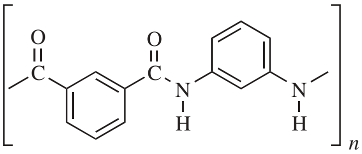
POLYAMIDES, AROMATIC

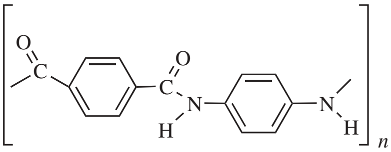
1. Introduction

Aromatic polyamides first appeared in the patent literature in the late 1950s and early 1960s, when a number of compositions were disclosed by researchers at DuPont (1–3). These polymers were made by the reaction of aromatic diamines with aromatic diacid chlorides in an amide solvent. Over one hundred examples of aromatic polymers and copolymers described in patents were listed in a 1989 book (4). Another extensive list of polymers was provided in the previous edition of this encyclopedia 5).

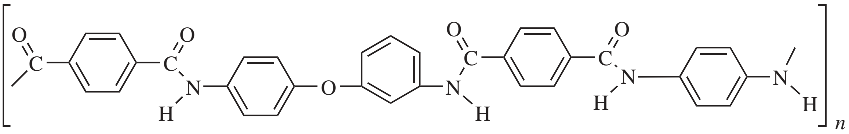
Forty years later, after the expenditure of much time and money, the number of commercially important aromatic polyamide polymers has been reduced to three, two homopolymers, poly(*m*-phenylene isophthalamide) (MPDI) and poly(*p*-phenylene terephthalamide) (PPTA), and one copolymer, copoly(*p*-phenylene/3,4′-diphenyl ether terephthalamide) (ODA/PPTA) (6):



poly(*m*-phenylene isophthalamide) MPDI



poly(*p*-phenylene terephthalamide) PPTA

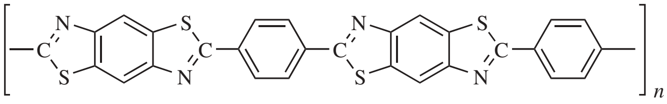


copoly(*p*-phenylend/3.4′-diphenyl ether terephthalamide ODA/PPTA

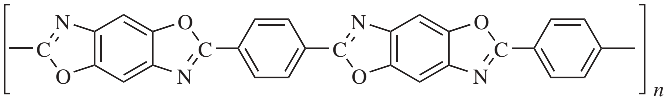
Because fibers from these aromatic polyamides have properties that differ significantly from the class of fibers known as polyamides (see Polyamides, Fibers), the U.S. Federal Trade Commission adopted the term “aramid” as designating fibers of the aromatic polyamide type in which at least 85% of the amide linkages are attached directly to two aromatic rings.

The important properties of this class of polymers include thermal and chemical stability and the potential for high strength and modulus. Aliphatic polyamides melt at temperatures below 300°C, whereas most aromatic polyamides do not melt or melt above 350°C. Aramids also exhibit greater chemical resistance and low flammability. These properties derive from the aromatic character of the polymer backbone that can provide high chain rigidity. Aromatic polyamide fibers can have very high strength and modulus, and these properties persist at elevated temperatures. Because of their low density, aromatic polyamides have higher specific strength and modulus than steel or glass. In recent years, design engineers have been able to utilize these unique properties to create products which protect personnel from fire, bullets and cuts, reduce the weight of aircraft and automobiles and hold oil drilling platforms in place.

There are several other aromatic polymers, not polyamides, but which form fibers with high chain rigidity and similar properties. These would include poly(*p*-phenylene benzobisthiazole) (PBT) and poly(*p*-phenylene benzobisoxazole) (PBO) (Chap. VII of Ref. (4)):



poly(*p*-phenylene benzobisathiazole) PBT



poly(*p*-phenylene benzobisoxazole) PBO

There is no systematic nomenclature for aromatic polyamides; however, several codes can be found in the literature. Poly(*m*-phenylene isophthalamide) is referred to as MPD-I or MPDI, poly(*p*-phenylene terephthalamide) is referred to as PPTA or PPD-T, and copoly(*p*-phenylene/3,4′-diphenyl ether terephthalamide) is referred to as ODA/PPTA or HM−50. Another important polymer, although not available in commercial quantities, is poly(*p*-benzamide), PBA. Codes will be used throughout the article to refer to these materials.

2. Sources of Ingredients

The principal ingredients for the manufacture of aromatic polyamides on a commercial scale are the diamine and diacid chloride monomers, plus the solvents used for the polymerization reaction. The chemical processes reported to be used for preparation of each of these ingredients are described in this section.

2.1. Solvents. The key polymerization solvents are readily available from several sources. They are: dimethylacetamide (DMA), dimethylformamide (DMF), *N*-methyl-2-pyrrolidinone (NMP) and hexamethylphosphoramide (HMPA).

2.2. Monomers. *m*-Phenylene diamine (MPD) can be prepared by the continuous liquid phase hydrogenation of *m*-dinitrobenzene at moderate temperatures (7). One process employs a dispersion of the *m*-dinitrobenzene in water (8); another uses a solvent, such as DMF, which dissolves both reactant and the MPD product (9). Catalysts for the hydrogenation include platinum, palladium and nickel that must be recovered by filtration. Purification steps include vacuum distillation.

p-Phenylene diamine (PPD) can be made in a two stage process (10). In the first stage aniline and sodium nitrite undergo diazotization to form benzenediazonium chloride, which in turn reacts with excess aniline to form the intermediate, diphenyltriazine. At low pH, diphenyltriazine is rearranged into para-aminoazobenzene. Finally, para-aminoazobenzene is cleaved by catalytic hydrogenation into PPD and aniline. The aniline is recycled to the first-stage reaction. The PPD then undergoes a series of purification steps, including vacuum distillation.

3,4′-Diaminodiphenyl ether (3,4′ODA) can be prepared from 3,4′dichlorodiphenyl ether by treatment with aqueous ammonia in the presence of an amide solvent (e.g. NMP), using copper as a catalyst (11). Dichlorodiphenyl ether is prepared by treating the sodium salt of *p*-chloro phenol with *m*-dichlorobenzene in the presence of aqueous NaOH, followed by removal of the water and subsequent treatment with dimethylene glycol diethylether and CuCl (12).

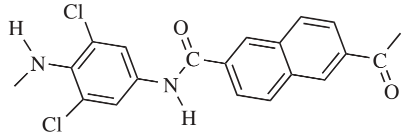
Phthaloyl chlorides (ICL and TCL) are made by at least two processes, both involving the chlorination of phthalic acid. In the first (13), xylene is chlorinated by a photochemical reaction to form hexachloroxylene. The hexachloroxylene then reacts with phthalic acid to give the corresponding phthaloyl chloride and byproduct HCl. Phthaloyl chloride is purified by double distillation. To produce isophthaloyl chlorides chlorides (ICL) by this reaction, *m*-xylene and isophthalic acid are the starting materials. To produce terephthaloyl chlorides (TCL), the process starts with *p*-xylene and terephthalic acid. Phthaloyl chlorides can also be produced by reacting intermolecular anhydrides of the corresponding acids with phosgene in the presence of an amide catalyst such as DMF or DMA (14).

