

PATENT SPECIFICATION

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(54) POLYAMIDE FIBRES

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to polyamide fibers having a novel structure and improved properties prepared by an improved spinning process.

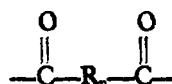
U.S. Patent 3,414,645 describes a dry spinneret wet spinning process in which solutions of wholly aromatic polyamides are extruded through a gaseous medium into a coagulating bath, followed by stretching in a wash liquid, washing, drying and hot drawing to produce filaments.

German 1,810,426 (Offenlegungsschrift) teaches the use of certain optically anisotropic dopes of carbocyclic aromatic polyamides in wet spinning processes to afford fibers of good strength as-spun, i.e. without a drawing or heating process. A high temperature treatment with tension raises the strength to higher values. It has been found that these heating processes may adversely affect certain fiber properties for many uses. Heating causes an increase in crystallinity and generally a reduction in fiber toughness and breaking elongation. The fibers may become brittle on heating, reducing their value for such uses as tire cords.

This invention provides as-spun polyamide fibers and film having unusually high tenacity as compared with prior art fibers and film of the same polymer and a process for preparing the polyamide fibers and film.

This invention provides a fiber or a film or a polyamide having an inherent viscosity of at least 2.5 and consisting essentially of recurring units I and II, or III, or I and II and III, wherein:

I is



II is



and III is



and when units I and II are present in the polymer they are present in substantially equimolar amounts, R, R' and R'' groups, which may be the same or different, are divalent radicals, n is zero or the integer one, and at least 95 mol % of the total R, R' and R'' radicals in the polymer consist of single rigid radicals (as hereinafter defined) with extended bonds (as hereinafter defined) or a series of such rigid radicals linked together directly by extended bonds, with the proviso that rigid ring radicals may be linked by azo or azoxy groups, said fiber or film having a filament or film tenacity of 18 to 40 gpd., a filament or film breaking elongation of 3.5 to 8.0%, and crystalline regions with a primary apparent crystalline size of 0 to 52 Å.

Preferably the polyamide has an inherent viscosity of at least 3.0, more preferably 4.0 and most preferably 4.5. Preferably the fibers or film have an LCO value of at least 20.

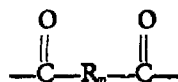
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The fibers and films of this invention are characterized by unusually high levels of tenacity in combination with moderate levels of elongation which affords high toughness at low to moderate degrees of crystallinity as indicated by the apparent crystallite size.

A preferred class of fibers and films has an LCO value of at least 10 and more preferably at least 20. Tenacities of filaments of the invention may range from 18 to 32 grams per denier (gpd) or higher, elongations from 3.5 to 7% or higher, toughness values from 0.40 to 1.5 gpd or higher and modulus values from 300 to 800 gpd or higher. Fibers having a modulus of at least 400 are preferred. The fibers have orientation angles of from about 30° to 12°.

This invention also provides a method of preparing a polyamide fiber or film which comprises extruding a dope through an orifice through a layer of inert non-coagulating fluid and then into a coagulating bath, the dope comprising a polyamide and a solvent consisting essentially of sulfuric acid of at least 98% concentration, chlorosulfuric acid or fluorosulfuric acid and mixtures thereof at a concentration (C) of at least 30 grams of polymer per 100 ml. of solvent, the polyamide having an inherent viscosity of at least 2.0 but not less than 2.8—0.05 (C—30) and consisting essentially of recurring units I and II, or III, or I and II and III, wherein:

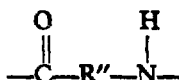
I is



II is



and III is



and when units I and II are present in the polyamide they are present in substantially equimolar amounts, R, R' and R'' which may be the same or different, are divalent radicals, n is zero or the integer one, and at least 95 mol % of the total R, R' and R'' radicals in the polyamide consist of single rigid radicals (as hereinafter defined) with extended bonds (as hereinafter defined) or a series of such rigid radicals which are linked together directly by extended bonds with the proviso that rigid ring radicals may be linked by azo or azoxy groups.

Preferably the polyamide concentration is 40—56 g/100 ml solvent. Preferably the dope is solid at 25°C and is extruded at 40 to

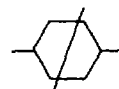
120°C. It is most preferred that the dope is extruded at 70 to 90°C.

Figure 1 shows a schematic view of one type of apparatus for carrying out a process suitable for preparing the fibers of this invention. Figure 2 is a drawing of a fiber section. Figures 3, 4, 5 and 6 are graphic of a complete and half diffraction pattern dotted arcs have the lowest photographic density. In solid arcs the thickness is proportional to the photographic density. Figures 7 and 10 are drawings of a densitometer trace of a selected area of a fiber section. The respectively. Figures 8 and 9 are drawings of a portion of a densitometer trace.

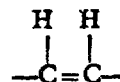
In Figure 1, a spinning dope is pumped through transfer line (51) through a spinning block (52), through the orifices of spinneret (53) through a layer of gas (55) and into a coagulating liquid (56) in spin tube (60) through which the filaments (54) are conducted. A strong as-spun multifilament bundle (65) is passed under guide (57) and is wound up on a rotating bobbin (59). The coagulating liquid (56) flows from container (61) through spin tube (60) and falls to container (62) from whence it is returned by pump (63) and tube (64) to container (61).

The essential portion of the polymer consists of polyamide units (including polyoxamide units when n is zero), which provide stiff chains. As-spun fiber and film prepared in accordance with the present invention from copolyamide, i.e. wherein R or R' is a mixture of at least two different radicals or wherein units I, II and III are present, will have an elongation of at least 4.5% whereas products prepared from homopolyamide will have an elongation of at least 3.5%.

By the expression "rigid radicals" is meant (a) the ring radicals: single ring or fused multi-ring aromatic carbocyclic or heterocyclic radicals, *trans*-1,4-cyclohexylene



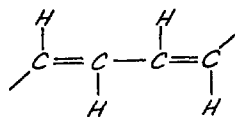
and 1,4 - [2,2,2] - bicyclo - octylene and (b) the linear unsaturated radicals: vinylene



and ethynylene $-\text{C}\equiv\text{C}-$. It will be understood that monomers containing amino groups directly attached to linear unsaturated radicals are not stable and hence vinylene or ethynylene cannot serve as R' or that portion of a R'' radical attached to



By the expression "extended bonds" is meant chain-extending bonds of the radical (as determined by the true bond angle) which are essentially coaxial (as in p-phenylene,

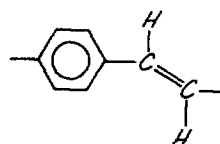


or 2,4'-trans-vinylene

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or parallel (as in 1,5-naphthylene

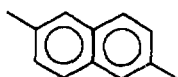


The latter radical may also serve as R''.

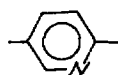
and *trans*-1,4-cyclohexylene) and oppositely directed. These polymer structures additionally have the characteristic of forming anisotropic or liquid crystalline phases when mixed with certain strong protonic acid solvents, as will be discussed in greater detail in a later section. Preferred radicals with extended bonds suitable for R, R' and R'' are *trans*-1,4-cyclohexylene, 1,4-phenylene, 1,5-naphthylene, 2,6-naphthylene

R, R' and R'' are intended to include substituted and/or unsubstituted radicals. The substituents, if any, should preferably be non-reactive (e.g., thermally) during subsequent processing of the polymer, e.g., heat treating of a shaped article thereof. Such reactivity is undesirable in that it may cause branching and cross-linking of the polymer and may adversely affect the dope and/or fiber properties. Among the preferred nonreactive substituents may be named halogens (e.g., chloro, bromo and fluoro), lower alkyl (e.g., methyl, ethyl and isopropyl), methoxy, cyano, and nitro. Generally, it is preferred that no more than two (and more preferably no more than one) suitable substituents be present per single radical. Preferably no more than 20 mol % of the total R, R' and R'' radicals in the polymer should be substituted R''.

