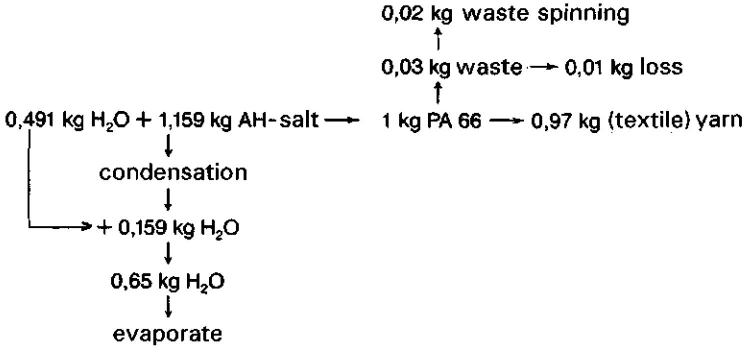
(2.13)

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 × 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:



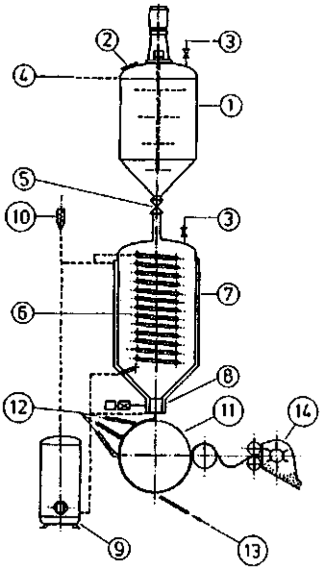


Figure 2.28 Flow Diagram of a PA66 batch type polycondensation

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

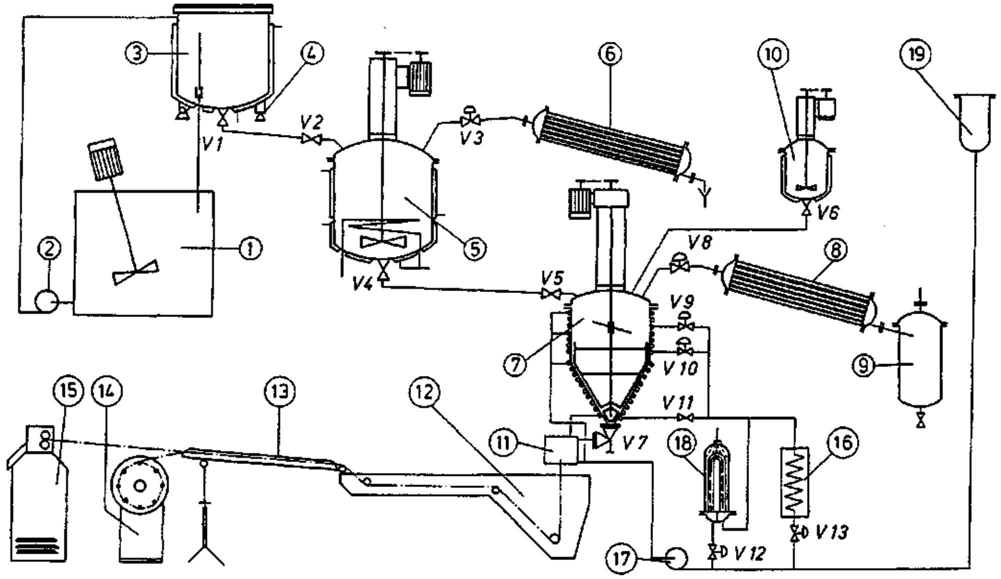


Figure 2.29 Flow sheet of a two-stage autoclave polycondensation for PA66

1 AH-salt dissolver and storage bin
2 Supply pump
3 Measuring vessel
4 Weighing scale
5 Pre-polycondensation autoclave (≤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

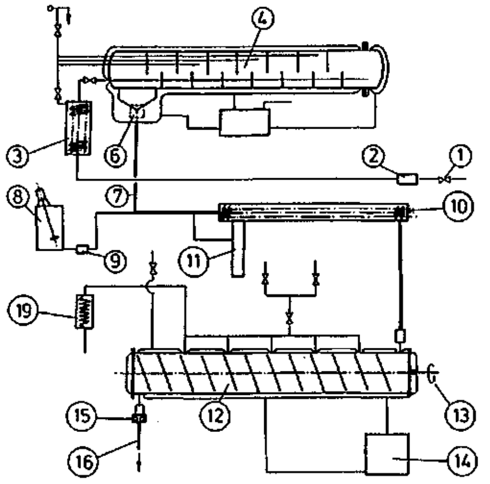


Figure 2.30
Flow diagram of a continuous PA66 polycondensation installation [74]

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	

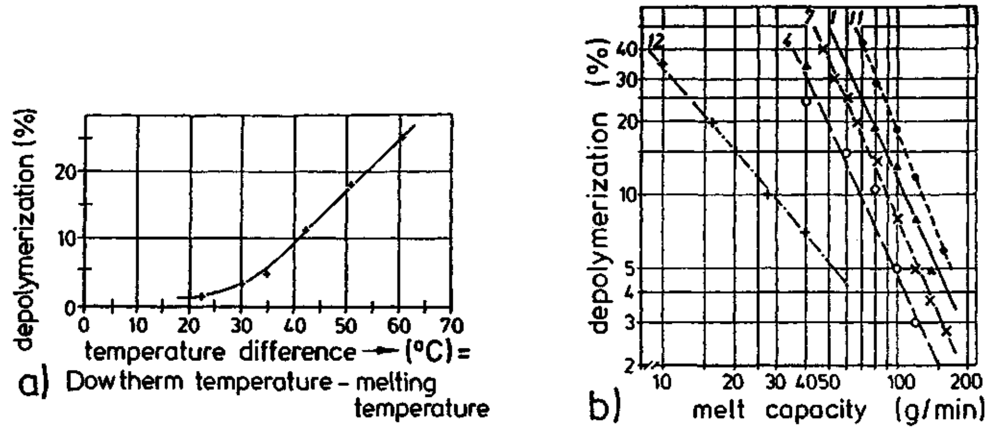


Figure 2.31 Influence of the difference between the Dow temperature and the melting point on the depolymerization (*a*) and the melt capacity *Q* (*b*) for different melt grid systems [86]

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

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

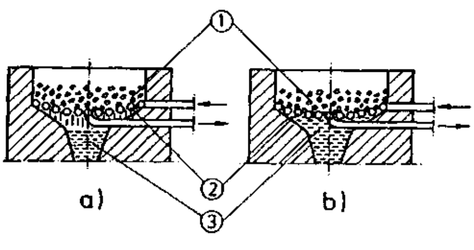


Figure 2.32
Operating scheme of the Dow vapor melt grid
a) Polymer melts by contact with the grid and fills the sump below
b) Sump is filled to the grid and thus reduces the contact area and simultaneously decreases the melt capacity
1 Chips
2 Dow vapor condenser pipe grid
3 Melt in sump

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 $0.05 \pm 0.01\%$ 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 × 8 ends and 150 dtex × 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 × 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.

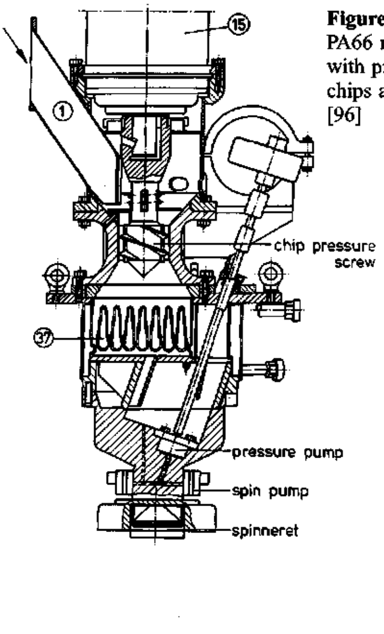


Figure 2.33
PA66 melt grid spinning head with pressure screw onto the chips and a booster pump [96]

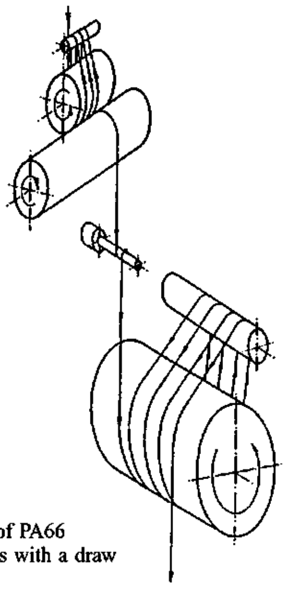


Figure 2.34
Cold drawing of PA66 textile filaments with a draw pin

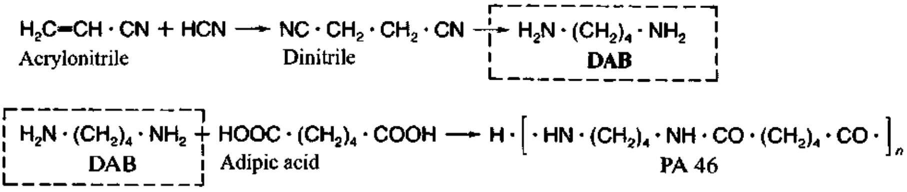
- The cooling air should meet the filaments as closely under the spinneret or the hot shroud as possible [97]. For fine textile titers a bosom shaped airflow profile is useful and for staple fibers, BCF and industrial filaments a constant airflow profile. The air temperature should be ≤ 14 °C.
- For 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 f1 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 ($\eta \approx 3.6 \ldots 3.8$) 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 POY and 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:



$$\underset{\text{Acrylonitrile}}{H_2C{=}CH\cdot CN} + HCN \longrightarrow \underset{\text{Dinitrile}}{NC\cdot CH_2\cdot CH_2\cdot CN} \longrightarrow \boxed{\underset{\textbf{DAB}}{H_2N\cdot (CH_2)_4\cdot NH_2}} \qquad (2.15)$$

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

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 $\approx 14 \ldots 16\%$; $E = 46 \ldots 49$ cN/dtex; $E_{wet}/E_{dry} \approx 62\%$; shrinkage at boiling $\approx 8 \ldots 10\%$, 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).

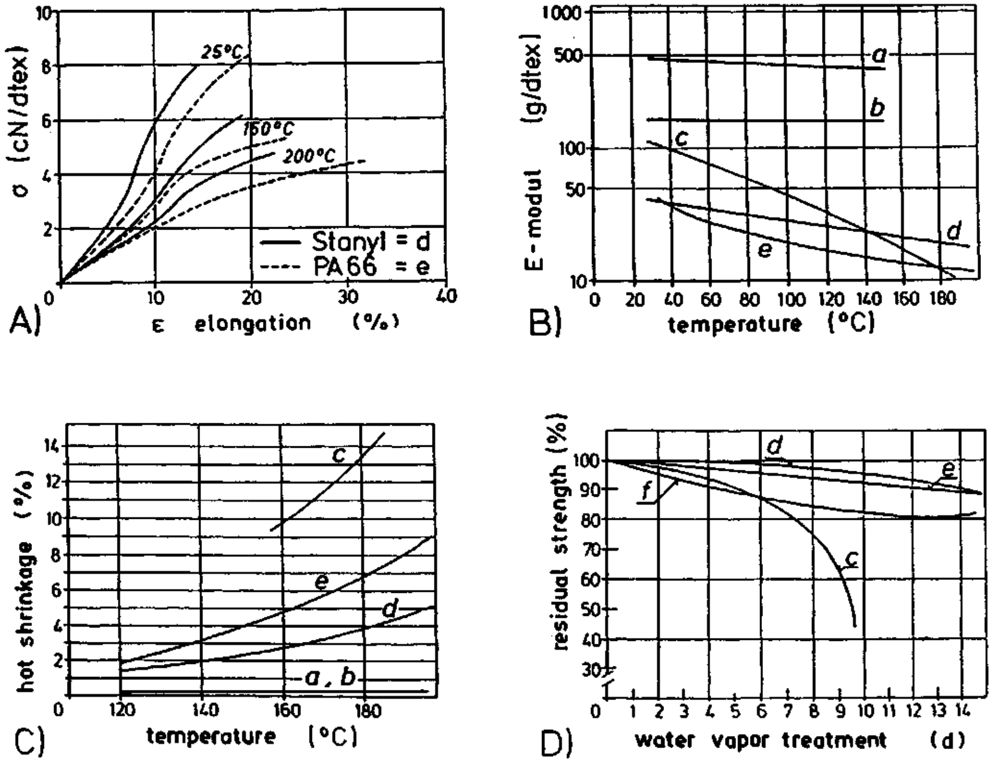


Figure 2.35 *A*) Stress (σ)/Strain (ε) diagram of "Stanyl" PA46 and PA66 multifilaments at different temperatures [101]
B) Elastic modulus as a function of temperature [101]
a) Kevlar, *b*) rayon, *c*) PET, *d*) PA46 "Stanyl", *e*) PA66, *f*) PA6
C) Hot shrinkage β as a function of temperature
a, *b*) rayon, Kevlar, *c*) PET, *d*) PA46, *e*) PA66
D) Residual strength $\sigma_{\text{res.}}$ 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.

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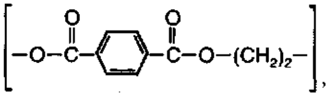
This laurinlactam can be polyadded as free amino acids to a polymer. This process can be accelerated significantly by adding acids similar to the end group stabilizers. The polymer is very thermo-stable, so that the polymerization can be done at temperatures up to 300 °C [112].

2.3 Polyester (PES)

2.3.1 Introduction

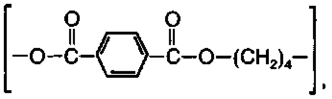
Even though a great number of polyesters [114] has been evaluated by now, only a few of them are around that can create good fibers and are crystalline with a melting point between 220 and 280 °C, and only three of them gained significance in fiber production:

Polyethylene Terephthalate
$T_G \approx 70 \cdots 80$°C; $T_S \approx 260$°C



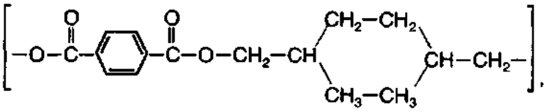
(PET) (2.17)

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



(PBT) (2.18)

Polyester from 1,4-Dihydroxymethylcyclohexane
and terephthalic (Kodel®)
$T_G \approx 60 \cdots 90$°C; $T_S \approx 250 \cdots 300$°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).

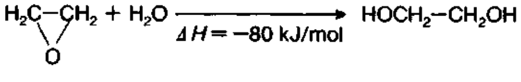
2.3.2 Production of Dimethyl Terephthalate (DMT), Terephthalic Acid (TPA) and Ethylene Glycol (EG)

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.

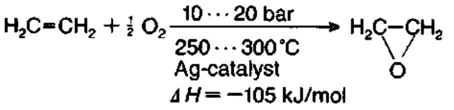
The best known process for the production of terephthalic acid is from Amoco [125]: p-xylene is changed directly to raw terephthalic acid by a radically catalyzed liquid filament oxidation at 200 °C and 15...30 bar in acetic acid with Co-Mn catalysts and Br bonds [126–129]. For example 48.8 parts of 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]:



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

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,

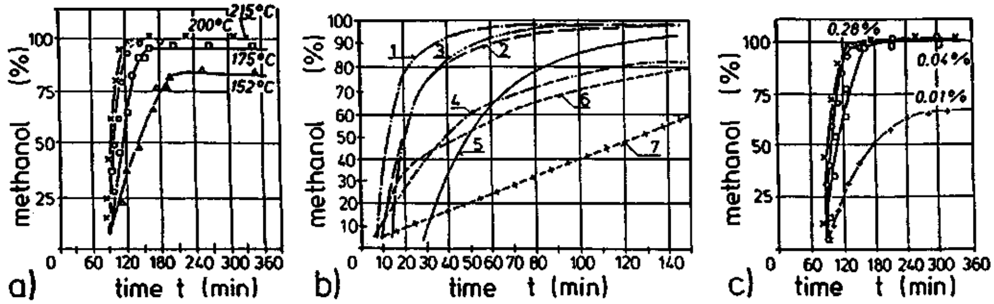


Figure 2.36 Methanol separation during the transesterification of DMT
a) With addition of 0.2% $Zn(CH_3COO)_2$ + PbO with the reaction temperature as parameter [142]
b) At 200 °C with different catalysts (0.14% metal acetate) as parameter (*1* Cd-, *2* Zn-, *3* Co-, *4* U-, *5* Pb-, *6* Na-, *7* Ni-acetate)
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 lack of metal acetates, etc. more stable than transesterification polymers. The stabilizers can also be added after esterification together with the antimonial catalysts [154].

A number of patents [155–163] describe further details and process possibilities.

2.3.3.3 Polycondensation of Diethylene Glycolterephthalate to Polyethylene Terephthalate

In praxis diethylene glycolterephthalate (DGT, monomers) is polycondensated under vacuum (empty about 0.1 mbar of the vessel, with material about 0.5 mbar) over 3...6 h, usually 4...5 h, at 270...295 °C for normal viscosity ($[\eta] \approx 0.63 \ldots 0.67$)—usually with metal acetates (Me-Ac) and antimony trioxide as catalysts.

The process parameters and catalysts have to be set very precisely, because polycondensation reacts quite sensitive to them. Table 2.10 presents an overview over the influence of catalysts, and Fig. 2.37 over the polycondensation process in time [144]. A good overview with numerous literature and patent references can be found with *Ludewig* [130]. Mostly used are antimony derivatives [164, 165] besides a metal acetate and (less frequently) titanium [166] and germanium [167] compounds. Viscosity and the creation of COOH-groups are of major importance here (Fig. 2.38). $Sb(OCH_3)_3$ and $Zn(CH_3COO)_2$ are the most stable catalysts against aftereffects, with respect to COOH-groups especially the latter one (groups I and II in Table 2.10). For long term thermostabilization triphenyl phosphate (Fig. 2.39) or triphenyl phosphite are suited instead of the formarly used phosphoric acid. This also influences the rate of polycondensation [164]: with $Sb(CH_2COO)_3$ only very little (graphs 1 and 2), but with $Co(CH_2COO)_2$ (graphs 3 and 4) and $Mn(CH_3COO)_2$ (graphs 6 and 7) more.

For the practical application some engineering companies recommend the following catalysts:

—for the autoclave process:	Sb_2O_3 + CoAc	(for DMT + glycol)	[169]
	Sb_2O_3 + Na Mg-Ac		[170]
—for the continuous process:	Sb-Ac + Mn-Ac	(for DMT + glycol)	[170]
	Sb-Ac	(for TPA + glycol)	[170, 171]

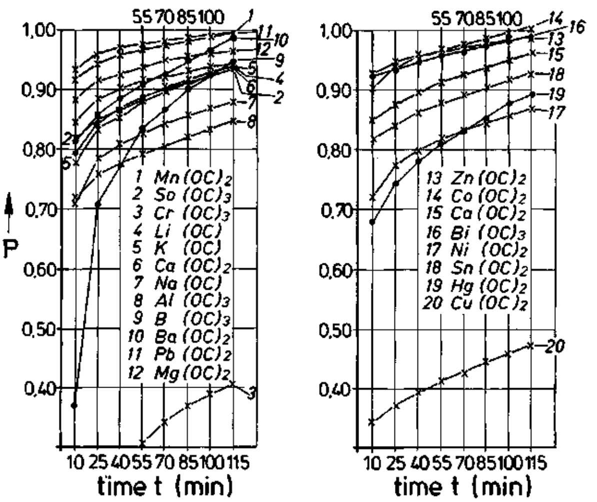


Figure 2.37 Polycondensation reaction as a function of time for diethylene glycol terephthalate with catalysts as parameters (concentration $1.2 \cdot 10^{-2}$ mol/mol ester)

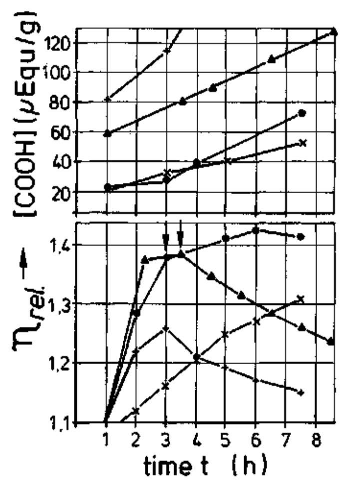


Figure 2.38 Influence of the catalysts on the viscosity and carboxyl end groups during the polycondensation of diglycol terephthalate; ↓ = polycondensation stopped; melt stored at 280 °C under pure nitrogen;
Catalysts: ● $Sb(OCH_3)_2$,
▲ $Zn(CH_3COO)_2$, × $Cu(CH_3COO)_2$,
+ $Ni(CH_3COO)_2$

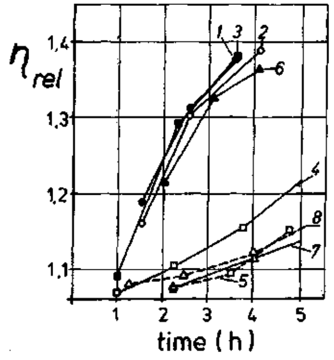


Figure 2.39
Viscosity increase of PET with different polycondensation catalysts and the addition of triphenylphosphate:
1 ● – ● $Sb(CH_3COO)_3$
2 ○ – ○ $Sb(CH_3COO)_3$ + triphenylphosphate
3 ■ – ■ $Co(CH_3COO)_3$
4 □ – □ $Co(CH_3COO)_3$ + triphenylphosphate
5 □ ··· □ $Co_2(PO_4)_2 \cdot 8H_2O$
6 ▲ ··· ▲ $Mn(CH_3COO)_2$
7 △ – △ $Mn(CH_3COO)_2$ + triphenylphosphate
8 △ ··· △ $MnNH_4PO_4 \cdot H_2O$

During the production and processing of PET melts several side reactions and decompositions can appear [172, 30]:

- Ether formation: Typical are up to 2.5 mol-% diethylene glycol contents. This ether formation has negative consequences: The melting point is lowered to $(270 \pm 2) - 2.3x$ (mol-% DEG) K respectively by 5 K/weight-% DEG. To reduce this effect more than 98% DEG should be produced during esterification or transesterification. Polyester chips should contain less than 1.1 weight-% DEG. Polyesters with Ti-, Co-, Zn- or Sb-catalysts have a lower melting point by the clear formation than those with Ca-, Mn-, Fe- or Pb-catalysts as well as a lower thermostability.
- Figure 2.40 [168] shows that the use of Mn-Ac + Sb_2O_3 and triphenylphosphate at temperatures under 285 °C is the least damaging condition to transport the melt in less than 30 min respectively at temperatures under 280 °C in less than 60 min dwell time to solidification. Results are primarily the lowering of the molecular weight due to the chain cracking and the resulting reduction of the melt and solution viscosity, the increase in carboxyl end groups, and a discoloring of the polyester (Table 2.10). Among other things this will lead to a reduction of the achievable filament tenacity. To produce a thermo stable polyester melt it is necessary to avoid the formation of carboxyl end groups already during polycondensation: on one level by using temperatures under 285 °C and also by using adequate catalysts and possibly by using thermo stabilizers or TPA as a starting material. Also transporting the melt at < 280 °C and (if necessary) increasing the temperature in the extrusion block to the optimal extrusion temperature of up to about 310 °C by reducing the melt pressure (see Chapter 4.6.11 and Fig. 3.4) reduce the decomposition to a minimum.

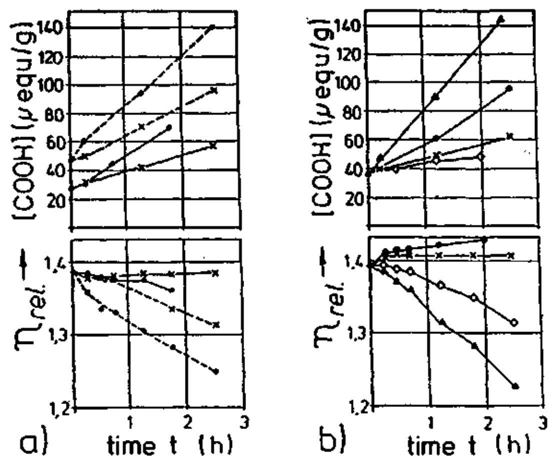


Figure 2.40
Viscosity and carboxyl end groups of PET during heating:
a) At 280 °C (X) respectively 290 °C (□) under pure nitrogen with different catalysts: catalyst 1: $Mn(CH_3COO)_2 + Sb_2O_3$ + triphenyl-phosphate catalyst 2: $Zn(CH_3COO)_2 + Co(CH_3COO)_2 + Mn(CH_3COO)_2 + Sb_2O_3$
b) ● 270 °C, × 280 °C, ◇ 290 °C, △ 300 °C

- Thermo-oxidative decomposition: The thermo-oxidative degradation is essentially dependent on the partial oxygen pressure and the temperature [172]. Here vinylester groups are formed as starting points for link reactions; (good) catalysts only have little influence on this. To analyze this, differential thermo analysis (DTA) and thermogravimetry (TG) are suited. Oxidation moves and increases the peak from just under the melting point to ≤200 °C [165] together with an increased loss of weight. Adding mixes of phosphoric and brenz catechin phosphoric acid esters with thermophenoles increases the stability and reduces the absorbed amount of oxygen (Fig. 2.41). This is especially noticed when parts with relatively large surface area (e.g. PET dust from the rotary dryer) enter the melt during the process, and the thermo oxidatively damaged dust surface leads to graining and gel formation [176].
- Hydrolytic decomposition: Sufficient drying and dry storage of the chips are some of the most important steps in the production of polyester filaments. Even smallest amounts of humidity reduce the average degree of polymerization during melting considerably as shown in Table 2.11 [177]. Only 0.01% H_2O in the PET chips cause a 10% decomposition of the melt. Chips of 4.7 mm length and an initial humidity content of 0.004% will contain 0.025% after 30 min in normal air and 65% relative humidity, and powder (40 mesh) will gain 0.125% humidity. When these chips are melted in the extruder at 285 °C, the melt coming from the spinneret does not form filaments. Therefore PET chips must be dried prior to further thermo processing to ≤0.004% water content and stored and transported under N_2 or air with a dew point of under −40 °C. Another example: PET with a molecular weight of 19,400 has 100 units per chain. One water molecule with a molecular weight of only 18 is sufficient to break this chain into two parts, e.g. of 50 units each with a molecular weight of 9700 that will not form filaments. The presents of one water molecule as a percentage of the initial molecular weight equals a water content of 0.092%. One split chain like this per 20 to 30 not split chains prevent filament formation: this results in the required water content of ≤0.004% in the polyester chips to make them spinnable.

Table 2.11 Calculated Hydrolytic Decomposition in Dependence of the Water Content of the Polyethyleneterephthalate

Water content		$\bar{P}_{na}$	$\bar{M}_{na}$	$[\eta]$	$\eta_{rel.}$	Decomposition [%]	
%	mol					$[\eta]$	$\bar{P}_{na}$
		110	21 182	0.692	1.388		
0.01	0.118	98	18 974	0.64	1.356	7.5	10.5
0.02	0.236	89	17 152	0.69	1.331	13.3	19
0.05	0.589	69	13 366	0.50	1.273	27.7	37
0.1	1.176	46	8 894	0.38	1.207	45	58.2

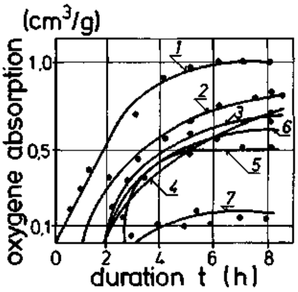


Figure 2.41
The kinetic of oxidation of PET filaments with different stabilizers:
1 Without stabilizer, with 4,4-thio bis (6-tert butyl-m-cresol) (CAO·6) + brenz catechin phosphoric acid
2 4,6-tert-butyl phenylester (BPSPE) + H_3PO_4
3 2,6-diisobornyl methylphenol (DIBMP) + BPSPE
4 DIBMP
5 DIBMP + tri-p-tert-butyl phenylene phosphite (TBPP) + H_3PO_4
6 TBPP
7 CAO·6 + BPSPE

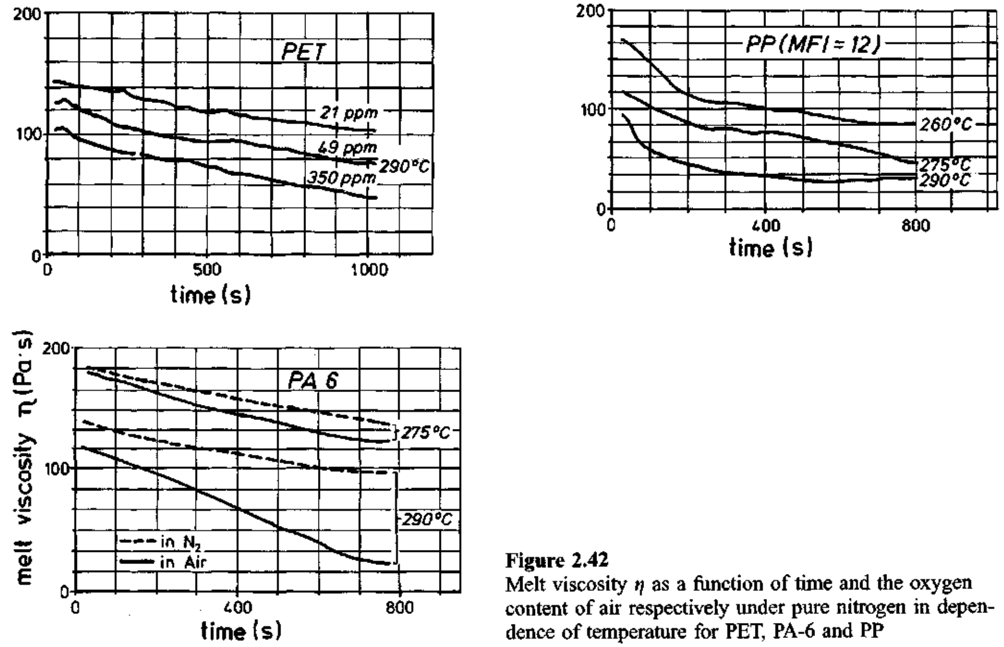


Figure 2.42
Melt viscosity η as a function of time and the oxygen content of air respectively under pure nitrogen in dependence of temperature for PET, PA-6 and PP

Additionally Fig. 2.42 shows that depending on the practically possible parameters the melt viscosity not only of PET but also of PA-6 and PP decreases similarly with time, and this already significantly after 10...15 min.

On the topic of solid phase afterpolycondensation see Chapter 4.5.

Calculating the reaction order of PET polycondensation [178] is still under discussion in the available literature: On the basis of viscosity measurements [179] an order I reaction is shown; others conclude an order II reaction from the glycol formation [180]. It seems most likely that an order III reaction occurs, because the time dependent graphs match the measured results best. Also the gross reaction order, i.e., the back and forth reaction, equals the order III reaction. In a given case it is only possible to follow the degree of polymerization and compare it to one of the three differential equations that describe the reaction order [178].

Pigments to influence luster, color, etc. are mainly used for dulling. See Chapter 6.8.1 about the use of TiO_2.

Spin dyeing the polyester black has been done for a long time, especially with soot and small additions of antimon trioxide. The melt pipes that were used for dyed or black melts need to be thoroughly cleaned before they can be used again for natural melts. Therefore the soot or dyestuff should be added as late as possible to the process, so that the installations stay clean up to that point. Thus additives are usually added as a master batch in powder form or as chips in the extruder entrance or in a melt blender dosed in right before extrusion. This is also true for dosing into the melt flow of a continuous polycondensation installation.

2.3.3.4 Properties of PET Melts and Chips

After polycondensation the melt is extruded into water, most practically with under-water-chip cutters (see Chapter 4.3, "Chip Cutting"), cut into chips, directly mechanically dehydrated, crystallized, and then dried to $\leq 0.004\%$ water content (see Chapter 4.5) and thus melted again and spun. The properties of well spinnable PET chips for textile filaments and fibers are explained in an example in Chapter 10. Generally spinning of the following products from PET chips can be assumed with the mentioned intrinsic viscosities $[\eta]$, measured in phenol-dichlorobenzene 60 : 40/25 °C:

PET chips for	$[\eta]$ in dl/g [170]
low pilling staple fibers	0.40...0.50
staple fibers wool types (W)	0.58...0.63
cotton types (Bw)	0.60...0.64
HT-HM cotton types (high tenacity, high modulus)	0.63...0.70
textile filaments	0.65...0.72
technical yarns	0.72...0.90
tire cord yarns	0.85...0.98
films/foils	0.60...0.70
injection mold, blow forms	0.90...1.00
bottles	0.75...0.8

The deviation range for staple fibers is $\leq \pm 0.02$ or better and for all other yarns $\leq \pm 0.015$. In the autoclave system for polycondensation there is a delay between starting and completing melt extrusion of about 20 min (equivalent to 2.4 tons from a 4.5 m^3 polycondensation autoclave), which will lead to quality differences in the chips (Fig. 2.40 and 2.42). This makes intimate blending necessary to achieve at least a higher average value. The product of a continuous polycondensation is more homogenous.

Due to the water cooling the chips are in the amorphous phase and have to be crystallized prior to drying to avoid sticking or sintering during the heat up for drying or in the extruder entry zone.

Amorphous chips stay gray under UV-light, while crystallized chips fluoresce light blue. When testing the crystallization for drying only a few individual chips may remain uncrystallized.

Of the many existing definitions of viscosity [104, 130], for polyethylene terephthalate only the relative solution viscosity $\eta_{\text{rel.}}$ and the intrinsic viscosity $[IV]$, or limit viscosity $[\eta]$, is used. For conversions the Huggins formula is applied. If here $\eta_{\text{rel.}}$ is measured in a PET solution in phenol/tetrachlorethane (1 : 1)/20 of 25 °C of in phenol/dichlorobenzene (1 : 1)/25 °C as 0.5 or 0.1 g/dl, so the Huggins constant $K = 0.35$. Thus

$$[\eta] = \frac{1}{0.7}[\sqrt{1 + 1.4(\eta_{\text{rel.}} - 1)} - 1] \tag{2.22}$$

$$\eta_{\text{rel.}} = 1 + [\eta](91 + 0.35[\eta]) \tag{2.23}$$

These formulas can be used quite well between $\eta_{\text{rel.}} = 1.2$ respectively $[\eta] \approx 0.4$ and $\eta_{\text{rel.}} = 1.7$ respectively $[\eta] = 1.163$. Other possible formulas show up to 10% deviation.

To determine the molecular weights and their distribution one can apply several methods [104, 130]: Membrane osmosis, steam pressure osmosis, sedimentation during centrifuging, or light diffusion. More simple and in praxis sufficiently exact is the indirect method by the formula corrected towards [130] and via the degree of polymerization:

$$\bar{M} = (\eta_{\text{rel.}} - 1.059) \cdot 10^{4.8} \text{ respectively } \bar{P} \approx \bar{M}/192 \tag{2.24}$$

This formula provides useful results for $M \approx 10{,}000$ to 40,000.

To determine the melt viscosity there is also a mathematical relationship to the molecular weight that is based on $\eta = K \cdot M^{3.5}$ (with $K = 3.6278 \cdot 10^{-12}$) [130], but its results deviate considerably from measurements. Therefore it is better to use Fig. 2.43 that is based on an interpolation of measurements of the melt viscosity as a function of the melt temperature with the intrinsic viscosity as the parameter. In praxis the melt viscosity of textile polyesters at spin temperature is about 2500...3200 P and of tire cord qualities about 10,000...15,000 P.

The dependence of the temperature on the melt viscosity can be described by [130]

$$\eta = C \cdot e^{E/RT} \tag{2.25}$$

The humidity content of the chips can be determined according to the C.-Fischer method or with the DuPont Moisture Tester. Because it is necessary to obtain the extremely low humidity value of $\leq 0.004\%$ it is important to mention the measured value and the measuring method due to the significant variations.

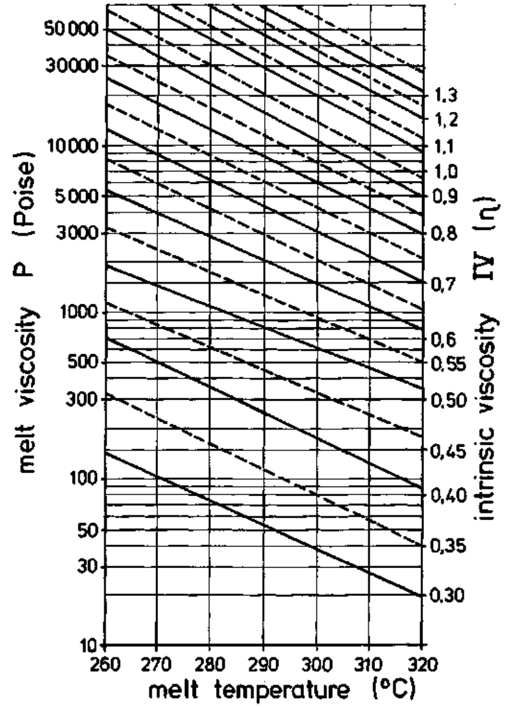


Figure 2.43
Relation between melt viscosity η, intrinsic viscosity $[\eta] = \mathrm{N}$ and the melt temperature T (°C) of PET

The melting point can vary between 255 and 265 °C; this is based in the chip history as well as in added mixtures like DGT or in different measuring methods. Table 10.7.2.2 shows a sample specification of well spinnable PET chips.

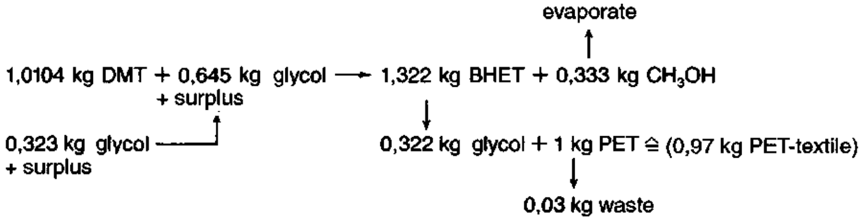
2.3.4 Autoclave Polycondensation to PET

- From DMT and ethylene glycol:
  DMT is delivered either in bags (paper-aluminum-PE coated), in barrels or in silo trucks. It has to be emptied in clean, dust free rooms into storage tanks with a loosening device. Then it is transported pneumatically to the weighing tanks or directly to the melt or solution tanks see (*2*) in Fig. 2.44) with a throughput of about 2 t/h. When delivering melt [180, 181] (to avoid the cost for DMT crystallization, packing and re-melting in heated specialty transporters) it is necessary to observe the thermal burden of the DMT. Figure 2.44 shows a process diagram [179] and Table 2.12 the corresponding specifications for an installation size of 1000 kg PET/batch. Ethylene glycol can be stored outside in aluminum vessels, that should be steam-heated, because at −11 °C the risk of freezing exists. Feeding the glycol into the process is done through measuring units, e.g. oval rotary counter. It is important to protect against humidity because of the hygroscopicity.

  In (1) the necessary EG quantity (645 kg EG/1000 kg PET) is prepared, mixed with the additives and heated to 175...180 °C. Parallel to this 1010.4 kg DMT are melted in (2) at 175 °C. The transesterification autoclave (5) is slowly heated to 180 °C, EG is filled in and then the melted DMT is added slowly. The temperature is increased over 1.5...2 h to 195...200 °C and kept at that for 1...1.5 h, evaporating 326 kg methanol. The glycol steam is refracted in the reflux condensor (6), while methanol transfers into the drain condenser (7) and runs as condensate into the collection tank (8). The β-hydroxyethylterephthalate (BHET) is pressed from (5) with 1.5...2 bar N_2 into the heated (220 °C) polycondensation autoclave (9); its temperature is raised over 1...1.5 h to 280...285 °C and kept there for 2…3 h. Polycondensation is finished when no more glycol drains into the glycol receiving tank and a (reproducible) desirable melt viscosity (about 2800 P for $[\eta]=0.63$, Fig. 2.43) has been achieved. This melt viscosity can be measured with a torque measuring apparatus in the agitator shaft or (not quite as exact) by the power consumption of the three phases drive motor of the anchor or helical agitator. It follows a fast (if possible) extrusion through the casting head (16) onto the casting wheel (17) into completely desalted water and the chip cutting (18). The chips are then pneumatically (19) transported to the collection and weighing tanks (20, 21). Weight into batches, the chips then transported into the rotary dryer (22), then they crystallize at 130…140 °C and dry at about 165…180 °C and 0.1…0.5 mbar for about 12 h: the last 2 h allow the chips to cool to about ≤ 80 °C, and then they are filled and transported to the spin or storage tank.