3. Polymer Properties

3.1. Chemical Structure. A wide variety of aromatic polyamide polymers and copolymers have been disclosed in the patent literature. Table 1 provides a partial list of structures, the inherent viscosity of the polymer (a measure of molecular weight), and two thermal characteristics of the polymers. Many additional examples can be found in the literature (4,5).

With the exception of the A-B type polymer, poly(*p*-benzamide), the polymerizations are of the A-A plus B-B type. A further distinction can be made between monomers with para orientation, e.g. PPTA and those with meta orientation, e.g. MPDI. The meta oriented polymers are less easily crystallized, and therefore usually remain in solution throughout the polymerization. In some cases they can be spun into fibers directly from the polymerization medium. Para-oriented polymers, on the other hand, will tend to crystallize as they reach a certain chain length, so that they precipitate from the polymerization solution. This can limit the level of molecular weight that can be achieved, as will the nature of the solvent and the polymerization temperature.

Another important characteristic of the monomers is the presence of pendant groups attached to the aromatic ring. These pendant groups include alkyl, halogen, alkoxy, cyano, acetyl, and nitro. In addition to the simple phenylene compounds, diamines and diacid chlorides based on naphthalene and 4,4′-biphenyl have been used. A variety of monomers with bridging units have also been explored, of the form:



where X can be oxygen, sulfur, sulfone, keto, amine or isopropylidene.

Thus the number of chemical structures that could be (and has been) explored is quite large, especially when one considers the possible copolymer combinations.

3.2. Physical and Chemical Properties. Molecular Weight The number average molecular weight (M_n) of aromatic polyamides is generally in the range of 10,000 to 30,000, which is typical of condensation polymers. Because the measurement of M_n and M_w (weight average molecular weight) is difficult and time consuming, the molecular weight of aromatic polyamides is commonly characterized by a dilute solution viscosity parameter termed "inherent viscosity" (η_{inh}). Inherent viscosity is an approximation of "intrinsic viscosity" ($[\eta]$), which, in turn, is classically related to molecular weight by the Mark–Houwink equation.$[\ \eta\ ]$=kMwa

Values of k and a in this equation have been measured for several aromatic polyamide solutions in 96% sulfuric acid (15,16).

PPTA	$k = 0.008$	$a = 1.09$
poly(tetramethyl-*p*-phenylene terephthalamide)	$k = 0.0063$	$a = 0.96$
poly(*p*-phenylene-2,5-dimethyl terephthalamide)	$k = 0.0021$	$a = 1.16$
MPDI	$k = 0.013$	$a = 0.84$

k has the units mL/g (divide by 100 to obtain the more commonly used units for η_{inh} of deciliters/g).

The viscosity/molecular weight relationship deviates from the Mark-Houwink equation at high levels of molecular weight (15). For PPTA this nonlinearity is pronounced above $M_w = 40{,}000$. Thus at high levels of molecular weight, inherent viscosity will be somewhat misleading as an indicator of M_w.

Inherent viscosity is defined as:ηinh=ln(tsoln/tsolv)/c

Where t_{soln} is the flow time for the polymer solution in the viscometer, t_{solv} is the flow time of the solvent and c is the concentration of polymer in the solution specified as 0.5 g/dL (17). Thus η_{inh} has the units of reciprocal concentration. Different solvents have been used. For the *p*- oriented polymers, the normal solvent is 96–98% sulfuric acid. For the *m*- oriented polymers amide solvents are often used in place of sulfuric acid.

Molecular Weight Distribution The polydispersity index (M_w/M_n) for PPTA has been estimated by gel permeation chromatography to be near 2 for low molecular weight polymers and nearer to 3 for polymers with $M_w > 35{,}000$ (15).

Thermal Properties High melting point is one of the key distinguishing properties of aromatic polyamides. (In most cases the melting point exceeds the decomposition temperature, so that the material chars). A number of scientists have studied the thermal characteristics of aromatic polyamides via Differential Thermal Analysis (DTA). Data for melting point are included in Table 1. The melting points of these polymers were empirically identified with the endothermic phase transitions from DTA measurements. One study did not detect a melting point for PPTA (18) while another (19) did (530°C). This has been attributed to molecular weight differences.

Thermogravametric Analysis (TGA) provides a measure of polymer thermal stability. In this test polymer samples are heated at a programmed rate and sample weight is recorded as a function of temperature. Two studies (18,19) made TGA measurements and reported the temperature for 10% weight loss (see Table 1). The thermal stability of these polymers is lower in air than in nitrogen.

Solubility Solubility of selected aromatic polyamides in a variety of solvents has also been measured (18). In general PPTA is soluble only in strong acids, such as sulfuric, hydrofluoric and methanesulfonic acids (all of the polymers cited are soluble in these acids). MPDI is also soluble in the amide solvents (DMF, DMA, and NMP) and in dimethyl sulfoxide, as are most of the substituted variations of these two polymers. Solubility in the amide solvents is increased by the addition of salts such as LiCl and $CaCl_2$. This class of polymers is generally not soluble in formic acid or *m*-cresol, which are common solvents for aliphatic polyamides.

Analytical and Test Methods The properties described above are all determined by well known techniques in polymer chemistry. A description of each of the methods can be found in textbooks (17).

4. Polymerization

4.1. Laboratory Synthesis.

Solution Polymerization Most of the examples in the patent literature utilize solution polymerization. In this technique, an aromatic diamine is dissolved in an amide solvent and a stoichiometric quantity of an aromatic diacid chloride is added to the diamine solution while stirring vigorously. Important factors include monomer stoichiometry, ingredient and solvent purity, anhydrous conditions, diamine concentration (and therefore polymer concentration), and temperature of the starting diamine solution.

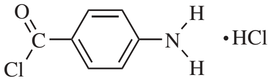
The primary polymer properties that are sought in these polymerizations are high polymer molecular weight and freedom from impurities that could impact the properties of products prepared from the polymer. All of the factors listed above can affect molecular weight. Stoichiometric imbalance will lead to excess ends that cannot react. Impurities, including water, can react with the active ends of one of the monomers. High temperature can lead to side reactions that produce unreactive ends. Since the reaction between an acid chloride and an amine is highly exothermic, the heat generated can significantly increase the temperature of the polymerizing solution. The extent of the temperature rise will depend on the diamine concentration and the degree of cooling.

For polymers that remain soluble in the polymerizing medium, such as MPDI in NMP, the reaction is rapid even at low temperature. For those that do not remain soluble, the choice of solvent becomes very important. More powerful solvents can produce polymers with higher molecular weights. Lower temperatures can also retard the precipitation of the polymer.

A 1965 book (21) discusses low temperature solution polycondensation at length, although it does not deal with the reaction of aromatic diamines with aromatic diacid chlorides by this method. The book also discusses interfacial polymerization.

A mechanism for these low temperature polymerizations has been proposed (p. 115–9 of Ref. (4)). It involves an initial stage in which the amine reacts with an acid chloride liberating a molecule of HCl. The HCl, in turn, forms a complex with either an unreacted amine end or a molecule of solvent. An equilibrium is established between the amine hydrochloride and the solvent hydrochloride that depends on the basicity of the solvent. The first stage proceeds until half of the amine has reacted; at which point nearly all of the amine ends have formed an HCl complex. The second stage of the reaction is much slower and depends on the availability of free amine.