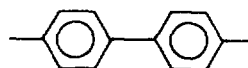
2,5-pyridylene



4,4'-biphenylene



trans,trans-4,4'-bicyclohexylene



radicals and 1,4-phenylene groups linked by *trans*-vinylene, ethynylene, azo or azoxy. In addition, R may be *trans*-vinylene, ethynylene, *trans,trans*-1,4-butadienylene

A preferred class of the polymers of the group described above are those polyamides (n being the integer one) wherein R and R' are selected from the group 1,4-phenylene, 4,4'-biphenylene, 2,6-naphthylene, 1,5-naphthylene and *trans*-1,4-cyclohexylene; R is additionally selected from the group 2,5-pyridylene and *trans*-vinylene; R'' is 1,4-phenylene; and at least 50 mol % of the total of R and R' is wholly aromatic. Of this preferred class of polymers, the most preferred are those wherein R is selected from the group 1,4-phenylene, 4,4'-biphenylene, 2,6-naphthylene, 2,5-pyridylene, *trans*-1,4-cyclohexylene and *trans*-vinylene; R' is selected from *trans*-1,4-cyclohexylene, 1,4-phenylene and mixtures of 1,4-phenylene with up to 50 mol % of 4,4'-biphenylene; R'' is 1,4-phenylene; with the provisions that (a) at least 75 mol % of the total of R and R' are wholly aromatic and (b) at least 75 mol % of either R or R' is 1,4-phenylene.

The chains of the linear condensation polymers of the invention may include up to 5% (mol basis) of radicals not conforming to the above cited description, e.g., not having extended bonds, or non-rigid.

It is to be understood that these non-conforming radicals differ in their effect on the

properties of the as-spun products. Thus, rigid radicals such as m-phenylene, whose chain extending bonds are neither coaxial nor parallel and oppositely directed, and highly flexible radicals such as hexamethylene and dexamethylene will ordinarily be used in small proportions, whereas radicals such as 4,4'-biphenylene may be used in larger amounts, up to 5% to yield fibers which still exhibit the unusual combination of properties of products of the invention. While not preferred, a small proportion of the amide units in the linear condensation polymer chain may be replaced, if desired, by other stable non-amide-forming units, e.g., ester-forming units or urea or sulfonamide-forming units. In general, such products are more difficult to prepare and are more restricted in their utility.

The polymer to be spun may be a homopolymer, random copolymer, ordered copolymer or blend of homopolymers and/or copolymers of the above description. The usual additives such as dyes, fillers, delusterants, UV stabilizers, anti-oxidants, etc., may be incorporated in the fibers and films of this invention.

Among the preferred polyamides may be named: poly(p-phenylene terephthalamide) (hereafter PPD-T); poly(p-phenylene p,p'-biphenyldicarboxamide); poly(p-phenylene 1,5 - naphthalene - dicarboxamide); poly(trans,trans - 4,4' - dodecahydrobiphenylene terephthalamide); poly(trans - 1,4 - cinnamamide); poly(p-phenylene 4,8-quinolinedicarboxamide); poly(1,4 - [2,2,2] - bicyclo-octylene terephthalamide); copoly(p-phenylene 4,4' - azoxybenzenedicarboxamide/terephthalamide); poly(p-phenylene 4,4'-trans - stilbene - dicarboxamide) and poly(p-phenylene acetylenedicarboxamide).

The polymers for use in this process are conveniently made by reacting suitable monomers in the presence of an amide type solvent by low temperature techniques as taught in U.S. Patent 3,063,966 to Kwolek et al. In order to obtain high molecular weight polymers the monomers and solvent should contain a minimum of impurities and the water content of the total reaction mixture should be less than 0.03% by weight.

Poly(p-phenylene terephthalamide) is conveniently made by dissolving 1728 parts of p-phenylenediamine in a mixture of 15,200 parts of hexamethylphosphoramide and 30,400 parts of N-methylpyrrolidone, cooling to 15°C. in a polymer kettle blanketed with nitrogen and then adding 3243 parts of powdered terephthaloyl chloride with rapid stirring. The solution gels and turns into a dry crumb-like material in 3 to 4 minutes. The stirring is continued for 1.5 hours when possible cooling to keep the product temperature at about 25°C. The polymerization is essentially quantitative and the final reaction mixture contains 7.5% polymer of

about 5.5 inherent viscosity (hereafter I.V.). The I.V. of the polymer from this system can be controlled by the ratio of monomer to solvent. Reduction of the amount of monomer from 9.83% above 8.64% gives a reaction mixture containing 6.5% polymer of 6.0 I.V. The use of about 11.7% of monomers gives a reaction mixture of 9.0% polymer of 2.5 I.V.

The crumb-like acidic product is vigorously stirred or ground with water in a Waring Blender or a colloid mill and the resulting polymer slurry filtered. The wet polymer is further washed by reslurrying with soft water to remove solvent and HCl and collected on a filter. This slurrying and filtering is repeated about four times in sequence followed by a final wash with distilled water. To aid in neutralization, one of the soft water washes may also contain sodium carbonate or hydroxide. The polymer is then dried at 120-140°C.

Polymerizations can also be carried out by the continuous mixing of the monomers.

Suitable spinning solvents consist essentially of sulfuric acid of at least 98% concentration, chlorosulfuric acid, fluorosulfuric acid, and mixtures of these acids. The sulfuric acid may be of greater than 100% concentration, i.e., fuming sulfuric acid. Sulfuric acid at a concentration of about 99.8% is preferred. Higher concentrations may be used, however, the presence of excess sulfur trioxide tends to degrade the polymer causing a reduction in the inherent viscosity. This could cause loss of filament tenacity. This degradation is time and temperature dependent so that if fuming sulfuric is used, the exposure time at elevated temperatures should be kept to a minimum. This definition of suitable solvents is not intended to preclude the presence of certain additives. Thus, hydrofluoric acid, halogenated alkylsulfonic acids, halogenated aromatic sulfonic acids, halogenated acetic acids, halogenated lower alkyl alcohols, and halogenated ketones or aldehydes can ordinarily be present in an amount up to about 30% of the total weight of the solvent and additive. The exact amount of additive that may be present will, of course, depend upon the particular solvent-polymer combination that is employed. The use of fluorosulfuric (rather than sulfuric) acid, or lower polymer concentrations permits the use of a greater amount of an additive. In general, the greater the percent of halogen present in the additive, the greater the amount of additive that can be used up to the limit of phase separation. Trifluoromethanesulfonic acid can ordinarily be present in an amount equal to the weight of the above sulfuric acids. Additionally sulfones, chlorinated phenols and nitrobenzene can be used as a solvent additive in lesser amounts than the halogenated additives described above.

The water content of the dope should be

preferably controlled to be less than 2%. Excessive water can interfere with the formation of dopes suitable for spinning and also lead to excessive degradation of the polymer.

5 The relatively dry polymer (preferably less than 1% water) should be mixed with a "dry" solvent under conditions minimizing exposure to atmospheric moisture and the dope stored under a dry atmosphere.

10 The dopes should be mixed and held during the spinning process at as low a temperature as is practical to keep them liquid in order to reduce degradation of the polymer resulting in lower I.V. values. Exposures to temperatures over about 90°C. should be minimized.

15 A particularly useful method is to continuously prepare the dope and feed directly to the spinnerets, thus minimizing any holding time. If batch processes are used and dopes are to be stored for later use, they may be frozen to a solid form, preferably under a blanket of dry nitrogen. Such solidified dope can be crushed to granules or powder and subsequently used to feed a screw melting device leading to a spinneret.

20 The concentration (C) of the dope is defined herein as grams of polymer per 100 ml of solvent at 25°C. By "solvent" is meant the actual sulfuric acid plus any solvent-additive present. At least 30 grams, preferably 40 grams, of polymer per 100 ml of solvent should be employed. Where the solvent is sulfuric acid of 98 to 100% H_2SO_4 , this corresponds to dopes containing at least 14, preferably at least 18, weight % of polymer. Preferred dopes for the instant spinning process employ between 40 and 56 grams of poly-(p-phenylene terephthalamide) having an I.V. of at least 3.0 per 100 ml of acid. This amounts to between about 18 and 22 weight % of polymer in the previously mentioned acid dopes.