The beginning of the polycondensation process can also be moved up into the transesterification autoclaves: this gives the installation a better timewise utilization, i.e. transesterification and prepolycondensation occur in (5) at up to 225 °C. However, the methanol transferring into (8) contains more glycol. This reaction takes 3.5…4 h; 0.2 h of pressing the BHET follow, 3.0…4.2 h polycondensation in (9) and 0.3 h extrusion. By timing the transesterification and polycondensation times well, two polycondensation autoclaves can be served by one transesterification autoclave.

The reaction process and the mass balance can be shown as follows:



(2.26)

- From TPA and ethylene glycol:
  Here only the entrance phase through direct esterification (inclusive) is different than from DMT: In a Z-kneader or high viscosity mixer (e.g. a double cone mixer, Fig. 2.119) or in a continuous paste mixer glycol and TPA are prepared in a mol relation of about 1 : 1.2 for 30…60 min at 30…40 °C and transported to the direct esterification in an autoclave with an enlarged inside heat exchange surface. This autoclave (Fig. 2.45) [182] contains in its lower part co-centrical heated ring surfaces and a heating jacket that heats the contents at 1.5…2 bar over 1.5…2 h to 250…260 °C at the end. For the whole time water and glycol are evaporated at the top; the glycol condenses in the reflux condenser above and returns to the autoclave. After only approximate stoichiometric esterification the

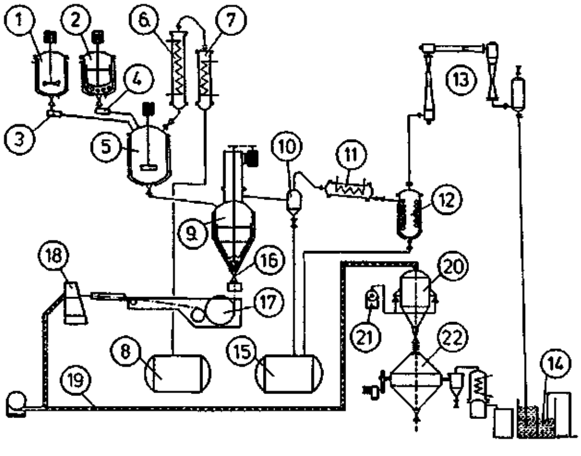


Figure 2.44
Simplified flow diagram of the batch PET polycondensation (definitions of the positions and technical data of the example see Table 2.12)

Table 2.12 Specifications for the PET Autoclave Polycondensation according to Figure 2.44

Position	Description	Design like figure #	Size per 1000 kg PET/batch
–	DMT-(salt-) storage tank, vertical or horizontal, with loosening device, 1.45641 or A1, emptying via dosing device, dust free filling		2500 l × m*
–	DMT transportation device, 1.4541, pneumatic, dust free		> 3000 kg/h
–	EG storage tanks A1 tanks with inside steam heating coils to outside > + 5°C	4.38	800 l × m*
–	EG pumping station with quantity measuring, switch, filter, pipes, 1.4541 –observe height difference		$> 4 m^3/h$
1	EG preparation vessel with heating jacket for up to 185°C, 1.4541, stirrer	4.10a	1000 ··· 1200 l drive 1 kW
–	Addition vessel for glycol and additives with stirrer		100 l
2	DMT melter, vessel with heating jacket and inside coil for up to 185°C, 1.4541, anchor agitator	4.10a	2500 l
3, 4	Basket (star) filter, 1.4541, with heating jacket		
5	Transesterification autoclave, 1.4541 with heating jacket, 1.0425 (=H II) for up to 230°C with (*turbo) stirrer	4.10b	3000 l 2.5 kW
6	Reflux condenser, inside 1.4541, jacket and inside coil with dephlegmator (entrance side)		
–	Gooseneck pipe with temperature element		
7	CH_3OH drain cooler, jacket and inside coil	2.29 (8)	
8	CH_3OH collection tank	2.29 (9)	430 × m*
9	Polycondensation autoclave, inside 1.4541 with heating jacket, 1.0425 (=H II) for up to 320°C, pressure ≤ 10 bar) and vacuum (0.1 mbar) proof, anchor agitator, for $[\eta] = 0.67$, flat, for higher $[\eta]$ more spiral, three-phase current drive 60/30 rpm, double functioning slide ring gasket, glycol superposed and water cooled, conical bottom, foam dome	4.10c	2650 l 20 kW
16	Bottom valve to (9) and casting head (34 stringths, i.e. 100 kg/15 min) DN200	4.17	
10	Centrifugal drop separator		
11	Flow down condenser, advance idling, jacket and inside coil cooling		
12	Vacuum condenser, centrifugal entry, jacket and inside coil cooling		
13	Steam vacuum jet, for 3.5 ··· 5 bar saturated steam, 5 stages (empty ≈ 0.1 mbar)	2.22 (5)	$\leqslant 0.1$ mbar
14	Condensator tank, barometric positioning	2.22 (7)	
15	Glycol tank – to recycling		
17	Casting wheel into water better under water chip cutter	4.33/5.35	for 30 stringths
18	Ribbon chip cutter	in 15 min	
19	Chip transportation, pneumatic	4.15	> 1000 kg/15 min
20, 21	Chip container and weighing device		> 3000 l
22	Bi-conical vacuum dryer, 0.1 mbar empty or continuous crystallizer and dryer	4.46 4.56	2100 l/ $\leqslant$ 185°C

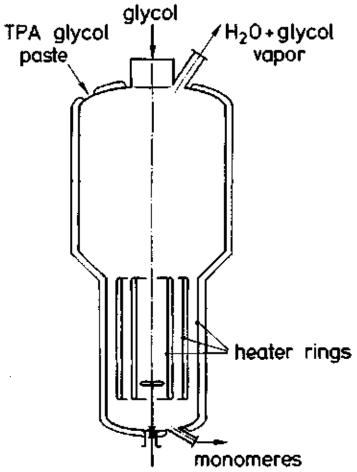


Figure 2.45
Autoclave for direct esterification of TPA with enlarged inner heat exchange surface [142]

monomer (= BHET) is removed at the bottom and then transported into the polycondensation autoclave (pos. 9 in Fig. 2.44). Further reaction occurs as described for that figure. Some of the quoted patents mention that 10...20% of the oligomer content are stored in a separate autoclave or remain in the esterification autoclave to serve as an initiator for the next TPA-glycol batch.

Autoclave polycondensation to PET is recommended:

- when PET production is newly started; if uniform production quantities of more than 20 t/24 h result, it is possible to change to the continuous process;
- for frequently changing special products;
- for productions of less than about 20 t/24 h.

2.3.5 Continuous Polycondensation to PET

2.3.5.1 Processes and Apparatus for Trans- and Direct Esterification

- From DMT and ethylene glycol:
  The first significant patents [183–186] by DuPont were transformed into installations between 1952 and 1956. Transesterification is done in a reaction column (Fig. 2.46) [183] respectively position 6 in Fig. 2.48. The rotor-finisher principle was patented in 1953 (Fig. 2.47 [184] respectively position 14 in Fig. 2.48). Between the column and the finisher two sequential vacuum prepolymerization vessels are positioned (10, 12) since 1953. The finisher (15) for some time has been a single disc or a spoke wheel reactor. The first patents of German companies in this area are from 1952 [192] and 1957 and later [189–191]. Japanese patents mostly date after 1960 [193], and the first continuous polycondensation staple installation dates 1962/63 [184].
- From TPA and ethylene glycol:
  These modern installations are usually also suited for DMT. The differences are only in the initial step.

Figure 2.49 shows such a flowsheet as well as the most important process data [171]. Raw materials can be HP- or MP-TPA or QTA [195] as well as DMT. QTA is not as pure and can lead to corrosion problems, if not all contact areas are made from materials 1.4541 (≈AISI 304) or better. Further process data can be found in [182] as well as the reaction sequence from DEG to the finished polymer (similar to Fig. 2.54).

Figure 2.50 shows that the processes of different engineering companies are quite similar for DMT as well as for TPA as a raw material.

Another process is shown in Fig. 2.50 [182], that can use DMT (a) as well as TPA (b) as raw material. In (a) DMT is dosed into the melter (4) and melted, while EG (1) is prepared and stored in (2). Starting from the reactor (6), where either hot EG and DMT melt are mixed, or the TPA-EG paste from (4) is started, both processes are the same. Here four reactors are positioned in sequence (6, 7, 9, 10). From the last reactor the intermediate product flows into the finisher and then it is pumped to stringth casting or to direct spinning (12).

In this connection, Table 2.13 mentions data regarding the filter fineness, raw materials and the energy consumption [171]. It should be noted that the filters and pumps can encrust after using antimone trioxide as a catalyst due to reduction to (metallic) antimone for a long time, what can cause problems especially for the spin pumps. Chapter 6.6.3 mentions the cleaning procedure hereof.

A continuous PET polycondensation is advantageous if a uniform polymer with a capacity of $\gg 20$ t/24 h is to be produced for a long period of time. It can be taken into account that many additives are added briefly before spinning or extrusion.

The uniformity of the relative solution viscosity of a PET melt with $[\eta]$ values usually between 0.63 and 0.75 from a continuous polycondensation can be given with values better than ± 0.01 or even up to ± 0.002 for $[\eta]$.

2.3.5.2 Finisher

The originally patented double shaft finisher (Fig. 2.47) is still being built today (Fig. 2.51). Because the interior of the finisher must remain free of sublimation and decomposition products and the viscosity of the melt is considerably higher than for polyamides (see Fig. 2.21), the one shaft finisher and the shaftless finisher have been developed and proved successful. Model trials with the one shaft finisher are published in [197].

A cross-sectional view of the finisher (item 11 from Fig. 2.50b), the HVS reactor (=High Viscosity Self Cleaning) [44, 54] is shown in Fig. 2.52 and the corresponding outside view in Fig. 1.13. In addition to the heating/cooling jacket also the rotor and the shaft are heated to the same temperature. The self cleaning of all parts that have contact with the product is done by scrubbers that clean the inner jacket surface, the shaft and the individual rotor arms at each revolution, so that no long term decomposition or cracking products can develop. The rotors and their arms must be constructed very strong due to the high viscosity and the high volume.

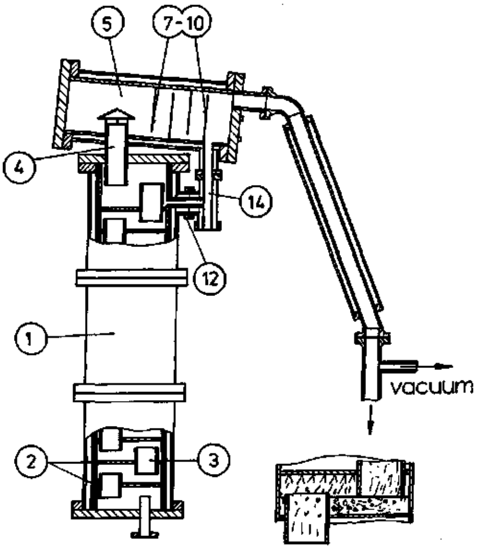


Figure 2.46
Transesterification column for DMT and ethylene glycol to diethylene glycol [183]

1	Column
2	Plates, some of them heated, with
3	Overflow and drain
4	Overhead steam evaporation (CH_3OH)
5	Condenser
7–10	Throughflow resistor
12, 14	Reflux

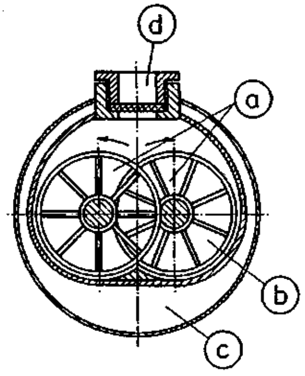


Figure 2.47
Double shaft finisher with wheels [184] (compare Fig. 2.51)
a) Wheels, covered with wire mesh sieves
b) Evaporation spaces
c) Dow vapor heating room
d) Evaporated glycol vapor to condenser

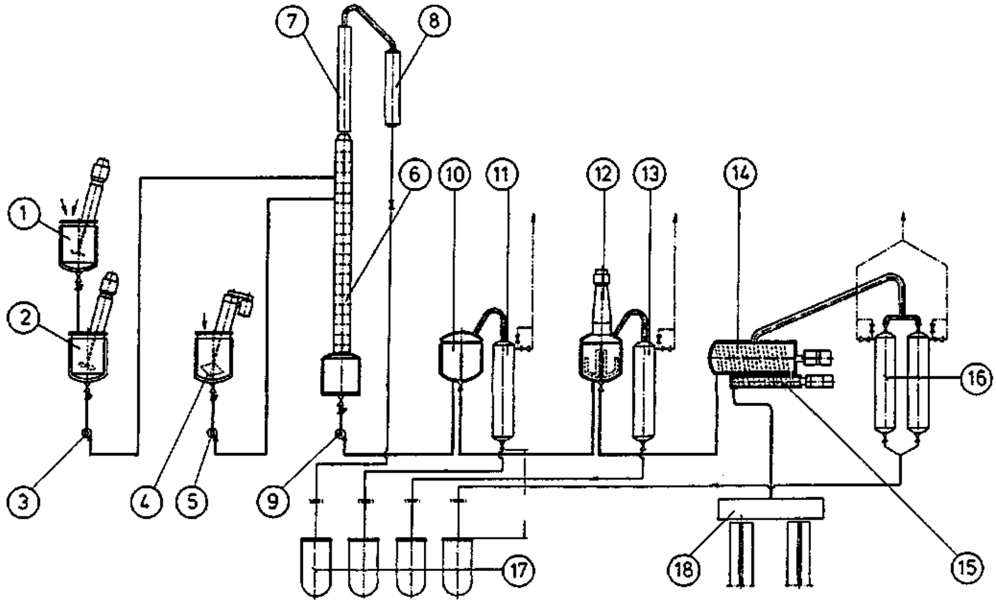


Figure 2.48 Flow diagram of a continuous PET polycondensation for DMT and ethylene glycol as raw materials [74]

1	Glycol preparation vessel	*11, 13*	Glycol discharge condenser
2	Storage for prepared glycol	*12*	Prepolymerizer
3, 5, 9	Dosing pumps	*14*	Disc or screw finisher (similar to Fig. 2.21)
4	DMT melter	*15*	Polymer extrusion screw
6	Transesterification column	*16*	Glycol vacuum condensers
7	Reflux condenser	*17*	CH_3OH- and glycol receiving tanks
8	CH_3OH discharge condenser	*18*	Direct spinning equipment
10	Vacuum flasher		

Today also a shaftless one rotor finisher is manufactured (Fig. 2.53 [199]). The shown finisher has a rotor diameter of 2.60 m and a length of about 6 m. It is made from a stainless steel pipe ring construction and consistently dips with the lower part into the melt sump at the bottom, takes the melt along to the top by the rotation, while depending on the viscosity a more or less developed film flows down, allowing the film to evaporate on both sides. Here, too, the inner wall is continuously scrubbed.

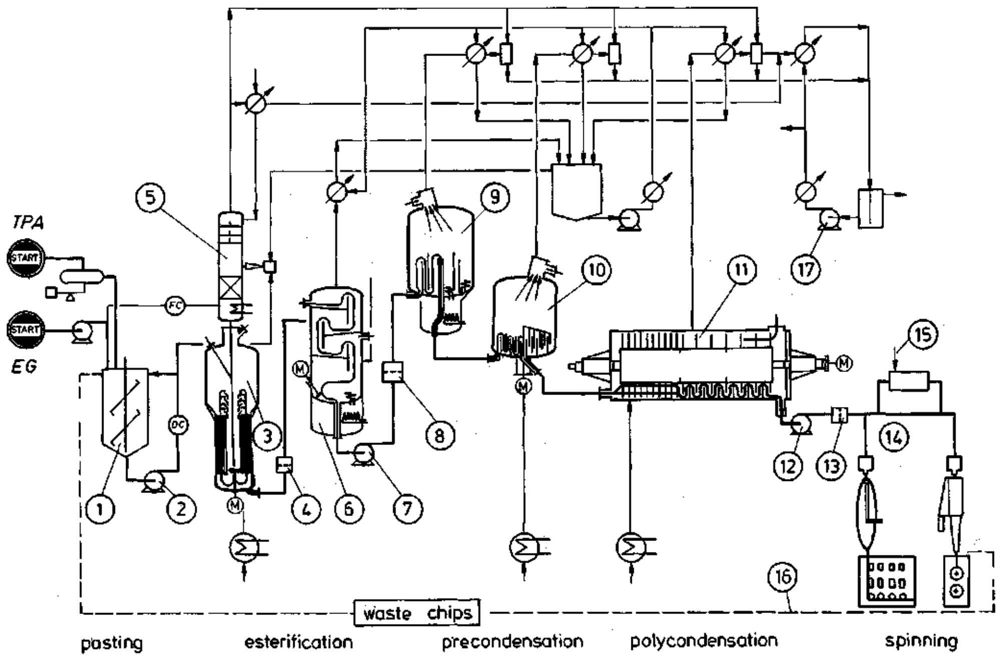


Figure 2.49 Continuous PET polycondensation for TPA and glycol as raw materials (Karl Fischer GmbH, [171])

– Continuous weighing scale for TPA or DMT
– Dosing pump for ethylene glycol
1 Mixer/kneader for TPA and EG
2, 7 Dosing pump for paste respectively DEG
3 Esterification autoclave I
4, 8 Filters
5 Reflux column for separation of water (methanol) and glycol
6 Esterification autoclave II
9 Flasher
10 Prepolycondenser
11 Polycondensation finisher
12 Discharge (gear) pump
13 Non-stop filter
14 Heated pipe to fiber or filament spinning
15 Possible additive injection
16 Possible polymer waste recycling to 1
17 Vacuum installation

Process data of the continuous polycondensation of TPA and EG to PET [171]:

EG : TPA-mol relation	1.12 . . . *1.18* . . . 1.28		
Paste mixer (1)	$t_V = 45\ldots60$ min	$T = 30\ldots40$ °C	
Esterification I (3)	$t_V = 1.5\ldots2$ h	$T = 250\ldots260$ °C	$p = 1.5\ldots2$ bar
Filter (4)			
Reflux column (5)	$R = 0.9\ldots1.2$		
Esterification II (6)	$t_V = 1$ h 45 min	$T = 255\ldots270$ °C	$p = 0.5\ldots1$ bar
Pump (7) and filter (8)			
Prepolycondensation I (9)	$t_V = 1\ldots1.5$ h	$T = 265\ldots275$ °C	$p = 50\ldots80$ mbar
Prepolycondensation II (10)	$t_V = 50\ldots60$ min	$T = 275\ldots280$ °C	$p = 5\ldots8$ mbar
Polycondensation	$t_V = 60\ldots80$ min	$T = 280\ldots285$ °C	$p = 1\ldots2$ mbar

= Finisher I (11) with shaftless basket type evaporator: $n = 0.5\ldots3$ rpm.

Product: PET melt with $[\eta] = 0.6\ldots0.65 \pm 0.005$ at 285 °C, i.e. textile quality

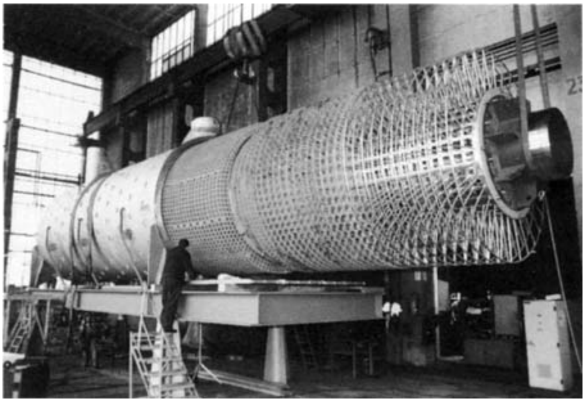


Figure 2.49 (*Continued*)

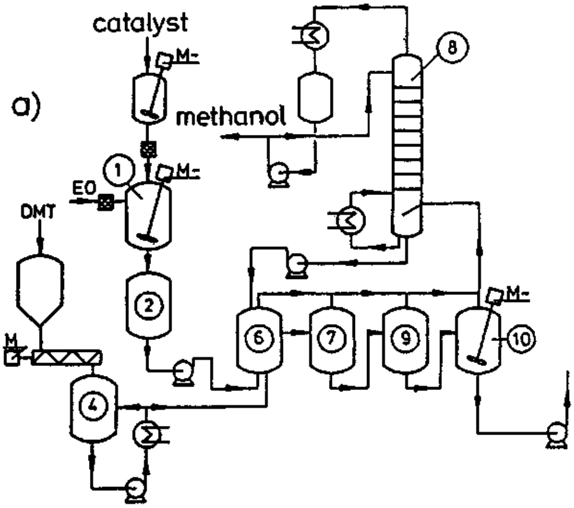


Figure 2.50a,b
Continuous PET polycondensation flow sheet for DMT or TPA and ethylene glycol as raw materials (Zimmer AG [182])

1 Glycol preparation
2 Storage for prepared glycol
3 Storage for either TPA or DMT
4 Premixer
5 Dosing pump
6, 7 Esterification
8 Transesterification column
9 Vacuum flasher
10 Vacuum prepolycondenser
11 Ring disc reactor (see Fig. 2.52)
12 Polymer melt to chip production or spinning

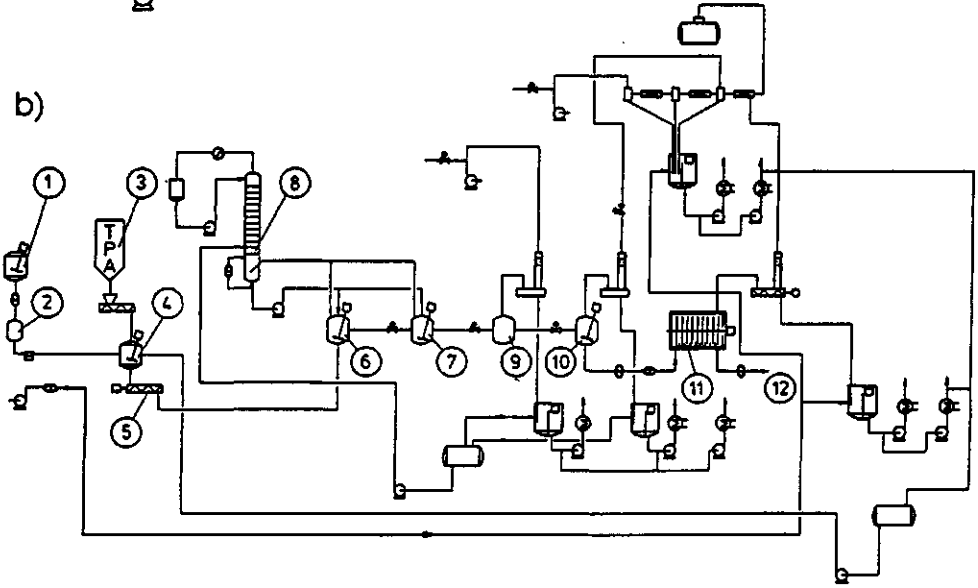


Table 2.13 Process Data of a Continuous PET Polycondensation Installation [171]

Filter fineness µm		Raw material consumption kg/1000 kg polymer		Energy and auxiliaries consumption per 1000 kg polymer	
EG	10	Pure terephthalic acid	858	Electricity	105 kWh
DMT (if)	10	Monoethylene glycol	338	Steam	210 kg
Catalysts	10	Catalyst	0.3	Cooling water (circa.)	42.5 m^3
TiO_2 suspension	2...3	Stabilizer	0...0.04	Cooled water (circa.)	320 MJ
DEG and		Additives	0...10.0	Completely desalted water	0.035 m
Precondensate	15	Dulling agent TiO_2	0...4.0	Fresh water	5.7 m^3
Impurities	none			Pure nitrogen	1.4 Nm^3
				Instrumental air	28 Nm^3
				Compressed air	32 Nm^3
				Fuel oil	58.5 kg

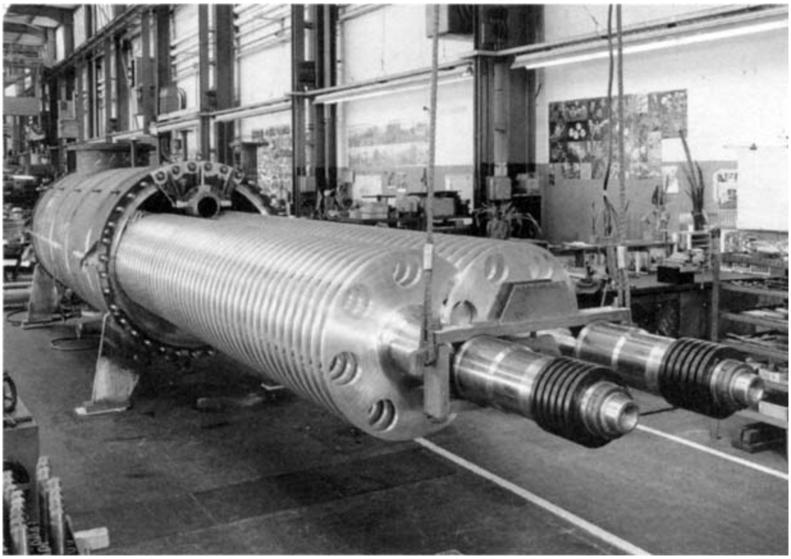


Figure 2.51 Double shaft finisher (reactor) opened, rotors drawn out to the front (Werner & Pfleiderer [199])

Rotor diameter (outer/inner)	800/342 mm
Distances of axis	574.5 mm
Clearance to wall	2 mm
Longitudinal disc spacing	93 mm
Inner length	4500 mm
Contact heating surface	10.67 m^2
Drive	36.7 kW
Inner volume	4.32 m^3
Revolutions, adjustable	0.8–7 rpm
Melt residual time for 1 rpm	48.5 min

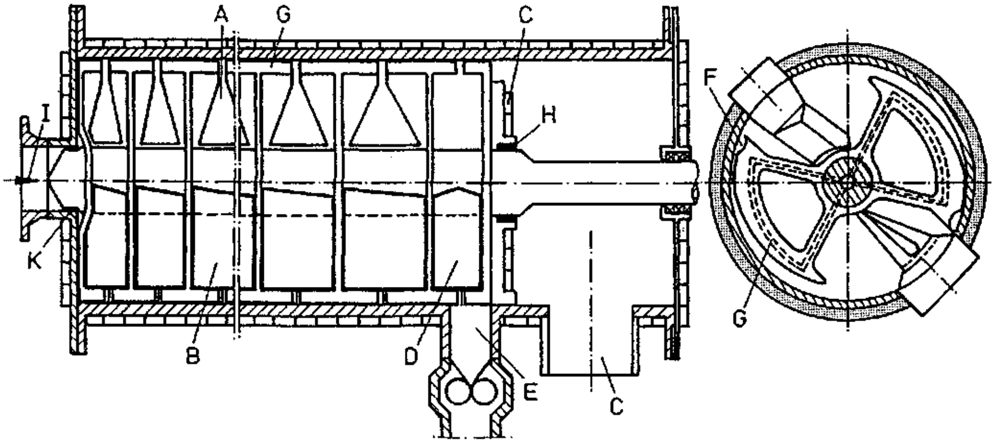


Figure 2.52 Longitudinal and cross-sectional view of a HVSR reactor (item 11 in Fig. 2.50b, Zimmer AG [44, 54])

A) Upper stator
B) Lower stator
C) Vapor suction
D) Discharge stator
E) Discharge with gear pump (Fig. 4.115)
F) Agitator with shaft and wings
G) Rotor with wall scrubber
H) Labyrinth seal
I) Intermediate product entrance
K) Friction bearing
L) Sealing for polymer viscosities of up to 10^4 Pa·s

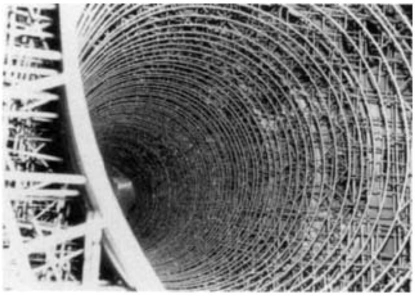
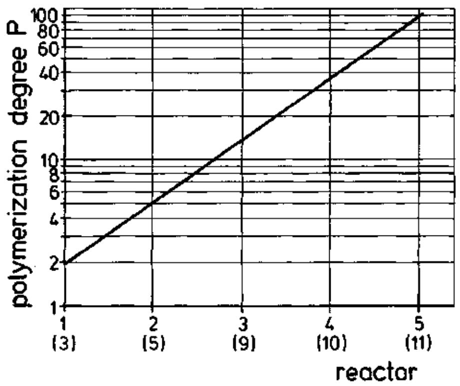


Figure 2.53
Inner view of a basket of a shaftless finisher type SR [199] (Werner and Pfleiderer)

The finisher is arranged into the overall process according to Fig. 2.22. The melt flows from (1) to (8). The pipe between the finisher dome and the corresponding vacuum condensers (3) should condense the glycol that contains a significant amount of monomers and oligomers. One of the two condensers can run while the other one can be cleaned without interrupting the process. A two or three phase steam jet injector provides the necessary process vacuum inside the reactor between 0.1 and 0.5 mbar, usually working with glycol vapor. The melt exits through jacket heated discharge gear pumps (Chapter 4.6.8.3). The earlier used single discharge screw is no longer being used.

The intrinsic viscosity IV = [η] and consequently the molecular weight and the degree of polymerization increase inside the finisher from the entry value to the set [η]-value (Fig. 2.54). To achieve a uniform product it is necessary to include a homogenization zone before the polymer exit.



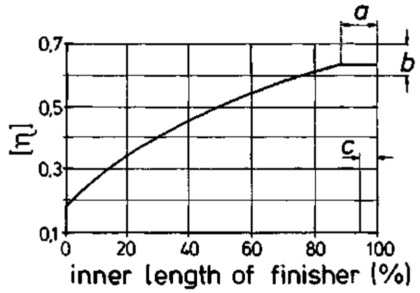


Figure 2.54 Typical [η]-curve of PET when passing the finisher length respectively as a function of the dwell time [91]
a) Homogenization
b) Control range
c) Discharge zone

2.3.6 Spinning and Drawing of PET

2.3.6.1 Route of PET to Spinning

The melt from the continuous polycondensation is pressed by the discharge pump of the finisher to the spinning heads on the shortest possible path. Additional non-stop filters are not necessary. Usual are melt velocities of 4...6 cm/s for pipes with an inside diameter of 32...100 mm. For $[\eta] = 0.6...0.7$ the melt and pipe temperatures should be ≤ 280 °C, and for $[\eta] \approx 0.9$ they should be ≤ 290 °C. The maximum dwell time is about 10 min. The pipes are formic gas welded and electro polished on the inside to $R_t \leq 0.4$ μm and, just like the valves, must not have any dwell corners or pockets. The spinneret packs can be used with or without stainless steel sand filters and contain a flat filter in front of the spinneret with 20 μm for the usual textile titers.

The chips are transported by air from the mechanical dehydration to drying, where they are either crystallized in vacuum dryers at 130...145 °C under continuous movement and then dried to a residual humidity of $\leq 0.004\%$ at 180 °C for a total of 8...12 h including a cool down time of about 2 h to about 80 °C. For larger capacities today continuous crystallizers and dryers are preferred that also crystallize the chips under constant movement at 140...145 °C and then dry them to a residual humidity of $\leq 0.004\%$ during a slide down the drying tower at about 180 °C with air or nitrogen with a dew point of under -40 °C.

Chip transportation and storage from extrusion are done with equally dry air or nitrogen. Above each spinneret two chip vessels in sequence are suggested with the lower one of such size that it is possible to continuously spin while the upper one is filled and rinsed with nitrogen (Fig. 4.45).

The spin extruder size should have 10...20% reserve capacity according to Chapter 4.6.4. Screw lengths of 25 or 30 *D* including 3 *D* for the mixing torpedo are suggested. The melt pressure at the tip of the screw is between 100 and 130 bar for textile qualities, and for tire cord qualities between 400 and 500 bar. The former ones require spin pumps for 150...200 bar pressure difference, the latter ones high pressure spin pumps for up to 1000 bar.

For larger installations non-stop large surface filters should be installed according to Fig. 4.129 with the option of loss free switching. Melt pipes and distribution pipes, spin beams, melt valves, extrusion blocks and spinnerets can be selected according to the Chapters 4.6.5 to 4.6.11. With the appropriate cooling in the quenching chamber relatively tight spinneret bore gauges are possible, up to about 3 mm for textile titers.

2.3.6.2 Spinning and Take-Up of PET Filaments

From experiences and publications today the following preferred take-up speeds are to be expected:

- for staple fibers (cotton type) >1300, preferred 1700 m/min,
- for textile filaments for draw texturing: with POY velocities between 3200 and 3600 m/min [130], nearly up to 5200 m/min,
- for FOY yarns ≥5600 m/min up to 8000 m/min. These filaments will still have a residual draw of 15...10%,
- for textile ROY yarns with a spinneret take-up of 1300...1700 m/min and an integrated draw ratio before the winder of 3.4 to 5,
- for tire yarn so far a spinneret take-up of 600 up to 800 m/min and an integrated draw ratio to 3000...3400 m/min. In new installations from 1992 the spinneret take-up is 1100...1200 m/min and an integrated draw ration to winding at over 6000 m/min.

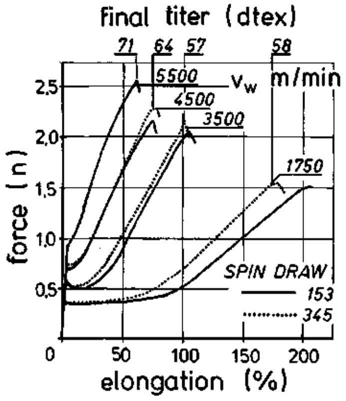
Figure 2.55 shows the stress strain curve as a function of take-up speed [200]. The elongation at the breaking strength drops with increasing speeds, while the specific tenacity increases. Additionally Fig. 2.56 shows the achievable specific breaking strengths and the possible residual draws from trials and the literature [1–5] as a function of take-up speeds for not yet drawn filaments. The maximum tenacity is reached around 5000...6000 m/min spinneret take-up, while the residual draw even at 10,000 m/min is about 1.1. These results show the same tendency as those of [201]. At 5000 m/min the final spin values for diameter, orientation, crystallization and birefringe are achieved about 60 cm below the spinneret, i.e., within 10 ms. At 9000 m/min this only takes about 10 cm respectively 1 ms.

From stability evaluations about the spinning process it is possible to conclude the minimum individual filament titer (see Fig. 2.57):

$$T_{\min}[\text{dtex p.f.}] = f[Q \cdot \sqrt{\ln(v_L/v_o)}] \qquad (2.27)$$

(T = individual filament titer, Q = spinneret bore throughput in g/min, v_L/v_O = spin draw ratio).

According to this the filament titers in the area A are well spinnable, while those in area B will lead to many breaks. The reason for this is the melt fraction (thick-thin spinning) that occurs at shear rates of about $10^5\ \text{s}^{-1}$ [204]. Another investigation [200] discusses the relations between individual filament titer (2.5...4.3 dtex), spinneret take-up (1750...5500 m/min), spin-draw ratio (153...613) at the breaking tenacity (2.0...4.0 cN/dtex), breaking elongation (in %), the initial elastic modulus (18...70 cN/dtex),



Spin take-up speed m/min	Spin draw ratio	Draw ratio	Final titer	Yarn fineness tenacity cN/dtex	Elongation at breaking strength %
1750	1:153			1.75	206
3500	1:153	1.411	58	2.45	104
4500	1:153	1.266	64	2.64	177
1750	1:345			1.77	175
3500	1:345	1.444	57	2.52	100
4500	1:345	1.266	64	2.80	78
5500	1:345	1.148	71	3.10	61

Figure 2.55
Stress-strain diagram for PET yarn spun with different take-up speeds

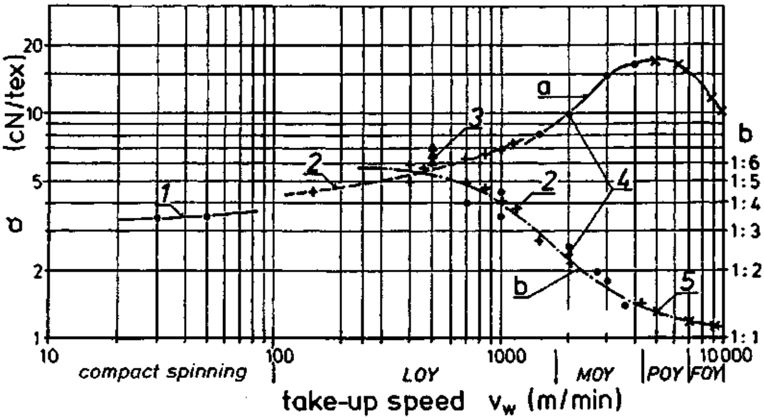


Figure 2.56 Breaking strength (a) and residual drawability (b) of PET filaments (not postdrawn) as a function of the take-up speed v_W (graphs 1...5: measured by different tests in different plants)

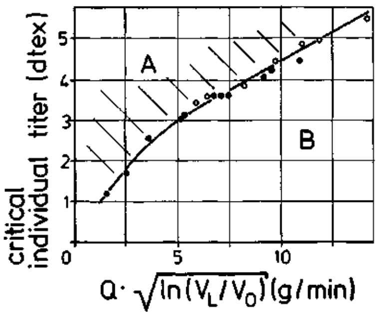


Figure 2.57
Critical titer of PET filaments as a function of melt supply and spin draw [201]
A) Spin range; polyester $M_n = 22{,}000$, melt temperature about 310 °C, take-up velocity 5000...10,000 m/min.
B) Range with high number of filament breaks, spinneret throughput 0.5...5.2 g/min·hole, spinneret hole diameters 0.25...1 mm shear rate $< 10^5\ s^{-1}$

the shrinkage force (300...3300 cN/mm^2), the draw modulus (0.6...7.5 cN/dtex), the crystal size (30...65 Å) and the extrusion velocity through the spinneret bore (4...40 m/min) as well as the dye absorption (in mg dyestuff/[g]fiber with a well marking dyestuff (about 7...11 before and 1...4 after drawing) and a badly marking dyestuff (10...11 before and about 4...10 after drawing). For the latter one it is notable that dye take-up increases considerably with increasing spin take-up. This is confirmed by practical experiences in the carrier free and pressureless dyeing of polyester filaments that are spun with a take-up speed of over 7000...8000 m/min; this guides into an economic advantage over the traditional polyester dyeing under pressure or with carrier.

The influence of the other mentioned parameters can be summarized as follows:

- For higher spin distortion ratios (153 → 613) the increase in the breaking strength slow down, both with respect to the extrusion speed as well as with respect to the take-up speeds (Fig. 2.58).
- The breaking elongation reacts in the opposite way. In the range of about 4000 m/min a spinning induced crystallization sets in [203].
- The initial modulus increases with increasing spinning speed, while the spin distortion ratio has no influence. Higher individual filament titers show a lower initial modulus because of the slower cooling due to the higher heat capacity.
- The shrinkage force increases with higher take-up speed and higher distortion ratios (> 345). Higher individual filament titer however lowers it.
- The dynamic draw force—for the residual draw—increases with higher take-up speeds, parallel to an increase in spin distortion ratio and shrinkage.