Poly(p-benzamide) PBA is an interesting case. One monomer from which a high molecular weight polymer can be made is *p*-aminobenzoyl chloride hydrochloride:This monomer can be synthesized from *p*-aminobenzoic acid and thionyl chloride, forming the intermediate, sulfinyl aminobenzoyl chloride, followed by treatment with dry HCl in ether (22). When this monomer is dissolved in an amide solvent such as DMA, an equilibrium is set up between the amine hydrochloride of the monomer and the solvent hydrochloride. Some free amine is formed and the polymerization proceeds. As one would expect this monomer is extremely sensitive to water and heat.



Poly(m-phenylene isophthalamide) MPDI is an example of a polymerization in which the polymer remains soluble in the polymerizing medium. Suitable solvents are NMP and DMA with the possible addition of LiCl or $CaCl_2$. MPD is dissolved in anhydrous solvent at a concentration of up to 1.0 mole/liter and cooled to 0°C, stirring vigorously. Solid ICL is added and the stirring is continued for 30 minutes. The resulting polymer remains in solution and has an η_{inh} of 1.8 (3).

Poly(p-phenylene terephthalamide) PPTA provides an example of a polymer that has very limited solubility in suitable solvents. In the laboratory, PPD is dissolved in an amide solvent in concentrations up to 0.5 mol/L. The solution is cooled to near 0°C, stirring vigorously. Solid TCL in an equal stoichiometric quantity is added and within a few minutes the solution becomes opalescent. Vigorous stirring is continued as the polymerizing mixture solidifies and then breaks into particles with the consistency of wet sawdust. This crumb can then be neutralized with dilute caustic, washed with water and dried. The resulting polymers exhibit η_{inh} as high as 6.0 (23).

Because polymerization will proceed much more slowly when the polymer becomes insoluble, the selection of the solvent has an important effect on the level of molecular weight that can be achieved. Solvents using mixtures of

HMPA and NMP or HMPA and DMA produce polymers with higher molecular weight than any of the three solvents alone (24). Similarly, salts can be added to amide solvents to increase the solubility of PPTA and thereby increase the η_{inh} level that can be obtained (24). The combination of NMP and $CaCl_2$ is especially useful for providing high molecular weight PPTA (25). Another approach for increasing the level of molecular weight that can be attained is the use of an acid acceptor, such as tertiary amines (26) and tributyl amine (27).

Copolymers A large number of copolymer compositions have been prepared, many by low temperature solution polymerization, including ODA/PPTA (28, 29, pp 145–172 of Ref. (4)).

Interfacial Polymerization Some of the earliest reports of the preparation of aromatic polyamides employed interfacial polymerization. In this technique the diacid chloride is dissolved in a solvent with limited water solubility, and then added to an aqueous solution of the diamine with vigorous stirring. The aqueous solution contains a base that neutralizes the HCl that is generated. One example is the preparation of MPDI using tetrahydrofuran as the solvent for ICL (2).

This process is difficult to develop at a commercial scale. A modified process for producing MPDI allows the ICL and MPD to react slowly in a solution without an acid acceptor. This reactive solution is then added to an aqueous solution containing an acid acceptor and stirred vigorously to build molecular weight in an interfacial type polymerization. This process gives higher molecular weight than solution polymerization techniques and therefore, improved fiber properties. This is the process that Teijin uses to produce the polymer for their MPDI product, Teijinconex® (30).

Vapor Phase Polymerization PPTA can be formed by vapor phase polymerization at temperatures above 250°C (31). The polymer produced appears to have a high degree of branching, which makes the spinning of fibers with high strength more difficult. Improved products may be formed by using an acid acceptor that would permit shorter reaction times (32).

4.2. Commercial Processes. There are relatively few commercial products based on aromatic polyamides. These are listed in Table 2. Processes for producing the polymers, for those products where reliable information has been published, are described below.

MPDI The commercial process for MPDI has been proposed (5) based on the patent literature (33). A block diagram of the process is shown in Figure 1.

The “diamine” noted in the Figure is actually a 9.3% solution of MPD in DMA in the patent example, and the “diacid chloride” is molten ICL. The MPD solution is cooled to −15°C, while the molten ICL is supplied at 60°C. The heat of reaction brings the temperature of the effluent from the mixer to 74°C. This effluent is then cooled before $Ca(OH)_2$ is added to neutralize the HCl formed in the polymerization reaction. Finally, the polymer solution is blended, deaerated and filtered before being pumped to storage for use in spinning. The MPDI of the patent example has an η_{inh} of 1.65.

A second polymer process is the modified interfacial polymerization described earlier (30). In this process, the polymer is isolated and dried, then redissolved for spinning, as shown in Figure 2

PPTA The commercial process for PPTA has been proposed (5) based on the patent literature (34,35). A block diagram of the process is shown in Figure 3

In this process, PPD is dissolved in HMPA and then mixed with molten TCL in a series of mixers equipped to remove some of the heat of reaction. The polymer/solvent crumb is then washed with water, filtered and dried. For health reasons, HMPA has been replaced by NMP/$CaCl_2$ as a solvent.

A similar process has been described for the production of PPTA for the Twaron® process (10), although the polymerization reaction is done in batch reactors. The solvent is NMP containing $CaCl_2$. The polymer has a molecular weight (M_n) of 18–19,000.

ODA/PPTA The polymerization process for producing ODA/PPTA has been described (6,28,29). PPD and 3,4′ODA are dissolved in a solvent such as NMP and then reacted with TCL to form the copolyamide. The composition is likely 50% 3–4′ODA and 50% PPD. When the reaction is complete the HCl formed is neutralized by the addition of $Ca(OH)_2$ to give a stable viscous solution that is suitable for spinning. The inherent viscosity is in the 2–3 dl/gm range and the polymer concentration is around 6 wt%. The process is quite similar to that shown in Figure 1 after accounting for the use of two diamines.

5. Processing of Aromatic Polyamides

Most of the aromatic polyamides we have discussed so far have high melting points that prevent the type of melt processing common to aliphatic polyamides, polyolefins, and other polymers. Thus, most applications are based on forms of the polymer that can be prepared from solutions of the polymers. These would include fiber, films, and pulp.

Techniques for processing polymer solutions are well known (See Fibers, Manufacture) and include wet spinning and dry spinning of fibers and solution casting of films. In order to minimize the cost of commercial processes, large numbers of fibers must be handled together, at high speed and with minimum interruptions to the operation. Commercial processes for forming aromatic polyamide products are described in this section, focusing on the types of solution that are employed and the methods used to coagulate the fibers and complete the development of the fiber structure. Wet Spinning MPDI A flow diagram for the wet spinning of MPDI to form Teijinconex® is shown in Figure 4(30).

The process involves dissolving the dry, salt-free polymer in an organic solvent at low temperature and then heating the dispersion to near 100°C to form a clear solution. This solution is wet spun into an aqueous solution containing a high concentration of an inorganic salt. The coagulated fiber is washed, and then drawn and post-treated. The fiber has excellent mechanical properties.

Figure 5 describes another wet spinning process for MPDI (38).

Dry Spinning MPDI The dry spinning of MPDI from a DMF/$LiCl_2$ solution into an air column maintained at 225°C has also been described (3). After the fibers thus formed are drawn 4.75X and the remaining solvent and salt removed by extraction in hot water, they exhibit a tenacity of 0.6 GPa and an elongation of 30%.