25 It may be noted that the useful solvents all have high density (H_2SO_4 1.83, HSO_3Cl 1.79, HSO_3F 1.74 g/ml). Use of such high density solvents leads to a much higher volume fraction of polymer than when alkylamides like hexamethylphosphoramide and dimethylacetamide (densities about 0.9 to 1.0 g/ml) are used. High volume fraction is also provided by the high concentrations of polymer in the dopes.

30 In the present invention it is useful to use as high a dope concentration as possible. It has been found in general that the tenacity of the fibers produced increases with the concentration of the dope from which they were spun. Dopes of useful concentrations are solid at room temperature and melt to spinnable liquids when the temperature is raised. Increasing temperature causes polymer degradation as shown by loss in I.V.

35 It is desirable that the extrusion of a dope result in a fiber with an I.V. of at least 2.5.

A given fiber I.V. can be obtained by starting with a polymer of a moderate I.V. and processing to keep degradation to a minimum or by starting with a higher I.V. and processing for more severe degradation. For purposes of the present invention, the I.V. of the polymer in the as-spun fiber (assuming appropriate washing and drying to prevent undue degradation) is taken as the I.V. of the polymer in the dope as it is extruded. Thus, the I.V. of the polymer in the dope as it is extruded should be at least 2.0 and should be no less than $2.8-.05(C-30)$ where (C) is as defined above.

40 The spinning dopes of the present invention possess unexpected stability. It appears that the "acidity" of the sulfuric acid is reduced by the presence of high concentrations of the stiff chain polyamides. Dopes are made of PPD—T polymer of 4.88 I.V. in sulfuric acid (100%) at concentrations of 46, 21.8 and 3.7 g./100 ml. The dopes are heated for 3 hours at 100°C. Polymer isolated from the heated solutions has an I.V. of 4.2, 2.8 and 1.9 respectively. Further evidence for reduced "acidity" of the concentrated dopes is the fact that PPD—T dopes of 46 g./100 ml. are substantially non-reactive with aluminum metal at 70—80°C. whereas dopes of 25 g./100 ml. concentration react vigorously.

45 It has been found advantageous in some instances to deaerate the liquid dope at reduced pressure prior to spinning.

50 The dopes or polymer-solvent system used in this process behave much like polymer melts. A typical dope of 46 grams of PPD—T of about 4 I.V. in 100 ml. of 100% sulfuric acid may have a bulk viscosity of about 900 poises at 105°C. which increases on cooling to about 1000 poises at 80°C. and then rapidly increases upon further cooling until the dope solidifies to an opaque solid below about 70°C. The bulk viscosity increases with higher inherent viscosities at a given concentration and temperature. The liquid dope referred to above is a turbid, translucent liquid at temperatures below about 135°C. at which temperature it becomes relatively clear.

55 Thus far, dopes containing about 49 grams of PPD—T per 100 ml. of sulfuric acid represent the highest concentration that can be handled in the conventional mixers, transfer lines and spinning equipment because of the extremely high bulk viscosity of the mixes. When the usual technique of lowering the viscosity by raising the temperature is used, excessive degradation of the polymer occurs. The use of more effective mixers in combination with more efficient cooling in the mixer will permit the use of higher concentrations. The viscosities at these higher concentrations are a function of the polymer-solvent system used.

60 In general, dopes can be extruded at any temperatures from the lowest at which they

are sufficiently fluid to be handled up to about 120°C. Since the amount of degradation is dependent upon the time and temperature, temperatures as low as practical should be used, preferably below 90°C. Preferably the dopes are extruded at 70—90°C. If higher temperatures are desired for any reason, the equipment should be designed so that the exposure time of the dope to the elevated temperature is kept at a minimum.

The spinning dopes of this invention are unusual. At room temperature most are solid. As the temperature is raised, they melt, becoming less viscous and translucent to transparent. They are optically anisotropic, i.e., microscopic regions of a given dope are birefringent; a bulk dope sample depolarizes plane polarized light because the light transmission properties of the microscopic areas of the dope vary with direction. This characteristic is associated with the existence of at least part of the dope in the liquid crystalline or mesomorphic state. These dopes exhibit anisotropy while in the relaxed state.

For a well mixed dope of given composition and concentration, the temperature at which melting occurs is fairly reproducible and reversible. This melting behaviour is accompanied by an absorption of heat as indicated by differential thermal analysis. The melting temperature of solidified dopes can also be determined by measuring the intensity of polarized light passing through a thin sample and a 90° crossed analyzer as the temperature is raised. The melting temperature is that temperature at which the transmitted light intensity increases rapidly. In general, the melting temperature increases as the concentration increases. For example, PPD—T/sulfuric acid dopes of 32, 40 and 46 g./100 ml. acid show melting temperatures of 40—50°C., 63—65°C. and 72—82°C., respectively. A dope that is incompletely mixed and has a distribution of phases of different concentration will have a broadened melting range.

As the temperature of a molten, anisotropic dope is increased, a point is reached at which the amount of anisotropic phase begins to decrease. This temperature (T_a) can be determined by a measurement of the change in the scattering of polarized light at small angles (e.g. 1°) on passing through a thin layer of dope. T_a increases with the concentration of the polymer, e.g., for PPD—T/H₂SO₄ dopes of 32, 40 and 46 g./100 ml. concentration T_a values are found to be about 80—100°C., 82—135°C. and 110 to 122°C., respectively. Even above these temperatures the dopes are largely anisotropic and give good results in the present process, but highest tenacity fibers will be obtained by the spinning of dopes at temperatures above the melting point and below T_a .

Extrusion conditions are discussed in terms

of spinning conditions for fibers in the following section. It will be understood that the comments can apply to the extrusion of films.

Spinnerets and all other apparatus parts should be constructed of materials resistant to the strong acids used.

The diameters of the holes (orifices) and the ratio of the length of the capillary/diameter of the hole (L/D) in the spinneret are not critical. Strong fibers have been obtained with round orifices ranging from 1.0 to 10 mils (0.025 to 0.25 mm) diameter and having a L/D ratio of from 1.0 to 8.3. The process is also operable with non-round holes of various shapes including narrow slits—.02 × .05 mm. or .02 × 25 mm. or .175 × 75 mm for example.

The spacing of the holes is not critical and would be dictated by construction materials and by the threadline stability produced in spinning.

The jet velocity (designated "JV") is the average velocity of the dope in the spinneret capillary as calculated from the volume of dope passing through an orifice per unit time and from the cross-sectional area of the orifice may range from 17 feet/minute (fpm) (5.1 meters/min.) or lower to 1150 fpm (350 meters/min.) or higher. The minimum value for a given dope and orifice is determined by the ability of the dope to jet continuously and cleanly. The smaller diameter orifices will display a higher minimum jet velocity than larger orifices.

The spin stretch factor (SSF) as expressed herein is the ratio of the velocity of the fiber as it leaves the coagulating bath to the jet velocity. Spin stretch factors of as low as 1.0 or lower and as high as 14 or more can be used. The minimum spin stretch factor to be used with a particular spinning dope and orifice is determined by the ability to form a filament of relatively uniform denier and the desired physical properties. The maximum useful spin stretch factor is limited by filament breakage in the process. In general, increasing the spin stretch factor from a low value at a given jet velocity affords fibers with higher tenacities and moduli and lower elongations and denier. One skilled in spinning will readily adjust orifice diameter, thickness of the gas layer, jet velocity and spin stretch factor for a given spinning dope and apparatus to obtain a fiber of the desired denier and physical properties.

It is essential that the spinneret face be separated from the coagulating bath by an inert fluid layer of gas or a non-coagulating liquid such as toluene, heptane, etc. The thickness of the fluid layer can vary from 0.1 to 10 cm. or more and preferably is from about 0.5 to 2 cm. thick. Use of larger thickness increases the opportunity for adjacent filaments to fuse together.