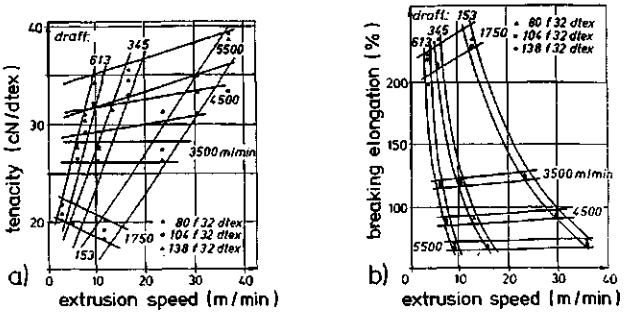


Figure 2.58 Breaking strength (a) and elongation (b) of PET-POY as a function of the spinneret hole extrusion speed v [252] with the take-up speed, denier per filament and spin draw as parameters

- The draw modulus = force in the initial region of the draw increases also with higher spin take-up speeds.
- The crystal size (from X-ray measurements) increases with higher spinning speeds.
- The birefringe (larger responds to a higher preorientation of the molecular chains) increases with higher spin take-up speeds; this increase is less for coarser deniers per filament at take-up speeds up to about 3500 m/min than for finer dpf; for over 4500 m/min the increased orientation due to the spin draw overshadows this.

2.3.6.3 Spinning and Drawing of PET Filaments and Tow

If the draw ratio during POY spinning is not sufficient for the final product, the filaments or the tow have to be drawn hot. This draw can be done either dry over hot cylinders and/or in hot air, or in hot water baths. Because of the important quantities of PET most of these issues are covered in Chapters 3.4 Drawing, 3.6 Draw Texturing and 4.10 Draw Twisting Machines, 4.13 Staple Draw Machines etc.

The necessary hot drawing has to be done just below the glass transition temperature. With the increase of the tenacity comes a reduction in elongation and filament cross-section. Figure 2.59 shows the influence of draw temperature on the draw zone, the neck point [131]. With increased draw speed the flow zone becomes more distinct, because the draw heat (generated by the draw energy in the filament) cannot dissipate as quickly. The better the heat transfer in the area of the neck point, e.g. drawing in hot water, the less distinct is this telescope effect.

During drawing the draw forces are also important as shown in Fig. 2.60. Because drawing should happen below the glass transition temperature and stays in the range of 1 : 3.4 to 5.5 depending on the end product for LOY yarns, for practical reasons one assumes a maximum draw force of about 10 g/tex. To

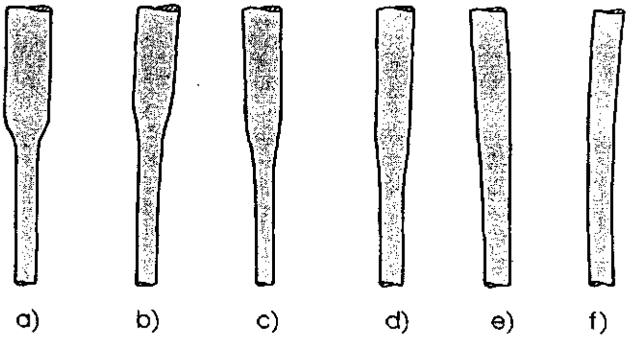


Figure 2.59
Influence of the draw temperature on the flow zone form (neck point) of an individual PET filament [130]
a) 70 °C, *b)* 71 °C, *c)* 72 °C, *d)* 73 °C, *e)* 74 °C, *f)* 75 °C

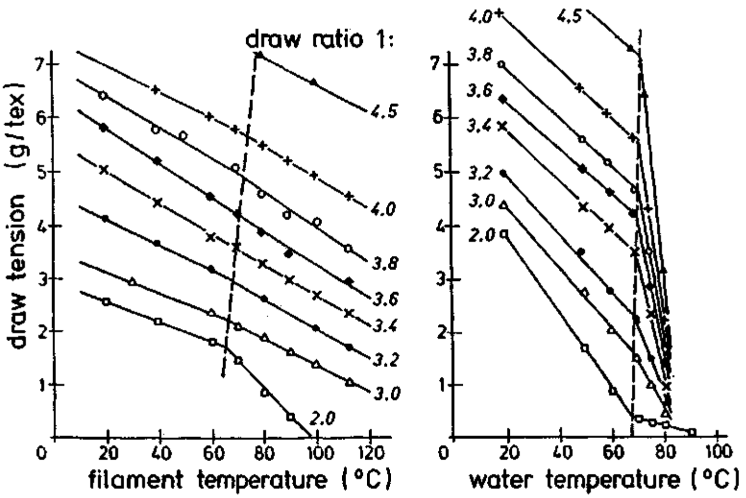


Figure 2.60 Draw tension σ of textile PET filaments and tows in air (left diagram) and in water, in dependence of temperature and draw ratio (1 : 2 to 1 : 4.5; draw speed 1000 m/min)

determine the drive power an efficiency of 0.5 is included for small machines between the drive of the draw unit and the drawing rolls. For larger draw units the efficiency has to be determined more precisely and can be as high as 0.8...0.9.

The large number of possibilities to produce filaments and fibers of different properties from PET by choice of polymer, spin conditions and draw conditions, can best be shown by a few examples:

- PET staple fibers can be blended with many natural and man-made fibers, and for this purpose have to match in titer and in the initial elastic modulus. The HM-HT-cotton type (high modulus, high tenacity) shows similar properties as fine cotton (Fig. 2.61a and b). The production is explained in Chapter 2.3.6.4 in more detail. The HM cotton type is meant for blending with cotton. The viscose type (d) is suited for blending with rayon and/or viscose staple (e). In spite of the different course of tenacity and elongation for more than 10%, the wool type (f) and the anti-pilling wool type (g) are particularly well suited for blending with wool (h). In all these cases the tenacity is about 50...70%

Table 2.14 Consumption of Raw Materials and Polymer Properties for PET Produced with the Zimmer Continuous PET Polycondensation Installation [170]

	Staple fiber	Textile yarn	PET bottles	PET films	Technical yarns	Tire yarn	
TPA	862...859	862...859	865	865	865...862	865	kg/1000 kg PET
EG	342...335	342...335			343...336		kg/1000 kg PET
TiO_2	0.4%	0.4%					
For chip production with Dual Chip Cutters 5 kg TPA/t and 2 kg EG/t have to be added.							
[η]	0.63	0.66	0.63	0.63	0.82	0.95	±0.015
COOH	28	28	28	28	22	19	mequ/kg
SP		258...260			256		°C
DEG	0.9...1.1	0.9...1.1		0.9...1.1	1.3	1.3	weight-%
WT	1.0...1.3	1.0...1.3					
Y.I. (granulated)	−10	−10	− − 1	− − 1	–	–	

higher than the natural or chemically made blending partners. This considerably increases the usage of the blends. To produce HM-HT and HM cotton types the fibers are appropriately spun from chips with $[\eta] = 0.7 \ldots 0.75$, while the wool used to be spun from $[\eta] = 0.63$, today mostly $[\eta] = 0.67$. To obtain the final properties requires certain aftertreatments, that are covered for example in Chapter 4 in the descriptions of machines and installations.

- PET-POY yarns for draw-texturing is spun from PET chips of $[\eta] = 0.67$ with a take-up speed (depending on the type of winding head and the filament titer) ≥3200, preferred 3600 (newly up to 5200) m/min with or without godet take-up from the spinneret. Further processing see Chapters 4.10…4.12.
- PET spun bond webs are taken up similar to POY yarn at the spinneret with 3000…5200 m/min quenched and then irregular laid onto a suction transport belt so that it cannot be drawn further. In spite of this a good PET web filament has a tenacity of 20 cN/tex and 30% elongation and 5% shrinkage at boiling. These properties are only achieved with filaments taken up from the spinneret at >5000 m/min.
- Finished PET filaments without after draw and about 20…23% residual draw can be produced with spin take-up speeds of over 7000 m/min if a suited PET polymer is available.
- Set and set-like finished yarns can be spun as trilobal filaments or as δ-shaped filaments with one over length side, cooled asymmetrically in a ≈400 mm long quenching chamber, taken up and wound with ≤7000 m/min.

2.3.6.4 Production of HM-HT Cotton Type Polyester Staple Fibers

These PET staple fibers (High modulus high tenacity cotton type) with 1…2.5 dtex per filament are gaining importance because of their ideal blending properties with cotton (graphs a and b in Fig. 2.61). A production installation is similar to Figs. 4.1 and 4.287. The polymer should have an intrinsic viscosity $[\eta]$ of $(0.67 \ldots 0.72) \pm 0.02$. Table 2.15 shows the most important properties of this fiber type compared to other PET staple fibers.

During spinning (with melt from continuous polycondensations as well as from spin extruders) even the slightest variations in temperature are important. Irregularities in the airflow during quenching can lead to differences in orientation and crystallinity, leading to irregular drawing. Spinneret take-up speed is around 1700…1900 m/min.

The spin tow is coiled after a good finish preparation into large cans, removed after similar storage, taken off and plied; it is lead over a septet through a preparation dip bath to pretensioning and preheating. The entrance to the first draw zone should be under little tension to allow the tow to run parallel and not twisted. The total tow should be evenly distributed over the width of the rolls. The seven rolls should be

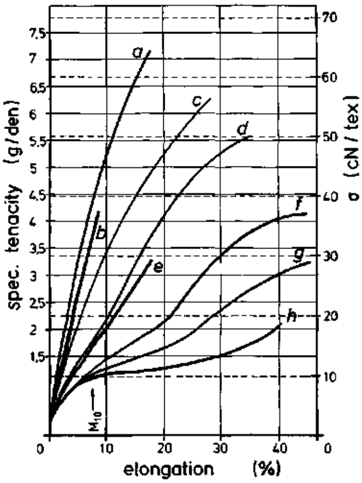


Figure 2.61
Typical stress-strain diagrams of PET staple fibers for comparison and blending with corresponding natural and viscose fibers
a) High modulus, high tenacity cotton type (HM-HTC type)
b) Cotton
c) High modulus cotton type (HMC type)
d) Viscose staple
e) Viscose rayon
f) Wool type
g) Anti-pilling wool type
h) Wool
(Recommendation by Zimmer AG [54])

Table 2.15a Important Data of HM-HT PET Yarn Types Compared to Normal Types

Fiber type, Degree of heat setting, Degree of draw	Tenacity cN/tex)	Elongation (%)	Shrinkage at boiling (%)	Crimp stability (%*)	Degree of crimp (%*)	Bulk/ elasticity
HT-HMT type, tension fixed, no shrinkage, heat setting, fully drawn	≥65	≤20	0	≥60	≥10	very strong
HT types, partially tension fixed, no shrinkage, heat setting, normal drawn	≥53	≤30	≤1	≥65	≥12	strong
MM types, no heat setting, normal drawn	≥53	≤30	>1	≥70	≥14	low
LM types without tension heat setting, full shrinkage, heat setting, normal drawn	≥40	≥35	varies	≥75	≥16	medium

*Data strongly depend on measuring methods

Table 2.15b Polymer Properties for Tire Yarn and Technical Yarns

	PET. directly spun		
Value	Cord yarn	Technical yarn	Low shrinkage yarn
Intrinsic viscosity	0.95±0.012	0.82	
DEG content Weight %	< 1.1	< 1.1	
COOH MEQ/g	< 18	< 20	
TiO_2 %	0...0.02	0...0.02	
Catalyst ppm.	300	230	
Heat stabilizer ppm.	30	30	
Water content weight %	≤0.003	≤0.003	
PET dust content weight %	<0.05	<0.05	
Yarn:			
IV $[\eta]$	0.88	0.75	0.75
dtex (drawn)	1100/182...210	–	–
Tenacity cN/tex	84	74	69
Breaking elongation %	12	14.5	22
Hot air shrinkage %	6	4	1.5

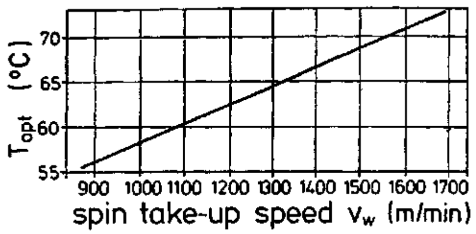


Figure 2.62
Optimum draw temperature $T_{opt.}$ as a function of the spin take-up speed v for PET with $[\eta] = 0.63$ (draw take-up speed = 120 m/min)

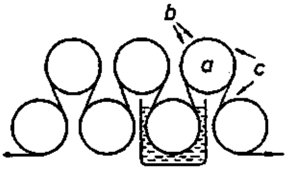


Figure 2.63
First draw septet of a PET-HM-HT fiber after-treatment line (Zimmer AG [54]) with draw bath below the fifth roll (a), draw range (b), and friction range (c) with hot draw plate effect

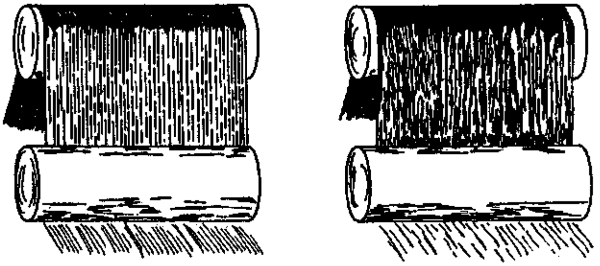
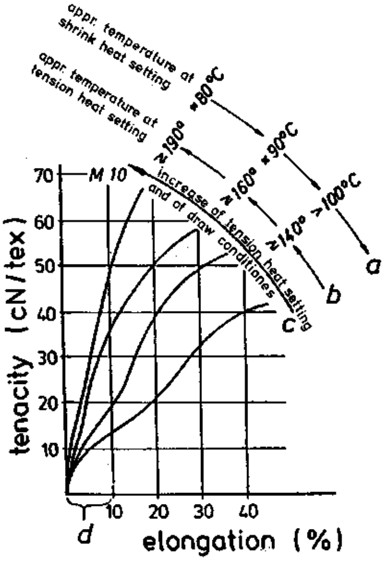


Figure 2.64
Uniform (on left) respectively uneven (on right) draw zone on the sixth roll of the draw septet (zone c in Fig. 2.63) [54]

heated to a temperature depending on the spin take-up velocity according to Fig. 2.62. According to a process by Zimmer AG [196] the fifth roll runs in a tempered draw bath (Fig. 2.63), so that a wet draw with ironing and slide effect occurs on rolls six and seven. At least these tow rolls have to provide the appropriate surface treatment for this. Drawing starts on roll six and is completed upon leaving roll seven into the next septet. The draw line on roll six (Fig. 2.64) should be as narrow and straight as possible (Fig. 2.64). Minor irregularities are corrected on roll seven by the ironing effect. An irregular draw can be recognized by the uneven exit from roll six and in the final product (e.g., long staple, differences in crimp, elongation and tenacity, high CV values). The temperature on the rolls must be better than ±1 °C. Fiber-to-fiber adhesion also influences the eveness of draw and crimp. To high fiber-to-metal friction can lead to increase fibrillary breakages.



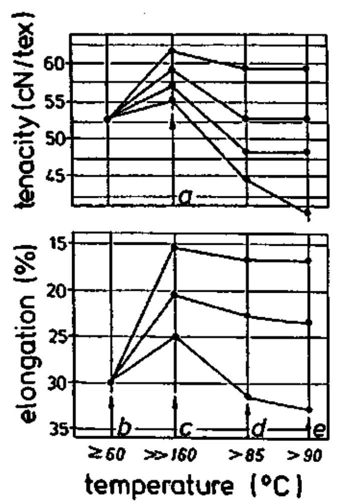


Figure 2.65
Influence of heat setting conditions on the PET staple fiber elastic modulus
- *a*) Approximate temperature during heat setting with shrinkage
- *b*) Approximate temperature during heat setting under tension
- *c*) Increase of the tension heat setting and draw conditions
- *d*) 10% modulus

Figure 2.66
Stress-strain behavior of PET filaments and tows during aftertreatment
- *a*) Influence of tension and heat setting with temperature and time progression
- *b*) Draw values after draw zone, temperature ≥ 60 °C
- *c*) Value after heat setting, temperature > 160 °C
- *d*) Value after stufferbox crimping, temperature > 85 °C
- *e*) Final value after drying, temperature > 90 °C

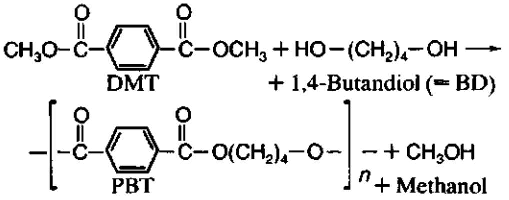
The tow is then cooled to under 100 or better 70 °C, then dried and heat set on large drums with constant speed and high tension above 160 °C and then cooled again to 100 or 70 °C at constant speed. This will result in tenacities of over 65 cN/tex with elongations under 20%, a boiling shrinkage of 0% and a 130 °C vapor shrinkage of less than 3%.

In order to maintain these data the tow shall not be heated beyond the heat setting temperature in any of the following processes, or the tenacity will decrease and the elongation increase. This is especially true for stufferbox crimping, where the mechanical work of the fibers transforms into heat inside the tow. Figure 2.65 shows the influence of different temperatures on the tension-elongation diagram. Figure 2.66 describes the development of tenacity and elongation during the fiber making process. An even crimp requires that the tow is fed absolutely straight to the crimp rolls. The resulting primary and secondary crimp is shown in Fig. 3.60. A high degree of crimp can be achieved by a sufficient 100 °C saturated steam treatment just before the crimper, because this will briefly drop the elastic modulus and make the tow more pliable. Inside the stufferbox the tow temperature should be above 80 °C but as far below the last heat setting temperature as possible. The latter can also be influenced by steam injection.

After leaving the stufferbox machine the tow should cool and dry at temperatures considerably below the heat setting temperature, cool to below the glass transition temperature and run towards the staple cutter; here the crimp is briefly pulled out by a tension roll to ensure uniform staple length.

2.3.7 Polybutylene Terephthalate (PBT)

Since its introduction around 1968, the production now increases annually about 10...15%, with increased 1,4 butandiol (= butylene glycol). Butandiol (BD) is primarily gained by the GAE process from acetylene and formaldehyde. New processes start with ethylene via promoethanol or with propylene via allylacetate and the oxo process. Polycondensation follows the scheme



(2.27)

or analog starting with TPA and with water as a byproduct. During the polycondensation butandiol is also regained.

According to *Zimmer* [120] the process can be executed in autoclaves as well as continuously with a choice of DMT or TPA as raw material. The process and the installations are similar to those for PET, however with the data corresponding to the raw material and the final product. The reactor vessels are equipped with inside heat exchange rings and agitator similar to Fig. 2.45. Chip cutting—if done—is the same as for PET as is the drying process. A solid phase aftercondensation is also possible.

For the continuous process from raw material entry (DMT and BD) to the finisher five autoclaves are needed; for TPA and BD only three. During the DMT process 85% of the byproduct methanol have 99% purity and 15% as a tetrahydrofuran (THF)-methanol mixture that is difficult to separate and can only be burned. The TPA process produces twice the quantity of THF in a watery solution with about 10 mol-% THF (of the TPA) but it can be sold well after destillation. The evaporated glycol can be re-entered into the process.

Table 2.16 shows the technical data for the process and the products. Yarns have a low moister regain (about 0.4%) and very good crimp stability—important for BCF yarns. The latter also depends on the correct heat setting temperature (between 160 and 200 °C). Considering the sales value of the byproducts, PBT yarn cost is already lower than PA-6 yarn cost. Another application is the combination with PET in bicomponent yarns to achieve crimp or dye effects.

Table 2.16 Raw Material Consumption, Polymer Properties and Yarn Properties of PBT [120]

PBT products with [η]	medium	high	after condensated
Raw material consumption [kg/t]		DMT process	TPA process
DMT resp. TPA		885	757
BD		442	472
Product specification			
Intrinsic viscosity [η]*	0.85	1.15	
Adjustment range	0.72...0.9	0.95...1.2	0.75...1.3
Standard deviation	±0.015	±0.015	±0.02
COOH groups [10^{-6} Equ]	40...60	40...45	25
Yellow index	8	11	
Melting temperature $T_S = 215°C$, glass transition temperature $T_g \approx 40°C$			
Yarn properties	POY, draw textured	BCF trilobal	
Take-up speed	[m/min]	3600	800
Draw ratio	1:	1.26	3.38
Titer	[dtex]	190f52	1200f60
Tenacity	[cN/tex]	30.9	26
Breaking elongation	[%]	24...32	35
Shrinkage at boiling	[%]	3...4	< 1
Degree of crimp	[%]	50...60	23
Crimp stability	[%]	≥90	67

*[η], calculated according to the Billmeyer formula for $\eta_{rel.}$, measured in a (3/2) phenol-tetrachlorethane

2.4 Polyolefines

Polypropylene was first spun in 1958, polyethylene in 1967 [517] and then discontinued until about 1985, even though it was known since 1933. Polypropylene today has the most significant growth rate (around 7% p.a., 300,000 t in 1995) in filaments, staple fibers and nonwovens compared to all other synthetic fibers. PE spin products today are only produced in very small quantities. Since the installations and machines for both productions are practically identical, it is sufficient to describe the polypropylene production. For polyethylene the different process parameters have to be considered, especially the melting point of 169 °C for PP respectively about 105...138 °C for PE depending on the type. The glass transition temperature is +5 °C for PP and < −70 °C for PE. This is particularly important for outdoor applications, because unmodified PP will become fragile in freezing temperatures.

2.4.1 Polypropylene (PP)

Just before 1957 *Natta* [205] transferred the polymerization process by *Ziegler* [204] onto polypropylene. Of its four stereo specific modifications (Fig. 2.67) only the isotactic polypropylene (b) with a melting point of 162...176 °C was suited for fiber production. After an introduction that raised high expectations there were many setbacks between 1960 and 1970 without sufficient additional qualities that PP textile production was discontinued in most places. Some goal oriented long term research and development made PP much later a textile material with remarkable properties at low cost, that since 1980 continuously gained relevance as the fourth synthetic fiber class next to PA, PET and PAN textiles (see Table 1.2) (since 1995 in third place before PAN).

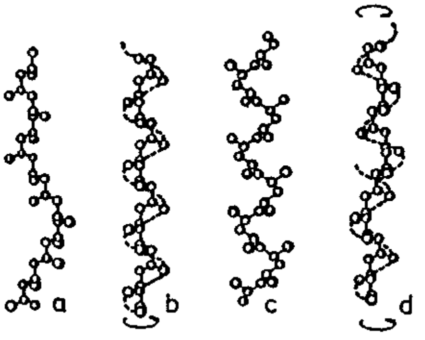


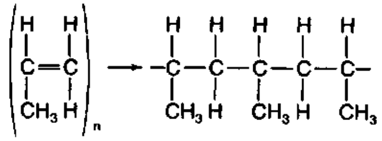
Figure 2.67
Stereo specific arrangement of polypropylene molecular chains: a) atactic, b) isotactic, c) syndiotactic, d) stereo bloc

A good overview of the development of polypropylene fibers can be found in [206] with many references, however only until 1982.

2.4.1.1 Production of Polypropylene

Propylene is a liquiefiable unsaturated carbonhydroxid in gas form resulting from the refinery of crude oil/petroleum with $S_P = -47$ °C that can be produced by two processes (typically in one case with a 16% yield): either as a byproduct with ethylene and higher carbonhydroxides during the high temperature pyrolisis of the petroleum distillation and natural gas fractionating or as a byproduct of gasoline during hydrolytic cracking of higher carbonhydroxides. The latter is the more frequently used process. To be processed for spinnable PP it is necessary for the propylene to be of $\geq 99.5\%$ purity, for molded parts production only 93% purity is sufficient.

The transition from propylene to polypropylene occurs according to the formula


$$\left(\begin{array}{cc} H & H \\ | & | \\ C & = C \\ | & | \\ CH_3 & H \end{array}\right)_n \longrightarrow -\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{C}}- \qquad (2.28)$$

that shows the four possible arrangements it can be polymerized into configuration (b) in Fig. 2.67 that is achieved with the help of Ziegler-Natta catalysts, in the sequence of the action:

$$\delta\text{-TiCl}_3 \text{ and } Be(C_2H_5)_2 \text{ better than } \alpha\text{-TiCl}_3 \text{ and } Al(C_2H_3)_3.$$

Today catalyst systems of the third generation are used that provide a higher selectivity for isotactic PP and a higher yield. They can be used in the (still mostly used) suspension polymerization as well as in the gas stage polymerization.

Polypropylene or LLDPE (e.g., with Cp_2TiCl_2/MAO [534]) produced with metallocene catalysts is atactic, while when produced with $Cp_2Ti(C_6H_5)$MAO results in selectively isotactic PP [535] (1 g catalyst for PP or PE); mol mass distributions of $M_W/M_n = 2 \ldots 2.5$ are realistic with a small distribution or MFI 1000 g/10 min.

Suspension polymerization is for example done in hexane or in n-heptane. Isotactic PP is not soluble in n-heptane; thus this is truly a suspension polymerization at under 100 °C during the process the not reacted propylene is evaporated, the suspension is centrifuged, washed with methanol and dried.

BASF [205] developed a polymerization process in the gas phase. The PP produced here or in similar processes gains relevance for spin qualities [206], even though the products vary considerably from those of the suspension polymerization.

In a few cases the PP powder is processed directly, but usually it is compounded in double screw extruders (Chapter 4), reduced to the desired molecular weight and cut to chips. The hot cut off with directly following water cooling produces a lens shaped chip. Cylindrical chips, like from under-water chip cutting, are rare.

PP is usually described by the following properties:

- Average molecular weight M_n—for spin qualities between $\leq 100{,}000$ and 300,000 or as average weight $M_w > M_n$;
- M_w/M_n—for Gauss distributions = 2, for commercial products between 3 and 10, usually around 5;
- M_v—average viscosity molecular weight; $M_w > M_n$ (usually 1.2 times) $> M_v$;
- $[\eta] = K \cdot {M_v}^a$ = intrinsic viscosity (Mark-Houwink formula) with $a \approx 0.8$ for PP and $K = (0.8 \ldots 1.1) \cdot 10^{-4}$, depending on the solvent and the temperature;
- *MFI* = Melt Flow Index—rate of extrusion of PP at 230 °C/2.16 kg or at 190 °C/10 kg load [207] in g/10 min.

Two typical molecular weight distributions are shown in Fig. 2.68, and the approximate relation between M_w, $[\eta]$, and $MFI_{230\,°C;2.16\,kg}$ in Fig. 2.69. Mathematically the relationship between the intrinsic viscosity and the melt flow index can be described as follows

$$\log[\eta] = A + B \cdot \log MFI \tag{2.29}$$

A and *B* are depending on the molecular weight and its distribution. In a limited *MFI* range *B* is almost constant; *A* then gives an approximate number for the molecular weight distribution. For a relatively wide distribution of the molecular weight $A \approx 0.50$ and $B \approx 0.197$. In [208, 209] experimental relations are

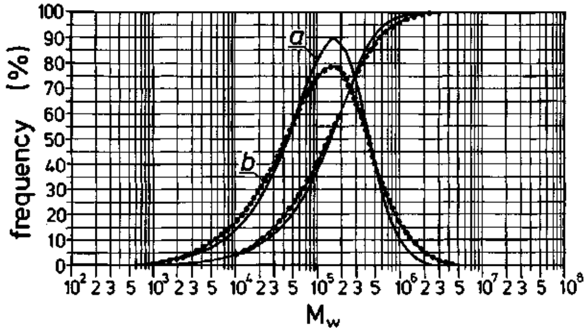


Figure 2.68
Typical molecular weight distributions of well spinnable and drawable PP products (Hüls AG [165])
a) Type P 2000 CR, especially for spun bond
b) Type PX 4439, especially for conventional and compact spinning and drawing

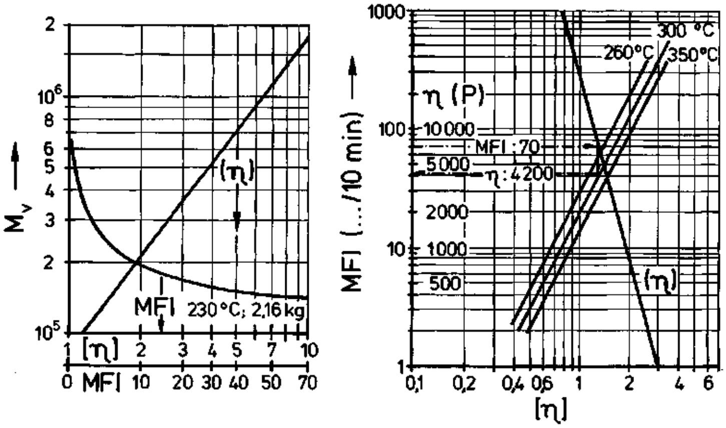


Figure 2.69 Approximate relation between *MFI* (e.g. 70), [η] (e.g. 1.4), melt temperature (300 °C) and melt viscosity (η = 4200 P, from trials)

mentioned for certain variables of different PP types. Rheometric measurements of the extrusion *MFI* can be made with the apparati in [210, 225] (see Fig. 7.30).

The selection of the correct PP type is essential for the spinning process. For low take-up speeds, e.g. for compact spinning machines, an initial polymer with *MFI* = 12 . . . 15 g/10 min can be decomposed with organic peroxides in the melt to *MFI* ≈ 20 . . . 35 g/10 min. With appropriate catalysts such polymers can be directly delivered from the polymerization process (see Fig. 2.70). High speed spinning processes, however, require a polymer with an extremely narrow molecular distribution and cannot bear overlong polymer chains that are left during the thermal decomposition. Here an initial polymer with *MFI* = 1.2 . . . 2.0 g/10 min is needed, even if the aspired *MFI* values are around ≥ 20 . . . 35 g/10 min. During the polymer selection the die swell also has to be taken into account.

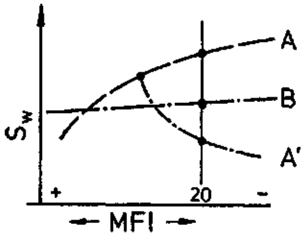


Figure 2.70
Die swell value S_w of PP depending on the production process
A) From suspension polymerization
A') From A) thermally decomposed to lower *MFI*
B) From the gas phase polymerization

In all cases the chips presented to the extruder must be homogeneous and well blended.

PP is relatively stable against heat and light; however, it needs to be protected against the related oxidations by stabilizers, especially against thermo-oxidative damage of the melt (Fig. 2.42) and during hot aftertreatment. High sheering forces in the melt can cause degradations in the molecular chains. Impurities in the polymer easily lead to photo degradation. Effective stabilizers against these influences are phenol derivatives [204], e.g. DBPC, antioxidant, santonox, inox etc., as well as peroxide decomposers, e.g. triphenyl phosphate, or absorbers as Cyasorb HV or Eastman Inhibitor, or energy suppressers as Ni-dibutyldithiocarbamate etc. For these and other stabilizers as well as for the metal desactivators the complete removal of the Ziegler-Natta catalysts is important (see Table 6.11).

As PP cannot be dyed in the traditional textile fashion, dyestuffs need to be entered into the melt as organic or inorganic pigments just as dulling agents and optical brighteners (see Chapter 6.8). These include organic fluorescence materials that absorb UV light at approximately 3000 Å and transform it into visible radiation of about 5500 Å. These additives must not have a negative influence on the stability of PP, on the physical properties of the products, and must remain stable during processing. Minor changes in color due to the process can be considered in the recipe.

With a small amount of additive the PP can be made dyeable: < 5% masterbatch mixed under the chips—for acid or disperse dyes provides good properties and better resilience. The extruder should have 30 · D screw length with good mixing; melt temperature is approximately 260 °C; chips need to be predried [536].

This multitude of additives and the three possibilities in Fig. 2.70 for the production of a PP with a specific *MFI* explain that there is hardly a wider range raw material than PP chips that can have slight variations from batch to batch, thus requiring a variety of process parameters.

The humidity content of PP chips is certainly < 0.05% and consists of humidity layer on the surface. Additional drying is usually not necessary. If done anyway, it only addresses the few molecular layers of surface humidity and the homogenization and slight increase of the chip temperature; this increases the homogeneity and slightly increases the extruder capacity.

2.4.1.2 Phenomena during PP Spinning

Even though spinning of PP has a lot of similarities to PET and PA-6 spinning considering the different parameters, there are some phenomena that appear more distinct than in other polymers. Figure 2.71 shows the spinning process for a single filament with the technical data for each area. The shearing at the

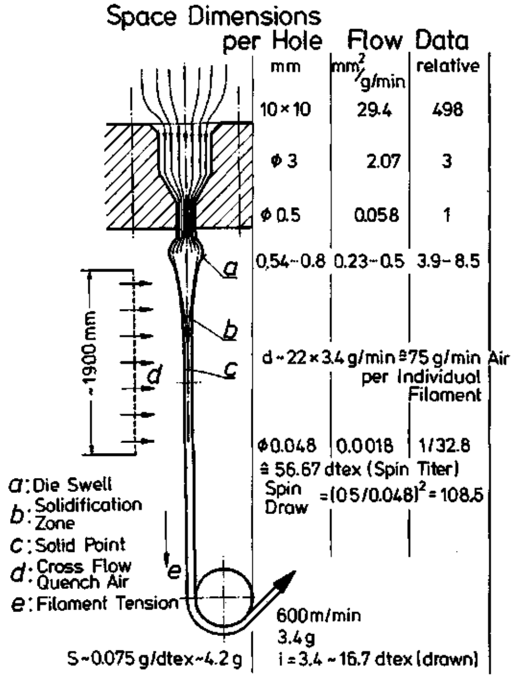


Figure 2.71
Melt and filament path during PP spinning (e.g. individual filament of carpet yarn)

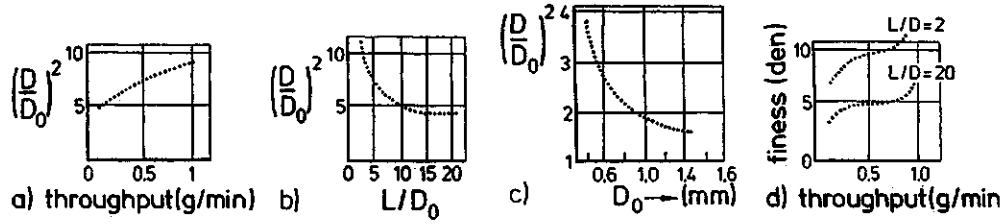
entry to the spinneret is quite small, but increases up to approximately 500 fold into the capillary. Due to the melt relaxation from about 30...60 bar in front of the spinneret to about 1 bar behind the spinneret bore, the filament diameter increases 2 to 3 fold; this is known as the die swell. In the following cross air quench the filament cools from the outside to the inside, soon reaches its solid phase and then its spinning filament diameter that is larger than the final filament diameter by the draw ratio.

The die swell depends on the production process of PP (see Fig. 2.70), the melt viscosity and temperature, the throughput per bore and its dimensions. Figure 2.70 curve A is valid for a polymer from the suspension polymerization that can be interrupted at any given *MFI* and results in a specific swell value of the PP. Due to the thermal degradation according to A′ the swell value can be reduced by increasing the *MFI*. For PP from gas phase polymerization the swell value is practically independent of the *MFI*.

The swell value decreases further with increasing temperature and lower viscosity (Table 2.17) and with a narrower distribution of the molecular weight. The influence of spin data is shown in Fig. 2.72: Die swell increases with the throughput and decreases as the $L:D$ ratio or the capillary diameter increase. This limits the diameter of the spinneret bore and thus the finest possible individual filament titer, not allowing a completely free choice of capillary diameter.

Table 2.17 Influence of Viscosity and Temperature on the Die swell of PP $Q = 0.5$ g/min; Diameter = 0.8mm $L = 16$ mm $= 20D$

Temperature	Die swell at	
	high viscosity	low viscosity
190	4.2	2.8
230	2.8	1.5
280	2.1	1.3



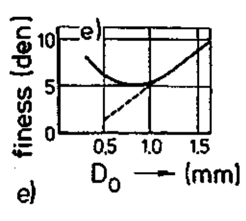


Figure 2.72
Influence of the spinneret hole geometry on the dieswell during PP spinning
a) Influence of the throughput Q at $T = 190$ °C, $D = 1$ mm, $L = 8$ mm, $[\eta] = 1.9$
b) Influence of the L/D ratio at $T = 190$ °C, throughput $Q = 0.3$ g/min × hole, other data as before
c) Influence of the capillary diameter for $T = 280$ °C, throughput $Q = 0.3$ g/min × hole, $L/D = 20$, $[\eta] = 1.9$
d) Influence of the throughput Q and L/D on the smallest filament titer
e) Influence of the capillary diameter D_0 on the smallest filament titer

The crystallinity of PP filaments increases during take-up from the spinneret; this can for example be shown through X-ray refraction [213]. Isotactic PP crystallizes in a monocline and a metastable hexagonal modification, where each three monomeric units form a screw thread with a fiber period of 0.65 nm. The rate of crystallization depends on the molecular weight, the history of the PP melt, and the temperature (Fig. 2.73). It is assumed that crystallization already starts in the air quench, as indicated by the magnitude of the half life time. It is also dependent on the take-up tension and reaches 53% at $3 \cdot 10^6$ Dyn/cm^2 $(= 0.033$ g/dtex$)$ and 58% at $10^3 \ldots 10^6$ Dyn/cm^2 $(= 1.1$ g/dtex$)$ [215, 216] (Fig. 2.74). The crystalline portion $(= d_{\mathrm{kr}})$ and the amorphous portion $(= d_{\mathrm{a}})$ are connected via the density (γ) that can be determined over $1/\gamma = x/d_{\mathrm{kr}} + (1 - x)/d_{\mathrm{a}}$ with $d_{\mathrm{a}} = 0.85$ and $d_{\mathrm{kr}} = 0.936$. The stereo regularity can be shown with fractionated solution methods (see for example Table 2.18) [217]. In the spinneret capillary there is a minor preorientation. The major portion of the orientation is created from the outside filament portion that solidifies first in the border phase between the liquid inside portion and the solidified filament portion.

The most important measurement for the orientation is the birefringence (Fig. 2.76) that increases significantly when crystallization is mostly completed. In this example it reaches a constant and final value after about 60 cm below the spinneret, which also concludes the filament formation in the spinning process. Figure 2.76 shows the relation between birefringe and orientation of the spun undrawn PP filament versus different production parameters [218]. High viscosity, throughput per bore and air velocity result in high spinning orientation as well as a low spinning temperature and a small individual filament titer. An afterheating zone below the spinneret also reduces the birefringe and the orientation.

The limit of the spinnability is reached when the filaments at the exit from the spinneret bore look like a saw tooth wire. This melt fracture is a periodically appearing instability in the spinning process that is due to a variation of the spinneret bore throughput [219]. The effect becomes stronger by increasing the melt shearing or the throughput per spinneret hole, the molecular weight and the polydispersity, and it becomes less with an increased melt temperature, reduction of the *L/D* ratio of the spinneret capillary and its entrance cone. If the effect cannot be removed by counteractions, a polymer with a lower and/or a narrower molecular weight distribution needs to be selected.