Spinning of PPTA Unlike MPDI, high molecular weight PPTA is not soluble in amide solvents, with or without the addition of inorganic salts. Formation of fibers from PPTA became possible when it was discovered that concentrated solutions of the polymer in 100% sulfuric acid had relatively low viscosity, could be spun at moderate temperatures, and that the PPTA did not degrade rapidly at those conditions (34). This discovery was the result of the study of nematic solutions of PBA and PPTA (22,34) and substantiated the theoretical predictions of Flory (39). A schematic of such a process is shown in Figure 6

The patent literature (34) describes a spinning process in which PPTA is dissolved in 98–100% sulfuric acid at a concentration of greater than 18%. The solution is pumped through a spinneret into an aqueous coagulating/quenching bath, with an air gap separating the spinnerets from the bath (40). The fiber is then washed thoroughly with water and dried.

Fibers formed by this spinning process are highly oriented even without the type of high temperature drawing common for other polyamide fibers, and have high stiffness (tensile moduli of 50–75 GPa). Even higher moduli (Kevlar® 149 has a modulus of 180 GPa) can be obtained by subjecting the fibers to a stretching process at high temperature (41–43). This would appear to be the basis for the high modulus versions of Kevlar® and Twaron®.

Wet Spinning of ODA/PPTA The literature (28,29) describes the wet spinning of the copolyamide, ODA/PPTA, from a solution in NMP and $CaCl_2$ that had been filtered and deaerated. The solution is then pumped through a spinneret into a hot water/$CaCl_2$ bath. Next the filaments are washed with hot water and dried. The dried fibers are subjected to 8.5× stretch in a heated cell containing 510°C nitrogen. The fibers have tenacities in the 2.6 to 3.3 GPa range, depending on the ratio of DPE to PPD. The process is similar to that described in Figure 5.

Post-Spinning Processes A significant portion of the aramid fiber sold in recent years has been in the form of staple, floc or pulp products that are produced by the fiber manufacturer. Short fiber products are produced by cutting continuous filament yarn into lengths that range from about 1 mm to over 100 mm. Products in the 1 to 6 mm length range are referred to as “floc”, while the longer products are called “staple”. All of the continuous filament products described previously are also offered in cut-fiber forms.

Pulp is highly fibrillated, high surface area (7–15 sg m/g) short length product that is made by passing an aqueous slurry of cut PPTA fiber through a refiner (10). MPDI is not offered in pulp form, but methods for producing pulp have been disclosed (44,45).

Film Casting of PPTA A technique has been developed for producing biaxially oriented PPTA film (46). A schematic of this process is shown in Figure 7

This process involves dissolving PPTA in sulfuric acid at concentrations that produce a liquid crystal state. The viscous solution is extruded through a die onto a drum or belt where it is subjected first to high humidity warm air. This can convert the film from an anisotropic solution to an isotropic one. This is important for the production of a balanced film (machine direction or MD compared to transverse direction or TD), because anisotropic solutions of PPTA have a strong tendency to fibrillate. This solution is then dipped into a coagulating liquid, such as dilute sulfuric acid, which sets the film. Next the film is washed with water to remove the acid, after which it is biaxially stretched to provide orientation and then dried. Finally, the film is heat treated while retaining the orientation.

6. Fiber and Film Properties

Physical, chemical, electrical, and mechanical properties of fibers are described in this section, with emphasis on commercially available fibers and the properties of importance in the markets they serve.

6.1. Fiber Structure.

An extensive description of the structure of PPTA (Kevlar®) fibers has been provided in a 1993 book (47), including a description of the crystal lattice (48), estimates of apparent crystallite size and percent crystallinity, a description of fibrillar and pleat structure, and evidence of a skin-core structure. Crystal lattice structure and dimensions for PBA and MPDI (Nomex®) fibers are also included, as shown in Table 3. The structure of Twaron® is essentially the same (10), while the crystal structure of Teijinconex® is nearly identical to the MPDI fiber in Table 3. PPTA fibers are highly crystalline, ranging from 68 to 95% crystalline depending on the heat treatment of the fiber and the crystallinity measurement technique. MPDI fibers are also highly crystalline, although the crystal lattice is quite different from that of PPTA (30).

It has been proposed that PPTA fibers have an unusual radial orientation of hydrogen-bonded sheets and a pleated structure (49). When this model is combined with proposals for a skin-core structure (50–52), one can visualize a comprehensive picture of PPTA structure.

6.2. Fiber Properties.

Most commercially available fibers are now available in a variety of forms, including continuous filament yarns of different deniers, staple products of various lengths, pulp, paper products, and some nonwoven fabrics. Physical and chemical properties have most often been determined for the yarn products, with the understanding that these properties would usually apply to the other forms as well. While there is some variation in properties among the various deniers, it is usually not large. Representative properties of the major types of commercial yarn are shown in Tables 4 and 5. These properties are taken from the catalogs published by each manufacturer (53). Test methods are described in Table 6.

The products available commercially at this time fall into several categories. The MPDI products provide high temperature durability, low flammability, inherent dielectric strength and excellent chemical resistance, combined with low modulus and high elongation. These products are well suited to fabrics for protective clothing, paper in electrical uses, and high temperature filtration applications. PPTA and ODA/PPTA provide high tensile strength and modulus, coupled with high use temperature and low flammability. The high modulus versions of PPTA provide value in protective apparel, ropes, and fiber optic applications, while the standard versions are used in asbestos replacement and rubber reinforcement markets. Figure 8 shows modulus vs. tenacity for a wide variety of fiber products.

6.3. Film Properties.

The two commercial aramid films are both based on PPTA. Aramica® is a homopolymer, while Mictron® is most likely a copolymer or a terpolymer. They provide excellent strength and stiffness, along with high temperature stability. Table 7 lists some of the key properties of these materials.

7. Uses

The properties of aromatic polyamide fibers and films are sufficiently different from those of the products that preceded them that many new uses and applications have been developed. Applications are summarized according to general market groupings, specifying the type of fiber or film used but not the specific product.

7.1. MPDI Fibers.

Textiles MPDI fibers have found a substantial market as the fiber used to produce garments designed to protect workers from the hazard of fire. Obviously this includes fire fighters and racecar drivers, but it also is becoming standard clothing for workers who operate in chemical factories and other places where the danger of flash fires is real. Key properties include: its inherent flame resistance; abrasion, wear, and chemical resistance which allows clothing to be washed and worn many times; and high elongation and low modulus which allows the design of comfortable clothing. Anti-static properties and other characteristics can be incorporated by use of fiber blends.

MPDI fabrics have also been used as a fire blocking material in aircraft seat upholstery, where regulations require such functionality. They are finding increasing use as a fire block in hospitals and as upholstery where fire resistance is important.

Another major market for MPDI fabrics is as bag filters for a number of industries, such as power plants, cement factories, and steel factories, where the ability to withstand hot, corrosive gases is critical.

Paper An equally important use of MPDI fiber are products in the form of paper. Paper can be made from a mixture of MPDI fibrids and floc (45). The mixture is slurried in water and processed on a conventional paper machine. The primary market for these papers is as electrical insulation in motors, generators, and transformers. The key properties are chemical resistance, good insulating characteristics, and high temperature stability.

Another significant market based on paper is that of honeycomb sandwich structures for aircraft interior floors and panels. The MPDI provides thermal stability during processing and, in the form of honeycombs, gives an exceptional stiffness to weight ratio.