The configuration of the spin tube (60)

and the character of the guide (57) in Figure 1 can affect the elongation and modulus in the as-spun yarn. At the same jet velocity and windup speeds, a straight tube generally produces higher yarn elongation and lower modulus than a tube constructed at its lower end. Similarly, a roller guide generally produces higher yarn elongation than a snubbing pin. Useful spin tube dimensions will vary with spinning speeds and yarn denier.

A variety of baths may be used to coagulate the fiber. Satisfactory results have been obtained with both aqueous and non-aqueous systems. Useful aqueous systems have ranged from pure water to systems containing high concentrations of sulfuric acid (70%), ammonium hydroxide, or salts such as calcium chloride, potassium carbonate or sodium chloride. Aqueous baths containing water miscible organic solvents such as methanol, and ethylene glycol are also useful. Examples of non-aqueous coagulation baths include 100% methanol and methylene chloride solutions containing 5 to 50% of methanol, N,N'-dimethylformamide or N,N'-dimethylacetamide. Bath temperatures ranging from -25°C. to 28°C. are preferred. It is considered that a wide variety of coagulants can be used at temperatures from subzero to 50°C. or more. More preferably the temperature of the bath is kept below 10°C. (most preferably below 5°C.) in order to obtain the highest tenacity in the filaments.

Because of the degrading effects of even small amounts of acid in the yarn, complete removal of the acid is very important in obtaining high tenacity fibers. Water alone or combinations of alkaline solutions and water may be used for its removal.

A convenient washing method is, to spray the thread line as it leaves the coagulating bath with an aqueous alkaline solution (e.g. saturated NaHCO₃ or 0.05N NaOH), remove surface liquid from the thread line with a wiping device (e.g. a sponge) or a jet, wash with water (ca 75°C.) to reduce the acid content to about 1% (on a dry fiber basis) and wind up on bobbins. Such bobbins can be stored for short periods (up to about 24 hours) in water or dilute alkaline solution before the final wash. Preferably the final wash (e.g. with 75°C. water) should reduce the acid or base content below 0.01% (on a dry basis).

While small amounts of yarn can be washed and neutralized on the bobbin, it is preferred that the yarn be washed as such in thin layers in flumes, on rolls with overhead sprays, on screens, belts or the like. In a continuous process the thread line can be washed and neutralized continuously at the same speed as the thread line at any point between spinning and wind up.

The thoroughly washed fibers can be dried on the bobbin with air at up to 150°C. The

fibers can conveniently be dried on heated rolls (e.g. 160°C.). If the fibers are dried while under a tension of less than about 0.3 gpd, which is a preferred method, the properties are not significantly changed. The use of tensions above 0.3 gpd reduces the elongation and increases the modulus from that obtained by tensionless drying.

The properties of the as-spun yarns can be altered by a heat treatment. Heating a yarn under tension, preferably in an inert atmosphere, at temperatures of 150°C. to 550°C. increases the yarn modulus from about 15 to 100% and reduces the yarn elongation by about 50%. The modulus increase is greater with increasing tension and temperature. Typical tensions and times of exposure used at 150°C. are about 2 to 12 gpd for 1.5 to 6 seconds and at 550°C. are 0.5 to 2 gpd for 1 to 6 seconds. At low and intermediate temperatures, the yarn tenacity is not significantly changed, but it may be reduced after treatment at 450°C. or more.

Yarns to be heat-treated are usually dry beforehand but the heat treatment effects can be produced on wet yarns direct from washing or on rewet dried yarns by slightly lengthening the time of heating.

Test Procedures

Inherent Viscosity

Inherent viscosity (I.V.) is defined by the equation:

$$I.V. = \frac{\ln(\eta_{rel})}{c}$$

where *c* is the concentration (0.5 gram of polymer or fiber in 100 ml. of solvent) of the polymer solution and η_{rel} (relative viscosity) is the ratio between the flow times of the polymer solution and the solvent as measured at 30°C. in a capillary viscometer. The solvent is concentrated sulfuric acid (95—98% H₂SO₄) unless otherwise specified.

Filament properties are measured on fibers that have been conditioned at 21°C. and 65% relative humidity (R.H.) for at least 16 hours unless otherwise specified. Yarn properties are measured on yarn that has been conditioned at 24°C. and 55% R.H. for at least 16 hours. All measurements are made in the fiber conditioning environment.

Tenacity (breaking tenacity) (Ten.), elongation (breaking elongation) (E), initial modulus (Mi), and toughness (breaking toughness) (Tou.) are obtained from breaking a single filament or a multifilament yarn on an Instron (trade mark) tester (Instron Engineering Corp., Canton, Mass.).

Single filaments are broken with a gage length (distance between jaws) of 1.0 inch (2.54 cm.). The results on 3 filaments are averaged. Yarns are given 3 turns per inch

(2.54 cm.) twist (under 0.1 gpd tension) and broken with a 10 inch (25.4 cm.) gage length. All samples are elongated at a constant rate of extension (10% elongation/minute for fibers having an E of under 8%, and 60% elongation/minute for fibers with E of 8 to 100%) until the sample breaks.

The denier of a single filament (d.p.f.) is calculated from its functional resonant frequency, determined by vibrating a 7 to 9 cm. length of fiber under tension with changing frequency. (A.S.T.M. D1577—66, part 25, 1968). This filament is then used for 1 break.

The denier of yarn is determined by weighing a known length (at 0.1 gpd tension); 90 cm. length is convenient.

The tenacity (grams/denier, g.p.d.), elongation (%), initial modulus (g.p.d.) and toughness (gram-centimeters per denier centimeter or simply g.p.d.) as defined in A.S.T.M. D2101, part 25, 1968 are obtained from the load-elongation curve and the measured denier. In actual practice, the measured denier of the sample, test conditions and sample identification are fed to a computer before the start of a test; the computer records the load-elongation curve of the fiber as it is broken and then calculates the fiber properties.

It should be noted that different values are obtained from single filaments (filament properties) and from multifilament strands (yarn properties) of the same sample. Filament tenacities are higher than yarn tenacities—typically about 1.2:1, filament elongations are higher than yarn elongation and filament moduli are lower than the yarn values. Unless specified otherwise all properties given herein are filament properties.

The physical properties of all yarns of the examples are measured with the yarn having 3 twists/inch (t.p.i.) (per 2.54 cm). This results in a different twist multiplier (T.M.) for yarns of different denier.

$$T.M. = \frac{(\text{twists/inch}) \sqrt{\text{denier of yarn}}}{73}$$

It has been observed that the initial modulus of a yarn decreases as the T.M. is increased. For example, the modulus of a 700 denier yarn (T.M. 1.08 at 3 t.p.i.) will be lower by about 5% than that of the equivalent 200 denier yarn (T.M. 0.58 at 3 t.p.i.).

Film tensile and elongation properties are measured on films that have been conditioned in the same environment and manner as used for yarns. Test results are obtained from breaking the film using a 2 inch (5 cm.) gauge length at 100% elongation per minute.

Dope viscosities are measured by a Brookfield Viscometer with a No. 7 spindle at 10 rpm.

The orientation angle of the fiber as discussed in "X-Ray Diffraction Methods in Polymer Science" by Leroy E. Alexander, Wiley-Interscience (1969) Chapter 4, p. 264, is determined by the following method. A wide angle X-ray diffraction pattern (transmission pattern) of the fiber is made using a Warkus pinhole camera. The camera consists of a collimator tube 3 in. (7.6 cm.) long with two lead (Pb) pinholes 25 mils (0.0635 cm.) in diameter at each end, with a sample-to-film distance of 5 cm.; a vacuum is created in the camera during the exposure. The radiation is generated by Philips (trade mark) X-ray unit (Cat. No. 12045) with a copper fine-focus diffraction tube (Catalog No. 14000320) and a nickel beta-filter; the unit is operated at 40 kv. and 16 ma. A fiber-sample holder 20 mils (0.051 cm.) thick is filled with the sample; all the filaments in the X-ray beam are kept essentially parallel. The diffraction pattern is recorded on Kodak No-Screen medical X-ray film (NS—54T) or equivalent. The film is exposed for a sufficient time to obtain a pattern which is considered acceptable by conventional standards (e.g., a pattern in which the diffraction spot to be measured has a sufficient photographic density, e.g., between 0.2 and 1.0, to be accurately readable). Generally, an exposure time of about 25 minutes is suitable; however, a lesser exposure time may be suitable, and even desirable, for highly crystalline and oriented samples to obtain a more accurately readable pattern.