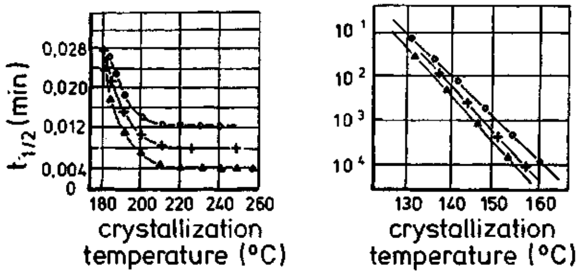


Figure 2.73
Structure and rate of crystallization of polypropylene
a) At 140 °C, depending on melt temperature during 1 h maintained before extrusion and crystallization
b) Depending on the crystallization temperature (M_{W}: °173,000, +357,000, △ 490,000 g//mol)

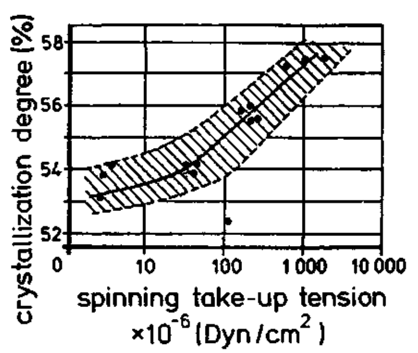


Figure 2.74
Degree of crystallization α of melt spun filaments as a function of spin take-up tension σ.

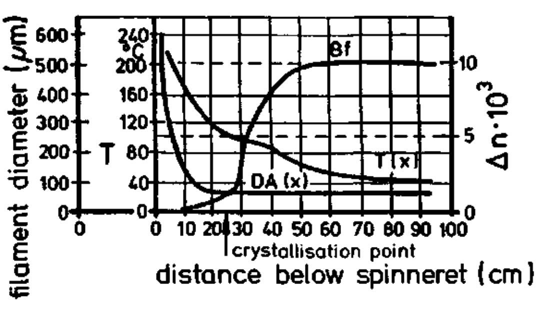


Figure 2.75
Effective filament diameter D_a, birefringence $Bf(\Delta n \cdot 10^3)$ and surface temperature T as a function of the filament distance from the spinneret L.

Table 2.18 Influence of Stereo Regularity on the Crystallinity of PP

Fraction	Dissolved in	Indissoluble in	Crystallinity T_m	
			%	°C
I		trichlorethylene	75...85	176
II		n-octane	64...68	174...176
III	n-octane	2-ethyl hexane	60...66	174...175
IV	2-ethyl hexane	n-heptane	52...64	168...170
V	n-heptane	n-hexane	41...54	147...159
VI	n-hexane	n-pentane	25...37	110...135
VII	n-pentane	ethyl ether	15...27	106...114

The "fish skin" effect that appears in the transition between spinning a smooth filament and the melt fracture is also not acceptable for further processing and it can be removed by the aforementioned measures. Possibly the additions of different additives or softeners may suffice. A faster take-up speed than the critical take-up speed results in a draw resonance (Fig. 2.77), that causes the individual titers to vary considerably while the total titer is constant. The periodicity is between 0.5 and 3 s; the diameters vary by up to ±20%. An isotherm afterheating zone below the spinneret increases the critical take-up speed and evens out the individual filament diameters. A lower take-up speed only increases the periodicities.

A similar effect comes from the periodic influence of the cross flowing quench air (Fig. 2.78), so that it is difficult to separate variances in titer relative to all the above mentioned influences.

Without looking at these effects in detail, there are simple criteria to determine the maximum take-up speed from the spinneret. It is possible to produce a diagram similar to Fig. 2.57 (for PET) for a specific type of PP; also the individual filaments break below the spinneret depending on the spin titer and the take-up speed (Fig. 2.79). Only values below the line allow the polymer to be spun well. For better spinnable PP polymers this line moves up and right. In this example a final fineness of 16.7 dtex per filament = about 57 dtex spin titer for carpet yarn can be taken up well from the spinneret at 700 m/min. At 800 m/min the filaments would break.

Many filament breaks directly below the spinneret can also be caused by too high shearing force in the melt in filters with too much fineness. Then there is a large number of crystals like forms at the bottom of the filters that broke off the melt and come out with it through the spinneret capillary, directly causing the filament break.

Of significant influence on the yarn quality is also the rate of surface cooling, especially for coarser individual filament titers, if the heat transfer from the filament inside to the surface is low compared to the heat dispersion from the surface to the quench air. Then an inside-outside effect is formed that can give a

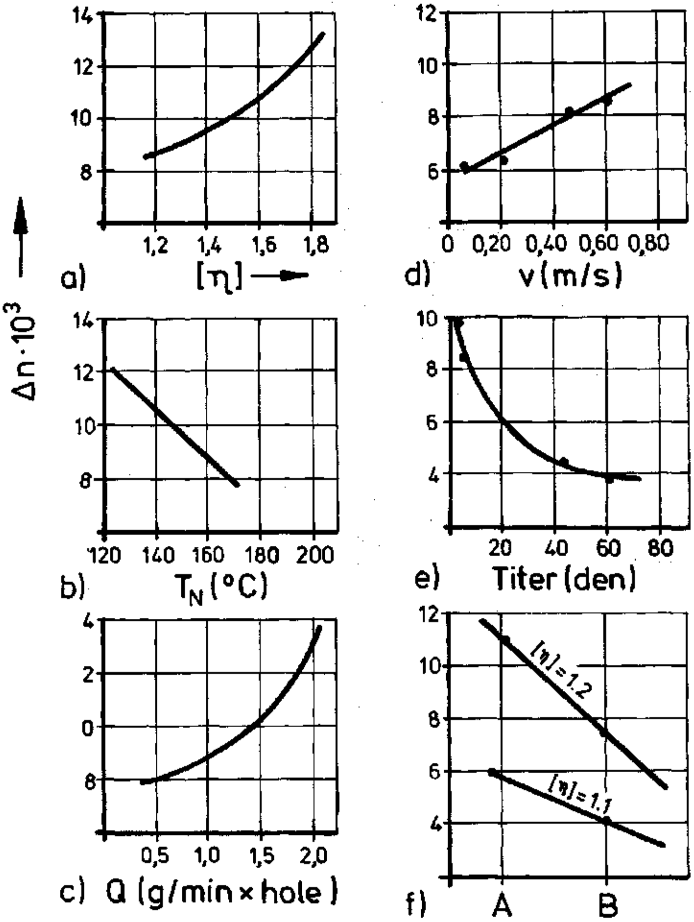


Figure 2.76 Relationship of the birefringence coefficient Δ*n* and
a) the intrinsic viscosity [*η*]
b) the melt temperature T_N
c) the throughput per spinneret hole *Q*
d) the quench air velocity *v*
e) the individual filament fineness
f) the hot shroud below the spinneret (A without and B with hot shroud)

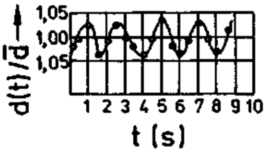


Figure 2.77
Pulsation of an individual filament diameter due to the take-up draw resonance directly below the spinneret ($L/D = 0$, $D_C/D = 4$, $\alpha = 60$; average filament diameter = 1.988 mm)

Figure 2.78
Uster diagram of two individual polypropylene filaments spun with take-up resonance
A) Normal take-up resonance
B) With very high spinning draw

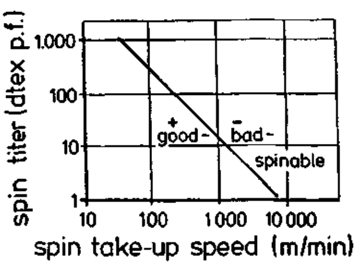


Figure 2.79
Maximum spinneret take-up speed (of the first godet) v for P as a function of the individual spinning fineness

brittle hand. But even a relatively slow filament cooling with radial temperature gradients in the range of 103 ...10^4 K/cm leads to radial birefringence differences of e.g., $3 \cdot 10^{-3}$ in the center and $4.5 \cdot 10^{-3}$ directly under the surface. Also asymmetrical cooling can lead to asymmetrical birefringence, e.g. from $25 \cdot 10^{-3}$ at the blow side and $17 \cdot 10^{-3}$ at the rearside [220, 221]. This effect can also be used to produce self-curling yarns, especially if they have trilobal or δ-cross-sections (see Chapter 2.3.6.3).

This finally results in stress strain diagrams of the not yet afterdrawn yarns, that even at 3500 m/min take-up speed show 130% elongation (Fig. 2.80) [222]. Besides different numbers for draw ratio and

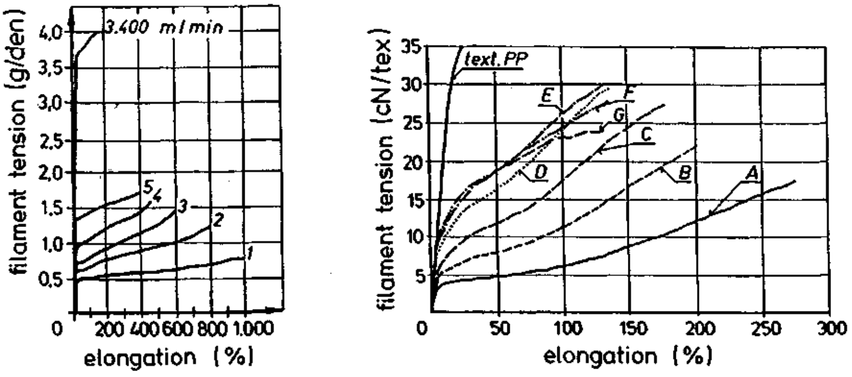


Figure 2.80 Stress-strain diagrams of undrawn PP multifilaments spun with different take-up speeds from the spinneret:
left [222]: Take-up speed v (m/min): 1) 8.4, 2) 36, 3) 116, 4) 170, 5) 258, *1*...*5* wet quenched; 3400 m/min = air quenched for comparison,
right [236a]: Take-up speed v (m/min): A) 1500, B) 2000, C) 2500, D) 3000, E) 3500, F) 4000, G) 4500; textured PP; draw textured PP for comparison

elongation the behavior of the filaments during POY spinning is similar to PET and PA. Here, too, it is not possible to obtain completely drawn filaments.

The final drawing is done over hot godets (during draw twisting) or over hot rolls and through hot draw ducts (for draw texturing and staple tow). The maximum draw ratio also depends on the crystalline structure: Hexagonal modified fibers can be drawn up to 1 : 6 to 1 : 9, monocline modifications only up to 1 : 3 to 1 : 4.5 [214]. The strong influence of draw temperature (Fig. 2.81) can be shown by birefringence [223].

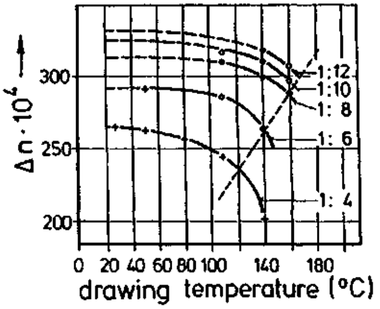


Figure 2.81
Influence of the draw temperature T and the draw ratio on the birefringence of PP $\Delta n \cdot 10^4$ [223]

2.4.1.3 Spinning and Aftertreatment of Polypropylene

There is hardly another polymer that can be spun in so many ways as PP, which is mainly due to its melt properties (e.g., high melt tenacity). Also refer to the following chart:

Spinning method	Final fineness (dtex) or diameter (mm)	Possible residual shrinkage (times)	Spinneret take-up m/min	Also refer to chapter or literature
Conventional POY[1]	1...40 dtex	3...7	500...1300	4.9
Conventional POY,	1...10 dtex	1.5...2.3	3000...4000	4.9
extremely slow				
• downwards, with air quench	3...150 dtex	3...7	20...120	5.1
• downwards, with water quench[2]	25...300 dtex	3...7	20...50	5.1.5
• downwards, with water quench	0.08...4 mm	4...7	20...50	[236]
• upwards, with air quench	3...300 dtex	3...7	20...50	5.1 [231]
Blown fiber	0.01...10 dtex	—	6000	5.4.1
Free fall spinning, upwards,	0.3...1.2 mm	—	0.7...2	5.5.6
electrostatic	0.01...0.3 dtex			Fig. 2.83
Foil yarn from flat foil	10...200 dtex			
from blown foil	900...3500 dtex	5...9	20...200	[235]
Upwards through meshed wires				
with air quench	3...70 dtex	1...2	10...30	5.2.2

[1] from this also with direct drawing: BCF and technical high tenacity yarns

[2] from this also technical and high tenacity yarns

Due to the low chip prices the transformation costs should also be kept as low as possible to obtain cheap fibers and yarns. This results in high capacity units (see also Chapter 1.4).

Larger spin extruders should have a screw length of $L = (28\ldots30)D$ with an entry zone $L_E \approx 8D$, a compression zone $L_K \approx (3\ldots5)D$, a metering zone $L_M \approx (11\ldots15)D$, and a mixing zone $L_T \approx 3D$, preferably with a pin torpedo. The deep compression of smaller extruders is usually around 3 and for larger extruders around 2.6. Grooved entry cylinders have shown to be just as limited in usefulness for spinning as decompression screws, that have a slightly lower core diameter in the last 4 or 5 threads of the metering zone. It is possible to use a dropping temperature profile, but usually a rising temperature profile is used: The entry is water cooled, the first zone is heated to 180...220°C, the second zone to 220...250 °C and then increasing to the desired temperature of 250...275 °C depending on the *MFI*. The measuring head and the extrusion head have the same temperature as the last screw zone, and they are either heated electrically or by dow vapor. The melt pressure at the screw tip for fiber and nonwovens is set at 50...100 ± 3 bar. Installing a non-stop candle filter (Chapter 4.6.9) is recommended. In front of every spin pump and every spin pack there should be easily exchangeable static mixers. Sieve filters in front of the spinnerets serve as fine filters and help to even the pressure. Almost exclusively the length of the spinneret bore is $L/D \approx 2$, sometimes 4. The hole diameter for final fineness of 10...20 dtex is around 0.6 and 0.8 mm, for staple fibers (wool type) around 0.5 mm, for textile POY yarns around 0.25...0.3 mm, and for fine titers around 0.2 mm.

The best cleaning method for all polymer contaminated parts is the vacuum pyrolysis (Chapter 6.6.6).

The following comments for practical applications can be given for Fig. 2.71:

- The die swell should be kept as low as possible by selecting specific polymers and spinning temperatures.
- Larger hole diameters lengthen the freezing zone and increase the yarn tension.
- Higher take-up speeds for constant fineness also lengthen the freezing zone, but only slightly change the yarn tension.
- A hot shroud below the spinneret lengthens the freezing zone, delays the filament thinning and cooling, and increases the yarn tension.
- Cooler quench air and/or higher quench air velocity result in faster filament thinning and higher yarn tension.
- Higher spinneret temperatures result in higher yarn temperatures along the first part of the filament axis, reduce the yarn tension, but have limited influence on the course of the diameter.
- Higher throughputs per spinneret with constant take-up speed increase the cooling time and cooling zone with little influence on the yarn tension.
- A change in the intrinsic viscosity $[\eta]$ has not much influence on the course of the diameter or temperature.
- Too fast cooling directly below the spinneret results in inside-outside effects.

There are two methods for air quenching:

- with normal cross or radial air quenches—the necessary cooling time is about twice what it is for PET; i.e., for the same take-up speed the cooling zone needs to be twice as long. A quench air velocity profile in dependence of the fineness as in Fig. 2.82 needs to be considered;
- fast cooling directly below the spinneret—the quench air exits with a turbulent velocity of 20...35 m/s from a 10...30 mm slot directly below the spinneret and is blown slightly upwards (Fig. 5.2b and 4.172) against the filament bundle. Due to the slow spinneret take-up speed of 20...50 m/min the specific cooling times are even higher than for LOY spinning with a conventional air quench. With high air velocities it is possible to arrange more filament rows behind each other with bore spacing of up to < 1 mm, so that an air quench width of 300...400 mm results in up to 90,000 bores. The capacity per spinning unit then is about 90 kg/h · position and is equivalent to those of conventional spinning units (Chapter 5.1). The melt must be able to withstand the 1000 fold higher cross-forces of the air quench. Since about 1989 this process starts to expand into the spinning of PET and PA-6 [228, 229] (Figs. 5.2...5.8).

The yarn take-up for LOY, MOY, and POY and winding are similar to those for PET. The high shrinkage has to be considered, however, especially for winding. Integrated drawing to FDY requires LOY take-up, possibly MOY take-up, with two subsequent draw zones. The first godet (or duo) is heated to 60...65 °C, the second godet to 130...140 °C, and the third one remains cold. When POY spinning textile titers the yarn has a residual shrinkage of 1.5 to 2.2%, depending on the PP quality [230].

BCF yarn with a final yarn size of 1350...2500 dtex and 15...20 dtex per filament is taken up with about 600...700 m/min from the spinneret, cooled in a 1.65...2.20 m long cross quench zone, and can

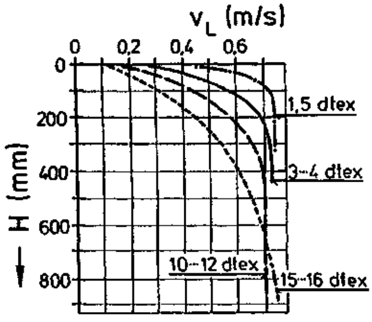


Figure 2.82
Quench air velocity profile v_L as a function of the distance below the spinneret and the individual titer

be drawn and air textured 1.00 m below and wound at 1800...2400 m/min. This requires a revolver winder with automatic bobbin doffer.

For conventional spinning of staple tow the length of the air quench is determined according to Fig. 3.18. Fine titers are not taken up from the spinneret at more than 1500 m/min, and carpet yarn titers with about 600...700 m/min and coiled into large cans. Up to 30 t/24 h per production line can be produced economically on compact spinning installations, while for $> \approx 40$ t/24 h per production line conventional installations are more economical.

Upwards spinning was first developed in England in 1974 [231, 232] and adopted later by several other companies (see Chapter 5.1, Fig. 5.1). In the fineness range of 2.2...100 dtex per filament the capacity is about 45 kg/h per position, and drops for 1.7 dtex per filament to about 33 kg/h per position. The power consumption is 1.2 kWh/kg fiber.

For the electrostatic spinning process (Fig. 2.83 [233]) the chips (6) are dosed onto the conveyor belt (1, 2) and melted at (7). Due to the electrostatic tension between the conveyor belt with the melt and the take-up belt (3,4) the filaments are drawn up out of the melt, cooled down, and are removed at (5) as a web. The fibers are very fine, but completely undrawn. There is no practical use yet.

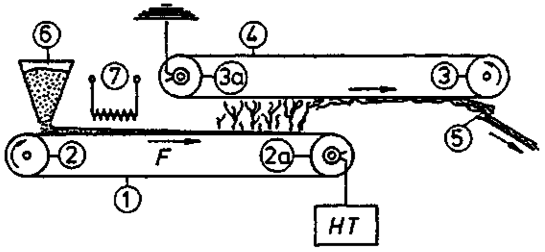


Figure 2.83
Scheme of the electrostatic spinning of PP [233]

Further spinning processes that are suited for PP, e.g., bicomponent spinning, compact spinning, spun bond spinning, blow fiber spinning, are described in detail in Chapter 5.

The requirements on the temperature eveness for PP are not as strict as for PET or especially PA, so that spinning beams can be divided into the respective number of zones and heated electrically with $\Delta T \leq \pm 3$ K. It is often useful to heat the extruder connecting head and the distribution pipes to the spinning positions electrically and control the zones individually (to a common temperature), and to only heat the spinning beam with oil or dow vapor.

2.4.1.4 Optimizing the Polypropylene POY Spinning Take-Up Speed for Draw Texturing

The different stress-strain diagrams in dependence of the spin take-up speed (Fig. 2.80a and also Fig. 2.80b for PET as well as Table 2.19) are more or less balanced by drawing while other characteristics as

Table 2.19 Changes of Specific POY-PP Yarn Properties before and after Draw Texturing (Results of Figures 2.55 to 2.61)

Spin take-up speed	m/min	1500	2500	3500	4500
Tenacity	cN/dtex	↗	↗	3.1(max)	↘
Max. crimp	%	↗	↗	↗	↘
Twist level	t/m	↗	↗	↗	↗
Density and melt enthalpy		↗	↗	↗	↗
After draw texturing					
Max. tenacity	cN/dtex	↘	↘	↘	↘
Draw ratio	1:	2.6	1.8	1.4	1.25
Breaking elongation	↘	↘	↘	↘	
Density		=	=	≈ 0.9	≈
Birefringence		=	=	$\approx 3 \cdot 10^{-4}$	↗
Crimp		↗	↗	↗	↘
Max. crimp stability	%	=	=	94	≈
Yarn tension behind spindle	cN	↘	↘	≈ 30	≈

Property: (↗) increases, (↘) decreases, (=) stays the same

especially the maximum crimp increase (Fig. 2.84). When comparing the improvements (↗) with the deterioration (↘) and the constant properties, the optimum take-up speed is around 3200...3500 m/min for subsequent false-twist texturing. Also the tenacity and elongation of the flat yarn are reduced with speeds above 3500 m/min, and the inner configuration of the filaments becomes more damaged [236a]. The overall properties of the draw textured materials are not quite at the level of draw textured PET-POY; however this is partially compensated by the higher volume and lower price.

2.4.1.5 High Tenacity Polypropylene Yarns

Technical PP-filaments with >7 g/dtex gradually gain importance. The PP chips should have $M_V \geq 150{,}000$ and the yarn a $CV \leq 7\%$ (Fig. 2.85). For $M_V \geq (5.5\ldots6) \cdot 10^5$ the tenacity barely increases. The molecular weight distribution also has to be quite narrow.

The chips are melted at the lowest possible temperature and with minimum shearing and then transported with high pressure to the spinneret, where the pressure is reduced to increase and even out the temperature. For example: Melt temperature at the screw tip 230 °C, in the spin head 235 °C, and when exiting from the spinneret 285 °C. The hot shroud should be optimized between 160...240 °C. The draw ratio can be between 1 : 8 and 1 : 10. The take-up speed when spinning into a water bath is 50...100 m/min and with an air quench 600...700 m/min. Chips with $[\eta] = 2.5\ldots3$ can produce yarns with a tenacity of 8.8...11 g/dtex.

It is also possible to start with chips with *MFI* (10 g/10 min at 230 °C/2.16 kg) at 275 °C spinning temperature. 5...20 mm below the spinneret the filaments are taken up into a water bath of 40 °C at 17.7...25 m/min and accelerate to 200 m/min after the second draw zone, resulting a draw ratio of 1 : (8...12.3). The resulting tenacity is between 8.7 and 10.4 cN/dtex with 25...30% breaking elongation and a 1% elastic modulus of 81...57 cN/dtex for 3.3...13.2 dtex per filament.

Figure 2.86 shows the scheme of the PP high tenacity spin-draw process with wet quenching [234], and Fig. 2.87 shows the process with air quenching. In both cases three draw zones are necessary.

2.4.1.6 Polypropylene Foil Yarns

PP filaments or fibers from foils can be produced from flat foils that are casted onto cooling drums, or extruded into a wet quench bath, or produced from blow foil with air quench. All three methods are known from the plastic industry and described sufficiently in the literature [235]. Table 2.20 shows the most important differences of these foils depending on their production process, the produced strips or strip types, and the end use. The "Barfilex" process [236] produces through a profiled flat foil spinneret

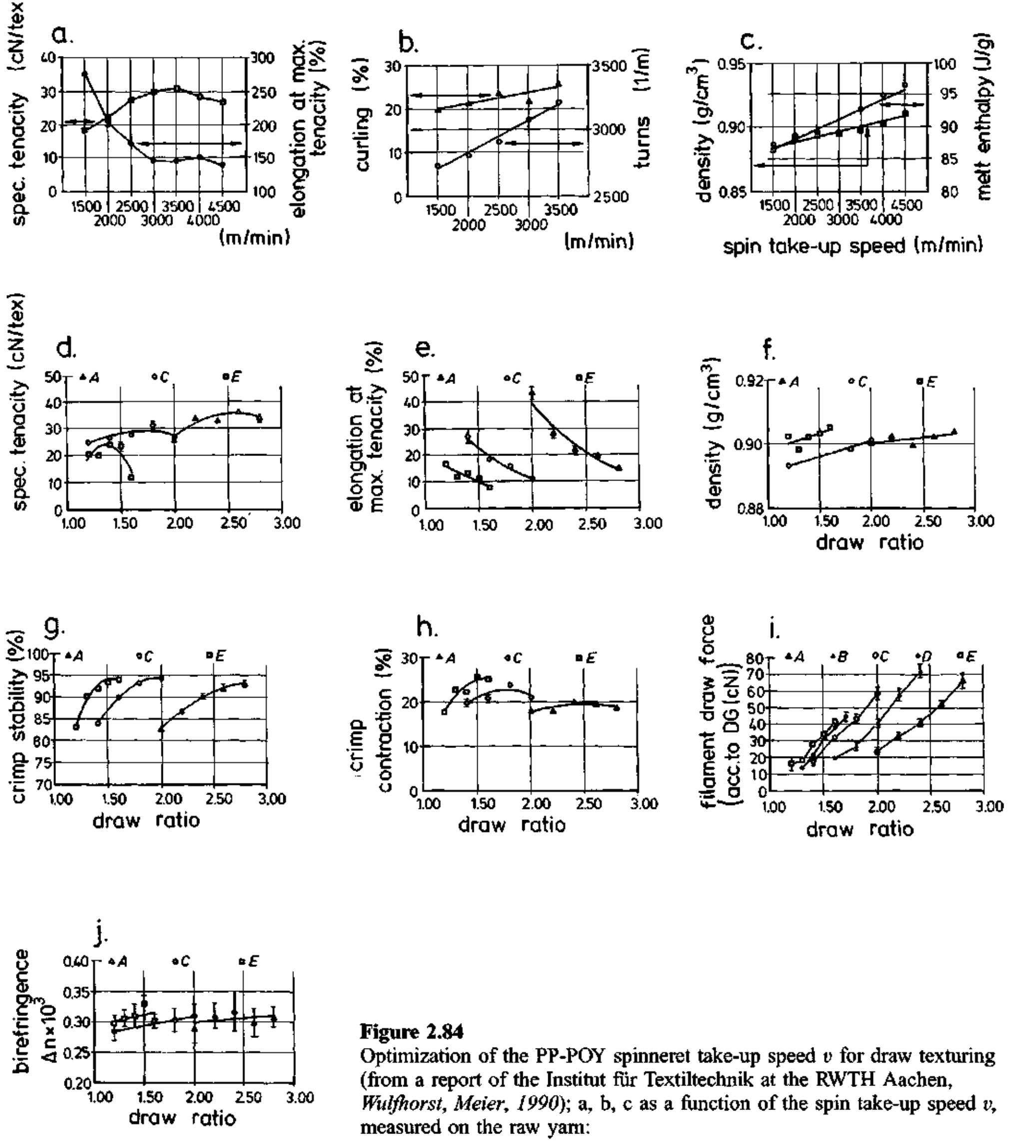


Figure 2.84
Optimization of the PP-POY spinneret take-up speed *v* for draw texturing (from a report of the Institut für Textiltechnik at the RWTH Aachen, *Wulfhorst, Meier, 1990*); a, b, c as a function of the spin take-up speed *v*, measured on the raw yarn:

a) Specific tenacity *F* (□) and elongation ε (○) at highest tenacity as a result of Fig. 2.84 right
b) Maximum crimp and the necessary t/m in the texturing zone (△ A, ○ C, □ E)
c) Density γ (□) and melt enthalpy Δ H (○)
d)..*f)* As a function of the draw ratio
d) Specific tenacity of the textured yarn
e) Elongation at highest tenacity of the textured yarn
f) Crimp density
g) Crimp stability
h) Curling
i) Filament tension after false twist spindle
j) Birefringence coefficient of the individual filaments

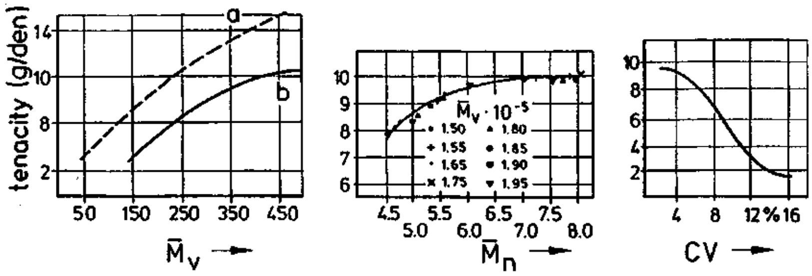


Figure 2.85 Influence of the molecular weight of PP on the achieved tenacity and the molecular weight distribution
a) Narrow distribution, decomposed, schematic
b) Wide distribution from untreated polymer chips
Right: corresponding CV values

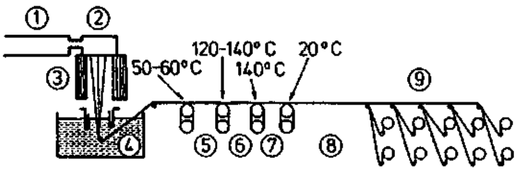


Figure 2.86
Process scheme for the production of high tenacity PP filament with wet quenching
1 Spin extruder
2 Spinning head with metering pump and drive
3 Hot shroud
4 Quench bath with chilled water
5 First draw zone (draw ratio 2...4)
6 Hot draw zone (draw ratio 1.2...2)
7 Stabilizing zone (draw ratio 1.01...1.1)
8 Finish oil application
9 Take-up winding

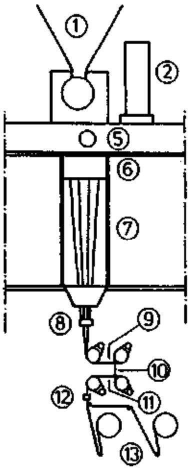


Figure 2.87
Process scheme for the production of high tenacity PP filament with air quenching
1 Spinning extruder
2 Control panel
5 Spinning head with metering pump and drive
6 Hot shroud
7 Air quench chamber
8...12 Four hot godets for three draw zones
13 Take-up

Table 2.20 Foil Yarns – Thickness Ranges and End Uses

Production Process	Production Range, undrawn, µm	Thickness Range, drawn, µm	End Use
Water Bath	60...250	15...50	Weaving foil yarn, also low shrinkage, binder twine, wire strand
Cooling drums	200	50	High modulus ribbons
Blow Foils	50...70	15...20	Carpet backing
Ribbon	$(2\ldots5) \cdot 10^3$	300...600	Packing ribbons

directly into water a sharply profiled film that is highly preoriented; upon drawing at a ratio of 1 : 10 to 1 : 11 it splices at the thin spots and results in the respective number of individual filaments.

Further processing is done as for monofilaments or in compact installations in a two-zone hot draw with subsequent preparation and winding on precision winding heads with filament tension control.

2.4.1.7 Comparison of Properties

Figure 2.88 shows some of the important properties of PP yarns and yarns from other fibers for similar end uses. The elastic recovery of PP is similar to that of PA-66 and above an elongation of about 10% superior to that of wool or PET. The recovery angle however is considerably smaller than for PA-66. Heat set PP yarns show a better pile recovery than non-set yarns. This is the reason why PP-BCF yarns can be very competitive to PA-BCF yarns.

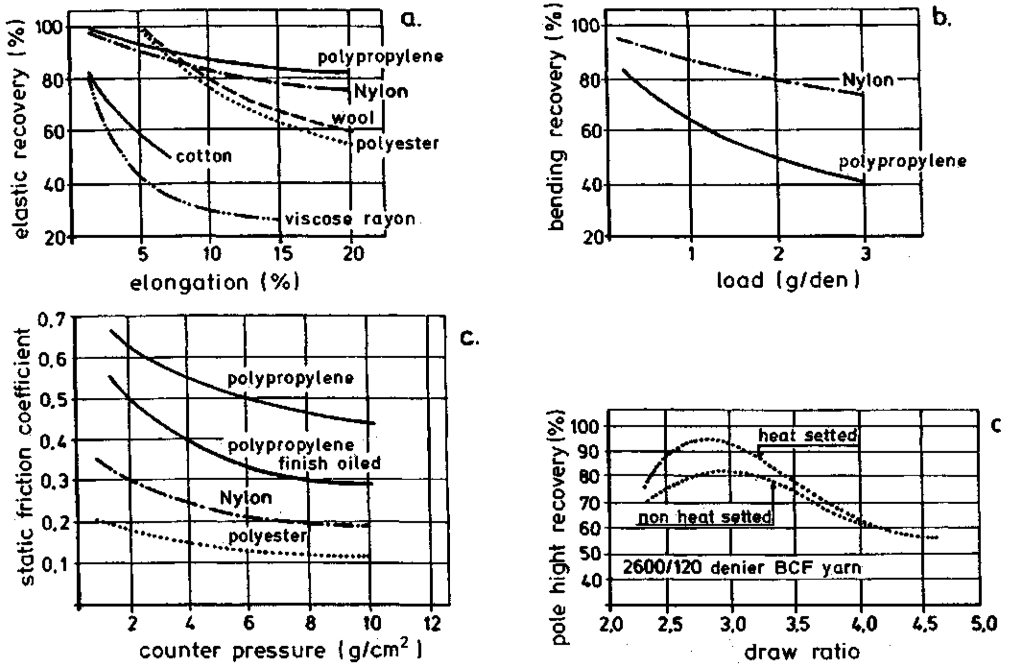


Figure 2.88 Some properties of PP yarns in comparison with other materials:
a) Elastic recovery of several polymer filaments and natural fibers
b) Bending recovery of PP and PA-66 filaments
c) Fiber to fiber friction coefficient (static), fibers of the same material
d) Pile height recovery of air textured PP-BCF yarn after same compression cycles (den 2600 f120)

For outdoors and wet applications PP is better suited than any of the other mentioned materials.

2.4.2 Polyethylene (PE)

Polyethylene (PE) was first produced in 1933 by ICI [510] at approximately 1000 bar/170 °C and 1938 by BASF [511] in a solution or emulsion at 40 bar and first had some relevance as a plastic material. Polymerization is according to the following schematic while releasing 25 kcal/mol:

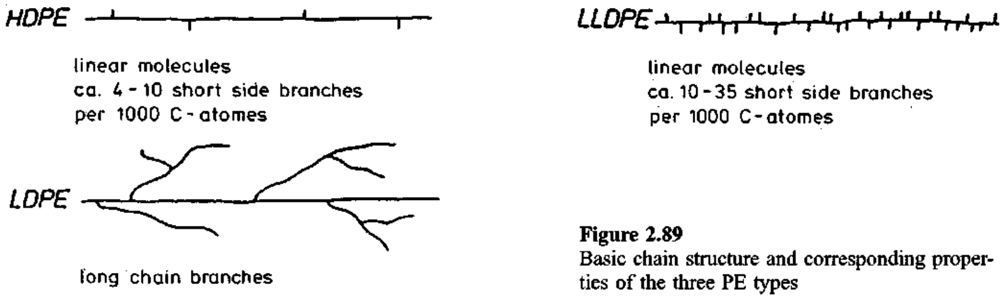


Figure 2.89
Basic chain structure and corresponding properties of the three PE types

$$R^{\cdot}+CH_2{=}CH_2 \longrightarrow R{-}\dot{C}H_2{=}CH_2 \xrightarrow{n\cdot CH_2=CH_2} R{-}(CH_2{-}CH_2)_n{-}CH_2{-}CH^{\cdot}{}_2 \tag{2.30}$$

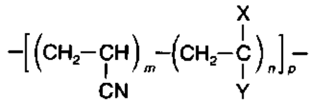
Three different double bonding systems can occur here: end steady without branches or with branches, or mid steady. According to the Ziegler process [513–515] especially titanium compounds and aluminum alkyls [514] are used as catalysts that can result in chain molecules of several millions molecular weight. The degree of branching is also important, as measured in CH_3-groups per 1000 °C-atoms in the main chain. Figure 2.89 shows the most important data of the three known polyethylene types and explains the type of branching. HDPE and especially LLDPE are used for spinning from melt to textile and technical filaments, while UHM-PE in the gel spinning process (Chapter 2.10) from solutions can be spun and drawn into yarns of extremely high tenacity [414].

The first industrial melt spinning appeared around 1965 in England [517]. This requires LLDPE or HDPE as pure, dry and dust free chips (just like for PP). Only spin dyeing as for PP is possible. The spin extruders mostly have screws with $L/D \approx 25\ldots30$ and a compression ratio of $1:4$ for small screw diameters and $1:2.5$ for $\approx$300 mm diameters D. Short compression screws are possible, but three zone screws are preferred. Filtration is recommended. Melt extrusion temperatures for LLDPE are around 135…145 °C and for HDPE around 170…190 °C. Considerable exceeding of these temperatures is possible; while in [517] the LOY process was used, the POY system is not used yet. Today, mostly the compact spinning method is used (Chapter 5.1) for the production of staple fibers. The draw ratios for LLDPE fibers are depending on the *MFI* $1:4.5$ to $1:7.5$. Textile properties as tenacity and elongation are shown in Fig. 5.6. Thus produced PE filaments are the softest known filaments.

Figure 2.90 shows the specific volume of the mentioned PE types next to PP and the specific heat as a function of the temperature [512]. It is also noted that the crystallinity of linear PE (HDPE) is considerably higher than of the branched LDPE; this is also shown in the stress strain diagram of the two types.

2.5 Polyacrylonitrile (PAN)

is split into three classes:



$$-\Big[\big(CH_2{-}\underset{CN}{CH}\big)_m{-}\big(CH_2{-}\underset{Y}{\overset{X}{C}}\big)_n\Big]_p{-} \tag{2.31}$$

- $m = 100\%$, $n = 0$—pure PAN (homopolymer) [237],
- $m \geq 85$ and $n8; \leq 15$ weight-% comonomers—usual PAN textile fiber of today, e.g., Dralon®; [238], Orlon® [239], Acrilan® [240],
- $m < 85$ and $n > 15$ weight % comonomers—known as the modacrylics.

Frequently used comonomers are vinyl acetate, acrylic acid methylester, methacrylic acid ethylester, vinyl chloride, vinylidine chloride, styrene, itaconic acid (-ester).

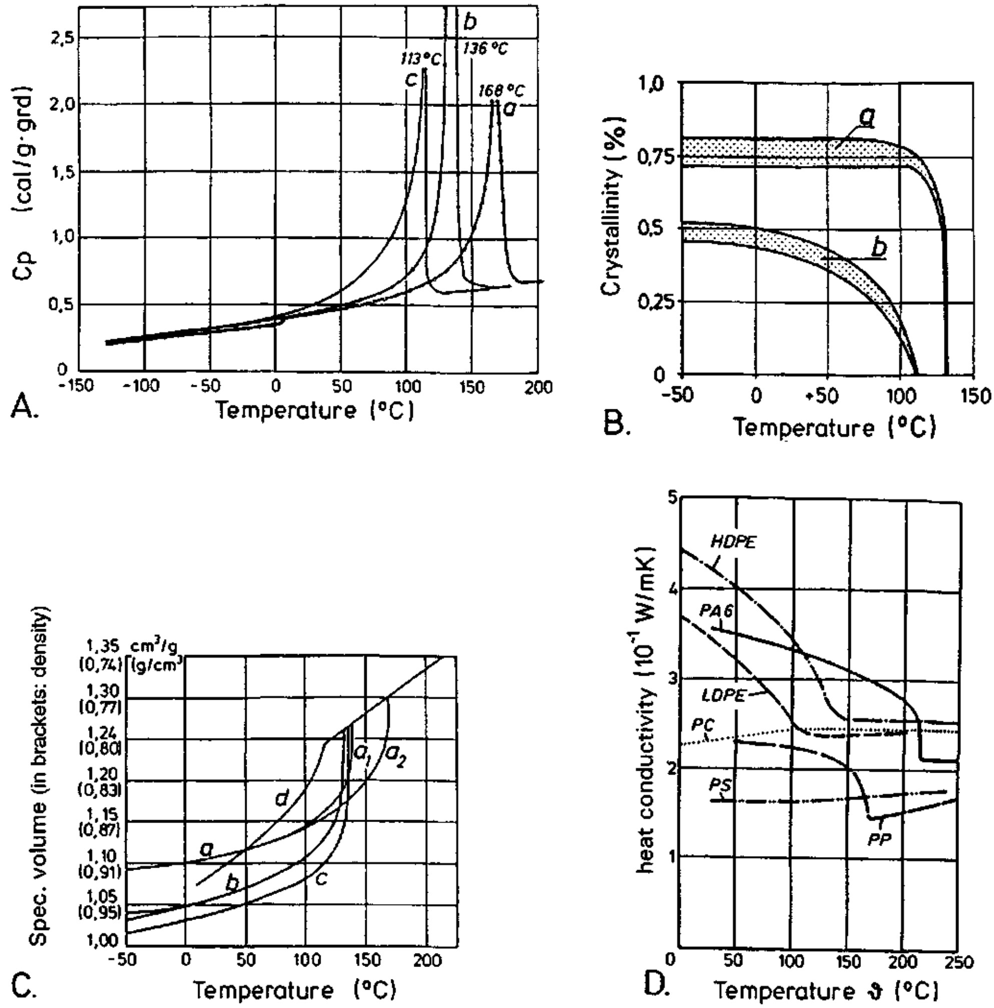


Figure 2.90 Specific heat c_P (*A*), crystallinity α (*B*), specific volume v and density γ (*C*) as well as the heat transfer coefficient λ (*D*) of PE and PP as a function of the temperature

A: *a*) Partially crystallized isotactic PP, $\varrho = 0.912$ g/cm^3
  b) Linear PE, 1.5 CH_3/1000 °C, $\varrho = 0.968$ g/cm^3
  c) Branched PE, 28 CH_3/1000 °C, $\varrho = 0.92$ g/cm^3
B: *a*) HDPE (linear)
  b) LDPE (branched)

The ranges are results of density differences, materials from different producers and also due to different measuring methods.