7.2. PPTA and ODA/PPTA Fibers.

Protective Clothing PPTA fibers have become the standard from which body armor for the protection of police and military personnel is made. The primary properties are high strength and light weight. These protective fabrics must be thicker than their fire protection cousins, but they still must be designed to be comfortable. PPTA is also used to make cut resistant fabrics for use in gloves and chain saw chaps.

Composites High strength and low weight provides the basis for the use of PPTA reinforced composites for the strength members in aircraft, boats, the transportation industry, and sports equipment. Related applications would include providing the protective shielding in lightweight helmets for the military and as rigid armor in military vehicles, police cars, helicopters and banks.

PPTA is also used in pulp form in a variety of automotive and industrial applications such as brake and clutch linings, gaskets, and nonwoven felts, where it has replaced asbestos. Key performance attributes are chemical resistance, thermal stability, and wear resistance.

Ropes and Cables Here, again, high specific strength and stiffness are important. Cables based on PPTA fibers anchor oil rigs and provide ship to shore mooring lines. PPTA fibers also provide tension reinforcement for fiber optic cables, where high stiffness and dielectric properties are key advantages. ODA/PPTA fibers are used in a variety of applications where high strength and abrasion resistance are important.

Rubber Reinforcement PPTA fibers were developed originally to replace polyester and steel as the reinforcing fiber in tires. That market continues to be important today, although it never reached the level envisioned in the 1960s. Key market segments today include high performance automobile tires, heavy-duty machinery and aircraft tires and, on the other end of the spectrum, puncture resistant, high performance bicycle tires. PPTA and ODA/PPTA are also used as reinforcement in rubber transmission belts and hoses.

Other Markets PPTA fibers are used to form nonwoven sheet reinforcements that are used as substrate for printed wiring boards where low thermal expansion or the ability to use laser drilling technology are important. Other applications for aramid fibers include cement reinforcement, the engineered lumber industry, boat sails, parachute fabrics, reinforcement in athletic shoes, pulp as a thixatropic agent—and the list could go on. Like most new materials, the development of new applications is a continuing process and is driven by the ingenuity of designers.

7.3. PPTA Films. Recording Media PPTA film provides a three to fourfold advantage in tensile modulus over polyester film which is the preeminent material of the industry. High temperature stability is another important feature in this market. These property advantages offer the possibility of substantial miniaturization, and are the primary basis for the development of this film. At this time, the markets and products are still in the development stage.

7.4. Resin and Fibrid Forms. More recently commercialized product forms of PPTA and MPDI are respectively, resin and fibrid. The resin (polymer) form is finding utility as a reinforcing agent or as a wear additive in a variety of thermoplastic matrices. The high surface area fibrid form is used as a thixatrope and as a reinforcing agent in coating, sealant, plastic, elastomer and composite applications.

8. Economic Aspects

Aramid products have now been commercially available for nearly 40 years. Table 2 provides a summary of current (as of 1999) capacities to produce these products, with total worldwide capacities of 19,000 metric tons of meta-aramid fiber, 43,000 metric tons of para-aramid fiber, and 600 metric tons of para-aramid film. Table 8 shows total world consumption of Aramid fibers between 1979 and 1998 (36), indicating sales near 90% of capacity for meta-aramid and near 60% for para-aramid. Sales of both types have been increasing at a rate of over 4.5%/year for the past 10 years.

Prices of Aramid products vary widely depending on the denier of the product and the part of the world the product is sold. In general, meta-aramids fall in the \$20−60/kg range while para-aramids fall in the \$10−30/kg range (36). Staple is less expensive than continuous filament yarn.

9. Health and Safety

No matter the process, the safety requirements in the production of aramid fibers and films are substantial. The monomers used in these processes are highly toxic and are sometimes handled at high temperatures (7). They require protective clothing and great care to avoid any contact. At least one potential solvent for the polymerization, HMPA, was found to be carcinogenic in rats (59) and was discontinued as the solvent for the commercial process. Sulfuric acid is used in the fiber formation of PPTA, and protective clothing is a requirement for all personnel who enter the spinning area. The high strength of PPTA fibers makes handling the yarn at high speed a hazardous enterprise, and special training of production workers is especially important.

PPTA and MPDI are relatively safe products that present minimal risk to human health and the environment. MPDI fabrics have been worn for over thirty years without significant effect on the skin, and PPTA products have a similar history. The Food and Drug Administration now provides that many forms of PPTA fiber may be safely used as components of articles that come in repeated contact with food.

During the processing of these fibers some respirable fibrous particles are always produced, and inhalation of these particles should be minimized. Adherence to good industrial hygiene practices for ventilation and cleanup will protect against significant exposure (60).

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Table 1. **Examples of Aromatic Polyamides**

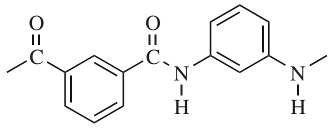
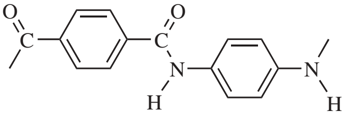
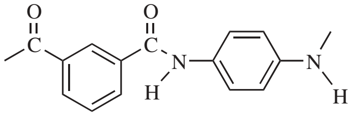
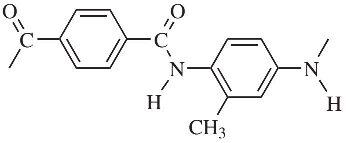
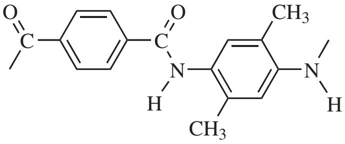
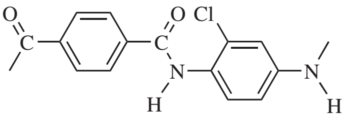
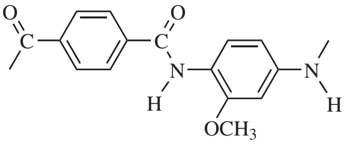
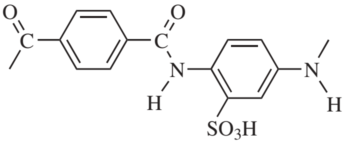
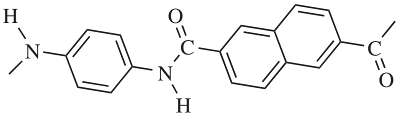
Polymer	η_{inh} (dl/gm)	Melting Temp from DTA (°C)	10% Weight Loss Temp (°C)	Ref
	0.83	435	458	(3)
	0.48	530	513	(18,19)
	5.0		568	
	0.46	422	452	(18,19)
	1.10		512	
	0.34	518	505	(18,19)
	0.32	545	487	
	0.67	496	473	(18)
	1.73	508	516	(19)
	1.29	402	435	(19)
		528		
	1.11	350	353	(19)
	2.48			(20)
	1.99			(20)