The arc length in degrees at the half-maximum intensity (angle subtending points of 50% of maximum intensity) of one of the principal equatorial spots is measured and taken as the orientation angle of the sample. The specific arc used for orientation angle determinations on fibers described in the following examples where more than one major arc is present is the one which occurs at the higher value of 20.

In one case, specifically poly(p-phenylene chloroterephthalamide), the diffraction pattern of the heat-treated fiber has been found in some instances not to contain any principal equatorial spots. When this occurs, two spots are generally observed, one on either side of the equatorial position. The orientation angle of these fibers is then measured on a suitable meridional arc (specifically the 006 reflection) using a diffractometer and this angle is compared to the orientation angle obtained on the corresponding arc by electron diffraction as described later.

The orientation angles of fibers of this invention are determined by a densitometer method from the x-ray film. The azimuthal intensity distribution of the diffraction arc is obtained by use of a Leeds & Northrup Microphotometer (Catalog No. 6700—P1)

whose electronic components have been replaced by a Keithley 410 Micro-Microammeter (Keithley Instruments Inc., Cleveland, Ohio). The output of this apparatus is fed to a Leeds & Northrup Speedomax (trade mark) Recorder, Type G.

In operation, the film is placed on the stage, the instrument is focused on the film, and the center of the diffraction pattern is made coincident with the stage center; both these centers are made coincident with the light beam of the instrument. The stage and mounted film are moved to permit the light beam to pass through the most intense area of the diffraction spot, the opposite spot is checked to insure true centering, and after any necessary fine adjustments are made, the recording of the azimuthal intensity trace through at least 360° rotation of the film is made on suitable coordinate paper. There is obtained a curve which has two major peaks in which the intensity axis is considered the vertical axis and the angular displacement the horizontal axis. A base line is drawn for each peak as a straight line tangential to the minima on each side of the peak. A perpendicular line is dropped from each peak maximum to the base line. Through the mid-point of each perpendicular line (i.e., the "half-intensity" point) is drawn a horizontal line which intersects each leg of the respective curves. The leg-to-leg length of each "half-intensity" horizontal line is converted to the degrees of arc as follows. The horizontal distance equivalent to 360° of angular displacement is determined by rotation of a given point through 360° followed by direct measurement of the horizontal displacement for such a rotation. For example, one of the two major peaks above may be used for this purpose. By direct proportion, the "half-intensity" leg-to-leg distance is converted to a degree value. The values for the two arcs are averaged and this is the orientation angle referred to herein. Values determined by this method have been shown to be precise to $\pm 0.7^\circ$ at the 95% probability level.

Method For Apparent Crystallite Size

X-ray diffraction scans of the fibers of this invention are different depending on the chemical structure, crystallinity and the degree of order and orientation in the fiber. A measure of apparent crystallite size (ACS) for each of the observed major diffraction peaks is calculated from data obtained from an X-ray diffraction pattern using a reflection technique to record the intensity trace by means of an X-ray diffractometer.

A Philips X-ray generator, wide angle diffractometer and electronic circuit panel are used to record the diffraction pattern. Approximately 1.5 meters of yarn is wound around a modified Philips sample holder with the axis of the yarn perpendicular to the

mechanical (2θ) axis of the diffractometer. The modification of the sample holder consists of cutting approximately 21 notches, 0.01 inches wide, along the edge of the holder and cementing a thin sheet of lead foil across the bottom side of the rectangular opening so that only the fibers on top will be exposed to the X-ray beam. Using Nickel-filtered Copper radiation ($1.5418\text{\AA}$), a trace of the diffracted intensity is recorded from 6° to $38^\circ 2\theta$, at a scanning speed of $1^\circ 2\theta$ per minute, a chart speed of 0.5 inches per minute, at a time constant setting of 2, with 0.5° scattering and receiving slits and employing a scintillation detector with a pulse height analyzer, 2θ being the angle between the undiffracted and diffracted beam. The full scale deflection of the recorder is set so that the entire diffraction curve remains on scale, which is linear, but with as large a response as possible and preferably with the maximum intensity at least 50% of the scale.

The diffraction scans or diffractograms observed for fibers of this invention consist, when the sample is crystalline, of a pattern of multiple peaks. In most cases two major peaks are located in the range of about 17° to $25^\circ 2\theta$ (for most samples 19° to $24^\circ 2\theta$). In a few cases one of the two peaks will be evident only as an inflection, which, however, will be sufficient to locate its position. Occasionally, only one major narrow crystalline peak is observed. The procedure used to obtain the apparent crystallite size (cf "X-ray Diffraction Methods in Polymer Science by L. E. Alexander, Wiley-Interscience, 1969, Chapter 7) is given below.

If the sample is not crystalline, a single very broad peak will be the only feature of the diffractogram. In this case the apparent crystallite size is taken as zero.

A base line is first established on the scan by drawing a straight line between the points on the curve at 9° and $36^\circ 2\theta$. Next, a vertical straight line is dropped from the top center of the selected peak to the base line, and a point midway between the top of the peak and the base line marked on this vertical line. A horizontal line is then drawn at this midpoint. This line may cut one shoulder of the peak or, if the minimum in between the two major peaks is low enough, both shoulders. The breadth of the selected peak at this point is obtained by either measuring the distance along the horizontal line from one shoulder to the vertical line and doubling it, or when possible the distance between both shoulders along the horizontal line. The distance is expressed as peak (or "line") breadth in radians, obtained by using the scale for 2θ (established on the chart previously) to convert the observed line breadth in inches or centimeters to degrees and, eventually, radians. If B is the observed line breadth in radians, the corrected line breadth β in radians is (cf.

Alexander, op. cit., p. 443),

$$\beta = \sqrt{b^2 - b^2 \lambda}$$

where b is the instrumental broadening in radians. The instrumental broadening constant b is determined by measuring the line breadth of the peak located at approximately $28^\circ 2\theta$ on the diffractogram of a silicon crystal powder sample supplied by the manufacturer of the X-ray equipment (Philips Electronic Instruments, Mount Vernon, N.Y.). The constant b is this line breadth in radians. The instrument settings used are: scanning speed $0.125^\circ 2\theta$ per minute, time constant setting 8 and chart speed $1''/\text{min}$.

Finally, the *apparent crystallite size* associated with the selected reflection is given by

$$\text{ACS} = \frac{K \lambda}{\beta \cos \theta}$$

where:

- K is taken as one (unity)
- λ is X-ray wavelength ($1.5418\text{\AA}$ here)
- β is corrected line breadth in radians (see above)
- θ is the Bragg angle ($1/2$ of the 2θ value of the selected peak, as obtained from the diffractogram).

The *primary apparent crystallite size* (PACS) used in the structural definition of the products of this invention is defined for those fibers having more than one major crystalline peak as the apparent crystallite size calculated for the peak which is located at the smaller (smallest) value of 2θ .

In this measurement, it is recognized that line breadth is affected by strains and imperfections in crystals (which are of unknown magnitude), as well as by crystallite size, and for this reason the value of crystallite size obtained is called *apparent*.

Values determined by this method have been shown to be precise to $\pm 2\text{\AA}$ at the 95% probability level.

QUANTITATIVE LATERAL CRYSTALLITE ORDER TEST

Introduction

The test, which involves the application of electron diffraction to thin fiber sections, demonstrates that the products of this invention have a unique lateral arrangement of crystalline planes which can be shown to be associated with the improved tenacity of the products. The preferred structure has one set of planes whose average position is parallel to planes that contain the fiber axis and radius.