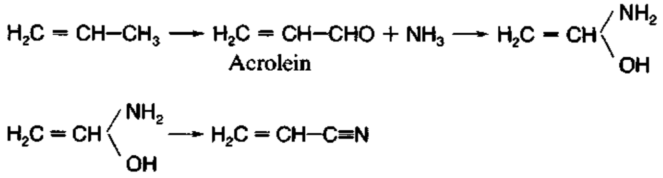
C: *a*) PP, *MFI* $i_5 = 250$ °C $= 1.9$ g/10 min, a_1 = heating up, a_2 = cooling down
  b) HDPE, $\varrho = 0.95$ g/cm^3
  c) HDPE, $\varrho = 0.965$ g/cm^3
  d) LDPE, $\varrho = 0.918$ g/cm^3
D: Heat conductivity coefficient of various thermoplastic materials

Already in 1931 *Rein* [242] found the first solvents for PAN calcium rhodanide, 1942 dimethylene formamide (DMF) and N-methylpyrolidone [242]. Only a few months later in the USA the solvents DMF and Tetramethylsulfon [243, 244] were patented. In Japan [245] PAN was solved in potassium or sodium rhodanide, and the solution was coagulated in ethanol or propane [245]. Already in 1944 DuPont started the production of PAN filaments that were later known as "Fiber A" [246]. 1952 the company Casella (later acquired by Bayer) followed. Installation sizes and plant capacities were published in 1981 according to Fig. 1.9. Since 1985 the Orlon capacities are being reduced and since 1995 stopped, while Dralon capacities are slowly increased. Courtelle® [248] and Beslon® [249] are both polymerized and spun in salt solutions, and today are used as good precursors for carbon fibers. The capacities however are negligible compared to those of PAN. In Asian countries PAN capacities are still increased; in the other countries significantly reduced (Table 1.2, Fig. 1.8) with a clear structural break since 1990.

2.5.1 Production of Acrylonitrile (=Vinylcyanide)

$CH_2 = CHCN$

Acrylonitrile today is mostly produced according to the Sohio process [251] from propylene and ammonia. Different methods are only due to the applied catalysts and the reaction sequence [251]:

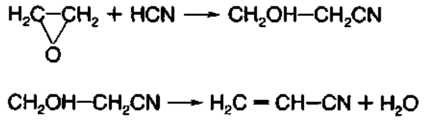


$$H_2C = CH-CH_3 \longrightarrow \underset{\text{Acrolein}}{H_2C = CH-CHO} + NH_3 \longrightarrow H_2C = CH\begin{matrix} NH_2 \\ OH \end{matrix}$$

$$H_2C = CH\begin{matrix} NH_2 \\ OH \end{matrix} \longrightarrow H_2C = CH-C{\equiv}N$$

(2.32)

An other two phase process starts with ethylene oxide and prussic acid and then leads via ethylene cyanhydrin



(2.33)

By direct addition of prussic acid to acetylene according to the process by *O. Bayer* and *P. Kuntz* in 1939 (DRP 728 767) acrylonitrile can be synthesized:

$$CH \equiv CH + HCN \longrightarrow H_2C = CH-CN$$

2.5.2 Polymerization to Polyacrylonitrile (PAN)

Polymerization of acrylonitrile without and possibly with comonomers is theoretically simple. However, producing well spinnable PAN-polymers at an industrial scale is extremely difficult. Detailed investigations are published by *Hunyar* et al. [252–260] as well as in US and German literature [261]. PAN cannot melt; it decomposes below the melting point and therefore has to be polymerized in a solvent or in emulsion systems. In the latter it is gained as a powder that is filtered, washed and dried. Only processes that can produce a very fine powder are possible, because coarse powders make the solving before spinning difficult. In practice, solution polymerization is done only with a few solvents (see Table 2.21). About 56.5% of the world capacity are gained by precipitation polymerization and solved for further processing in DMF for dry spinning and in DMF or dimethylacetamide (DMAC) for wet spinning. The remainder is polymerized in solution, degassed and filtered, and finally wet spun. The polymerization

Table 2.21a PAN Solutions and Spinning Baths

Solvent		Spinning solution		Precipitation			PAN from
%		concentration %	temperature °C	contents	portion %	temperature °C	
100	DMF [238, 239 265]	17...25	30...60	DMF water	40...60 60...40	5...25	precipitation polymerization (Redox System)
100	DMAC [240]	20	30...50	DMAC water	40...65 60...35	20...30	
100	DMSO	20	30...50	DMSO water	50 50	10...40	
50 50	NaSCN water	10...15		NaSCN water	10...15 90...85	0...20	solution polymerization
54 4 42	$ZnCl_2$ NaCl water	10		$ZnCl_2$ NaCl water	14 1 85	15...25	
70 30	HNO_3 water	10...13		HNO_3 water	30 70	3	
90...85 10...15	Ethylene glycol carbonate water	15...30		Ethylene glycol carbonate water	20...40 80...60	40...90	

Table 2.21b Distribution of the Capacities by Solvents (1976: Western Europe, America, Asia)

Solvent	Spinning system	% of total capacity	Example
Dimethylformamide	dry	22.5	DuPont, Bayer
Hydrous rhodanide solution	wet	23.8	Courtaulds
Dimethylacetamide	wet	21.5	Monsanto, Mitsubishi
Dimethylformamide	wet	12.5	Hoechst-Kelheim
Nitric acid	wet	10.8	Asahi Chem.
Hydrous $ZnCl_2$ solution	wet	4.4	Toho Rayon
Dimethylsulfoxide	wet	2.7	
Ethylene glycol carbonate	wet	1.8	Rumania

equipment is similar for both processes except for the precipitation, extraction/washing, drying and solving.

2.5.2.1 Theoretical and Experimental Basis

Summaries about the polymerization reactions of acrylonitrile (ACN) and comonomers are found in *Hill* [261], *Hunyar* [245] and *Falkai* [247]. Industrial scale production works almost exclusively with the solution suspension polymerization in a Redox system to produce the PAN powder or with the solution polymerization for the direct production of spinnable solutions (see Table 2.21).

- Solution suspension polymerization:
  A 7% ACN-H_2O solution with a Redox system of potassium persulfate and sodium bisulfate will lead to polymerization after a short induction period under stirring at constant temperature; a fine grain quantity of PAN is precipitated, then filtered, washed, dried and ground. This polymer can be dissolved in DMF or DMAC at normal temperature without further movement. The molecular weight results from $^{r}M = \eta_{\text{spec.}}/K \cdot C$ with $K = 1.5 \cdot 10^{-4}$ and $C =$ mol concentration per dm^3, e.g., $C = 5\ g/dm^3 \cdot 55\ dm^3$. The intrinsic viscosity $[\eta]$ for a polymer with a molecular weight of 100,000 is normally around 2. A good polymer has a narrow distribution curve.

  When using as an initiator system per weight part potassium persulfate 1/3 weight part potassium metasulfide and 400 times its quantity in cm^3 ferroamonsulfate solution (from 0.4768 g ferroamonsulfate in 1 dm^3 H_2O + 5 cm^3 n-H_2SO_4) at constant pH = 2, the molecular weight ($\bar{M}$ = average molecular weight) results as in Fig. 2.91. When the rpm of the agitator is increased from 40 to 160 rpm, $\bar{M}$ increased by about 30%, and from 0 to 300 rpm by about 45%.

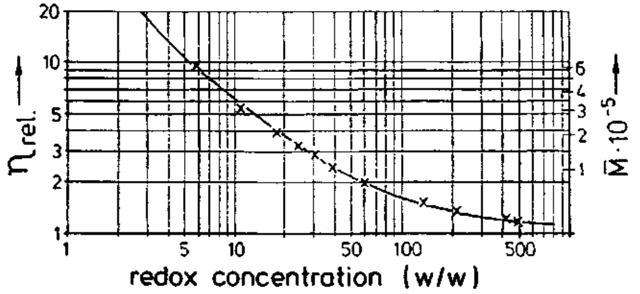


Figure 2.91
Functional relation of the relative viscosity of acrylonitrile polymer on the redox concentration during polymerization

Adding a few ppm metal ions (e.g., Cu^{++} or Fe^{+++}) increases the reaction speed considerably (Fig. 2.92). The increase of the reaction speed by persulfate and reduction additives can also lead to a reaction end before all monomers have been polymerized. The optimum relation is 1 mol persulfate : 2 mol thiosulfate.

Other trials polymerized 1.32 mol ACN (fresh 2 × distilled, $n_D = 1.3917$) per dm^3 H_2O with the Redox polymerization initiators $K_2S_2O_8 : K_2S_2O_5 : (NH_4)_2Fe(SO_4)_2$ in the weight relation 100 : 33 : 10 at 40 ± 0.2 °C under N_2 atmosphere. The results are shown in Figs. 2.93a through c: First the average molecular weight increases to a maximum with a maximum conversion of 30…40% and then drops after that. The degree of polymerization reaches after 40…60 min with a slight potassium persulfate concentration (1.2…1.8%) a clear maximum.

According to a US patent the process is done with a 28% suspension in water with a pH value set through H_2SO_4 at 3.0. Per kg H_2O three additional solutions are continuously added: one with 3.77 g $NaClO_3$ per kg ACN, a second with 13.5 g Na_2SO_3 per kg ACN, and a third with 6.4 g H_2SO_4 per kg ACN with a current velocity of 147.5 $cm^3/h \cdot kg\ H_2O$. After 7.5 h the pH value reaches a constant 2.5, the PAN concentration 24.8%, and the ACN concentration 3.5% under nitrogen.

- Solution polymerization:

Already before 1960 ACN and comonomers were polymerized in aqueous solutions of $ZnCl_2$ or HNO_3, later also in NaSCN and thus prepared for direct spinning.

First trials with continuous polymerization systems [282] with $K_2S_2O_8 : K_2S_2O_5$ in the ratio 3 : 1 with small additions of ferrum (II) amoniumsulfate at pH = 2.5 showed an increase in conversion of 50% after 4.5 h and to 80% after 8 h with a consistent molecular weight of 140,000 at 35 °C, that dropped to 90,000 at 55 °C. With more than 1% $K_2S_2O_8$ the molecular weight dropped from 140,000 to 90,000 at 1.87%. Larger autoclave volumes resulted in higher yields, emaille and glass installations resulted in a higher molecular weight than stainless steel. The polymer is then filtered and washed, dried in air 60 . . . 70 °C and ground finely. Figure 2.94 shows the degrees of polymerization of PAN produced in this manner.

In 1980 the solution polymerization of acrylonitrile in DMF was described in presence of azobiisobutyronitrile (AIBN) at 50 . . . 60 °C [247]:

- The polymerization of ACN in DMF happens proportional to the monomer concentration (Fig. 2.95a).
- The speed constant from $-dM/dt = k \cdot M^{3/2}$ depends on the initiator concentration (Fig. 2.95b).
- Polymerization in DMF is too slow for practical applications, and the process is too complicated for the period of 24 . . . 72 h.

It can be concluded that for practical applications the solution polymerization is only possible in the mentioned aqueous salt solutions, while for processing in DMF solutions first the PAN powder must be produced that then is dissolved, filtered, etc.

2.5.2.2 Apparati and Installations for Polymerization

If they do not polymerize directly for a spin solution, most companies use the precipitation method [262–264], that first provides the PAN powder that then has to be solved again. The most simple installation for this purpose is made from a reactor autoclave with a stirrer and cooling jacket. ACN, comonomers, water and catalyst are pumped into the autoclave at a constant ratio that is maintained (water at 0 °C solves 7.2% ACN, at 40 °C 7.9%, and at 50 °C 8.4%). The resulting polymer is not soluble in water and can be gained in the form of fine grains. On a rotating drum filter salts and not conversed monomers are washed

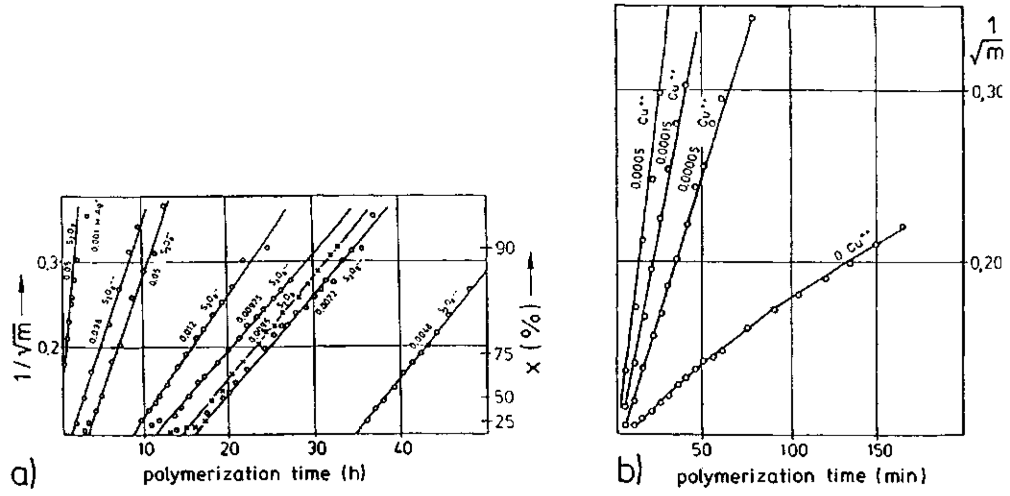


Figure 2.92 *a*) Catalytic polymerization of acrylonitrile with persulfate: Influence of (S_2O_3-) and acceleration effect of Ag^+ (figures near the lines in mol)
b) Catalytic polymerization of acrylonitrile with persulfate and thiosulfate: Influence of Cu^{++}

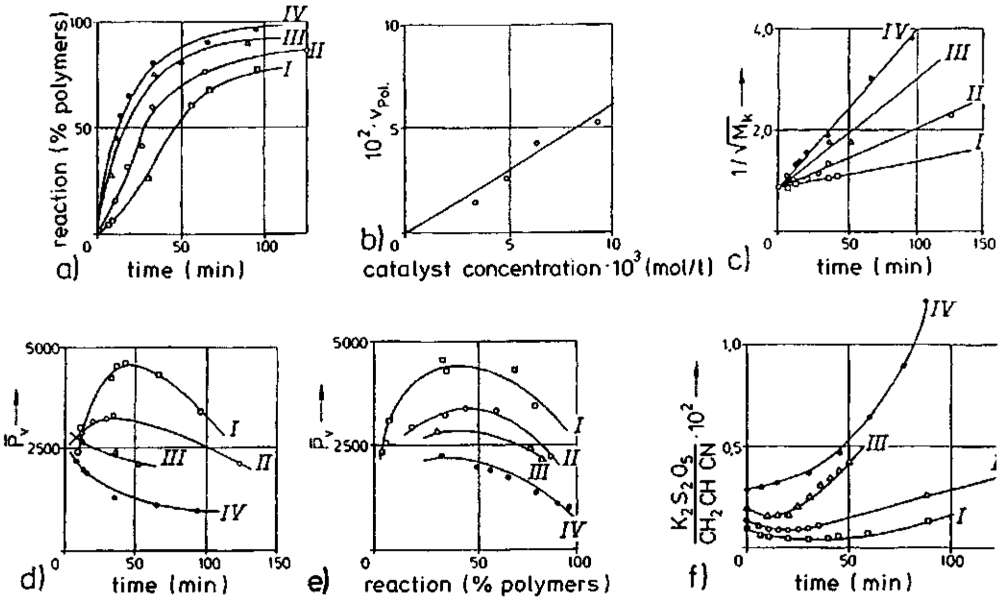


Figure 2.93 Various relations in the Redox polymerization of acrylonitrile:

a) Yield of acrylonitrile changed to polymer U as a function of the reaction time *t*

b) Polymerization velocity $v_{Pol.}$ as a function of the Redox concentration for ACN

c) Polymerization velocity as a function of the monomer concentration

d) Polymerization degree P_v as a function of the reaction time

e) Polymerization degree as a function of the conversion

f) Changes of the concentration ratios of potassium pyrolsulfide: monomers during polymerization

Concentration of the Redox system:

I: $3.3 \cdot 10^{-3}$, II: $5.0 \cdot 10^{-3}$, III: $6.6 \cdot 10^{-3}$, IV: $9.7 \cdot 10^{-3}$

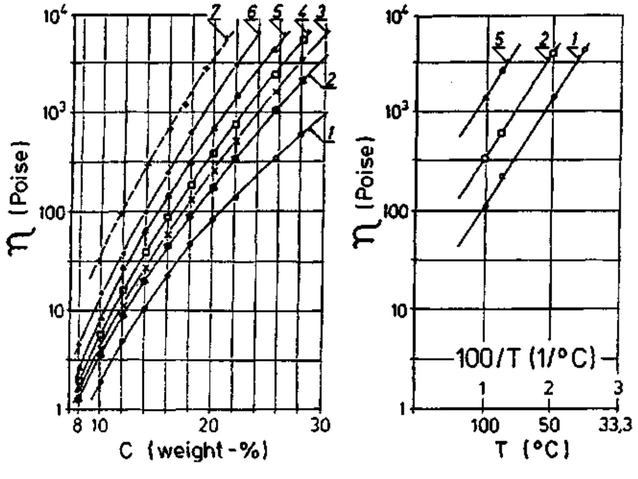


Figure 2.94 Viscosity concentration relation of different acrylonitrile polymers in N,N-dimethylformamide at 80 °C (left: single logarithmic scale) and as a function of temperature (right); concentration approximately 24% by weight

1 ○ PI: M = 85,800
2 ◆ Fe66: M = 100,000
3 × Fe67: M = 112,900
4 ◇ Fe59: M = 128,500
5 △ Fe60: M = 140,700
6 ● Fe62: M = 160,600
7 + in NaSCN: M = 112,900

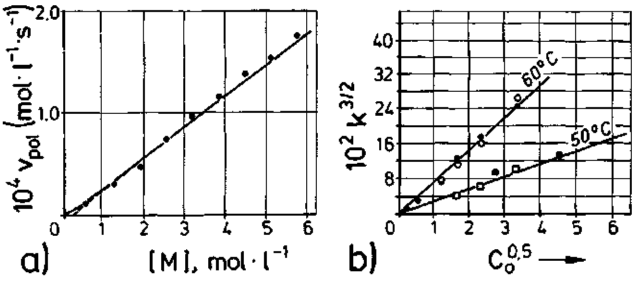


Figure 2.95

a) Polymerization velocity of acrylonitrile dissolved in N,N-dimethylformanide as a function of the monomer concentration [M] (initiator: azobisisobutyronitrile, 10^{-2} mol/l [247]

b) Constant *k* of the polymerization velocity as a function of the beginning initiator concentration c_0 of the solution polymerization of ACN in DMF (initiator: azobisisobutyronitrile)

out; then the filter cake is removed, dried, pulverized, etc. The washed out monomers can be recycled by distillation and re-entered into the autoclave.

The process scheme for a continuous ACN polymerization is shown in Fig. 2.96. Monomers (M_1, M_2), and water (W) are dosed through the pump system (P_1) and a dynamic mixer (M) from below into the first autoclave (A_1), where they slowly move upwards through a horizontally working high speed mixer stream and then are removed through the upper exit. Additives (Ad) are then added to the solution in front of the second high speed mixer (M) and the mix enters the main stream through a second pump (P_2). It then goes through a second autoclave (A_2), from bottom to top, also via horizontal mixing streams. Through an overflow this solution/partial suspension enters the third autoclave with a slow agitator, from which at the bottom a mixture of polymers, water, not conversed monomers is removed by a thick solution pump (P_3) and transported to filter washing (F_1). This polymer cake is then washed and filtered twice (F_2, F_3), pulverized in a hammer mill (H) and dried in a floating drying tower (T). The lighter dry powder is then blown into the filter head of the racking station (S) for racking or further processing.

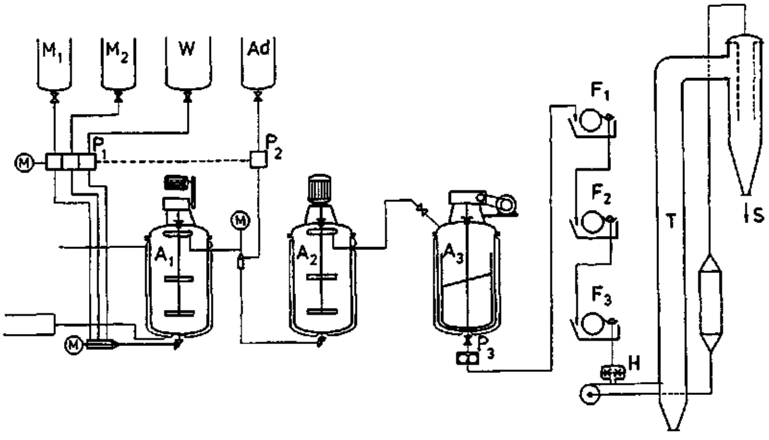


Figure 2.96 Flow sheet of an ACN Polymerization for a continuous process

M_1, M_2, W, Ad	monomers, comonomers, water, additives
P_1, P_2	dosing pumps
$A_1 - A_3$	polymerization autoclaves
P_3	discharge pump
F	triple extraction and washing (rotary filter)
H	hammer mill
T	floating tower dryer with
S	racking station for the polymer powder

For the process the initial pH-value is set by acids (e.g., sulfuric acid) to 1 to 4. The initiator concentration can be 0.1...5% of the monomer quantity. Polymerization is mostly practically performed at 40 to 55 °C. The exothermic polymerization heat is transferred through cooling of the autoclaves.

PAN produced by this Redox polymerization is a white powder with an average grain size of 20...100 μm. The usual average molecular weight M_w for further processing in spinning is between 80,000 and 100,000 and the respective viscosity $[\eta] = 1.18 \ldots 2.22$ dl/g, measured at 20 °C in DMF.

For storing PAN powder the risk of powder explosion should be pointed out.

During the solution polymerization conducted principally according the installation in Fig. 2.96, the solution flows through pump P_3 into a continuous de-aeration station and a large space filter into the spin storage tanks.

The only differences are that from the water tank (*W*), one of the water salt solvents is dosed in and the dosing pump (P_2) delivers directly into the entry autoclave (A_1).

In the de-aeration equipment as in Fig. 2.97 the solution film flows down the slant planes and turns each drop to the next plane. The vacuum should be only between 60...70 mbar, and the temperature between 40 and 50 °C, so that the solution concentration is maintained [272]. Filtration is very important for good spinnability and is usually done in water heated large space filter presses as known from the viscose industry (Fig. 2.98). They are made from a large number of wave shaped plates that can be pressed together mechanically or mostly hydraulically. The plates must be corrosion resistant and covered on both sides with filtration material that serves in open spaces for filtration and at the edges for sealing. Feeding is done in the middle of the head piece; the filtered solution flows through the inside of the plates into the plate corners for further processing. The filtration cake is removed from the filtration fabrics after opening the press. The size of the plates ranges from 300 × 300 mm (equal to about 0.15 m^2 filtration surface because of the two sides) to 2600 × 2600 mm (equal to about 10 m^2 filtration surface per plate). Process times for the necessary cleaning and the best suited filtration material can only be determined through experience.

Instead of processing the solution polymerization in a vessel cascade [273], it can also be processed in a flow tube [274]. This requires the addition of catalysts and radical formers like ammonium persulfate, azo-bis-isobutyronitril, p-toluolsulfone acid, butylhydroperoxide, boron components or ion radiation at suited positions.

The mathematical relations to the polymerization kinetics are explained in *Falkai* [247].

2.5.2.3 Installations to Dissolve PAN

For dry spinning PAN powder is usually dissolved in dimethylformamide (DMF), for wet spinning mostly in dimethylacetamide (DMAC), but also in DMF or seldom in DMSO. In the beginning of the dissolving process the polymer powder must be free of lumps and small solvated parts to avoid long dissolving times and insoluble particles. For this it is helpful to have a compact polymer core, thorough mixing, and a low temperature.

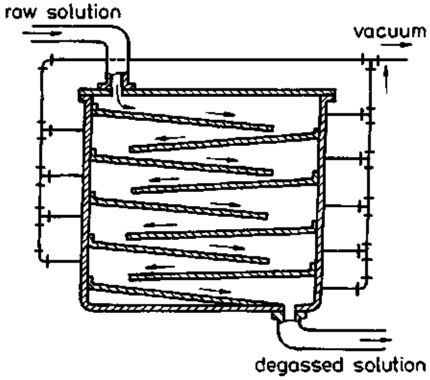


Figure 2.97
Scheme of a vacuum de-aeration equipment for a PAN solution (absolute pressure approximately 100 to 150 mbar)

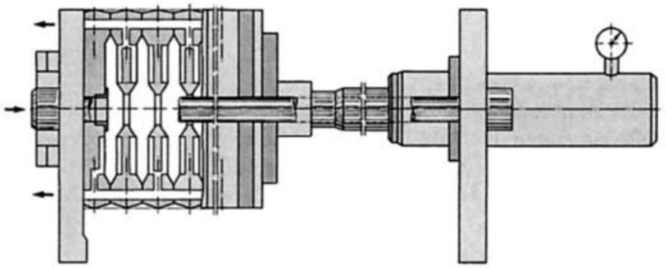


Figure 2.98
Scheme of a large space (multi-plate) filter press for a PAN solution [533] (Rittershaus & Blecher, Wuppertal)

The most simple dissolver is a stirring autoclave filled half way with a solvent, into which the powder is dosed under intensive stirring and under an inert gas. The ideal dissolving temperature is between 40 and 60 °C and may not exceed 80 °C, with a dissolving time of < 1 h. The process is exothermic; i.e., the autoclave has to be heated to the desired temperature in the beginning and then cooled to maintain the temperature.

A more intensive mixture and solution can be obtained in considerably less time by using a high shear mixer (Fig. 2.119).

A simple continuous dissolving installation with batch input is shown in Fig. 2.99: PAN powder is weighed and dosed from (*1*) into the tempered and measured solvent that has been filled into one of the two high shear mixers (*4*). Inside these mixers high rpm shear plates work to complete the initial dissolving process within about 30 min. This solution is entered into the autoclave (*5*) and mixed there under constant stirring at about 70 °C (for DMF). The pump (*7*) continuously removes solution and presses it through the two filters (*8*) into the second degassing autoclave (*5*) that is connected via pipe (*6*) to a vacuum of 60...100 mbar.

This solution is transported by pump (*7*) through another filter (*8*) into the spin storage tank (*5*) and homogenized under constant agitating. Pump (*7*) transports the solution through another filter (*8*) into the piping (*2*) to the spinning machine.

The solid matter concentration in the spinning solution is about 18...25% in DMF for wet spinning and about 23...30% for dry spinning. The pH value should be between 6.5 and 9.

The temperature of the solution in DMF for wet spinning is 20...60 °C and for dry spinning 110...140 °C, but must not exceed +5 °C in solutions in HNO_3. Too high deviations from the optimum temperatures for a specific solvent lead to geling and further to interlacing reactions. High viscosity and high molecular weights reinforce the geling, but narrow molecular weight distributions reduce this tendency [266]. Solutions in dimethylsulfoxide (DMSO) or ethylene carbonate or salt/water also tend to gel, while nitric acid can partially lead to hydrolysis of the nitrile components.

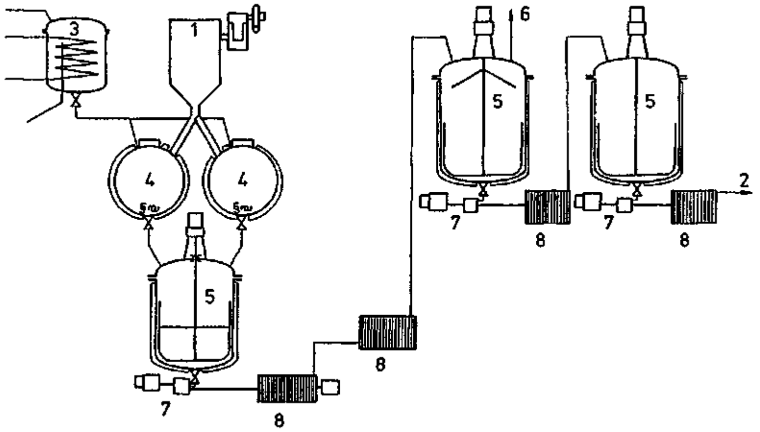


Figure 2.99
Flow sheet of a continuous PAN dissolving plant

1 PAN powder weighing tank
2 Piping to the spinning machine
3 Solvent weighing tank
4 High shear mixer (alternating working)
5 Several solution tanks in line
6 To vacuum de-aeration
7 Discharge pumps
8 Plate filters

Continuous dissolving plants for large capacities can follow the principle of Fig. 2.99. However it is useful to include entrance and homogenization steps [267, 268]. Double cone mixers and kneaders [269, 270] are the most important entrance steps, followed by a homogenization step and continuous deaeration, e.g., with a vertical pipe with heating jacket, where the solution flows on the inside walls after being dosed in through a ring slot. The gas is removed by a vacuum above, and the solution is removed from the sump [271].

Another fully continuous PAN dissolving plant was developed by Baker Perkins Ltd. and is described in [267].

2.5.3 Spinning and Aftertreatment of Polyacrylonitrile

The present global capacity of approximately 7000 t/24 h with over 99% staple fibers consists for about 25% of PAN/DMF solution that are dry spun, and about 12% that are wet spun. The largest European producer in this area [238] uses the dry spinning process, while the respective largest US producer [239] just discontinued the dry spinning process. The remaining PAN fibers are wet spun with about 22% in DMAC as the solvent [240].

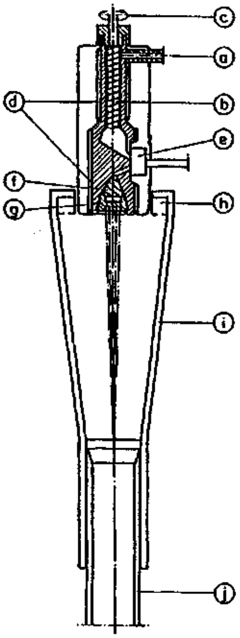


Figure 2.100
Schematic cross-section of a PAN melt spinning installation [267]
- *a*) PAN with plasticiser (e.g., up to 50% by weight DMF)
- *b*) Extruder screw
- *c*) Screw drive
- *d*) Electric heater belts
- *e*) Gear spinning pump with drive
- *f*) Afterheater
- *g*) Melt spinneret
- *h*) Solvent vapor sucking
- *i*) Telescope spinning tube (insolated)
- *j*) Spinning tube with electric heating and insolation

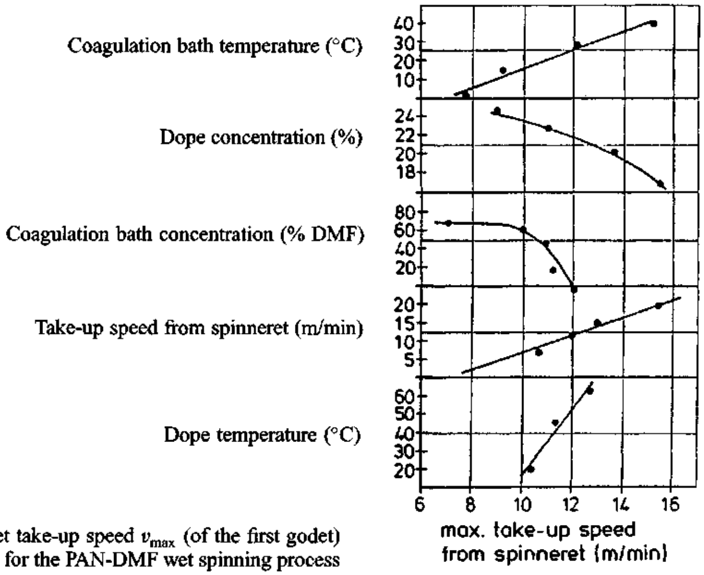


Figure 2.101 Maximum spinneret take-up speed $v_{\max}$ (of the first godet) as a function of various parameters for the PAN-DMF wet spinning process

After the three possible spinning processes the PAN tows enter a quite similar aftertreatment. As PAN solution spinning and aftertreatment are covered in Chapter 4 as an example for the equipment and machine design, the following references may suffice:

- Chapter 4.14: Dry Spinning Installations
- Chapter 4.15: Solution Wet Spinning Installations
- Chapter 4.15.2: Draw- and Wash Baths
- Chapter 4.15.3: Aftertreatment Equipment for Dry Spun Fiber Tow

Additionally the incorrectly named "Melt Spinning Process for PAN" [267, 276, 277] shall be mentioned here. For this process the PAN powder is pasted with 30...60% of a plasticiser, e.g., cyclic tetramethylenesulfon for DMF, and extruded with an extruder and gear pumps into one or several dry spinning tubes. The rubber like mass is said to have 168 °C at 105 bar at the spinneret. At over 920 m/min take-up speed 1 g/den are achieved. It is said to be possible to achieve up to 6000 m/min. Figure 2.100 explains the principle of this installation [267]. Excessive and varying delay times for the PAN paste increase the risk of decomposition.

A hydrating polymerization process avoids this risk of decomposition. The polymer is formed just before the spinneret [278–281] and then spun directly as a solution. These extracted and undrawn filaments yield for 2...5 dtex per filament a tenacity of 1.0...1.5 g/den and crimp at tension free hot water treatment. An industrial scale use of this process is not yet known.

The conditions for the PAN solution and the wet spinning with DMF as a solvent are shown in Figure 2.101. The optimum spinneret take-up speed is between 10 and 12 m/min, resulting in a tow speed after drawing of 45...50 m/min. Practical experience shows that it is difficult to form a wet spin tow for finer final titer than 2.5...3 dtex per filament. Therefore the dry spinning process is better for finer individual titers. For coarser than 13...15 dtex per filament after drawing the wet spin process is better. An overview over PAN solvents and the responding spin baths are shown in Table 2.21.

To produce finer individual filament titer than about 2.5...3 dtex, it is recommended to heat the tow coming from the aftertreatment on 8...16 drums to over 180 °C and to draw them in a hot air duct at 200 °C to the desired individual titer, cool them on water cooled drums and then crimp and cut them.

2.6 Polyvinyl Chloride (PVC)

Cheap and easily obtainable raw materials and excellent isolation properties, especially against cold, characterize these fibers. Due to the cancer suspicions during the production of PVC the interest has dropped considerably. The low temperature stability, beginning shrinkage at 75...80 °C, a low softening point and sensitivity against dry cleaning add to this. Applications are found primarily in filters, flame retardant home furnishings, underwear for extremely cold areas and products without electrostatic.

2.6.1 Production of PVC

PVC was first produced in 1913 [286–289] and was registered in the same year by *Klatte* as a patent for fibers. The non-chlorinated PVC fiber with 56.8% chlorine content and the postchlorinated version with 64% chlorine content was processed to staple fibers in Wolfen 1930 [290, 291]. Mixed polymers with vinylidenchloride (Saran®) [295, 296] and with acrylonitrile (Vynion N®, Dynel®) [297] followed.

Industrial scale processes for the production of vinyl chloride are thoroughly discussed in the literature [301–304].

For polymerization there are four different processes, but for production of spinnable products only the emulsion polymerization [305] and the suspension polymerization [306] are possible. The degree of polymerization should be between 1000 and 1500. Instead of the theoretical chlorine content of 56.8% BASF products claim 53.1% and products by Rhodiaceta 56%. This product without postchlorinating was called “PCU”. Further process details are given in [301–314]. The PVC powder produced this way has particle sizes of 0.01 . . . 0.1 μm.

Post chlorinating of PVC to chlorinated PVC (CPVC) is done in different media, e.g., tetrachlorcarbonate or under radiation. CPVC is then produced as a white powder with a chloride content of 64% with a maximum solubility in acetone and improved solubility in other organic solvents. Another process is described in [315].

The mix-polymer Saran® [316] is gained from vinylchloride and vinylidenchloride [316–324]. Further mix-polymers were evaluated for filament and fiber production, e.g., with vinlylacetate [324], acrylonitrile [325], allylester [326], unsaturated ether [327], methacrylicacidester and acryloacid methylester [328], Styrene [329] or mixtures with 13% vinyl chloride and 2% acrylonitrile [321] or with 7.5% acryloacidethylester [318] with polyvinylden chloride.

PVC also has to be stabilized, because it is light sensitive [335] and sensitive to oxidation [336–339] and will form polyenes.

2.6.2 Solving and Spinning of PVC and VC-Copolymers

The equipment and installations for solving PVC are similar to those for PAN (see Chapter 2.5.2.3). Temperatures and exposure times as well as solvents must be suited to the used polymers. It is important to filter at least twice before extrusion.

Extrusion equipment is also very much like the one for PAN, i.e., one can use the

- dry spinning process: Table 2.22 shows some principle values in comparison to PAN and acetate. Processes and spinning conditions are more like for acetate;
- or the wet spinning process.

For the latter extrusion of a 20 °C PVC solution in acetone is done through 2500 holes/spinneret into a slightly acetic aqueous coagulation bath. The collected filaments are washed in contra-current water, drawn by 150%, lubricated, crimped in a stuffer box and cut to staple fibers. After hot air drying they are opened and packed in bales.

In the dry spinning process in France mixtures of sulfurcarbonate/acetone and in Japan of acetone/benzene are used and stabilizers are added. In a different dry spinning process 35% by weight PVC are solved in 65% by weight solvent of 40% sulfurcarbonate and 60% acetone, extruded through spinnerets with 0.08 mm bores into 3.5 m long spin ducts heated to 125 °C, with the yarn being taken up at 135 m/min with a titer per spinneret of 374 dtex for 40 holes per spinneret. The yarn is drawn in two stages in a water bath of 40 cm length and 95 °C by 540%. The finished yarn has a titer of 78 dtex, a tenacity of 27 cN/tex and a breaking elongation of 10%. In modern installations speeds of up to 400 m/min can be reached.

2.6.3 Syndiotactic PVC

A lower polymerization temperature of the VC [347] favors the formation of syndiotactic parts [348], whereas the crystalline portion, the freezing temperature and the melting temperature increase [349]. By polymerization of VC at $-10\ldots-20$ °C the glass transition temperature for PVC can increase to 105 . . . 110 °C, the melting temperature to about 275 °C, and the chemical resistance can be increased. This polymer is solved in hot cyclohexanon [350] and extruded into a coagulation bath of water, cyclohexanon and an additional solvent, e.g., ethanol or acetone. The filaments are then washed, drawn in boiling water to a ratio of 1 : 7, dried under high tension and at high temperature, heat set and stabilized under pressure in vapor [351].