Table 2. **Commercial Products Based on Aromatic Polyamide Polymers**

Polymer	Type of Product	Trade Name	Capacity (metric tons/yr.)	Manufacturer
MPDI	fiber	Nomex®	15,900	E.I. duPont deNemours & Co.
MPDI	fiber	Teijinconex®	2,300	Teijin Company Ltd
MPDI	fiber	Fenylon®	900	Russian State Complex
PPTA	fiber	Kevlar®	29,900	E.I. duPont deNemours & Co
PPTA	fiber	Twaron®	11,000	Accordis (Twaron Products bv)
PPTA	fiber	Fenylon ST®	1,300	Russian State Complex
ODA/PPTA	fiber	Technora®	800	Teijin Company Ltd
Aramid Copolymer	film	Mictron®	400	Toray Industries, Inc.
PPTA	film	Aramica®	200	Asahi Chemical Ind Co, Ltd

[a] Data for fiber capacities from SRI International

Table 3. **Crystal Lattice Parameters of PPTA, PBA and MPDI**

	PPTA	PBA	MPDI
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Space Group	$P2_1/n\text{-}C_{2h}{}^5$	$P2_12_12_1\text{-}D_2$	$P1\text{-}C_1{}^1$
Lattice Constant			
a, Å	7.80	7.71	5.27
b, Å	5.19	8.14	5.25
c, Å	12.9	12.8	11.3
a, degree			111.5
B, degree			111.4
γ, degree	90		88.0
Number of chains in a unit cell	2	2	1
Density, g/cm^3			
Calculated	1.50	1.54	1.45
Observed	1.43–1.45	1.48	1.38

Table 4. **Properties of Aramid Fibers**

Trade Name		Nomex®	Teijinconex®		Kevlar®		Twaron®		Tech-nora®
Polymer		MPDI	MPDI		PPTA		PPTA		ODA/PPTA
Fiber Type		430	Std	HT	K-29	K-49	Std	HM	
Property	Test Method								
Density, g/cm^3	a	1.38	1.38	1.38	1.44	1.44	1.44	1.45	1.39
Equilibrium Moisture Content, % at:									
65% RH	b	5.2	5.2	5.2	4.0	3.7	6.5	2.5	1.8
95% RH	b	7.0	9.0	9.0	6.5	6.3	–	–	–
Tensile Properties at Room Temperature									
Strength, GPa	c	0.59	0.61–0.68	0.73–0.86	2.9	3.0	2.9	2.9	3.4
Elongation, %	c	31	35–45	20–30	3.6	2.4	3.6	2.5	4.6
Modulus, GPa	c	11.5	7.9–9.8	11.6–12.1	71	112	70	110	72
Thermal Properties									
Specific Heat, J/kg-K	d	1260	1050	1050	1420	1420	1420	1420	1680
Thermal Conductivity, W/m-K	e	0.25	0.11	0.11	2.5	2.5	–	–	0.5
Coefficient of Thermal Expansion, cm/(cm-°C)	f	1.8×10^{-5}	1.5×10^{-5}	1.5×10^{-5}	-4.0×10^{-6}	-4.9×10^{-6}	-3.5×10^{-6}	-3.5×10^{-6}	-6×10^{-6}
Heat of Combustion, J/kg	g	28×10^6	–	–	35×10^6	35×10^6	–	–	–
Flammability, LOI, %	h	28	29–32	29–32	29	29	29	29	–
Decomposition (in N_2) Temperature, °C	j	400–420	400–430	400–430	520–540	520–540	520–540	520–540	500

Tensile Properties Measured at Elevated Temperatures								
Tensile Strength, GPa measured at T=								
150°C	k	0.46	0.48	0.69	2.5	2.7	–	–	–
200°C	k	0.39	0.41	0.64	2.2	2.6	–	–	–
250°C	k	0.32	0.35	0.57	2.0	2.4	–	–	>1.7
Tensile Modulus, GPa Measured at T=									
150°C	k	10.6	6.1	8.6	60	91	–	–	–
200°C	k	9.9	5.1	7.0	58	89	–	–	–
250°C	k	9.4	4.3	6.1	–	–	–	–	>37
Tensile Property Retention									
Hot Air Exposure — % Strength Retained after:									
100 h @ 180°C	l	100	99	99	95	–	86	–	98
1000 h @ 180°C	l	99	95	95	60	–	80	–	85
100 h @ 250°C	l	95	85	85	35	–	55	–	75
1000 h @ 250°C	l	73	75	75	<10	–	–	–	25
Saturated Steam Exposure — % Strength Retained after:									
400 h @ 120°C	l	–	70	–	25	–	–	–	100
100 h @ 140°C	l	–	86	–	–	–	–	–	–
1000 h @ 150°C	l	70	<50	–	–	–	–	–	–

To convert strength and modulus values to cN/dTex, multiply GPa by 10.0 and divide by density (g/cm^3) To convert cN/dtex to gpd, multiply by 1.133;

Table 5. **Chemical Resistance of Aramid Fibers**

Trade Name		Nomex®	Teijinconex®	Kevlar®	Twaron®	Technora®
Polymer		MPDI	MPDI	PPTA	PPTA	ODA/PPTA
Chemical	**Time (Hrs)**/Temp (°C)	**Percent Strength Retention**				
40% H_2SO_4	100/95		28			90
10% H_2SO_4	100/21	90–100	98	90–100		
10% H_2SO_4	1000/21		95	69	35	
10% HCl	1000/21	20–60		35	10	
10% HNO_3	100/21	60–80	90–100	20–60		
10% HNO_3	2200/21				15	
10% NaOH	100/95		<10			75
10% NaOH	1000/21	90–100	90	46		
40% NaOH	1000/21	80–90	76			
28% NH_4OH	1000/21	90–100	90–100	90–100	65	
0.01% NaClO	1000/21	90–100		16		
10% NaClO	100/95					55
0.4% H_2O_2	1000/21	90–100	56–75			
10% NaCl	1000/21	90–100			100	
100% Acetic Acid	1000/21		90–100		90	
90% Formic Acid	100/21	90–100	90–100	90–100		
90% Formic Acid	100/99	60–80	90–100	0–20		
100% Acetone	1000/21	90–100	90–100			
100% Acetone	100/56	80–90		90–100		
100% Benzene	1000/21	90–100	90–100	100		
100% Ethyl Alcohol	1000/21	90–100	90–100	100		
100% Ethyl Alcohol	100/77	90–100		90–100		
50% Ethylene Glycol	1000/99	80–90	90–100	60–80		
10% Formaldehyde	1000/21	90–100	90–100			
100% Gasoline	1000/21	90–100	90–100	90–100		
100% Methyl Alcohol	1000/21	90–100	90–100	90–100		
100% Perchloroethylene	10/99	90–100		90–100		
100% Tetrahydrofuran	1000/21		90–100			

[a] Measurements made after 3 months (2200 hrs) of exposure at room temperature.