In the test procedure the major (i.e., most

intense) equatorial reflections in the conventional fiber x-ray diffraction pattern (obtained in the method for apparent crystallite size) are identified. Most fibers of this invention have two major reflections corresponding to d-spacings of from about 3.9 to $4.9\text{\AA}$ and are designated as "Class I Structures". Some fibers have only one major reflection corresponding to the same d-spacing range and are designated as "Class II Structures". An electron diffraction unit is calibrated so that the above major reflections can be identified in the electron diffraction pattern of specified thin fiber sections, since this test procedure is only concerned with those major reflections.

The densities of the major reflections in the electron diffraction patterns are measured in a specified manner and a lateral crystallite order (L.C.O.) value calculated.

Section Preparation

The fibers (or films) to be tested are heated relaxed or under low tension for a period of the order of about 10 seconds at a temperature in the range of $400\text{--}500^\circ\text{C}$. with the exact conditions selected to avoid decomposition or degradation of the fiber. This heating is conveniently done by passing the fiber through a nitrogen filled heated metal tube under tension just sufficient to prevent contact with the tube.

A well-aligned bundle (about 1 mm. in diameter and 5 cm. long) of fibers is embedded in epoxy resin. A short segment is cut from the preparation and glued to the end of a tapered rod as a holding tool.

Heated film samples are most easily embedded using small "BEEM" capsules (e.g., from Ladd Research Industries, Burlington, Vermont). A cut is made in the tapered tip of a capsule along a diameter to admit the specimen, which is inserted into the cut with the edge of the film at 45° to the capsule axis. The capsule is then filled with epoxy resin and polymerized.

Sections 0.1 to $0.2\ \mu$ thick are cut from the embedded fiber or film samples preferably using a diamond knife and a microtome designed for preparing very thin sections (e.g., the "Ultratome" by LKB of Stockholm, Sweden) at a cutting speed of 1 mm./second or less. The samples should be oriented while cutting so that the knife edge is perpendicular to the long axis (direction of extrusion) of the fiber bundle of film and is parallel to the thickness direction of the film.

Fibers and films having a class I structure are cut at an angle of about 45° to the long axis of the sample.

Fibers and films having a class II structure are cut so that the molecular chain axis is essentially normal to the surface of the section (established by using a polarizing microscope with a universal stage).

The film section should be prepared in such a way that it contains at least one long side (parallel to cutting direction) and one short side (normal to cutting direction) which are original extrusion surfaces.

- Usable sections should be of such a quality that they do not contain excessive knife marks, chatter marks, wrinkles or compression distortions (see D. Kay, "Techniques for Electron Microscopy", Second Edition, page 220; F. A. Davis, Philadelphia 1965).

Electron Diffraction

- The fiber sections prepared above are transferred to electron microscope grids and placed in the conventional high resolution position of an AEI EM-6G electron microscope operated at an accelerating potential of 100 KV. The half-plate mask is turned into position. The microscope is set for diffraction and the diffraction coarse focus is turned one click counterclockwise (i.e., to produce a magnification of about 600X) from the diffraction focus position. The section to be studied is then rotated until the long axis (approximately parallel to the cutting direction and passes through the center of the section) of the fiber (or film) section is perpendicular to the edge of the half-plate mask. The selected area aperture (hereafter "aperture") (having an effective diameter of about 1 micron in the object plane) is placed along the short axis (through the center of the section and perpendicular to the long axis) of the fiber section centered at a point that is one or two aperture diameters from the edge of the fiber section (this will be referred to as the S-position). The diffraction pattern is then focused, the photographic film (DuPont Ortho-S) is advanced a little more than half-way into the column and the pattern recorded. The diffraction coarse focus is again turned one click counterclockwise and the aperture moved to a position along the long axis of the fiber section and centered at a point that is at a distance of one or two aperture diameters from the edge of the fiber section (this will be referred to as the L-position). The diffraction pattern is focused, the photographic film is advanced all the way into the column and the diffraction pattern recorded. The process is repeated for at least three different fiber sections.

- Figure 2 depicts the arrangement of a fiber section (2) (cut at 45°), the aperture (4) and the edge (6) of the half-plate mask in the microscope image prior to taking an S-position diffraction pattern. Also shown are the long axis (8) of the section perpendicular to edge (6), the short axis (7), and the position (9) of the aperture for the L-position pattern.

Sections of a film are oriented as above. The aperture is placed at any point one or two diameters in from either of the two long

edges of the section and at a point one or two aperture diameters from the short edge of the section near its center for the S- and L-positions respectively.

The above procedure, after processing the film, yields three photographic negatives each having two electron diffraction (e.d.) patterns and a line (made by the edge of the half-plate mask) for each pattern.

Figure 3 depicts a typical e.d. pattern taken in the S-position of a poly(*p*-phenylene terephthalamide) fiber of this invention. An index line (18) has been drawn through the center of the pattern parallel to the edge of the half-plate mask. The pattern has pairs of diffraction arcs (10, 12 and 14) with each arc of a pair being located by equal radii (from the center of the pattern). Each arc of a pair has its point of maximum density (hereafter "maxima" for arcs corresponding to the major equatorial reflections in the x-ray fiber pattern), as measured in an azimuthal direction, located on a line, not shown (hereafter "center line") passing through the center of the pattern. The center is obscured by a circular region of high density (16) caused by the incident electron beam. Arcs 10 and 12 are identified as the major reflections for this class I structure and therefore have "maxima".

Figure 4 depicts an e.d. pattern taken in the L-position of the same section as used for Figure 3. In this and succeeding Figures the dense portion about the center (20) has been omitted and only the major reflections are shown.

Figure 5 depicts an e.d. pattern in the S-position. The locations of maxima (10, 11 and 12) correspond to the major reflections by x-ray.

A section of a fiber that is not a part of this invention that is typical of poly(*p*-phenylene terephthalamide) fibers prepared by conventional wet spinning yields e.d. patterns similar to Figure 4 in both the S- and L-positions.

Quality Tests for Diffraction Patterns— Class I Structures

Suitable e.d. patterns have features as follows:

- A. At least one pair of maxima with a center line that is parallel (within $\pm 30^\circ$) to the index line and one of the following arrangements.
 - (1) a second pair of maxima with a center line that is parallel (within $\pm 30^\circ$) to the index line (cf. Fig. 4), or
 - (2) a second pair of maxima with a center line that is perpendicular (within $\pm 30^\circ$) to the index line (cf. Figs. 3 and 5), or
 - (3) a diffraction ring (i.e., a major 360° arc without maxima)

- (4) In some instances the above type patterns may have a second pair of maxima having equal radii to one of the above maxima (cf. Figs. 5 and 6).

5 B. Two major diffraction rings

If features A or B are not realized, a new diffraction pattern set should be made on another section, or another diffraction pattern made on the same section with a slightly displaced selected area aperture position.

If the center lines of two pair of maxima are mutually perpendicular (within 30°) in the S-position pattern then the same reflections in the L-position must be either (1) on center lines that are parallel to one another (within 30°), cf. Figures 3 and 4, or (2) on the original mutually perpendicular (within 30°) center lines with the inner and outer reflections interchanged. The absence of condition (1) or (2) is evidence of cutting distortion and new sections should be cut and examined.

The maxima and/or major rings in a set of patterns for a given sample are designated as "a" or "b" by inspection of the S-position pattern.

If the S-position pattern has maxima on a line perpendicular (to within $\pm 30^\circ$) to the index line (cf. Figs. 3, 5 and 6), then all rings and/or maxima in both the S- and L-position patterns which correspond in radius [from the center of the pattern] to these maxima are to be labelled "b" and the other major maxima or rings, if they are present, are labelled "a".

If there are no maxima on a line perpendicular (to within 30°) to the index line, and if (1) two pairs of maxima exist that can be connected by lines parallel (to within 30°) to the index line, cf. arrangement of Fig. 4, or (2) if both reflections are complete rings, or (3) if a pair of maxima and a ring are present then the outer (greater distance from the center of the pattern) pair of maxima or outer ring is to be labelled "b" and the inner one "a".