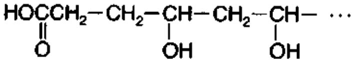
Table 2.22 Solvents and Important Data for Dry Spinning Processes (VC-polymers and Copolymers, PAN)

Raw materials	Solvent	Molecular weight	Concentration % of weight	Spinning tube		*T* [°C]		Take-up speed m/min
				length m	*D*	spinneret	tube	
Polyvinyl chloride	Acetone (1)+ Sulfurcarbonate (1)	34000	30	3.5	–	70	125	170 [1]
CPVC (postchlorinated)	Acetone	–	45	–	–	75	130	– [1]
Vinyl Chloride (90%) + Vinyl Acetate (10%)	Acetone	26800	27	–	–	50	130	250 [1,2]
Vinyl Chloride (80%) + Acryloacid methylester	Acetone (1) + Methylene chloride	–	20	–	–	–	80...100	80...100 [5]
Vinyl Chloride (60%) + Acrylonitrile (40%)		–	20	6	20	0	85...120	50...200 [2,4]
Polyacrylonitrile	Dimethylformamide > 8000		25	2.5	–	130	400	90 [5]
Acetyl cellulose	Acetone	40000...80000	20...27	4...8	10...25	56...59	60...95	150...500 [6]

(1) F-Pat. 913919 and 913927 (Soc. Rhodiaceta)
(2) US-Pat. 2418507 (Carbide & Carbon Chem. Corp.)
(3) US-Pat. 2420565 (CCC)
(4) US-Pat. 2404714 (Du Pont)
(5) Ullman, P., Enzyklopädie der technischen Chemie, 3rd edition, Urban & Schwarzenberg, Berlin

2.7 Polyvinyl Alcohol (PVAL)

Polyvinyl alcohol



$$\mathrm{HO\underset{\underset{O}{\|}}{C}CH_2{-}CH_2{-}\underset{\underset{OH}{|}}{C}H{-}CH_2{-}\underset{\underset{OH}{|}}{C}H{-}\cdots} \tag{2.34}$$

is gained from polyvinyl acetate (PVA) that was first produced in 1912 [352]. 1924 the gas phase reaction from acetylene and acetic acid was accomplished [353]. By saponification of PVA with an alkali or by transesterification and saponification PVAL is gained [354]. In a formaline solution [355] in presence of catalysts these yarns become water proof with acetale bonds between adjacent hydroxyl groups. After some significant improvements especially in tenacity, elongation and knot strength, production was started in 1950, rising to about 100,000 t/a in 1970 (Table 2.23), but dropping again to about 65% by 1986.

Table 2.23 PVAL Fiber Production 1970 (approx. 35% Filament and 65% Staple Fibers)

Country	Company	Trade name	Production (t/a)
Japan	Kuraray	Kuralon	32,700 } 70,000
	Nitivy Co.	Vilon	
	Unitika	Mewlon	
South Korea	Korea Vinylon Fiber	Mikron	
		Mikulan	
USSR	Vinol		7,000
PR China	(in Beijing)		20,000
			≈ 100,000 ... 120,000

A detailed overview over the processes and installations is found in *Sakurada* [356] and in the diagram in Fig. 2.102.

2.7.1 Production Process up to the Spinnable Solution

1 mol acetylene and 1 mol acetic acid after transferring over a zinc impregnated active charcoal at 200 °C will result in vinyl acetate. In water/methanol this will react by saponification with NaOH to vinyl alcohol and sodium acetate. The unstable vinyl alcohol groups then polymerize to polyvinyl alcohol under formation of a carboxyl group. This substance is still water soluble, but it can be spun wet or dry.

In the appropriate mol ratio PVA powder will precipitate, and it is continuously weighed and washed in cold water to clean from impurities as sodium acetate, sodium hydroxide and residues of acetic acid. The surplus water is pressed out in a screw decanter up to a defined quantity. After possible intermediate storage with another weighing this PVAL is entered into a dissolving plant, similar to the one for PAN in Fig. 2.99. As opposed to PAN solutions here all the apparati are vapor heated, and at a constant temperature of 100 °C within a few hours a processable solution with 10...18% dry substance and a viscosity of up to 4 Pa·s (as measured at 20 °C) is produced. This solution must be filtered several times during the preparation and prior to spinning, de-aerated, and temperature homogenized. Additives as TiO_2 are also added here.

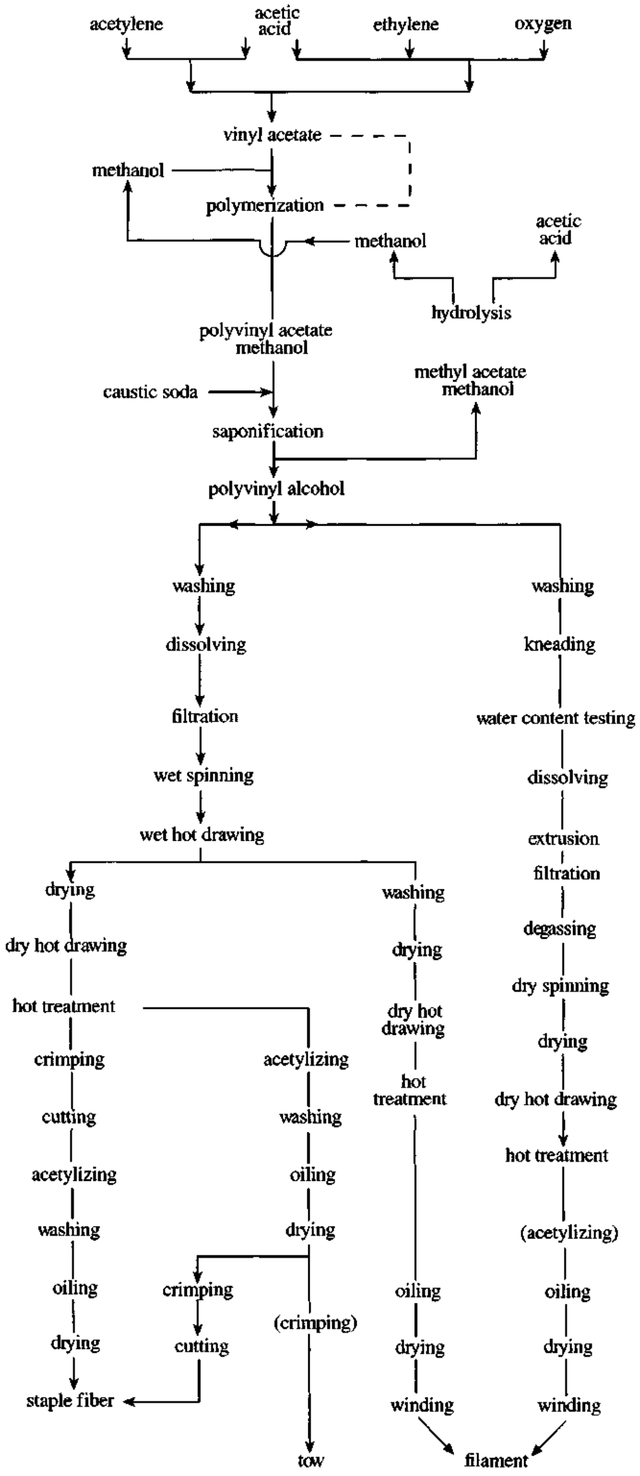


Figure 2.102 Block diagram for various processes for the production of PVAL fibers resp. tow or filaments

2.7.2 Solution Wet Spinning

The majority of PVAL with a degree of polymerization of about 1700 and a spinning viscosity at 90 °C of 4...15 P is wet spun. The spin bath in quantities of 2 cm^3/g solution contains 15...16% sodium sulfate in water at 40...50 °C. Different from the wet spinning machines described in Chapter 4.15 PVAL is spun upward through a spinning tube as in Fig. 2.103. Depending on the end use spinnerets with 2000 holes of 0.15 mm diameter up to 60,000 holes of 0.1 mm diameter are used—in the case of high hole number in star or segment arrangement (Fig. 4.140). The spinnerets are made from gold or gold-platinum alloys. Already about 6 cm above the spinneret the filament reaches its final undrawn diameter. Drawability drops with increased spinning tube length (30...150 cm: 14 : 1...10 : 1); at the same time the tenacity increases from 8.1 to 10.5 g/dtex. The take-up speed out of the spinning tube is ≤ 5 m/min, and the exit speed from the spin bath should be within ± 50% of this value.

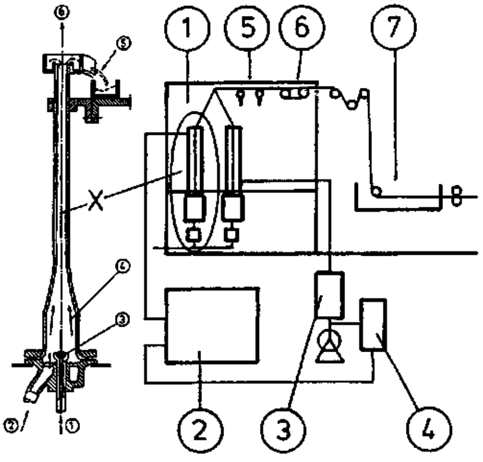


Figure 2.103 Schematic Drawing of a Wet Spinning Machine for PVAL
Right: Wet Spinning Part
1) Spinning machine
2) Spinning bath preparation
3, 4) Filters
5) Plying of the filaments
6) Tow take-up
7) Post coagulation bath
Left: Upwards working wet spinning tube for PVAL
1) Spinning solution
3) Spinneret
2, 4) Coagulation bath
5) Coagulation bath overflow
6) Filament take-up.

As PVA is thermoplastic it can be drawn in a hot salt solution bath, over hot drums or in hot air. Hot aftertreatment follows at 220...230 °C for 40...180 s. Crystallization is completed after 10 s. Thus fibers and filaments with tenacities according to Fig. 2.104 are produced.

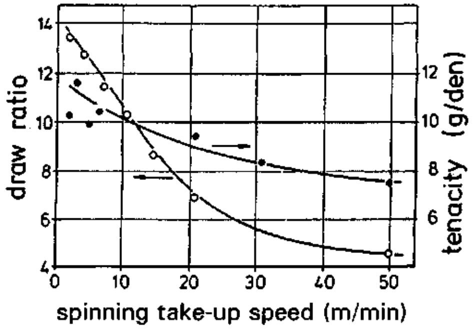


Figure 2.104
Tenacity and Draw Ratio of PVAL filaments as a function of the spinning take-up speed *v*

Indissolubility in water is achieved by a hardening process with interlacing of the hydroxyl groups of the PVA with aldehydes and acids under acetyl formation, especially in multi phase formaldehyde baths under higher temperature (see Table 2.24 [358]) with subsequent washing, crimping, drying and staple cutting.

Table 2.24 Composition of the Hardening Baths for PVA Fibers (%)

Composition	1st bath	2nd bath	3rd bath
Sulfuric acid	10.0	20.0	5.0
Sodium sulfate	23.0	20.0	–
Zinc sulfate	3.0	3.0	–
Formaldehyde	3.5	3.5	16.5
Water	60.5	53.5	78.5

With a known horizontal multifilament spinning process for PVA the polymer has a molecular weight of about 1600. The solution is spun with 18% concentration 5 g/min through a spinneret with 100 holes of 0.08 mm each into a NaOH bath with 350 g/l at 40 °C 150 cm bath length, take-up speed is 16...47 m/min.

2.7.3 Dry Spinning

The application is quite rare. The spin solution of 43% concentration at $M \approx 1700$ and 160 °C is deaerated after several filtrations and extruded with (for example) 500 cm^3/min through a spinneret with 211 holes of each 0.1 mm diameter into a dry spinning tube with air at about 50 °C, and taken up at 110...160 m/min. After direct drawing over two hot and one cold godet duos with a 1 : 11...13.4 ratio the yarn is wound at 1300...2000 m/min.

Another dry spinning process spins the PVA solution with 90...95 °C into 40...60 °C air with 60...85% relative humidity, taken up at 350...650 m/min and hot drawn in two stages to 1 : 7 to 8.5 to achieve filaments with 5 g/dtex tenacity.

In difference to the PAN dry spinning process (Chapter 4.14) for PVA hot spinning air is entered into the spinning tube about 1 m below the spinneret to keep the solution tenacity high.

The dry spun PVA filaments also require a formaldehyde aftertreatment etc., to remain water indissoluble as described before.

Filament and fiber properties as well as their applications are discussed in detail in [356].

2.8 Spandex or Elastane Yarns (EL, also PUR)

These highly elastic yarns (in the USA referred as Spandex [364], in Germany according to DIN 60 001 as Elastane [365]) have a breaking elongation of over 200%, preferably over 400%, and recover immediately and almost completely to the original state if the tension is removed. Textured yarns that recover due to their fiber geometry like springs or coils are not covered by this term.

Spandex yarns are made from high grade polymers with a high weight portion of segmented polyurethanes. The recovery is based on the structure of the amorphous (i.e., soft) connections between crystallized (i.e., hard) blocks [366].

Polyurethane (PUR) was first synthesized in 1937 [367]. The direct synthesis in high polar solutions (e.g., in DMF) was described in 1951 [370]. The reaction spinning system was used for this in 1949. 1958 Lycra® [372] and Vyrene® [373] were introduced to the market with better elastic properties than rubber yarns. 1992 the production was about 60,000 t/a, almost exclusively multifilaments of 20...2500 dtex and individual titers of 4...20 dtex per filament.

Table 2.25 shows the major trade products, spinning systems, producers and raw materials. Since 1988 the world capacities increase significantly with the dry spinning system dominating the scene. 1995 melt spinning came up also, but did not reach the same quality until 1996.

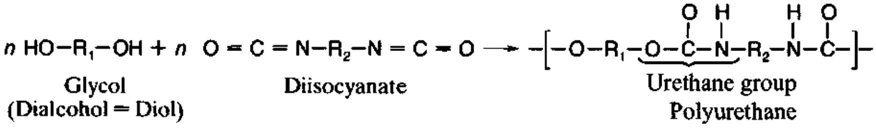
Table 2.25 Trade Products (1978) of Polyurethane Filament Yarn (Sticked Multifilaments)

Trade name	Producer	Components
Dry spinning systems		
Dorlastan, type X-200, X-220	Bayer AG, Germany	PES/MDI/semicarbazide derivative
Type V-400, V-420		PES/MDI/diamine
Lycra type 124 (123)	DuPont, USA, N-Ireland	Polyether/MDI/hydrazine
Type 126 (121, 127 133)	Holland, Canada, Brazil	Polyether/MDI/diamine
Type 128		PES/MDI/diamine
Asahi Spandex	Asahi Kasei, Japan	Polycaprolatonester/MDI/diamine
		Polyether/MDI/diamine
Espa	Toyobo Co., Japan	Polyether/MDI/diamine
Neolon[4]	Teijin, Japan	Polyether/MDI/aminohydrazide derivative
Opelon	Toyo Products	Polyether/MDI/hydrazine
	(Toray and DuPont, Japan)	Polyether/MDI/diamine
Wet spinning system		
Fujibo-Spandex[1]	Fuji Spinning Co, Japan	PES/Polyether/MDI/diamine
Lynel[2]	Fillatice, Italy	Polycaprolactonester/MDI/diamine
Chemical spinning system		
Glospan	Globe Mfg. Co., USA	PES- or copolyether ureathane/TDI/diamine
Enkaswing[3]	AKZO, Spain	PES urethane/TDI/diamine
Spancelle	Courtaulds, UK	PES urethane/MDI/diamine

1) License Amflioten (until 1978 also production of "Numa" by Ameliotex)
2) previous "Unel" Union Carbide, USA
3) License Globe Mfg. Co.
4) Production discontinued 1979
MDI = diphenylmethane-4,4′-diisocyanate, TDI = toluylene diisocyanate

2.8.1 Production of the Polyurethanes [374, 375]

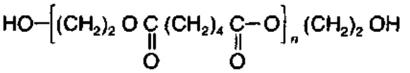
The most commonly used process is over several phases with



$$\underset{\text{(Dialcohol = Diol)}}{\underset{\text{Glycol}}{n\,HO-R_1-OH}} + n\,\underset{\text{Diisocyanate}}{O=C=N-R_2-N=C=O} \longrightarrow -\left[-O-R_1-\underbrace{O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}}_{\text{Urethane group}}-R_2-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-\right]-\atop\text{Polyurethane} \qquad (2.35)$$

a) Formation of simple linear polyurethanes according to the diisocyanate polyaddition process [376] Simple and well suited for the production of fibers is the polyurethane from butylenglycol [= 1,4-butandiol, $HO(CH_2)_4OH$] and hexamethylene diisocyanate [= 1,6-hexane diisocyanate, $OCN(CH_2)_6NCO$, Desmodur H [377]].
b) Formation of the elastomeric polyurethane block copolymer [378], a segmented polyurethane. For this a large portion of the glycol is substituted by long chain low $T_{melting}$ dihydroxyl compounds with $M \approx 2000$ during the polyadditon reaction in a). The alternation units have different sizes and consist partially of soft and partially of hard segments, connected through urethane bonds [379].
   b1) Formation of the soft segments [380–382] and preparation of their connections. The produced polymer with $S_P \leq 50$ °C and $M = 1000\ldots3000$ g/mol (= macro glycol) can be a polyether-glycol, e.g., polytetrahydrofuran $H-(HO-(CH_2)_4)_n-OH$ [377] or polyester glycol from the

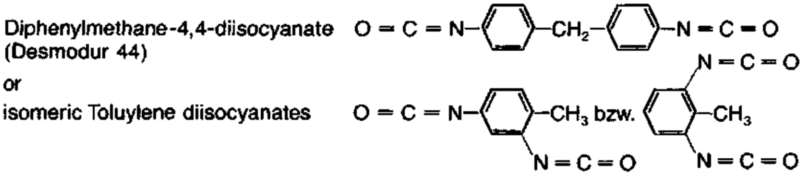
polycondensation of a dicarbonic acid with little glycol surplus, e.g., from adipic acid and ethylene glycol:



$$HO-\left[(CH_2)_2\,O\,\underset{\underset{\displaystyle O}{\|}}{C}\,(CH_2)_4\,\underset{\underset{\displaystyle O}{\|}}{C}-O\right]_n(CH_2)_2\,OH \tag{2.36}$$

or a mixture of these glycoles.

b2) By chain enlarging the hydroxylene end-groups with diisocyanates the prepolymer is formed with urethane bonds. For this mostly aromatic diisocyanates are used, e.g.,



(2.37)

which requires the diisocyanates to be used with a surplus of 3 : 2 to 2 : 1.

c) The chain length increase and the formation of hard segments, the actual polyaddition, is performed in a high polar solvent (DMF or DMAC [380]). The prepolymer is dissolved in the solvent and caused to react with a surplus of a low molecular diamine (e.g., ethylene diamine or m-xylene diamine or hydrazine) or diol (ethylene glycol or 1,4-butane diol).

The product of the reaction can form hydrogen bonds in the solvent with a physical reticulation of the hydrogen atoms and the urethane bonds.

For reaction spinning the chain lengthening and the polymer formation can be moved into the spin bath.

The structure of the finished segmented polyurethane is shown as a model in Fig. 2.105 [387]: Short chain crystalline areas of 2.5 . . . 3.5 nm and $M \approx 500 \ldots 700$ are held together by "soft" chains of about 15 . . . 30 nm and $M \approx 2000 \ldots 4000$. The latter prevents flow under tension and causes the recovery when tension is removed.

The reticulation can also be done by vulcanization of the finished filament with sulfur [388, 389] or by subsequent chemical reticulation of a mixture of a copolymer of 70% ACN, 20% ethylacrylate and

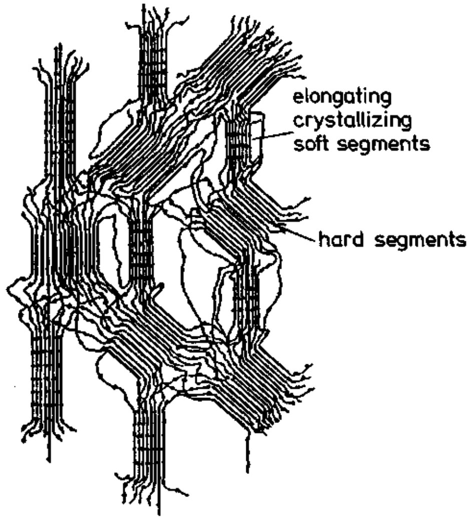


Figure 2.105
Schematic structure of a polyurethane elastomer in a low drawn state (about 200%, according to *Rinke*)

10% methacrylamide with a rubber like component from 70% ethylacrylate, 20% ACN and 10% methacrylamide [390].

Elastomers that are lengthened with glycol can be melt-spun, e.g., for bicomponent spinning of Monvelle® [389]. Elastomeric yarns on the basis of polypropylene [391] do not yet have sufficient recovery.

2.8.2 Installations and Apparati

The above mentioned complex production process can be run on a small scale in an autoclave by sequencing the individual steps, but for a production scale it is better to operate with a series of sequenced autoclaves (Fig. 2.106). The first autoclave A_1 is used to form the prepolymer. Macrodioles with a surplus of diisocyanate are entered into A_1 and solvents from the storage vessel L_1 are added. Both have the size of 70 l per 100 kg batch. Autoclave A_2 is heated to 50...90 °C. Under the same conditions solvents are added from L_2. During the transport of the prepolymer to autoclave A_3 it is filtered again and solvents from the storage vessel L_3 as well as additives are mixed in the static mixer M. In the autoclave A_3 the prepolymer is polymerized at temperatures above 10 °C with more additives. The finished solution has about 20...25% solids and a viscosity of 50...150 Pa·s. It is then transported via filtration and deaeration into the spin storage tank. The separation of the polymerization into two sequential autoclaves is advantageous. The process can be done continuously.

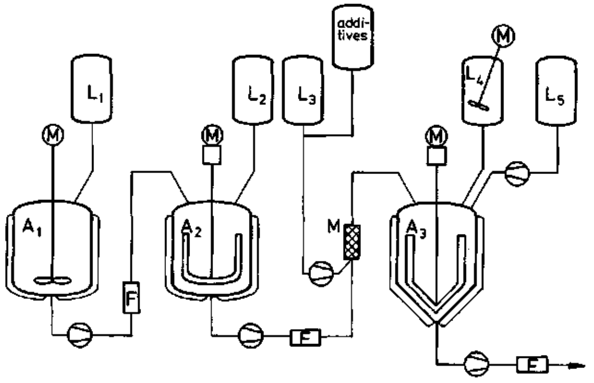


Figure 2.106
Batchwise polycondensation of PUR, in three stages (see text)

2.8.3 Wet Spinning System and Equipment

The solution (usually in DMF or DMAC) can be spun and coagulated in aqueous precipitation baths. As in Fig. 2.107, the solution is extruded through a vertical spinneret front into a 3...5 m long spin bath and taken up from there with grooved rolls at 5...20 m/min. The grooved shape is supposed to give the individual filaments in the multifilament yarn a false twist that lutes the yarns. A low draft ratio follows as does a multi phase extraction against the flow. Drying follows at about 50 m/min on large drums; here the filaments from a beginning 50...80% humidity and 0.5...2% solvent content are dried. The contact drying starts at 180...200 °C and goes to 220 °C in a second step. On the way to the next aggregate the filaments are drawn to a speed of 150...250 m/min and heat-set at temperatures above 230 °C under constant length. After cooling and finishing the filaments are wound on friction winding heads with 4 to 8 packages with yarn tensions of less than 0.01 g/dtex.

Only because of this aftertreatment and heat setting the filaments obtain their optimum properties. A temperature of 250 °C may not be exceeded. The wet spinning process is only interesting for coarse

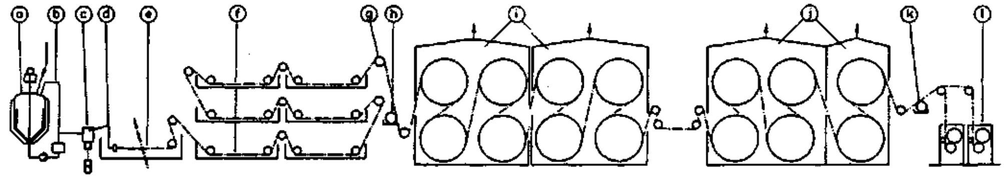


Figure 2.107 Flow sheet of a PUR elastomer wet spinning plant
- *a*) Spin dope container (solution from the last autoclave in Fig. 2.106)
- *b*) Dope circulation system and support to
- *c*) Spinning pump with drive
- *d*) Spinning pipes with spinnerets
- *e*) Coagulation bath (up to approximately 5 m length)
- *f*) Extraction and washing
- *g*) Co-sticking of individual filaments
- *h*) Oiling
- *i*) Contact dryer (in two stages)
- *j*) Contact heat setter (in two stages)
- *k*) Finish application
- *l*) Winding heads

individual and total titers, because it requires a too expensive and complicated aftertreatment compared to the dry spinning process.

2.8.4 Dry Spinning Processes and Installations

The dry spinning process is considerably more simple than the wet spinning process with aftertreatment. Today more than 80% of the spandex production is dry spun.

The highly viscous elastomer solutions (about 20–25% in DMF or DMAC, viscosity about 50...150 Pa·s) are pressed from the head pipe to the multi hole spinnerets with the help of gear pumps through a thin layer heat exchanger, so that the solution is heated to about 5...20 K below the boiling point of the solvent. According to DuPont [392, 395] this is done with large area round spinnerets with up to 16 hole fields, and the stream from the pump is divided hydraulically (see Fig. 2.108). *Fourné* [396] uses 4 to 16 individual spinnerets that are each supplied with an individual pump stream that is heated all the way to the spinneret at the spinning temperature of the solution. The spinning tube is just like the regular PAN dry spinning tube (Chapter 4.14.2) and is shown with 8 spinnerets in Fig. 4.332 (see Fig. 2.108d). Other spinneret arrangements see Fig. 2.108. The length of the yarn way in the tube is about 6...7 m. In its upper part there is a postheating zone for the inert gas (e.g., N_2) for up to 380 °C, and in the lower part a fine stainless steel fabric arrangement to laminarise the flow. The tube can be heated by liquid heating jackets in two or three zones from about 300...340 °C in the upper to 140...180 °C (for DMF and DMAC) in the lower zone. The number of the lower filament exits is equal to the number of the spun multifilaments.

Table 2.26 shows a typical yarn number range with the respective data per spin tube.

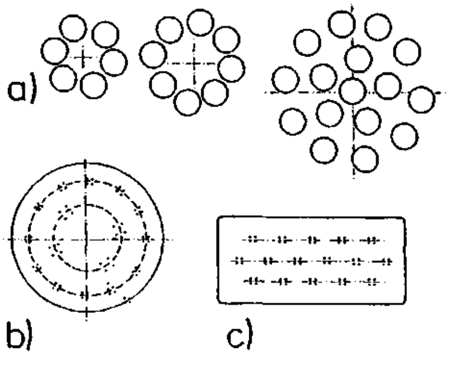


Figure 2.108
Spinneret arrangement for dry spinning of elastomeric filament yarns
- *a*) According to *Fourné* (6, 8, and 16 fold)
- *b*) According to DuPont (16 fold, European patent 0182 615)
- *c*) For a Japanese rectangular spinning tube with 16 spinnerets
- 8 spinnerets/tube (*Fourné*): See Fig. 4.330b

Table 2.26 Yarn Number Ranges. Take-Up Speeds and Spin Pumps for Elastomer Dry Spinning

Filaments/tube × dtex	Take-up speed m/min	Spinning capacity per filament[1)] g/min	Solution[1)] g/min	Spinning pumps size × rpm[1)] cm^3/revolution	Type
16 × 22	800...600	1.76	7.65	0.6 × 12.7	4 × 4
16 × 44	800...600	3.52	15.3	0.6 × 25.5	4 × 4
8 × 88	800...600	7.04	30.6	1.2 × 25.5	4 × 2
8 × 150	600...450	9.0	39.1	1.2 × 32.6	4 × 2
8 × 240	600...400	14.4	62.6	1.8 × 34.8 2.4 × 26.1	4 × 2
4 × 310	600...400	18.6	80.9	2.4 × 33.7	2 × 2
4 × 470	500...350	23.5	102.2	3.0 × 34.1 4.5 × 22.7	2 × 2
2 × 940	400...300	37.6	163.5	4.5 × 36.3	1 × 2 2 × 1)

[1)] For the higher take-up speed

The multifilaments with round or bean shaped individual filament cross-sections are drawn below from the spin tube. First they are adhered together either by the older false-twist method or by a newer air intermingling method to make a "quasi-monofil yarn" after passing by a yarn succer and a yarn cutter. Then they receive preparation and are drawn off via two godets, the speed of the second can be adjusted independently. They are spread to the bobbin gauge and pass by electronic yarn sensors to the respective bobbins, if possible with a doffer [Chapter 4.9.5] (Fig. 2.109 [400, 401]). The usual bobbins for an eight fold winder are 73.7 mm inside diameter by 80.2 mm outside diameter for yarn packages of up to 185 mm diameter by 57.25 mm traverse.

The wound yarns can still contain up to 0.5% solvent that can be reduced to toxiologically harmless values either by vacuum extraction or by drying at 70...80 °C or by sufficiently long storage.

2.8.5 Reaction Spinning Processes

Since the transformation of the NCO-prepolymers and aliphatic polyamides to high molecular urethane only takes parts of a second, it can be combined with the forming of elastomeric yarns [393, 394]. If for

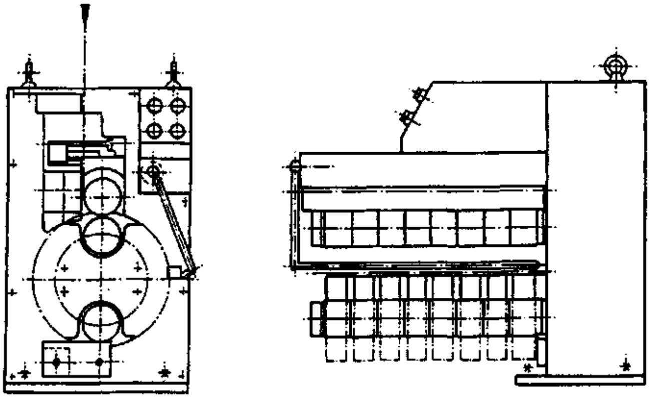


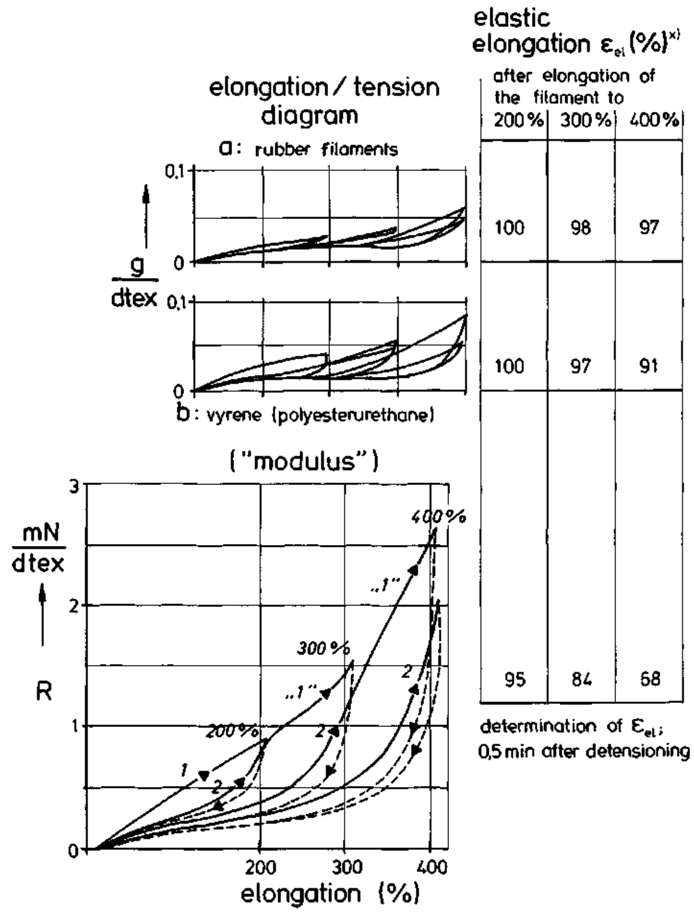
Figure 2.109 Automatic doffer winder for 8 elastomeric yarn bobbins (IWKA [537], left: for 350...1000 m/min × 0.52 kg/bobbin); for 4 yarn packages (Comoli Fermo [400], see Fig. 4.230)

example such a prepolymer is spun by including a triol like glycerin in spin baths of aliphatic diamines with portions of triamines (e.g., ethylene diamine with diethylene triamine), a relatively strong skin from cross linked polyurea urethane is formed by immediate NCO-amine reaction, that allows the thread being drawn off. The complete hardening is done either in hot pressurized water or in diamine/alcohol solutions or in toluol solutions. Thus the cross linked prepolymer structure creates a linked and segmented elastomeric yarn that is insoluble. However only a small portion is produced by this process.

2.8.6 Properties

Dominant properties are the high elasticity and the good recovery of about 100% at up to 200% elongation and of over 97% at 300% elongation. Also important is good abrasion resistance for blends with other textile materials.

Physical processes during yarn elongation and recovery as well as properties, processing, and uses are described in [374]. An example for the stress-strain diagram and subsequent recovery is shown in Fig. 2.110. Figure 2.111 also shows the maximum elongation as a function of process temperature respectively the exit temperature at the end of the dry spinning tube. Tenacity and elongation are difficult to measure as with the increase in testing length significant cross contraction occurs. In general terms the following ranges hold true: Tenacity about 0.54...1.17 cN/dtex, breaking elongation about



elastic elongation ε_{el} (%)x) after elongation of the filament to 200%	300%	400%
100	98	97
100	97	91
95	84	68

determination of ε_{el}; 0,5 min after detensioning

Figure 2.110
Stress/Strain diagrams of PUR filaments with stepwise elongation and relaxation (200%, 300%, and 400% elongation)
a) Elastic rubber filament
b) Polyester urethane yarn

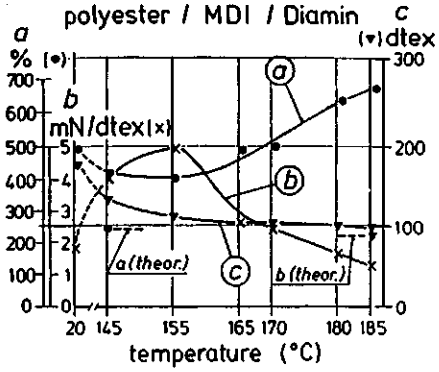


Figure 2.111
Changes of elastic filament properties (polyester/MDI/diamine) with increasing respectively decreasing orientation (hot air setting with 100% pre-elongation)
a) % elongation
b) Tension at 300% elongation ("modulus")
c) Yarn number in dtex (in a heated tube of 1 m length, 1 : 2 predrawn, i.e., from 2 m/min to 4 m/min)

Table 2.27 Physical Data for Selected Elastomeric Yarns

	Softening temperature °C	Melting temperature °C	Density g/cm^3	Moisture regain at 65% RH
Dorlastan V400	≈175	≈275	1.19	1.0
Enkaswing	210/220	250/260	1.2	≈1
Glospan/Cleerspan	215	–	1.20	<1
Lastralene			1.21	1.3
Lycra T-124 and T-126	200	–	1.2	1.3
Lycra T-128	175	–	1.3	0.8
Numa	225/230	270	1.20	1.0
Spanzelle	225	275	1.2	1.0
Vyrene	180/190	245	1.32	1.0

Light refraction slightly double refractive (optically positive)

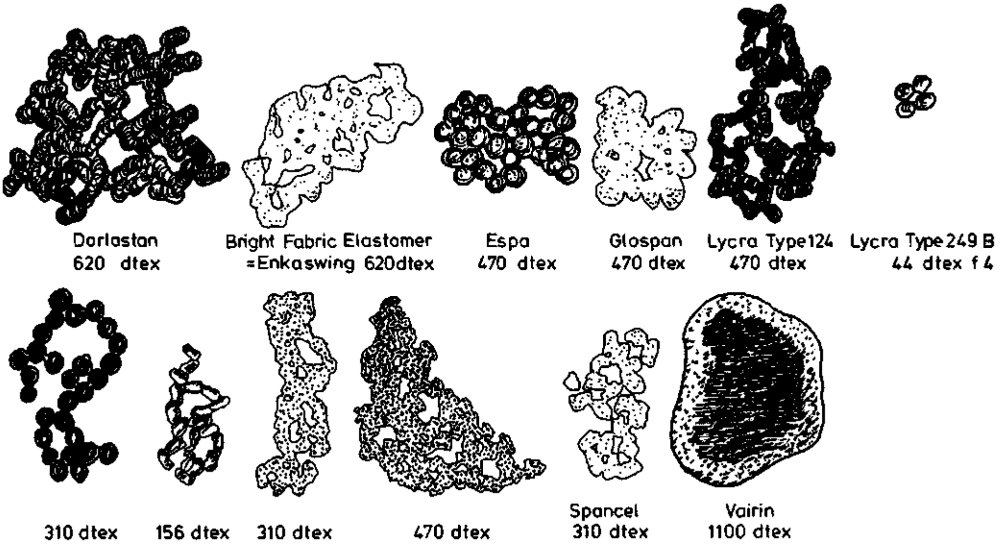


Figure 2.112 Cross-sections of polyurethane elastomeric filaments (according to *P. A. Koch* and *A. Nettesheim*) and of dtex 44 f4

400 . . . 750% of the original length, relative wet tenacity about 78 . . . 98%. Further physical data are shown in Table 2.27. Figure 2.112 also shows the divers filament cross-sections of some commercial products.

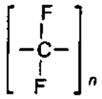
Due to the high elasticity special techniques are needed in processing; compared to rubber yarns the tenacity is three times as high and the abrasion resistance is considerably higher, so that most elastomeric yarns are much better suited for blends.

2.8.7 Polyurethane Hard Fibers

Within this fiber group only Perlon U® 518 and Igamid U® were of temporary significance. Perlon U® differs form PA 66 in the structural formula by an additional oxygen atom between the CO- and the $(CH_2)_4$ links; this lowers the melting temperature to about 184 °C. The production of hexamethylene diisocyanate and 1,4 butane diol is described by *Fourné* [46]. The molecular weight is between 9000 and 10,000; beyond 14,000 some cross linking starts to occur. The melt is unaffected by air and is extruded by nitrogen pressure, cut into chips or spun directly or via extruders at 210 . . . 225 °C to bristles. Drawing at a ratio of 1 : (3 . . . 4) should take place within 3 . . . 4 h after extrusion.

2.9 Polytetrafluorethylene Fibers (PTFE)

The polymerization of CF_4 to



$$\left[-\overset{F}{\underset{F}{C}}- \right]_n \qquad (2.38)$$

is either done under pressure in presence of NbF_5 or via radical with air oxygen or with peroxides in water. The highly exothermic reaction increases in speed as the pressure grows. Molecular weight and degree of polymerization cannot be measured properly. The molecules are probably without branches. Measuring via carboxyl end groups results in $M \approx n \cdot 10^5$ to $n \cdot 10^6$ [405]. The best known trade name is Teflon® [406, 408]. A similar fiber from polytrifluorethylene $-(-CHF-CF_2-)_n-$ is Hostaflon® [407].

2.9.1 Spinning and Drawing of the Filaments

PTFE has a high viscosity of about 10^{10} Pa · s even at 380 °C and starts to degrade already at temperatures around 360 °C. Solvents for solution spinning are not yet known. For a suspension spinning process a specific polymerization sequence is needed, and tape like parts occur with over 30% that have about 0.1 μm width and five times the length at 0.001 μm^2 cross-section. An emulsion from this, e.g., with cetane as an additive, can be spun by paste extrusion with tenacities according to Fig. 2.113.