Table 6. **Test Methods**

Note	Property	Test Description + ASTM Reference
a	Density	Density gradient tube at 21°C - ASTM D1505-96
b	Equilibrium Moisture Content	Fiber is bone dried and then exposed to the specified humidity at room temperature for >24 hrs
c	Tensile Properties	Instron Tester. Details depend on type of fiber. ASTM D885-85 (1.1 TM) For Kevlar®; D885 M for Twaron®; DuPont Test Method 12002 for Nomex®.
d	Specific Heat	Differential Scanning Calorimeter-ASTM E 1269
e	Thermal Conductivity	Guarded-Comparative Longitudinal Heat Flow - ASTM E 1225-87
f	Coefficient of Thermal Expansion	Untwisted fiber is held at constant tension, then length changes are measured as temperature is cycled between 25 and 150°C
g	Heat of Combustion	Oxygen Consumption Calorimeter - ASTM E 1354-97
h	Flammability—LOI	Oxygen Index - ASTM D 2863-97
j	Decomposition Temperature	Differential Thermal Analysis, ASTM E 1356-91
k	Tensile Properties vs. Temperature	Sample and Instron acclimated for 5 min prior to testing as above (c)
l	Exposure Tests	Samples exposed to specified conditions, then reconditioned to RT and 55% RH before testing as above (c)

Table 7. **Properties of Aramid Films and Papers**

	Mictron®	Aramica®	Nomex®	Thermount®
Reference				
Polymer	PPTA	PPTA	MPDI	PPTA
Form	film	film	paper	paper
Source	Toray	Asahi	DuPont	DuPont
Type		M type	410	N710
Thickness, μm	25	25	127	97
Density, g/cm$_3$	1.50	1.40	0.87	0.64
Mechanical Properties (MD/TD):				
Tensile Strength, GPa	0.5	0.5/0.3	0.1/0.05	0.2
Elongation, %	60	15/25	16/13	1.5
Tensile Modulus, GPa	13/9	19/10	–	5.4
Initial tear strength, kg	–	25	3.3/1.6	–
Melting Point, °C	Does not melt	Does not melt	Does not melt	Does not melt
Long-term Heat Resistance, °C	180	ca. 200	ca 200	ca 200
Thermal Expansion, (1/°C × 10$-^5$)	0.1	0.2	–	−0.7
Moisture Absorption, % @ 75% RH/ Room Temp.	1.5	2.8	–	1.6 @ 55% RH
Electrical Properties:				
Dielectric Constant @ 1 KHz	–	4.0	2.4	3.9
Dissipation Factor @ 1 KHz	–	0.02	0.006	0.02
Volume Resistivity, Ω-cm	5×10^{17}	10^{16}	5×10^{16}	–
Surface Resistivity, Ω	–	10^{16}	10^{16}	–
Dielectric Strength, KV/mm	300	230	25	82

[a] epoxy impregnated laminate.

Table 8. **Consumption of Aramid Fibers (thousands of metric tons)**

Year	1979	1986	1992	1998
meta-Aramids				
United States	4	5	5	7
Europe and Russia	1	4	4	7
Japan and Asia	<1	1	3	3
Total	6	10	12	17
para-Aramids				
United States	5	9	8	10
Europe and Russia	<1	4	8	12
Japan and Asia	1	1	3	3
Total	6	14	19	25