Quality Tests for Diffraction Patterns— Class II Structures

50 Suitable e.d. patterns have features as follows:

- A. a single ring in both the S- and L-position patterns or
- 55 B. a pair of maxima with a center line that is within 25° of being (a) parallel or (b) perpendicular to the index line in the S-position pattern and an L-position pattern having a pair of maxima with a center line that is within 25° of being perpendicular or parallel to the index line for conditions (a) and (b) for the S-position, respectively.
- 60

Densitometry

The processed film bearing the e.d. pattern is examined with a Joyce-Loebl Microdensitometer using a $10\times$ objective, 20:1 ratio arm, 1.6 d wedge range and a 4 mm. square slit. Each pattern of a class I structure is scanned along a center line connecting the maxima most nearly parallel to the index line or in the absence of maxima in that area (e.g., for a ring) along the index line. Class II structures having a uniform ring as the major reflection are scanned twice through the center of the pattern, (1) parallel and (2) perpendicular to the index line. A pattern of a class II structure having a pair of maxima are scanned along the center line of the maxima and on a line through the center of the pattern perpendicular to the center line.

Figure 7 depicts densitometer trace (24) made along the center line of maxima (10) of the pattern of Figure 4. The peaks (26) and (28), (designated "a" and "b") are due to maxima (10) and (12) in Figure 4. Maximum density plateau (30) is due to the darkened center and a base line is shown.

Analysis of Densitometer Traces

The test requires that the ratio between the heights (proportional to densities in the e.d. pattern) of the peaks be known and the peaks designated "a" or "b" by reference to the e.d. pattern. Because the peaks may be close and interfere with each other, correction for this interference (if present) must be made. The method of doing this and the definition of peak height, are discussed below. In all cases a curved background line (32)—cf. Fig. 8—is drawn with a flexible curve rule between the bottom (34) of the center trace (35) and the lower outer portion of the trace (36).

1. Traces having two resolved peaks

The outer shoulder (27) of the inner peak (26) is extended by a straight line (38) drawn parallel to the essentially linear upper portion of the outer shoulder (29) of the outer peak (28). The inner shoulder of the outer peak (28) is extended by a line (40) drawn parallel to the essentially linear upper portion of the inner shoulder of the inner peak (26). The peak height of a peak is the smaller vertical distance between the peak (1) the background line or (2) the extension of the shoulder of the other peak. In Figure 8 the peak height of peak (26) is measured on the vertical (42) from the peak to the background line. The peak height of peak (28) is measured on the vertical (44) between the peak and the extension (38) of the shoulder.

2. Traces having two peaks, one resolved and one an inflection

These are resolved in an analogous manner

to the above—cf. Figure 9. A piece of tracing paper is placed over the trace and a horizontal fiducial line drawn. The portion of the trace which includes the inflection (28) of the unresolved peak and the shoulder (31) of the inflection is drawn on the paper. The paper is then shifted, keeping the fiducial line horizontal, so that the drawing of the shoulder blends into the shoulder (27) of the resolved peak and the lower shoulder (33) of the inflection. The drawing is transferred—by carbon paper—to the original trace to give a corrected shoulder (44). The peak height of the inflection (28) is the maximum vertical separation between the original and the corrected shoulder of that peak. The peak height of the resolved peak (26) is the vertical distance from it to the background line.

3. Traces having a single peak

The peak height is the vertical distance from the peak to the background line.

A. Traces with two peaks, neither resolved

The peak heights are considered to be equal and the ratio of the two peak heights is taken as one, cf. Figure 10 which depicts a half scan of the pattern of Figure 6.

Calculations

The sum of the densities of the major diffractions measured in a half scan (center outward) should be at least 0.5 above the density of the background line.

The scan of the entire pattern should give a substantially symmetrical trace, with the heights (measured above the background line) of the left-hand and right-hand peaks associated with the most intense maximum in the pattern each being no more than 20% from the mean of the left- and right-hand values.

Based on the structural factors which determine peak heights, a parameter, A , has been selected as a measure of the degree of preferred structure in the products of the invention. For class I structures $A = (a/b)_S / (a/b)_L$ where a/b is the ratio of the peak heights of diffractions a and b and the subscripts S and L refer to the S - and L -positions respectively.

In the case of class II structures, $A = (H_1/H_2)_S / (H_1/H_2)_L$ where H_1 and H_2 are defined as follows:

In a (single) ring e.d. pattern, H_1 and H_2 are the peak heights in a scan perpendicular to the index line, and parallel, respectively. For an e.d. pattern having a single pair of maxima, H_1 and H_2 are the peak heights in a scan (a) perpendicular (within 25°) to the index line and (b) perpendicular to scan (a) direction, respectively. The subscripts S and L refer to a pattern taken in the S - and L -positions respectively.

A value of " A " (A_r) is calculated using the values of a and b on the right-hand half of the

densitometer trace for both positions. A second value of " A " (A_l) is calculated using the values of a and b on the left-hand half of the densitometer trace for the same patterns.

The Lateral Crystallite Order (L.C.O.) value for a fiber (i.e., for a given section) is the average of A_r and A_l for that section. If both values are finite, they are averaged directly. If the values consist of a finite value and an infinite value, the reciprocals of the values are averaged and the reciprocal of that average reported. If both values are infinite, the average is infinity.

Following is the average L.C.O. value and the range of values for 3 filaments examined for the examples using "?" as infinity.

Example	Average LCO Value	Range
I	i	i-i
IIA (a)	72	24-i
(b)	26	9.5-45
(c)	i	i-i
IIB	18	5.5-34
IV a	i	i-i
a ₁	i	i-i
b	34	29-38
b ₁	114	72-i
e	1.4	1.2-1.6
e ₁	11	3-25
f	68	62-79
f ₁	i	i-i
g	152	96-i
h	118	20-306
h ₁	35	27-44
i	i	i-i
j	1.6	0.9-2.8
k	i	i-i
k ₁	7.2	6.6-8.0
l	38	20-i
r	1.8	1.7-1.9

65

70

75

Example	Average LCO Value	Range	L.C.O. values for PPD—T filaments prepared by conventional wet spinning methods range from 0 to 4.5 with most of the values being about 1.0.
s	1.2	0.6–2.2	5
V a	44	15–i	
c	6.5	5.5–8.3	<i>Fiber Densities</i> Fiber densities are measured using the density-gradient tube procedure for plastics specified in ASTM method D 1505—68, Part 27, 1970, modified by using heptane-carbon tetrachloride at 25°C. as the liquid system for the density-gradient tube. The densities of four loosely knotted short (about 1 to 2 cm) lengths of filament or yarn are determined and the average value reported. Following are the values (to three significant figures) of density (in grams/cubic centimeter, g/cm³) for the fibers of the examples.
VIII d	72	15–132	
e	462	154–i	
f	105	35–i	
g	37	15–81	
h	65	12–110	
i	i	i–i	

10

15

Example	Table	item	density
I		as-spun	1.44
II A	VI	a	1.45
II A	VI	b	1.45
II A	VI	c	1.45
II B			1.42
IV	III	a	1.48
		a ₁	1.43
		b	1.42
		e	1.40
		e ₁	1.42
		f	1.41
		f ₁	1.42
		g	1.43
		h	1.43
		h ₁	1.46
		i	1.43
		j	1.47
		k	1.39
		k ₁	1.36
		l	1.43
		r	1.46
		s	1.40
V	IV	a	1.45
		b	1.46
		c	1.44
VIII	VI	d	1.45
		e	1.45
		f	1.44
		g	1.41
		h	1.45
		i	1.43

The wholly aromatic polyamide fibers of this invention will preferably have a density of at least 1.38 g./cm³ to assure that the fibers will not have an excessive amount of voids or bubbles that would significantly reduce the expected tensile strength.