The matrix wet spinning process is said to be more advantageous [409]. Here 60% by weight PTFE in the before mentioned size are suspended in an 8% viscose solution with the addition of alkyl- or acrylic polyglycol ether, then filtered and extruded at 20 °C through spinnerets similar to the viscose rayon spinnerets into a spin bath of 10% H_2SO_4, 16% Na_2SO_4 and 10% $ZnSO_4$ in water. The bath length is about 0.8 . . . 1.0 m, the spinneret hole diameter is 50 μm and the take-up speed is about 6 m/min. The filaments are then washed in 80 °C water and dried on drum dryers at 190 °C. The drying air has to be absolutely dust free as those particles are attracted electrostaticly and burn during sintering, thus causing black stains. The tenacity of the undrawn filaments is around 0.04 g/dtex.

For the subsequent drawing the yarn is heated on hot drums within about 9 s to 360 . . . 390 °C and drawn by the faster take-up to about seven times its length. Here the cellulose is burned off, and the PTFE

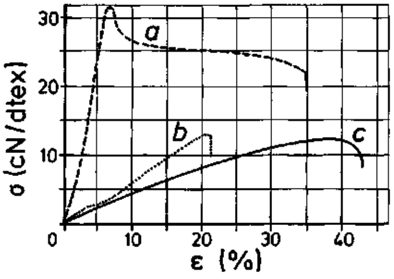


Figure 2.113
Tension elongation diagram of PTFE according to [6]

- *a*) Wet spinning with spinning transmitter (matrix process)
- *b*) Peel process according to Lenzing
- *c*) Dry spinning from a suspension

sinters to a multifilament with a tenacity of about 1.8 g/dtex at 18% breaking elongation—in this example with 2 dtex per filament. The yellow brown filaments can be bleached in boiling sulfuric acid with drip addition of nitric acid.

In a purely mechanical fiber formation process [410] the aforementioned powder is pressed in a cylinder to $\frac{1}{7}$ of the original volume eliminating all pores. The briquette is sintered in an oven without pressure to a homogeneous block, and cooling according to a specific sequence avoids any inner tensions. For the fiber formation the block is rotated and pressed against a beam of many fine steel blades that peel individual filaments from the block. During take-up these filaments are drawn to 4 to 7 times their original peeling length at 325 °C. Their individual titers are between 5 and 25 dtex per filament with a tenacity of 1.3 g/dtex and a breaking elongation of about 20%. The individual filaments are then plied to the desired total yarn titer, lubricated, dried and then wound. The yarn is pure white and very even. Figure 2.113 shows the stress-strain diagrams.

A Ram-extrusion plant (Fig. 2.114) for PTFE is very much like a piston spinning unit (Chapter 4.16) for batch production: The heater (*h*) is set so that the sinter temperature is not reached until the zones *i* through *l* for extrusion. The filaments that are extruded through the spinneret (*l*), are cooled like in melt spinning depending on the individual filament titer in air or water and then taken up, drawn, lubricated and wound.

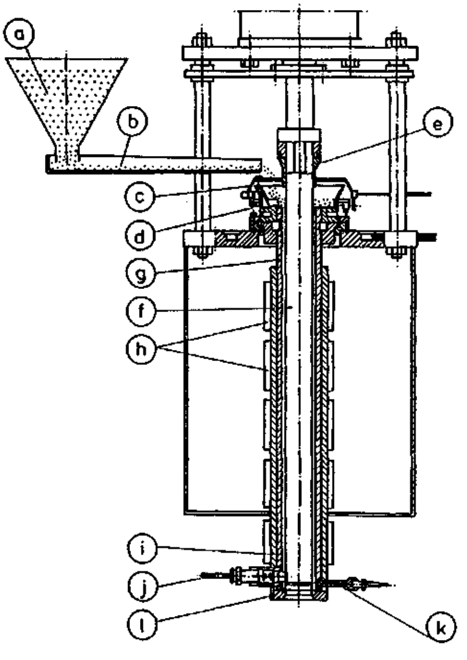


Figure 2.114
Schematic cross-section of a ram-extrusion plant for the production of filaments (PTFE, pitch, or gel)

- *a*) Dosing hopper
- *b*) Shaking groove
- *c*) Rotating distributor with skimmer
- *d*) Feeding cone
- *e*) Press ram
- *f*) Charge (filling)
- *g*) Barrel with
- *h*) upward cooling, downward heaters
- *i*) Spin pack with flat filter and spinneret
- *j*) Pressure sensor
- *k*) Temperature sensor
- *l*) Spinneret

2.9.2 Properties

PTFE is extremely resistant against heat and chemicals, UV-light and weathering, and it has the lowest known coefficient of friction. It is not wetted easily and remains flexible up to −190 °C and useful up to +260 °C. Further properties see fiber table in Chapter 11.

2.10 High Tenacity-High Modulus Filaments According to the Gel Spinning Process [412]

This solution (or probably melt) spinning process is primarily used for polyethylene with an extremely high molecular weight of $M \approx 3 \ldots 4.5 \cdot 10^6$. It can also be used for other materials with linear chain molecules without large branches as long as suitable solvents are known. Examples are PAN in DMF or DMAC, PVA in water +0.8% boric acid [413], possibly PVC and PTFE. From highly molecular PE yarns with a tenacity of over 50 g/dtex at 3...5% breaking elongation can be produced [414]. Even though this was known since 1957 [415], it has been applied only since 1980/1982 [416, 417]. Highly molecular PE is also only produced in small quantities [418], but growing slowly since 1996.

2.10.1 Principle

The high tenacity is achieved better the more statistically disoriented the carbon chains are in the solution (or melt) and the fewer shearing forces are applied during extrusion, so that all of the orientation is achieved during the drawing process [419]. Depending on the disorientation knotting of the molecular chains draw ratios of 1 : (30 to 40) can easily be achieved, 100-fold is considered normal, and over 1 : 1000 is possible. Figure 2.115 presents a model for this "shish-kebab spinning": A micro shish-kebab consists of chain folded lamellas and the filament structures above and below [420]. The lamellas can be fully drawn so that one pure long filament remains.

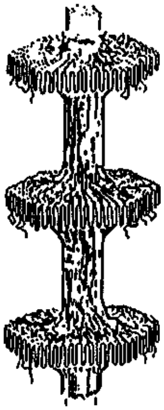


Figure 2.115
Model of a micro shish-kebab

According to [421] PE with $M_W = 1.5 \cdot 10^6$ was stabilized with 0.5% by weight di-t-butyl-p-cresol (DBPK) at 150 °C, then dissolved with 2% by weight in decaline at 130 °C, and spun through spinneret holes of 0.5 mm diameter according to the air gap process into a bath of decaline and water at 10 °C, extracted over a long distance, and drawn at 140 °C in a hot air oven. After a draw ratio of 1 : 32 the multifilament has an elastic modulus of 90 GPa, a tenacity of 3.0 GPa (≅ 36.5 g/dtex) and 6% breaking

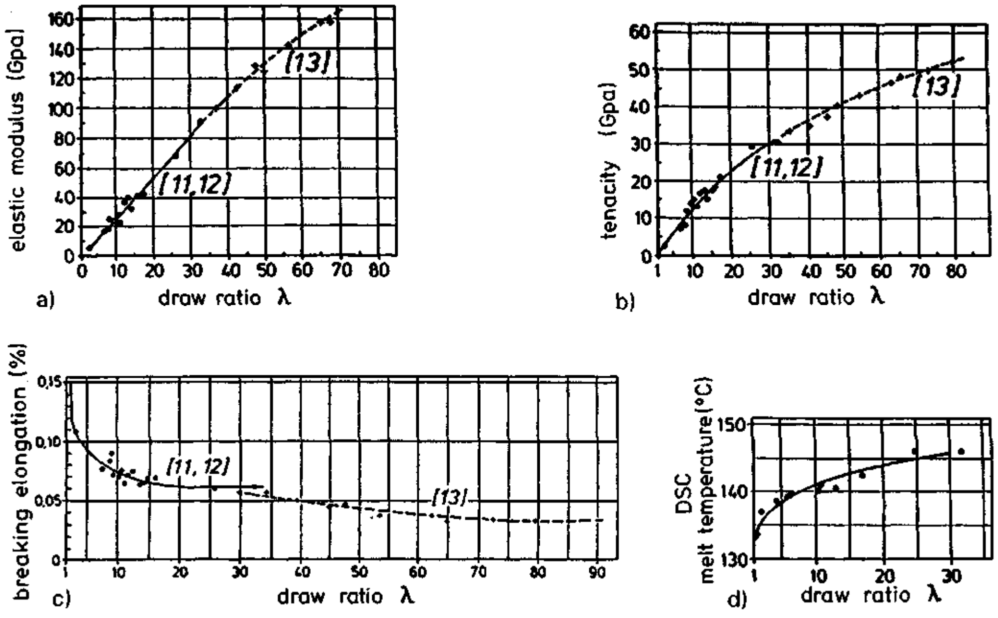


Figure 2.116 Properties of high molecular PE filaments as a function of the draw ratio, produced by the gel spinning process [11, 12, 13]
a) Elastic modulus
b) Breaking strength
c) Breaking elongation
d) DSC melt temperature [11, 12] as a function of the draw ratio

elongation. Figures 2.116a through d show the elastic modulus, the tenacity, the breaking elongation and the DSC melting temperature as a function of the draw ratio [422–424]. The draw ratio is also dependent on the temperature and the type of drawing: Wet drawing is limited to about 1 : 60 (Fig. 2.116, diagram b), while hot air drawing has achieved ratios of 1 : 90.

While the better solvent is decaline [425], paraffin oil is technically preferred, especially for working around 180...200 °C. Then the drawing is divided into a first stage of 1 : (2...4) directly following the coagulation bath, a second stage of up to 1 : 12 after extraction, and a third stage after drying at 180...200 °C in hot air with drawing over a long heated plate at ≥ 130 °C.

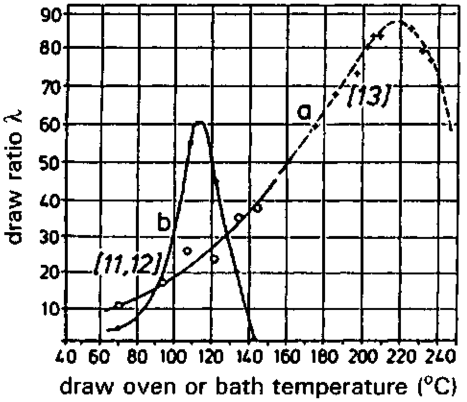


Figure 2.117
Maximum draw ratio as a function of the draw temperature for dry (a) and wet (b) gel filaments of high molecular PE ($M_W = 1.1 \cdot 10^6$)

2.10.2 Process, Machines, and Plants

Already at 2% PE concentration in paraffin oil viscosities of up to 20,000 Pa · s can occur, so that special solution plants become necessary. Also the necessary relaxation before the spinneret is different from other known spinning arrangements. Due to the high draw ratio and the low concentration the filaments exiting from the spineret are extremely thick.

Figure 2.118 shows the process diagram for the production of high tenacity gel yarns [417]: In the autoclave (10) the solvent (11) and the stabilizer (12) are mixed and heated for the paraffin oil to 140...170 °C. In the high shear mixer (15) the PE powder is pasted with this and homogenised in the twin screw extruder (18). This gel is then extruded by the spin pump through the spin head (23) into an air gap before the filaments enter into the coagulation bath (30). During take-up there is a hot air drawing zone between the godets (54) and (59). A long distance extraction (37) follows and so does hot air drying (45). This yarn can either be wound (52) and taken up from this bobbin, or it can be hot drawn continuously (63) to be wound at (72). At the appropriate areas lubrication and air tangling are added.

In the cross-section diagram 2.119 the principle of a high shear or double cone mixer is shown as well as in of Fig. 2.119b: Both conic open spiral blades comb with each other and transfer the mixing mass.

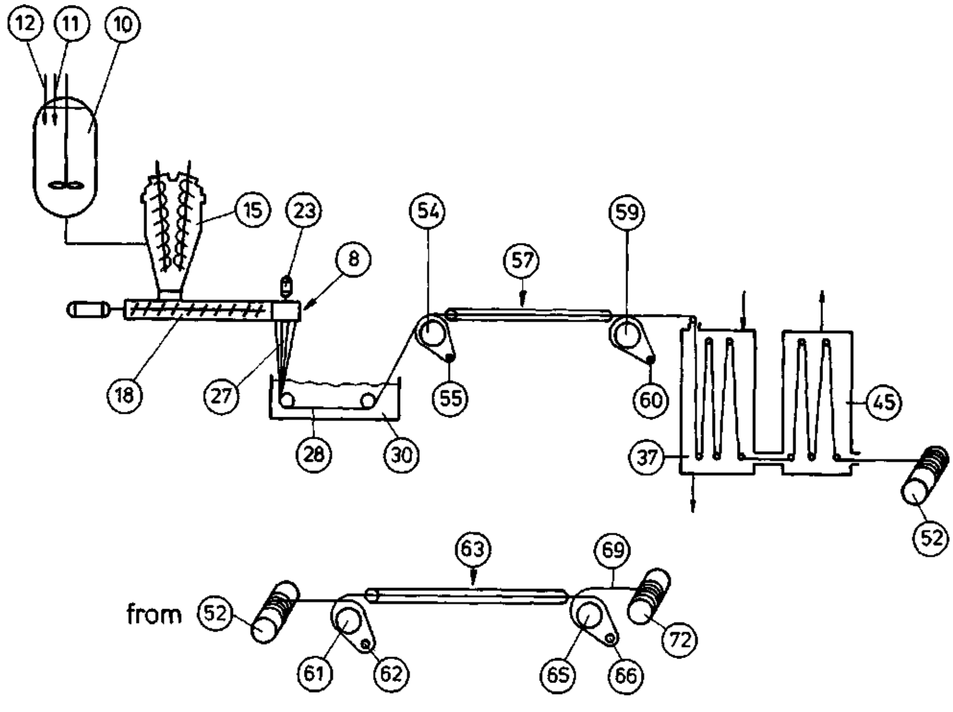


Figure 2.118 Process scheme for the production of high tenacity gel filaments

10	Dope preparation vessel	*59, 60*	Draw godet with idler roll
11, 12	PE and solvent supply	*37*	Extraction
15	High shear mixer	*45*	Dryer
18	Extruder screw	*52*	Take-up winder or continuous supply to
8	Spinning head with relaxation volume	*61, 62*	Supply godet with idler
23	Spinning pump with drive	*63*	Hot afterdraw duct or plate
27, 28	Gel multifilaments	*65, 66*	Draw godet with idler roll
30	Coagulation bath	*69*	Finish preparation and final filament
54, 55	Take-up godet with idler roll	*72*	Take-up winder
57	Hot draw duct		

Due to the screw like design and the low clearance to the wall the system is self cleaning and—very important for high viscosity—self emptying [427].

Double respectively twin screw mixing extruders are described in Chapter 4.6.4.2.

The relaxation tube (Fig. 2.120) before the spinneret consists of a jacket heated tube without anything inside. To avoid shearing forces filtration is only rather coarse. Therefore appropriate fine filters have to be arranged just before the spin pump. To spin the usual technical titers of 6 dtex per filament the spinneret holes have to have a diameter of ≈ 1.0 mm (6 dtex per filament $= 0.028$ mm filament diameter; at $c = 0.07$ and $i = 80$ the hole diameter becomes $0.028 \cdot \sqrt{(i/c)} = 0.95$ mm). A spinneret area of 60 mm diameter can contain a maximum of 140 holes and results in a spinning titer at the first godet of about 30,000 dtex with a yarn running width of 30...40 mm. For 5 m/min take-up speed a spin pump of 20 cm^3/revolution is needed. The first draw ratio is about 1 : 3 to 1 : 8. The individual zones for extraction and drawing (with an undefinable position of the draw zone) and the subsequent drying per ≥ 30 m way can be arranged according to Fig. 4.351, so that the plant parts are somewhat short. A directly following heat setting under costant length or with additional drawing improves the yarn properties.

Spinning trials with a solvent-free PAN gel with $M \approx 540,000$ ($\cong P \approx 10,200$) from a piston spinning machine proof the applicability of this process. Solvents can be DMF, DMAC, DMSO, or aqueous sodium isothiocyanide and spin baths from CH_2Cl_2 or DMSO/H_2O or NaNCS/H_2O and alcohol at temperatures of up to -30 °C. In the extraction bath one can work with acetone that evaporates on the way to the winder. The final drawing occurs in a separate step according to Fig. 2.118.

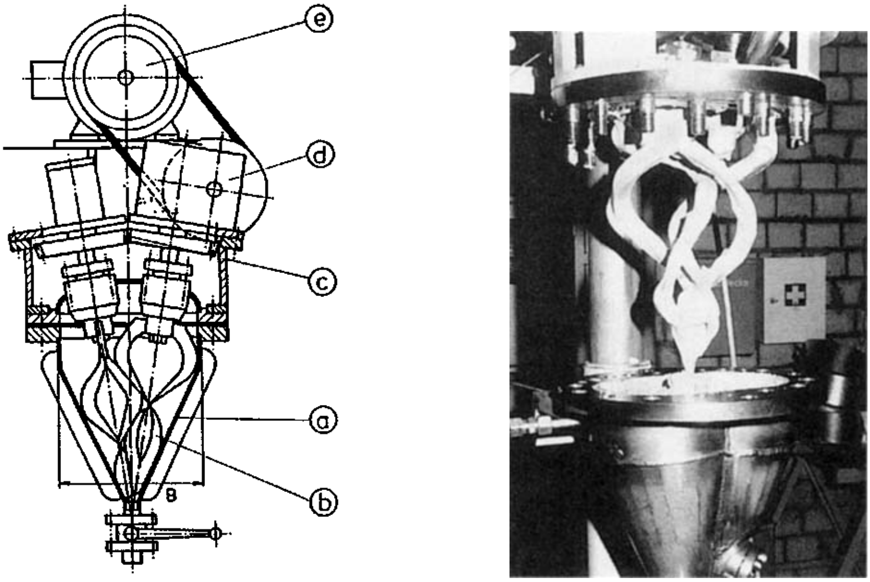


Figure 2.119a,b High shear mixer (=double cone mixer) [47]

Volume (l)	3	10	31	65	120
Width (mm)	203	515	702	884	1105

a) Double cone autoclave, jacketed
b) Combined double anchor agitator (combing)
c) Bearing housing
d) Worm gear box
e) Motor with adjustable speed drive

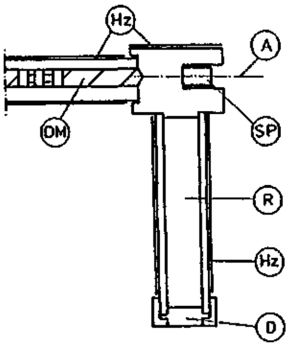


Figure 2.120
Relaxation volume (R) with twin screw mixer (DM), spinning pump (SP) with drive (A), spinneret (D) and heater elements (Hz)

2.10.3 Properties of PE Gel Filaments and Their Uses

For yarns produced by the aforementioned process tenacities, elastic moduli and elongations according to Fig. 2.121 are provided [429]. *Fourné* [424] has achieved much higher values with tenacities of 5 . . . 7 N/tex at breaking elongations of around 3% from a starting material with $M_W \approx 4.5 \cdot 10^6$.

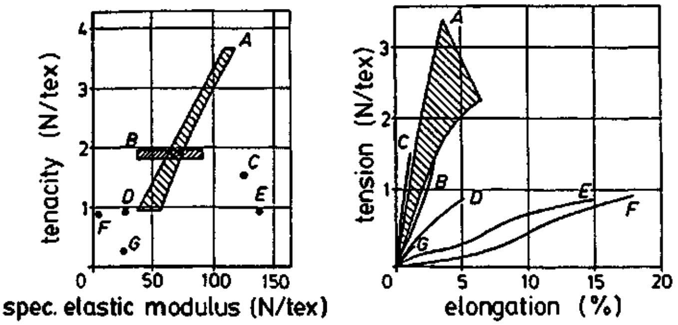


Figure 2.121
Properties of gel filaments "Dynema" compared to those of other filaments
A) HM-PE, gel spun
B) Polyaramid LM
C) Carbon filaments HS
D) E-glass
E) Polyester
F) PA 66
G) Steel

Comparative trials with melt spun PE achieved no more than 50% of the aforementioned values, even with drawing in several stages.

PAN yarns produced by this method can be drawn by a ratio of 1 : 5 to 1 : 28; in their optimum the tenacity was 43 cN/dtex and the initial modulus was 1450 cN/dtex. Higher draw ratios did not improve these values.

Most important uses fo these PE gel filaments are navel ropes, technical yarns for low temperatures and possible wet applications, and products with high tenacity and chemical resistance at temperatures under 80 °C. Other properties and uses see [429].

2.11 High Temperature and High Modulus Fibers

2.11.1 General Remarks

The definitions of "high temperature stable" (HT) and "high modulus" (HM) fibers include a variety of organic and thermoplastic fibers that have high glass transition temperatures and high decomposition temperatures, are difficult to ignite and do not feed the flame. Usually they can withstand continuous

Table 2.28 Physical Data of Aramides and Other High Tenacity Filaments

Fiber type	Trade name	Density (g/cm^3)	Tenacity cN/dtex	Breaking elongation %	Rel. loop tenacity %	Elastic modulus cN/dtex	Glass transition temperature °C	Melting temperature °C	Moisture regain %	O_2-index LOI value
Polyaramides	Kevlar	1.44		4…5	~50	300…400			≈1.5	31
	Kevlar 29	1.44	19	4		408				
	Kevlar 49	1.45	19	2.1	50…78	900…1000				
	Twaron	1.44				≈550				
	Twaron	1.45	24			≈850				
	Nomex	1.38	4.4…5.3	15…30	≈65	75…145			4.5…5	27…28
	Kermel 1	1.34	2.5…3	10…25		35…40			3.1	–
	Kermel 2	1.39	4…6	10…20		45…75			–	–
	PEEK	1.3					143	324		
	PSU	1.14…1.37		13			220 290			
	Polyarylates	1.2…1.44		50…40			173 188			
	Polyimides	1.41		32			315			
	HM-50	1.40	26.5	5.5		495			–	–
PA6	Polyamide 6	1.14					40		225	
PET	Polyester	1.39				75		260		
PE	PE-UHMT		30…50	6…3		600…1200		$\lesssim$146	0	
G	Glass	2.49…2.54				285…350				
	Basalt ≈2.6						–			
	Quartz	≈2.5						–		
	Boron Nitrate							–		
	Steel. drawn	7.75				270				
	Silicon carbide									
	Carbon HT	1.77				1320 1430				
	Carbon HM	1.91				1850 2700				
	Whisker. C-	1.9				5400				
	Fe-	7.8				260				

exposure to temperatures ≥ 180 °C without any notable damage. They also do not lose more than 40% of their tenacity after 500...1000 h exposure to 250...275 °C. Some can be exposed to long term heat of 350...450 °C. Over 450...500 °C all start to degrade rapidly. Weight losses occur in the inert gas atmosphere over 425 °C, and for para-linked polymers at about 550 °C. In Table 2.28 the physical data for polyaramides [430] and those of other fibers and materials are shown.

Aramides are distinguished into two groups: aramides with a tenacity of < 10, mostly < 6 cN/dtex and a breaking elongation of > 10 or > 15%, and aramides with a tenacity of > 12 or 20 cN/dtex and a breaking elongation of 6...11%. Aramides achieve the highest tenacity of all organic fibers; they compete with (graphitized) carbon fibers, PE gel fibers and steel wire. The specific elastic modulus ($E_{\text{specific}} = E/\gamma$ (in N · cm/g)) does not quite reach the values of carbon fibers, but it is higher than for steel or glass. The temperature—time relationship for Kevlar-29® is shown in Fig. 2.122. Kevlar® is more resistant to hydrolysis than PET, but less resistant to acids. As Kevlar® had a very promising market from the start, at least seven corporations followed with similar products within one decade after the patents by DuPont (*Kwolek, S.L.*, 1973 et al.) [430]. This class of fibers also includes polyether ketones (PEK, PEEK, etc.), polyimides (PI), polyamidimides (PAI), polychinazolindion, a heterocyclic polymer [431], polysulfones (PSU), and polyarylates (Table 2.28). Also some of the aromatic polyamides are part of this group. As they cannot be melted (except for rare exceptions), they are produced from aromatic diamines and aromatic dicarbonic acid dichlorides via interface condensation or via solution condensation. The solvents for this process should work with at least one, preferably both reaction partners, and possibly even with the resulting polymer (e.g., N,N-dialkylic acid amides, tetramethylurea, hexamethyl phosphoric acid amide, etc.). For the condensation the diamine is dissolved or dispersed in the solvent and the dicarbonic acid di-chloride is added under cooling in aequimolar quantities. The condensation temperatures are between -30 and $+100$ °C, preferably between -20 and $+30$ °C for 2...10 h and 15...25% solid contents. Solution agents (e.g., lithium chloride or calcium chloride) can increase the solubility. At the end of the condensation the resulting hydrochloric acid is neutralized (e.g., with calciumhydroxide, calciumcarbonate, ethylene oxide, or propylene oxide), degassed, and then the solution is led directly to the spinning process. Dry spinning, but preferably wet spinning is usually done from a solution with 15...25% solids at 4000...12,000 Pa · s, but even over 20,000 Pa · s. The relative viscosity of the solution should be $\eta_{\text{rel.}} \approx 1.4 \ldots 1.6$ (from a 0.5% solution in H_2SO_4 at 20 °C) to achieve good textile or industrial yarn properties. For high modulus yarns $\eta_{\text{rel.}}$ can reach ≈ 20. Coagulation bath temperatures are between 10 and 80 °C, and take-up speeds are 5...20 m/min for spinnerets with 72...200 holes, each 0.1...0.15 mm diameter [432].

For the dry spinning process the solution is extruded into about 200 °C inert gas and the take-up speed is about 100 m/min [433]. Then the filaments are drawn 1 : 1.1 to 1 : 1.3 in boiling water, washed at

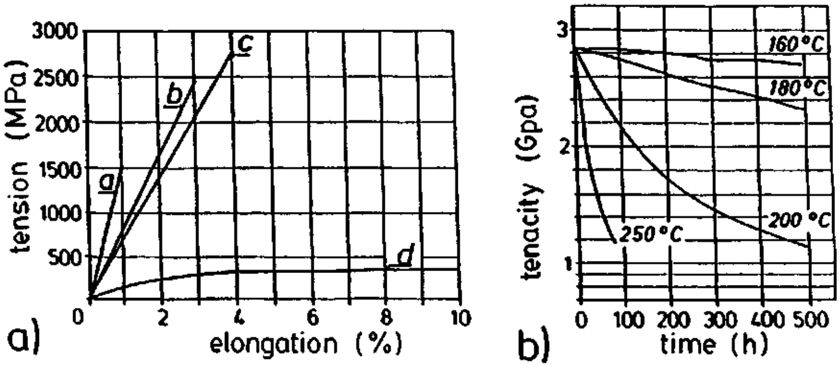


Figure 2.122 *a*) Schematic stress-strain diagram of “Filkar” (Toray) (a), “Kevlar” (DuPont) (b), “Technora HM 50” (Tejin) (c) and “Nomex” (DuPont) (d)

b) Time dependence of the tenacity of “Kevlar 29” yarn treated at different temperatures, measured at room temperature

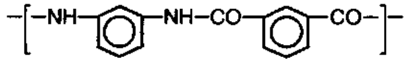
60 °C, dried and hot drawn dry at 220…350 °C by a ratio of 1 : 1.5 to 1 : 6. Lubrication, mechanical crimping and cutting follow.

Only inorganic special fibers allow higher use temperatures (Table 2.28).

2.11.2 Polyaramides

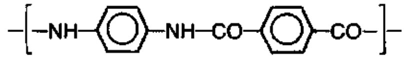
The best known aramide fibers are Nomex® (DuPont), Kevlar® (DuPont) and the similar Twaron® (AKZO) and Kermel® (Rhône-Poulenc) with the following structural formulas [430]:

Nomex



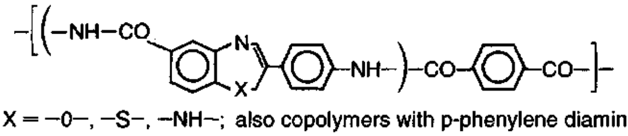
(2.39)

Kevlar
Twaron



(2.40)

Kermel



(2.41)

X = –O–, –S–, –NH–; also copolymers with p-phenylene diamine.

Nomex was first produced in 1966 [434]. It was made by polycondensation of isophthalic acid with m-phenylene diamine in DMAC [435], was then neutralized with $Ca(OH)_2$ and solution dry spun. In addition to the properties mentioned in Table 2.28 it should be mentioned: breaking torsion at 43…61 °C, hot water shrinkage at 95 °C: 1.5%, specific heat 1.2 J/kg K, heat conductivity 0.13 W/m K, decomposition temperature 371 °C, no loss of tenacity after 3000 h in 180 °C air, but after 1000 h at 260 °C drop to 65%.

Kevlar® [436, 532] and Twaron® are a PPD-T = poly-p-phenyl-terephthalamide. For the production a solution of p-phenyl diamine in HPT is mixed under cooling at 16 °C with terephthalic acid and then polycondensated between 60 and 95 °C under high shearing within a few seconds to a polymer concentration of 6 to 12%. The solvent is washed out, the polymer is dried and then dissolved in smoking H_2SO_4 at 80 °C, homogenized, filtered and spun according to the "Dry-Jet-Wet-Spinning" process (= air gap process) in a H_2SO_4-acidulous water bath. The highest mol-mass is achieved by mixtures of

HPT/NMP and DMAC/HPT of 1 : 2 respectively 1 : 1.4 [438]. At about 6…7% PPD-T concentration the solution becomes anisotropic [438] and can be spun as liquid crystal, i.e., the spun yet undrawn filaments have a very high tenacity [436], that can be increased by subsequent drawing and heat-setting at 350…450 °C.

In this solution "Dry-Jet-Wet-" spinning process the solution is spun through an air gap of only a few mm into an aqueous sulfuric acid spin bath that pours through a cone downwards. The yarn is drawn down through the downward flow and is separated at the lower end from the coagulation bath. Typical take-up speeds are about 100…200 m/min, but by bath additives (e.g., small air bubbles) they can be increased to 600 m/min.

To modify the properties one or two stage hot wet drawing zones can be included between washing and drying. Another modification is achieved by hot dry drawing at 400…420 °C after drying, especially to increase the tenacity. Further modification can be done by heat setting on hot drums at 420…450 °C; this is like dry aftercondensation (see Fig. 4.207).

Figure 2.123 shows the process diagram of a polyaramid air gap wet spinning machine with aftertreatment. The yarn speeds in the dry portion are 150 to 300 m/min depending on the yarn type; for single yarn aftertreatment up to 800 m/min have been reported.

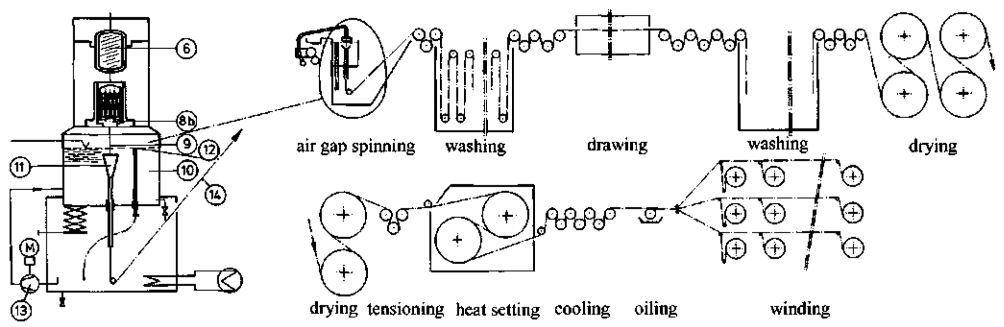


Figure 2.123 Left: Principle of the "Dry jet wet spinning" (=air gap spinning) of polyaramides
6) Dope-heat exchanger *11*) Spinning cone, with adjustable height
8) Pump block with spinneret *12*) Overflow for bath level
9) Air resp. inert gas gap *13*) Re-pumping of the spin bath
10) Spinning bath with *14*) Filament take-up
Right: Schematic drawing of a production plant for up to 124 parallel running polyaramid filaments (in a warp) of 800...about 2000 dtex each

2.11.3 Polyetherketone (PEK, PEEK, etc.)

These consist of basic aryl groups that are linked by oxygen and carboxyl groups (Fig. 2.124). These are semi crystalline polymers that are melted with spin extruders at 360...430 °C. The spinning heads as well as the spin pumps must also be heated to these temperatures. Additionally it is necessary to easily clean or exchange the parts that are in contact with the melt as it tends to decompose when not running. Quench duct cooling and lubrication, take-up, drawing and winding are as for PET-POY or PET-FOY. Figure 5.55 shows such a one position spinning machine for 2 filaments spinning and winding [486].

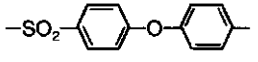
Polyetherketones were first produced in 1962 at DuPont and 1964 at ICI by condensation of acid chlorides under the Friedel-Crafts conditions [430]. High molecular products can especially be achieved in HF as a solvent with BF_3 as catalyst. A well-known trade name is Victrex® [445].

PEEK melt produced by the extruder spinning process has a viscosity of 400...500 Pa·s at 380 °C and a shear drop of 1000 s^{-1}, a viscosity of 350 Pa·s at 400 °C. Yarns produced under these conditions are continuously usable up to 250 °C with 5...6 g/dtex at 16% elongation and maintain 100% elasticity at up to 15% of their maximum tenacity. Produced are almost exclusively technical yarn titers with 6 dtex per filament. With the extruder spinning process with water bath cooling and afterdrawing coarse monofilaments can also be produced. Maximum crystallinity is achieved by afterheating at 256 °C.

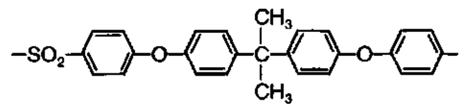
PEEK can only be dissolved in concentrated sulfuric acid. Important applications are reinforcement yarns and fabrics of laminates with carbon fibers [446]. It is said to have better radiation resistance than the traditionally used polystyrene. A doses of 1100 Mrad on a ^{60}Cobalt source finally resulted in the failure of a PEEK radiation protection.

2.11.4 Polysulfones and Polyether Sulfones

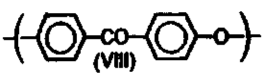
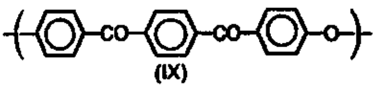
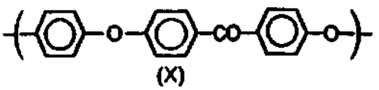
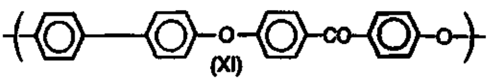
Both these materials have a similar structure:



Polyether sulfone 200 P [ICI]; $T_G \approx 230\,°C$ (2.42)



Polysulfone Udel® [Union Carbide]; $T_G \approx 192\,°C$ (2.43)

products:	A (°C)	B (°C)	C (°C)	continuous use temp.(°C)	density (g/cm³)
PEK:					
 (VIII)	T_G = 154 T_S = 367	166			
 (IX)	T_S = 384				
PEEK:					
 (X)	T_G = 144 T_S = 355	160 362	143 334	220…240	$\gamma_{crist.}$ = 1,32 γ_{amorph} = 1,26
PEEKK:					
 (XI)	T_G = T_S = 416	160			$\gamma_{crist.}$ = 0,48

viscosity of PEEK (at 1000s^{-1}) and at	360	380	400 °C
η_{melt}	480	400	350 Pa · s

Figure 2.124 Structure of polyether ketons with important properties

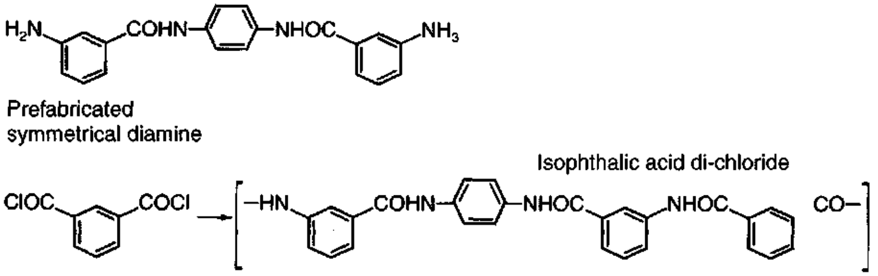
About the synthesis of these products see *Elias* [448]. They can be dissolved in DMAC and can be wet spun well after filtration.

Hollow fibers from this material are especially suited for reverse osmosis and gas phase separation (e.g., CO/H_2 or N_2/O_2). Spinning machines and spinnerets are described in Chapter 4.15.4. For the exact dimensioning and centering of the fiber walls, monofilaments are spun with individual dosing pumps, and the inside is filled with water and exactly dosed additives. After an inert gas distance of 200…500 mm the filaments run in a ≥ 2 m spin bath before their first contact with drums, pressure less if possible. Extraction then requires about 12…13 min treatment time in water at 10…14 m/min after drawing. After the subsequent drying the filaments are wound on very large diameter spools or reeled with a reel length just above the module length of the filter packages (Fig. 4.355).

Elias and *Vohwinkel* [430] report about properties.

2.11.5 Liquid Crystals

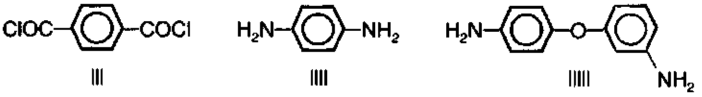
Filaments that obtain already a significant orientation of their macromolecules during spinning without afterdrawing (e.g., Kevlar® or Twaron®, Table 2.28), have a partially crystalline or partially oriented character in the solution or liquid phase [449]. This is especially achieved by polycondensation of orderly arranged co-polyamides from block components, e.g.:



(2.44)

Thus achieved higher crystallinity leads to improved thermal and mechanical properties. In the extreme case they are oriented so much during spinning that they are fully drawn during spin-winding.

Aromatic polyether amides as the Japanese HM-50 [450–452] are also part of this group. HM-50 is produced by polycondensation of terephthalic acid chloride (I) with a mixture of p-phenylene diamine (II) and 3,4′-diaminodiphenylether (III) in a polar solvent [450].



(2.45)

After neutralization with calcium hydroxide the solution is extruder spun to filaments. These are washed, dried and under extremely constant temperature around 500 °C afterdrawn.

Kevlar® or Twaron® form very long crystalline regions without long periodicity in the solution, i.e., the solution is liquid crystalline so that chain molecules are already parallel and oriented just as if drawn,

Table 2.29 Liquid Crystals as Aromatic Polyesters

Material	US patent applicant	S_P (°C)	Spinning temperature (°C)	T_G (°C)	Spinneret hole diameter (× length) (mm)	Take-up speed (m/min)
Aromatic polyester	4.224.433 23.11.1980 Celanese	345	360...370	130	0.18 × 0.25	150
Mix-polymer	4.267.289 9.5.1981 Celanese	280				
Aromatic polyester	4.265.802 5.5.1981 Celanese			285	0.188	60
Co-polyester	4.232.144 4.11.1980 Du Pont		320...340		0.23 × 0.46	549
Aromatic polyester	4.269.965 26.5.1981 Du Pont		396 335 279 340			549 549 457 549
Aromatic polyester	4.083.829 11.4.1978 Celanese		290 340		0.5 × 2.5	690
Aromatic polyester	4.130.545 19.12.1978 Celanese		290...320		as for PET 1...200 holes	

and they enter the fibers this way and provide long stretched crystal fibrils. Their thickness is between 5 and 20 nm, their widths are a multiple of this. The chain molecules lengthwise go through many crystalline areas; this results in the high tenacity.