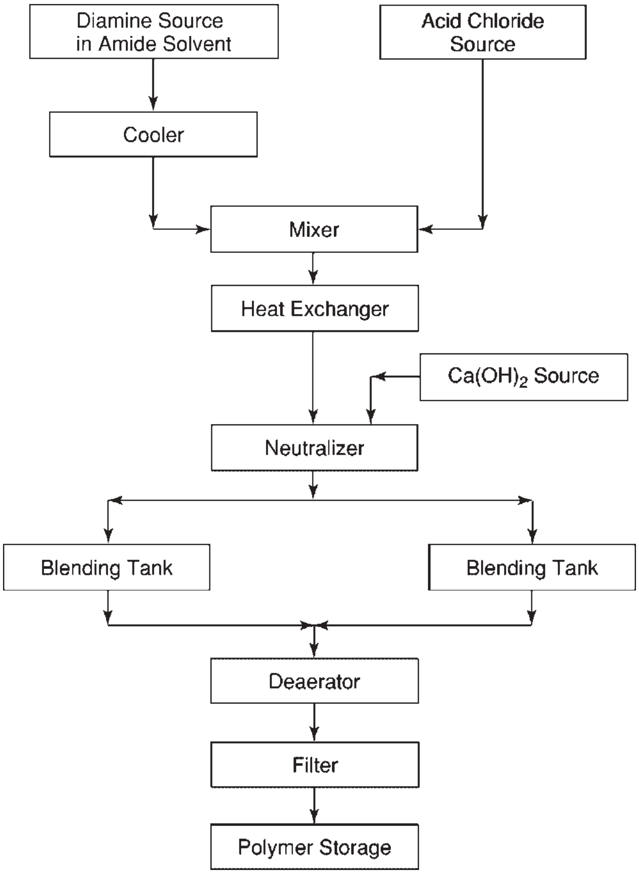


Fig. 1. Preparation of MPDI via low temperature solution polymerization

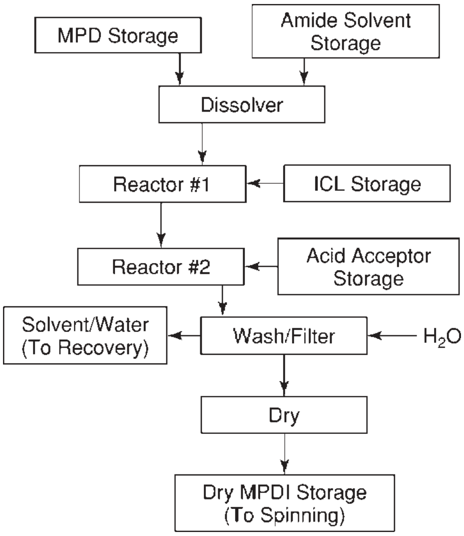


Fig. 2. Preparation of MPDI via interfacial polymerization

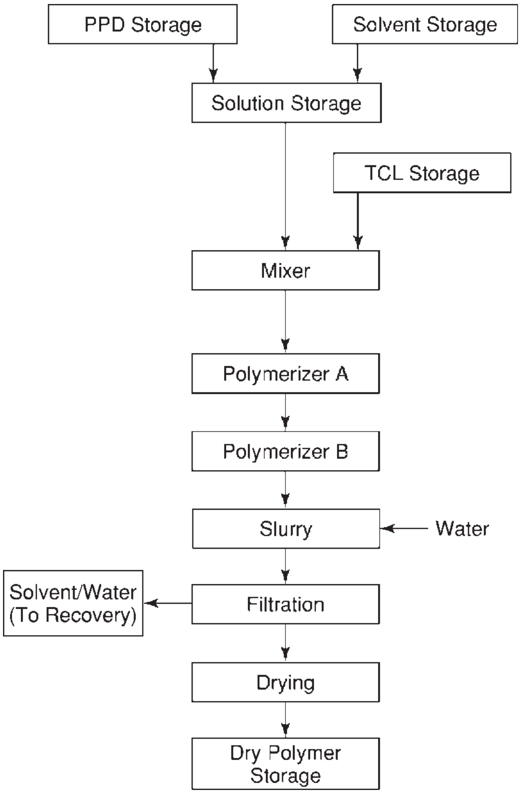


Fig. 3. Preparation of PPTA via low temperature solution polymerization

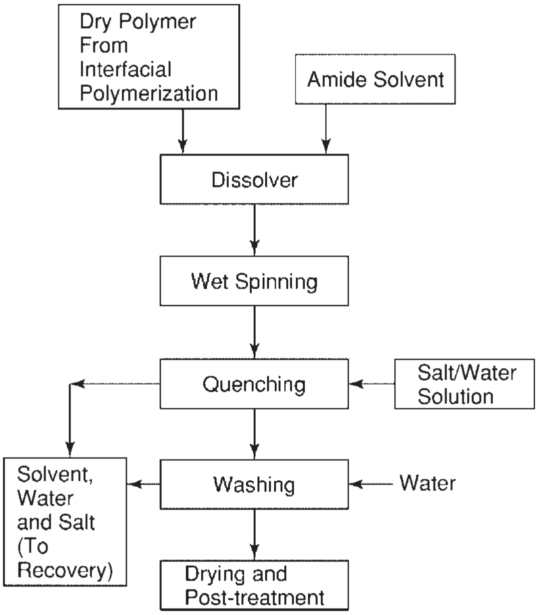


Fig. 4. Wet spinning of MPDI

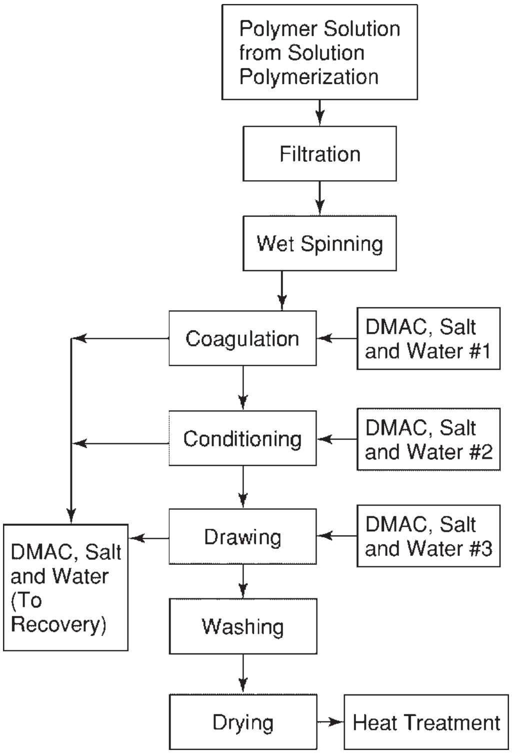


Fig. 5. Wet spinning of MPDI

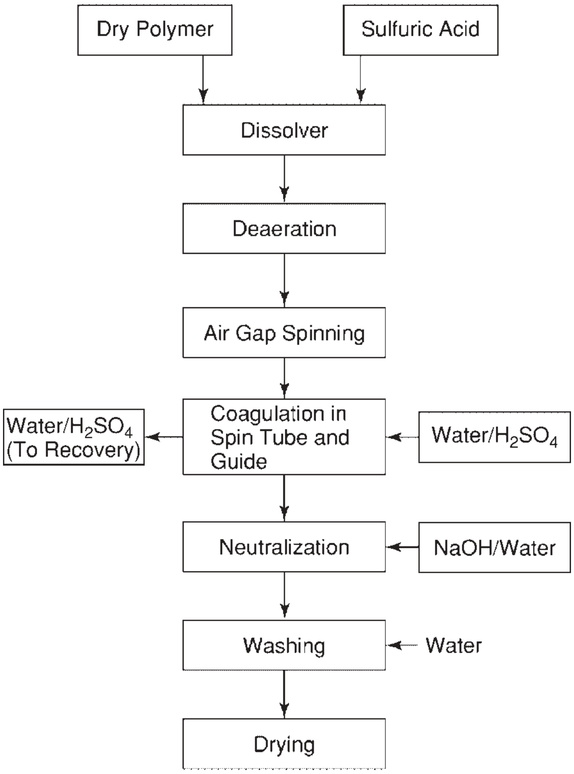


Fig. 6. Air gap spinning of PPTA

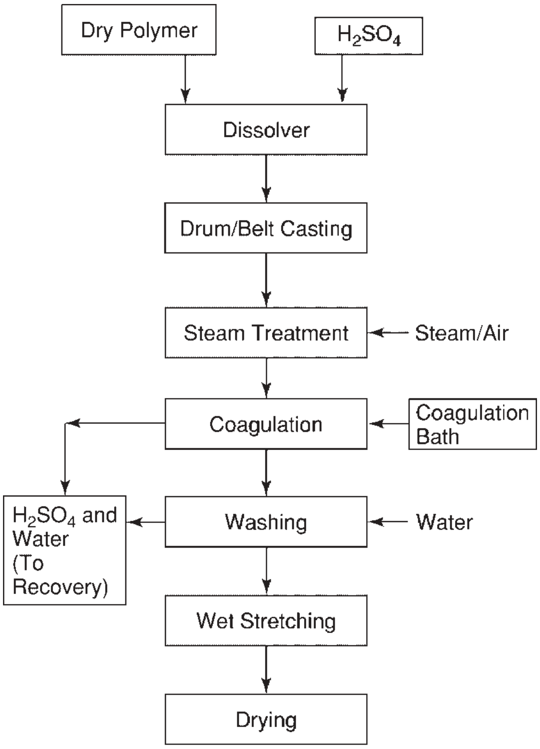


Fig. 7. Process for casting PPTA film

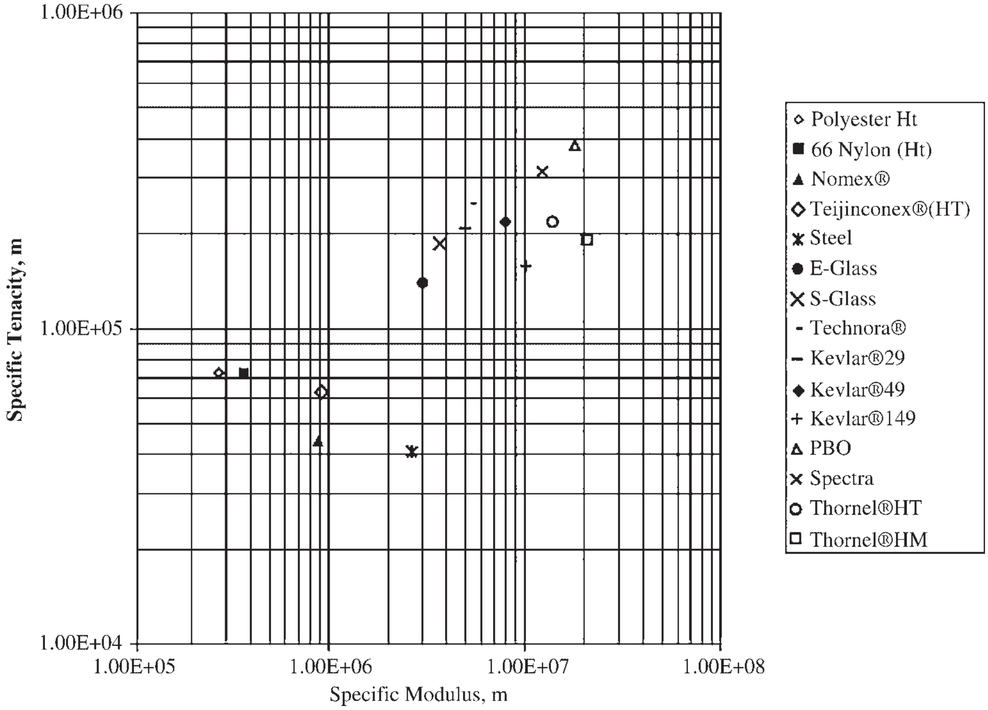


Fig. 8. Modulus tenacity map for industrial fibers.