Table 2.29 shows such liquid crystals and their US patents and some technical data. These are suited for melt spinning, mostly between 280 and 370 °C. Figure 2.125 shows a process flow sheet for a liquid crystal solution polycondensation plant: After preparation, e.g., of the diamines (A), dissolving (B) and continuous polycondensation in a vessel cascade ($C_1 - C_n$ with $n \geq 4$) follow. After degassing (D) the product is extruded onto a cooling conveyer belt (E), cut (F) and pneumatically transported under cooling to the storage tank (H).

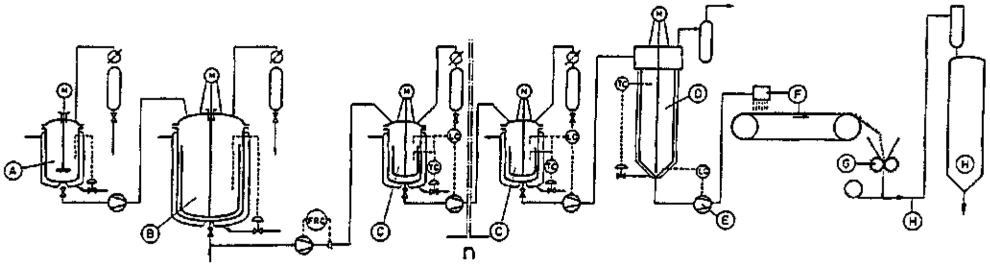
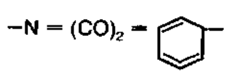


Figure 2.125a,b Schematic diagram of a (continuous) liquid crystal solution polycondensation in a cascade process

A) Preparation vessel	*E*) Metering pumps
B) Prepolycondensation	*F*) Casting head and cooling belt
C) 4 Cascade autoclaves in line	*G*) Granules
D) Continuous de-aeration	*H*) Pneumatic feeding and storage tank

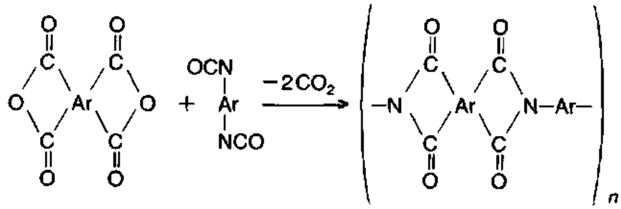
2.11.6 Polyimides

Part of the group of polyimides


(2.46)

are the polyamide-imides and the di-polyether-imides as well as those with heterocyclic groups [430]. Polyimide 2080® [519] can be wet or dry spun well from polar, organic solutions as DMF, just as P84® from solvents in DMF, DMAC, DMSO, or NMP (=N-methylpyrrolidon). Polyimide P84 is heat resistant up to 260...280 °C, and only loses 10% weight after 200 h in 400 °C air, about 30% weight at 450 °C. Glass transition temperature is around 315 °C. Carbonization happens without melting at > 500 °C.

The starting polymer for P84 [521] is produced in an one stage process by polycondensation of benzophenone tetracarbon acid dianhydrid with aromatic diisocyanates in a polar solvent and can be dry or wet spun directly.


(2.47)

The cross-section is bent trilobal, the color is a shiny golden yellow [521, 522]. 2 dtex staple fiber have the following textile data [522]: density 1.41 g/cm^3, tenacity 38 cN/tex at 32% elongation, loop and knot tenacity about 72 and 68%, elastic modulus 350 cN/tex, boil and thermo-shrinkage at 250 °C $< 1\%$. The fiber is difficult to ignite and has an LOI value of 36...38% O_2. Therefore it is particularly suited for hot gas filtration.

2.12 Other Polymer Fibers and Further Processes

Of the by now numerous new polymers only a few shall be mentioned here, that are produced by modified or completely different processes. The chemistry of these fiber raw materials is essentially described by *Falkai* [56], *Elias* [448] as well as *Elias* and *Vohwinkel* [430].

2.12.1 Silicon Dioxide Fibers

These are extremely temperature resistant and can be used in oxidizing atmosphere up to 1100 °C (see Table 2.28) [453]. They consist of 99.6% silicon dioxide and are acid resistant except for fluoric and phosphoric acid. Starting material is sodium silicate $Na_2O \cdot (3\text{–}4)\ SiO_2$, a highly viscous, oily, colorless liquid that contains 8% NaOH and 27% SiO_2 in aqueous solution, that under precipitation of silicic acid slowly decomposes. Therefore it must be stored under purest N_2. Sodium silicate is produced by melting 2 parts of quartz sand, 1 part of dehydrated soda and 0.1 part of carbon powder at about 1500 °C: $Na_2CO_3 + SiO_2 = Na_2SiO_3 + CO_2$. This finished glasslike mass is ground and dissolved in water under pressure [454].

According to a similar older process [455] sodium silicate is dissolved homogeneously in cellulose xanthogenate and spun in an acidic coagulation bath with even silicic acid distribution. Then the cellulose is pyrolized under N_2 and the filament annealed in air.

According to another process water soluble polymers with chain structure ($P \geq 2000$, e.g., polyethylene oxide with $P \approx 10^5$) are added to the sodium silicate/water solution and treated as aforementioned. This way one can also spin aluminum oxide in the γ-modification, zirconium oxide and similar materials.

For a new direct spinning process of sodium silicate data can be found in Table 2.30 [453, 456]. A normal dry spinning tube as for PAN or acetate at the appropriate temperatures is suited for this process. For winding on a tension controlled winder 0.8% spinning lubricant are added. The latter can consist of a 10% aqueous solution of a contact surface active ammonium salt [457].

The aftertreatment starts with about 1 min dip in n-HCl at 25 °C followed by washing in pure water until the product is free of Cl-ions (Enka-Type LT® [458]). This filament absorbs 10...15% water and can be completely dehydrated above 800 °C with about 10% length shrinkage. The fibers have 7...13 μm diameter with over 40% between 10...11 μm [453].

2.12.2 Polycarbosilane [430] and Silicon Carbide Fibers

Depending on the type, silicon carbide fibers are resistant in air up to 800...1250 °C. Further properties of polycrystalline inorganic fibers see Table 2.31.

Transferring dimethyldichlorsilane with sodium metal to dimethylpolysilane that changes by heating to 200 or 470 °C under inert gas of 30 bar to polycarbosilane:

$$\mathrm{H_3C{-}Si{-}CH_2{-}Si\cdots{-}CH_2{-}Si{-}CH_3} \tag{2.48}$$

Its molecular weight is about 2000 g/mol. Melt spinning at 160...200 °C and subsequent heating of the yarn in a separate process in a continuous oven (similar to Fig. 5.62) under inert gas to 1300 °C

Table 2.30 Dry Spinning Conditions for Water Glass [456] and Properties of Silicon Carbide Filaments

Water content:	15...30, preferred 20...25%
Mol ratio Na_2O:SiO_2	1 : 3 to 1 : 9
Temperature of the spin mass:	< slightly above 50°C
Spinning gas:	free of CO_2, preferred N_2
Spinning tube length:	≈ 2...8 m
Spinning tube temperature:	> 120°C
Take-up speed:	200...1000 m/min
Spin draw ratio:	≈ 20...100
Diameter of spinneret holes:	125...250 μm
Filament moister content at tube exit:	15...30% of weight
Tenacity of the filament:	7.5 19 26.4 g/tex
at take-up speed:	200 500 1000 m/min
Properties:	
Long term resistance to temperature in air:	up to 1100°C
Start of crystallization to α-crystao-balit:	after 1 h at 1350°C
Coefficient of thermal elongation:	$0.6 \cdot 10^{-4}\ K^{-1}$
Specific electric resistance:	$10^{13} \Omega \cdot cm$

Type:	*LT*	*HT*
Effective density (g/cm^3, 40% RH, 23°C):	2.0	1.8 g/cm^3
Tenacity:	800	270 MPa
	i.e., 40	15 cN/tex
Elastic modulus:	66	13 GPa
	i.e., 3.3	0.7 daN/tex
Breaking elongation:	1.5	2.0%
Moisture regain (40% RH, 25°C)		0.10 g/ fiber

results in a yarn from β-SiC. Its grain size is 5...7 nm, its tenacity 300 MPa and its elastic modulus about 300 GPa.

From dimethylchlorsilane and phenylmethyldichlorsilane [430] via polysilane styrene $[-Si(CH_3)_2-SiCH_3(C_6H_6)-]_n$, after spinning and heating to 1400 °C a polycarbonsilane with $M \approx (1\ldots4) \cdot 10$ g/mol results, that after further heating to 1400 °C splits off hydrogen, methane and benzene and transitions to black β-SiC whiskers.

It is also possible to start with a mixture of $ClCH_2Si-(CH_3)_2ClCH_2=CH-Si(CH_3)Cl_2$ and $(CH_3)_2SiCl_2$ with potassium in THF, that changes within 5 h at 66...68.5 °C [461]. These polycarbosilanes can also be extrusion-spun at 160...200 °C what is done from the spinneret to the bobbin under various external inert gases. The filaments may not be deflected on this way; this requires spindle driven winders. As the take-up speed increases the individual titer becomes finer and the yarn obtains more bending elasticity and is easier to wind.

2.12.3 Yarn Production via Carrier Filament

For yarns that cannot be produced by one of the aforementioned processes there are other methods, e.g.:

- Dissolving or dispersing in a spinnable carrier substance
- Growing from the gas or liquid phase onto a carrier filament
- Soaking the carrier filament with a solution or dispersion
- Minor additions that make the main substance more spinnable

In Table 2.32 some of the filaments are mentioned for which first a primary fiber is produced that then is transformed by reaction with the components mentioned on the right. Reaction components in gas form

Table 2.31 Properties of Different Poly-Crystalline Inorganic Fibers

Fiber	S_p (°C)	Density g/cm^3	Diameter µm	Tenacity N/mm^2	Elastic modulus · 10^{-3} N/mm^2	Specific tenacity Nm/g
Boron	2300	2.6	100	3000...4000	380...400	1150...1540
Zirconium oxide (Zircar. UCC)	2595	5.6...5.9	4...6	350...700	130...150	60...120
Boron nitride[3]	2980	1.85...2.10	4...6	350...1400	35...70	160...750
β-Silicon carbide	2700	3.2	7...10	3500	300	1090
Silicon carbide (Berghof)	2700	3.5	100	3000...3700	380...400	860...1080
Silicon carbide (AVCO)	2700	3.2	145	3500...4000	400...450	1100...1250
Aluminum oxide (Bayer)	2000	3.25	9	1200...1500	190...220	370...460
Aluminum oxide (Saffil. ICI)	2040	2.83	3	1000	100	360
Zirconium oxide (Saffil. ICI)	2715	5.6	3	700	100	130
α-Al_2-O_2 (FP fiber, DuPont)	2040	3.9	20	1380	345...379	

Fiber	Specific elastic modulus · 10^{-3} Nm/g	Specific surface m^2/g	Resistance to temperature in air °C	Resistance to temperature in inert gas °C	Remarks
Boron	144...152	< 1	500	1000	Tungsten core
Zirconium oxide (Zircar, UCC)	22...26.8	< 1	2480	2480	tetragonal, Y_2O_3-stabilizer
Boron nitride[3]	17...37.8		900	2500	
β-Silicon carbide	93.75		1300		
Silicon carbide (Berghof)	109...115	< 1	800		Tungsten core
Silicon carbide (AVCO)	125...140	< 1	800		Carbon core
Aluminum oxide (Bayer)	58.5...67.7	< 1	800	1100	
		Maximum usable temperature [°C]			
			S[1]	HT[2]	
Aluminum oxide (Saffil, ICI)	36	100	1000	> 1400	
Zirconium oxide (Saffil, ICI)	17.9	5	1400	1600	
α-Al_2-O_2 (FP fiber, DuPont)			900		Anal.: > 99% Al_2O_3

can for example diffuse into the primary fiber [463]. Boron nitride fibers can be spun as boron oxide fibers like glass fibers. Then at > 200 °C ammoniac is attached to the boron oxide, upon which at > 350 °C the formation of boron-nitrogen bonds starts while splitting off water. At > 1500 °C complete transformation takes place. Exact control of the nitrogen absorption and additional drawing at 2000 °C improve the tenacity and the elastic modulus of the BN fibers [464].

The other nitride and carbide fibers in Table 2.32 can be produced in a similar way.

Yarns, fabrics, and felts from cellulose fibers can be saturated with a water-soluble zirconium salt (with yttrium salt to stabilize the tetragonal modification of the zirconium oxide). During drying the salts precipitate in very fine distribution and are transformed to oxides at higher temperature. These formations are pyrolized and then freed from the carbon by annealing in air at much lower temperature than the sinter temperature. Here the smallest crystallites are formed that remain connected as zirconium oxide fibers.

Table 2.32 Fibers Produced by the Reaction Spinning Process

Fiber	S_P °C	Primary fiber	Reaction components
BN	3000 (Subl.)	B_2O_3	NH_3
TiN	2930	BN	$TiCl_4 + H_2$
NbN	2573	BN	$NbCl_5 + H_2$
B_4C	2350	C	$BCl_3 + H_2$
Mo_2C	2687	C	$MoCl_5 + H_2$
NbC	3500	C	$NbCl_5 + H_2$

2.12.4 Phenol-Resin Fibers

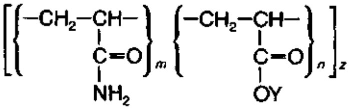
Highly interlaced phenol-formaldehyde resins with 74% C-content can be produced by a centrifugal spinning process (Chapter 5.6.1) with 0.2...0.3 dtex (about 4...6 μm diameter) and 10...60 mm staple length. The density is 1.3 g/cm^3, the LOI-index 39. After 24 h at 140 °C or after 6 h at 200 °C there is only a minor loss in tenacity. Phenol fibers can be carbonized at 800 °C with a yield of 50%.

2.12.5 Super-Absorbing Products (SAP) as Fibers

In water, these fibers absorb 50 to 150 times their own weight while the diameter increases for example for Laureal F® [467] by a factor of 23. Even with a web load of 3.5 kg/dm^2 more than 10 times the own weight remains attached without dripping or moistening the environment. Viscose or cotton without load only absorb about 30 times, wool 17 times and polyester 3 times their own weight. The Exlan® fiber consists of a PAN core and a SAP coat. Arco-Chemical [470] spins an only partially stabilized SAP polymer in an aqueous solution with the dry spinning process into air. According to [471] PP fibers can also be used as a carrier substance for already stabilized SAP powder [468].

To explain this unusual effect: The carboxyl groups in the polymer are solvated due to the contact with water or aqueous solution and they dissociate in the negatively charged carboxilat-ions. When gathering similar groups, these will electrostatically repel and the polymer group widens and accept water or similar matter in the open spaces. After stabilization, i.e. in the interlaced state, only swelling occurs. The resulting gel firmly holds the water by side valence bonds [469].

According to US patents [472, 473] it is also possible to start from hydrolyzed polyacrylo amides.



$$\left[\left\{-CH_2-\underset{\substack{|\\ C=O\\ |\\ NH_2}}{CH}-\right\}_m\left\{-CH_2-\underset{\substack{|\\ C=O\\ |\\ OY}}{CH}-\right\}_n\right]_z \tag{2.49}$$

(Y = hydrogen-aryl-ion or -alkali-ion, $m = 1 \ldots 100$, $m + n = 100$, $z = 1 \ldots 30$). Another starting material is acrylic acid.

It is also possible to start from a radical graft polymerization of ACN on starch [474]. After the alkali hydrolysis with the addition of carboxyl and carboxyl amide groups, the acid form of the resulting polyelectrolyte can be dried to a powder [476]. Instead of starch it is possible to use flour [476]. The dry powder dissolved in water becomes after neutralization a dispersion of highly swelled tightly packed gel particles almost without free water. A 10% dispersion has a viscosity of about 3 Pa·s, that can be reduced by stirring tixotropically to 0.003 Pa·s.

It is possible to extrude film or fiber. For spinning 50...80% SAP are mixed with 50...20% water and extruded like PAN paste (Fig. 2.100) in a dry spinning tube with a downward directed air stream of 40...80 °C, and the filaments are laid onto a conveyor as a fleece beneath the spinning tube. Then they are made water-insoluble in hot air at 70...120 °C or by aging at high relative humidity or radiation with ^{60}Co [477].

Applications are so far one way diapers, soil conditioners and seed encasements. Spun fibers are more advantageous than powder that can migrate. The fiber diameters are between 10 and 20 μm with large variations. The SAP fleece is protected on both sides by a thin PP spun bond (≈20 g/m^2).

2.12.6 Thermo Bonders

They are suited to lute textile fabrics. After cooling down again they have strong adhesive forces and are resistant to dry cleaning and laundry detergents. Two separate components or for example bi-component yarns from PE/PP with $S_P = 130\ ^\circ\mathrm{C}/169\ ^\circ\mathrm{C}$ fulfill these requirements: Ironing at 150 °C melts the PE and bonds the PP at the fiber intersections. However, the product is only little resistant to dry cleaning. Textile thermo bonders should therefore fulfill the following requirements:

- It must be possible to heat and process them from room temperature to 110...130 °C within 20 s on ironing presses with
- pressing with ≤ 0.4 kg/cm^2 with
- a minimum portion of thermo bonders with sufficient cohesion.
- They have to be highly resistant to dry cleaning detergents, especially tri- and per-chlor ethylene, laundry detergents, and possibly to boiling.
- It must be possible to produce powder or filaments or fibers.

Among the polyamides binary and tertiary co-polyamide systems fulfill these requirements. Caprolactam, PA 66, PA 610 and/or PA 12 salt [478, 479] are starting materials. Also co-polyester with melting temperatures of 150...200 °C [479–481] or PE ($S_P = 130 \ldots 140\ ^\circ\mathrm{C}$) and ethylene-vinyl-acetate copolymers ($S_P = 80 \ldots 120\ ^\circ\mathrm{C}$) can be used. Especially suited for spinning are copolyamide [47, 480] and co-polyester types [479, 481].

Figure 2.126 shows the melting temperatures of such a tertiary PA system that depending on the relative composition of the pure polyamides can be set to about 110 °C. With PA types from diamines and di-carbon acid instead of PA 66, it is possible to lower the melting points to about 80 °C without reducing the resistance to chemicals.

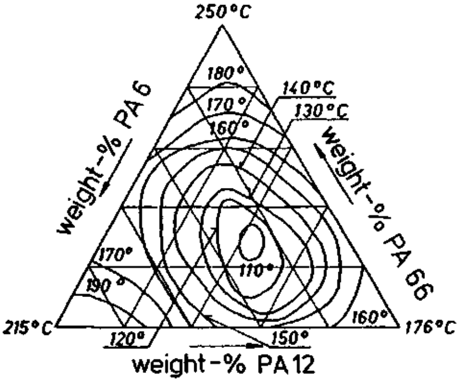


Figure 2.126
Melt temperature triangle of the copolymer of PA 6, PA 66, and PA 12

Copolymerization almost exclusively takes place discontinuously in autoclaves that are filled with the respective quantities of the individual monomers. If it is necessary to add water to PA 66 salt, one starts with a prepolymerization at about 190 °C, slowly reduces the pressure and afterpolymerization at about 20...40 °C above the melting point of the copolymer. The molecular weight can be set similar to PA 6 through growth inhibitors. The stringths are extruded into water and then cut. Powder is produced by cold grinding [482, 483] mostly with 20...25 μm diameter.

The granulate can be processed in regular extrusion spinning plants to a spun bond or melt blown web with low take-up forces. The spinning temperatures of $\approx < 220$ °C require liquid heating of the spinning beam or a low temperature Dowtherm® [484]. Drawing is not necessary. For the melt blown production [486] the compressed air temperature must be $\approx > 50$ °C above the spin melt temperature.

The spun formations after laying usually have to be stored for several hours to days to allow final crystallization and stop being sticky—until the next heat treatment for new adhesion. For winding the freshly spun web, it is therefore useful to combine/cover it with a special oily paper and calander and beam them together. This way it can also be cut to the desired width on roller blade cutters [487].

When spinning side-by-side bicomponent filaments the two components may not have more than 15% difference in viscosity at the exit of the spinneret. When spinning skin-core filaments the difference can be somewhat more. It is only important for exactly cocentric structures or for extremely thin coats (10...15%).

2.12.7 Organic Optical Fibers (POF)

Since about 1983 optical fibers made from polymers are replenishing glass filaments [488], especially for short distances. Raw materials are mostly polystyrene (PS) or polymethyl methacrylate (PMMA) with a thin fluorine skin. The conductivity loss (in dB/km) is still about 50 times as high as for special glass (GeO_2- or fluorine glass), but newer developments [490] reduce this loss to $\frac{1}{4}$ to $\frac{1}{5}$.

Even the slightest traces of metals and other impurities have to be avoided in the optical core, which makes an installation according to Fig. 2.127 [490, 491] for the production of these filaments particularly suited. The core material (2) is produced as a super pure PMMA cylinder and melted at the lower end (3) and extruded as a filament of 0.3...0.5 mm diameter. Simultaneously it is coated by a special fluorine skin of about 12 μm thickness at (3) that comes from a second cylinder (1). After air cooling at (4) it is drawn between the godet duos (6) in a hot air oven (5) in the ratio of up to about 1 : 2 and wound with about 20...25 m/min. The tenacity of the filament is about 9...11 cN/tex. Optical couplers were also developed for this.

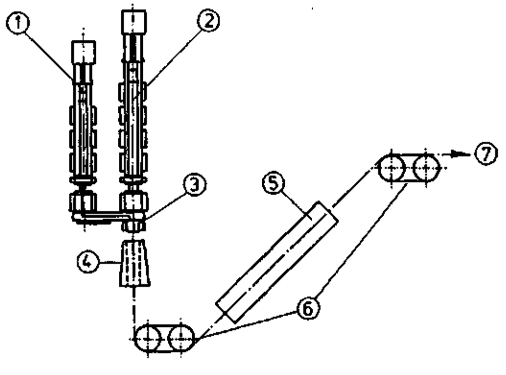


Figure 2.127
Bicomponent melt spinning installation for the production of light conductive plastic filaments [490, 491]
1) Piston type extruder for the skin material
2) Piston type extruder for the core both controlled for a synchronous quantity extrusion
3) Bicomponent (skin-core) spinneret
4) Air quench cooling
6) Godet duo take-up
5) Hot air draw duct
6) Draw godet duo
7) To (very large radius) winding

2.12.8 Electrically Conducting Filaments

Some polymers can be changed from their originally low conductivity by doting (see Table 2.33) to 2...3 digits of the conductivity of metals. Their weight specific conductivity is then only by a factor of 10^{-1} to 10^{-2} below that of well conducting metals. The conductivity still decreases over time; the materials have a moderate resistance against electrolyte solutions.

One of the polymers that can best be made conductive is cis-polyacetylene (PAC). It is produced by interfacial polycondensation (Chapter 2.12.9) by blowing acetylene onto the stationary surface of a Ziegler catalyst, e.g., $Ti(nC_4H_9)_4/Al(C_2H_5)_3$ at -78 °C [430]; this produces a thin non-homogeneous net

Table 2.33 Doting Component/Counter Ions and Electric Conductivity of Electrically Conducting Fibers1) and Metals

Polymer	Doting component/counter ion	Conductivity in S/cm
cis-poly-acetylene	I_2	$1.6 \cdot 10^2$
	Bi_2	0.5
	AsF_5	$1.2 \cdot 10^3$
	H_2SO_4	$1.0 \cdot 10^3$
	$(nC_4H_9)_4NClO_4$	$9.7 \cdot 10^2$
	$AgClO_4$	3.0
	Naphthalene sodium	80
Poly (p-phenylene)	I_2	$< 10^{-5}$
	AsF_5	500
	HSO_3F	35
	BF_4	10
	PF_6	45
	Naphthalene potassium	20
	Naphthalene lithium	5
Poly (m-phenylene)	AsF_5	10^{-3}
Poly (m-phenylene sulfide)	AsF_5	1
	AsF_3/AsF_5	0,3...0,6
Poly-pyrrol	BF_4	40...100
	$AgClO_4$	50
Poly (1,6-heptadiine)	I_2	0,1
	AsF_5	0,1
Poly (aluminum phthalate cyanine fluoride)	OBF_4	0.9
	$NOPF_6$	0,59

1) Data of the maximum electric conductivity according to [7] and from literature: "Symposium on Conducting Polymers", ACS Polymer Preprints 23/1 (1982), p. 73/138

Material	Density g/cm^3	Electric conductivity S/cm	Electric conductivity/density $M^2 \cdot g^{-1} \cdot \Omega^{-1}$
Copper	8.92	$6.5 \cdot 10^5$	$7.6 \cdot 10^4$
Gold	19.3	$4.1 \cdot 10^5$	$2.1 \cdot 10^4$
Aluminum	2.7	$3.7 \cdot 10^5$	$1.4 \cdot 10^4$
Iron	7.86	$1.0 \cdot 10^5$	$1.3 \cdot 10^4$
Lead	11.3	$0.5 \cdot 10^5$	$4.4 \cdot 10^3$
$(SN)_4$	2.3	$3.7 \cdot 10^3$	$1.6 \cdot 10^3$

layer, that can be pulled up as a filament. This cis-polyacetylene is not thermostable, starts to isomerise at 0 °C and changes above 100 °C quickly and irreversibly to the stable trans-isomer. The oxygen content in the environment has to be $< 5\%$. This doting happens over 1...2 d in the gas stage inside a vacuum chamber. At 0.05...0.25 mol-% saturation is achieved. The doting agent can also react in an inert solvent (e.g., $FeCl_3$ in nitromethane or sim.) during a dip time of only a few minutes.

According to a different process a carrier filament is pulled with the polymer that is to be made conductive through liquid air at −169 °C and then doted.

2.12.9 Interfacial Polycondensation Spinning [492]

Between the solutions of dicarbon acid chloride and diamines one can produce a polycondensation in the interfacial surface of for example non-melting polyamides [493]. Both components are dissolved in solvents that do not or only partially mix, e.g. one in water and the other in benzene. Then both are brought together in an extremely thin layer, as shown in Fig. 2.128, and the formed filament or film is taken up to the top [494]. Subsequent steps are possibly neutralization, washing, drying, preparation, and winding. This spinning process can in its most simple form be shown in a beaker. The process is a kind of reaction spinning.

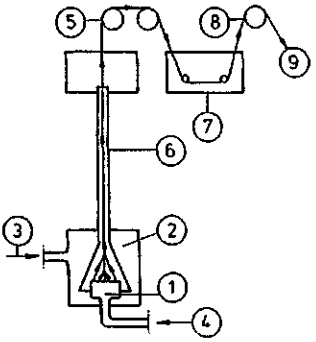


Figure 2.128
Schematic diagram of a filament spin process for interfacial polycondensation

- *1, 2*) Spinneret and spinning head
- *3*) Supply of diamine solution
- *4*) Supply of di-carbon acid di-chloride solution
- *5*) Godet take-up duo
- *6*) Filament formed in the boundary surface between the two solutions
- *7*) Washing bath
- *8*) Draw godet
- *9*) Filament to aftertreatment

2.12.10 Reaction Spinning

In the reaction spinning process the final chemical structure is not formed until after the extrusion into the coagulation bath, similar to spinning viscose. This way it is for example possible to extrude polyamide acids to filaments that are then changed by cyclohydration to polyimide filaments. Also some segmented polyurethane elastomer filaments can be produced by this process.

2.12.11 Emulsion and Suspension Spinning

According to this process filaments can be produced from non-soluble and non-melting polymers. First they are dispersed in a commonly spinnable mass, possibly with the aid of a spinning agent [495]. This dispersion is spun and treated following the process for the carrier substance, and the latter is then dissolved, melted, evaporated or pyrolized. The difficult part is to keep the dispersed mass together during the removal of the carrier. Size and form of the suspended parts are decisive for the coherence, the tenacity of the filament, etc. Parts of the size 5...1000 nm at a ratio of diameter to thickness of about 400:1 are advantageous [495]. Thus PTFE and others can be transformed into filaments [496], also mixtures of PVC with PVA or matrix fibril filaments from PA 6 and PET or ceramic that was spun and aftertreated in viscose solutions.

2.12.12 Electrostatic Spinning [497]

Here a polymer solution is charged by an electrode in an electrostatic field and then is sprayed at an electrode edge in the direction of the field lines of a strongly non-homogeneous field. The here formed plugs are pulled into the direction of the opposite electrode to a fine filament, while the solvent evaporated by temperature and/or vacuum. The formed fibers of about 1 . . . 10 μm diameter are collected at the opposite electrode and taken up continuously.

Electrostatic melt spinning with a starter melt film is described in Fig. 2.83.

2.13 Fibers from Natural Products [498, 499, 503, 504]

Some raw materials for synthetic fibers can be gained from natural products, e.g., tetrahydrofuran as a preproduct to adipic acid from pentane containing waste (corn cobs, oat shell, straw) or castor oil for sebacic acid. These preproducts have become uninteresting by now due to fully synthetic raw materials. This is different for fibers that contain a micelle of the original raw material as for example viscose [053] or cupro [503, 504], or that consist from its basic building substances, e.g., protein, casein, and alginate fibers. For an inorganic fiber basalt is a useful raw material.

2.13.1 Protein Fibers [500]

Originally it was considered as an ideal blend for wool, its importance has dropped considerably over the last twenty years. They might come back as artificial protein food fibers to cover the world demand for proteins. As raw materials soy beans and corn proteins are available, also casein and peanut proteins, etc. Protein can be gained with the help of bacteria from peanut waste [501] or from natural gas or crude oil waste [502]. Thus produced "textured foods" will some day have a tremendous market.

On the other hand Zein textile fibers (e.g., Vicara® in the USA (1948), Lanital® in Italy and Belgium, Marinova® in Belgium and in the German Democratic Republic, and Fibrolane® in the UK) have been discontinued.

The protein is first extracted from soybeans or corn and then gained by acid or rennet coagulation. Here the cross links must be denatured by splitting to generate stretched chain molecules that are suited for fiber formation. After drying and fine grinding the protein is dissolved in diluted soda lye. The solution has to mature to a viscosity of 100...200 P. Then it is de-aerated and after filtration spun in an aqueous coagulation bath that contains NaCl for food applications or formaldehyde and glucose or sulfuric acid for textile fibers. After 500...600 mm bath way the filaments are withdrawn through godets, plied, lightly drawn, neutralized, and rinsed in a long bath. Then they are cut to fibers or wound to a cake.

Figure 2.129 shows a process scheme for this process with notes for a production of 1000 kg dry protein fibers per 24 h.

The protein content of soybean, peanut, and corn flour is around 44...45%, and the prices in 1972 were about $\frac{1}{8}$ to $\frac{1}{12}$ of those for milk or meat protein that only contain half the protein content. The fibrous protein products roughly have the structure of beef or could be added to ground beef for "hamburgers". The interest disappeared with the shortage of proteins during the oil crisis.

2.13.2 Alginate Fibers

Alginic acid is extracted from dried and ground algae with a solution of soda and NaOH. After coagulation it is neutralized with soda and the soda alginate solution is spun in an aqueous bath with calcium chloride and a tenside. Thus produced fibers are soluble in alkali and soap solutions. Therefore they are used wherever such solubility is desired, e.g., for special effects in textile fabrics or for self-dissolving medical yarns.

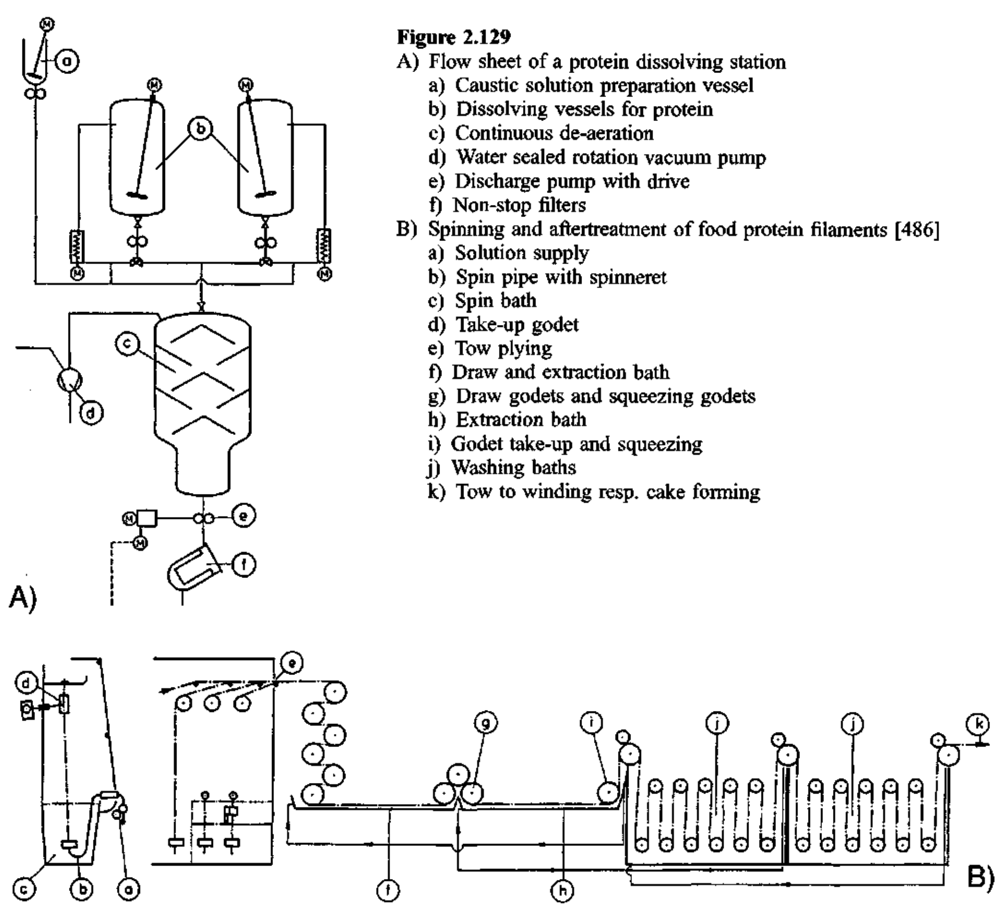


Figure 2.129
A) Flow sheet of a protein dissolving station
  a) Caustic solution preparation vessel
  b) Dissolving vessels for protein
  c) Continuous de-aeration
  d) Water sealed rotation vacuum pump
  e) Discharge pump with drive
  f) Non-stop filters
B) Spinning and aftertreatment of food protein filaments [486]
  a) Solution supply
  b) Spin pipe with spinneret
  c) Spin bath
  d) Take-up godet
  e) Tow plying
  f) Draw and extraction bath
  g) Draw godets and squeezing godets
  h) Extraction bath
  i) Godet take-up and squeezing
  j) Washing baths
  k) Tow to winding resp. cake forming

2.13.3 Filaments on Cellulose Basis

These filaments and fibers are part of the chemical fibers that are extensively described in the literature:

- Hydrate cellulose: e.g., viscose rayon [503] and cupro rayon or staple rayon [504],
- Acetylized cellulose as 2-, 2.5-, or triacetate [504],
- Nitro rayon that is no longer produced [505].

2.13.4 Basalt Fibers [507–509]

Basalt fibers are spun according to a process similar to Fig. 5.56 from the melt; filament breakages due to the centrifugal force or smallest contaminating enclosures are desired. To spin basalt filaments, e.g., in principle as in Fig. 5.56a and 5.57, highest melt purity is needed. To obtain this the basalt is melted and granulated with water by central removal from the melting pot. These chips are then melted again in a Pt-Rh-pot, lead to a spinneret from the same material according to Fig. 4.141 and spun gravimetrically through holes in the spinneret bottom at 1350...1420 °C. The filament bundle is taken up downwards at about 2000...5000 m/min, prepared at 1.00...1.20 m below the spinneret and wound contactless.

The raw material cost is $<\approx 1\%$ of the respective glass cost. Also does basalt have chemical advantages, especially with $>\approx 50\%$ SiO_2 and $<\approx 14\%$ Fe_2O_3, etc. (Table 2.34). In acidic compounds there is a slow corrosion [506]; the resistance against alkali media is good, even at higher temperatures, e.g., in cement; this is probably due to the ZrO_2 content. Filaments have a tenacity up to 700 °C of $(175\ldots215)\cdot10^7$ Pa and an elastic modulus of about $(7\ldots10)\cdot10^{10}$ Pa, both of which decline beyond 700 °C slowly to the highest useable temperature of about 1100 °C.

Table 2.34 Composition of Basalt (Weight %)

	Loss	SiO_2	TiO_2	Al_2O_3	$FeO_3 + FeO$	CaO	MgO	$Na_2O + K_2O$
Basalt from Berestovetsk (Ukraine)	1.7	50.0	0.65	16.25	14.55	5.0	0.35	2.75
Pyroxene Porphyrite from Khavochezersk	3.0	49.2	1.2	13.9	12.4	7.4	9.8	3.0
Basalt from Marneulsk (Georgia)	1.4	52.1	0.9	15.07	10.45	10.42	6.56	3.12

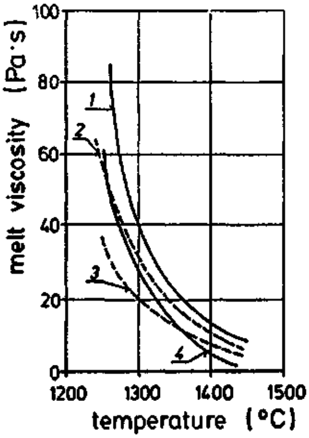


Figure 2.130
Melt viscosity temperature relation of basalt
1) Marneulsk
2) Aluminum-boron-silicate glass
3) Berestovetsk basalt
4) Pyroxene porphyrit.

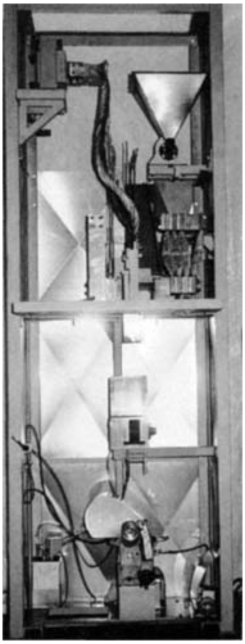


Figure 2.131
Melt spinning machine for melt temperatures of up to about 1450 °C and for direct winding take-up speed of up to 4000 m/min, as e.g., for basalt multifilaments [486] (see also Fig. 5.59)

During gravimetric spinning the filament fineness depends on the pressure in the melt column above each spinneret hole and the viscosity. The melt pressure is only (3...6) cm high · about 2.8 g/cm^3, and the viscosity is between 10...30 Pa · s (Fig. 2.130). This allows the calculation of the theoretical capacity per hole according to Hagen-Poisseuille $C_{theor.} = K \cdot H \cdot D^4 \cdot \gamma / L \cdot \eta$ with $K = \eta \cdot g/128 = 0.2408$, H = melt height in m, η = kinematic viscosity in m^2/s. The hole diameter can only be varied in a narrow range or the filaments will not form. With 9...12 µm filament diameter about 0.8 kg/24 h holes can be spun [507].

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$$\begin{array}{llll} \text{(1st order)} & -1/a_1\, dc_{A1}/dt = kc_{A1} & & \\ \text{(2nd order)} & -1/a_1\, dc_{A1}/dt = kc_{A1}{}^2 & \text{or} \quad = kc_{A1}\, c_{A2} & \\ \text{(3 rd order)} & -1/a_1\, dc_{A1}/dt = kc_{A1}{}^3 & \text{or} \quad = kc_{A1}{}^2 c_{A2} & \text{or} \quad kc_{A1}c_{A2}c_{A3} \end{array}$$

    (c_A = concentration with indices 1, 2, 3 for the respective solutions)

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