In general, at least parts of all of the following Examples illustrate both the product and process of the invention although Examples II, VI and VII are primarily for the purpose of illustrating the process. Except for the comparative test mentioned in Example VI, all spinning processes in the Examples are according to the invention.

The following fibers of the Examples are, however, comparative: the heat-treated fibers at the end of Example I; (g) and (h) of Example III in Table I; (d) in Table II; (c), (d), (e) and (j) of Example VI in Table V.

EXAMPLE I.

PPD—T of 5.4 I.V. is mixed in a beaker with sulfuric acid (99.7% H₂SO₄) in the ratio of 46 grams of polymer per 100 ml. of acid (20% by weight). The crude mixture of dough-like consistency is transferred to a mixing device consisting of two open top cylinders (each of about 250 ml. capacity) connected by stainless steel tubing which is also connected through a tee to a gooseneck that is temporarily plugged. Each cylinder has a filter pack [3—50 mesh screens/1—325 mesh screen/3—50 mesh screens, mesh/inch (mesh/2.54 cm.)] at its base. The mixing device is fitted to a pair of pistons which closely fit each cylinder. A small hole in each piston is opened for the initial fitting by each piston to insure the removal of air and then

closed. A water bath at about 95°C. is placed around the mixing device. After about 1 to 2 hours the polymer-solvent mixture is pushed by the pistons from 1 cylinder to the other for a total of about 5 cycles. With all of the mixture, now a dope, in 1 cylinder (and the connecting passage), the plug is removed from the gooseneck attached to the connecting passage and the gooseneck is connected to an electrically heated spinning block having a stainless steel felt filter (Dynaloy X5 made by Fluid Dynamics, Inc., of Morristown, N.J.) and a 0.5 inch diameter spinneret with 50 holes of 2 mil (0.05/mm)/diameter. The 95°C water bath is replaced around the mixing device and the initial length of the tubing. The short length of the tubing between the water bath and the spinning block (100°C.) is wrapped with a steam line.

The dope is pumped from the mixing device through the spinneret at 210 f.p.m. (64 m.p.m.) jet velocity through a 1 cm layer of air vertically into water at 4°C. using a spinning tube and windup similar to that shown in Figure 1 at a speed to give a SSF of 6.9.

The fibers after a thorough washing and air drying have an I.V. of 4.8 and a d.p.f. of 0.92.

A portion of the dried yarn is plied to a total denier of 183 and passed through a 10 feet long (3.05 meters) tube containing nitrogen at 525°C. under a tension of 1.4 gpd at a speed to give a residence time of about 2 seconds (300 fpm). The yarn is only drawn about 1.005 times its original length.

Properties of the plied as-spun and heat treated fibers are given below.

	as-spun	heat-treated
filament, Ten./E/Mi/tou.	26/3.7/750/0.50	21/2.2/950/0.23
yarn, Ten./E/Mi	22.8/2.8/811	20.5/1.7/1103
yarn, tou., gpd	0.314	0.164
orientation angle	11.2°	9.0°
apparent crystallite size	40 Å	109 Å

EXAMPLE II.

A

PPD—T polymer of 6.0 I.V. is added to sulfuric acid (99.7% H₂SO₄) at 40°C. in a water-jacketed commercial planetary mixer through a top entrance over about 2 minutes to give a ratio of 46 grams of polymer/100 ml. of acid. The mixer is sealed and placed under 68.5 to 76 cm. of Hg vacuum. The temperature of the water jacket is increased to 85°C. and the planetary mixing blades started at a slow speed. After about 12 minutes the jacket temperature is reduced to 77°C. which affords a temperature in the solution of between 79—82°C. Mixing is continued for about 2 hours. The solution then has a bulk viscosity of 2300 poises.

The dope is transferred to a glass-lined, water-jacketed (90°C.) kettle. A vacuum of about 69—76 cm. of Hg is applied for about 30 minutes to remove any air or bubbles caused by the transfer. The dope is pumped from the kettle through a transfer line closely wrapped with a water line (90°C.) to an electrically heated (80°C.) spinning block and attached gear pump. The gear pump meters the dope through another passage in the block to a water-jacketed (80°C.) spinneret pack containing a backing screen, stainless steel felt and a 0.5 inch (12.7 mm.) diameter spinneret containing 100 holes of 2 mil (0.051 mm.) diameter. The dope is extruded from the spinneret at a jet velocity of about 207 f.p.m. (63 m.p.m.) vertically through a 5 mm.

layer of air into 1°C. water in a spinning tube similar to that shown in Figure 1. Items a and b are made using a freely revolving roller under the spin tube to direct the threadline to the windup while item c uses a ceramic rod. The yarn is wound up at different speeds on a bobbin under a water (50°C.) spray. The bobbins of yarn are stored in a tank of water. The bobbins are then submersed in 0.1N NaHCO₃ and then further extracted with water (70°C.) on an advancing reel extracting device of the type shown in U.S. Patent 2,659,225. The extracted yarn is wound up and dried on the bobbins at 70°C. Properties of the dried yarn of 5.2 I.V. are given as items a, b and c in Table VI. These items have spin stretch factors of 1.5, 3.4 and 4.4 respectively.

B

A dope containing 46 grams of PPD—T (I.V. 5.9) per 100 ml of sulfuric acid (above 99% H₂SO₄) is mixed and extruded from a slot 2.5 mil × 0.35 inch (0.63 × 8.9 mm) at a jet velocity of about 64 feet (19.5 m) per minute through a 3.2 mm layer of air into a 1.6 × 25 mm vertical flume of 7°C. water and the film passed under a ceramic rod and wound up on a bobbin at a SSF of about 2.3. The bobbin is sprayed with saturated aqueous NaHCO₃ solution. After neutralizing, washing, and drying, the film of 871 denier has a Ten./E/Mi 18/5.7/360 when broken using a 2" (5cm) gauge length at 100% elongation per minute. Conditioning and testing is done in the environment used for yarns. The film has an I.V. of at least 5.0.

EXAMPLE III.

This example shows the use of other sol-

Dopes of PPD—T of 5.4 I.V. (4.6 for items f, k, m and n) and various acids and acids containing additives are prepared by hand mixing followed by 15 to 120

minutes of mixing in the mixing device of Example I. The dopes are extruded with apparatus similar to Example I through a spinneret with twenty 3 mil (0.076 mm.) diameter holes through a 1 cm. layer of air into 1°—3°C. water, wound up, thoroughly washed in water and air dried on the bobbin.

Specific conditions and results are given below. Solvents used are HSO₃Cl, HSO₃F, HSO₃F/H₂SO₄ mixture (49/51 by weight), and H₂SO₄ (100%) for items a, b, c, and d respectively. The solvent for item c is a mixture of FSO₃H and hydrofluoric acid and for items f-n a mixture of an additive and H₂SO₄ (100%) is used. Windup speeds used range from 608 (item j) to 2000 (item g) feet/minute (185 to 610 m.p.m.). The concentration of the spinning dopes ranges from 34 (item a) to 47 (item f) grams of polymer/100 ml. of solvent and additive. Other specific conditions and fiber properties are given in Table I.

It is observed that the use of the sulfonic acids as additives in items f and g affords a lower viscosity dope than with sulfuric acid alone.

The dope of item e containing hydrofluoric acid has a melting point that is about 50°C. lower than the melting point of a dope with fluorosulfuric acid as the solvent (e.g., item b) and can be spun at a lower temperature.

The fiber from item g has an unusually high as-spun yarn modulus. Similar high values have been obtained from dopes containing trifluoromethanesulfonic acid as an additive.

The amount of additive that can be tolerated, under normal spinning conditions, by merization are given in Table III. When 2 additive/solvent ratio for item f yields only a paste that cannot be extruded. The use of a 20/80 additive/solvent ratio for item m and 20% polymer gives a very viscous mixture that cannot be extruded. The use of a 40/60 additive/solvent ratio for item j gives only a dry crumb.

TABLE I

Item	Solvent Additive	Solvent	% Polymer	Spinneret Block Temp. °C.	S.S.F.	Filament Properties				
		Additive				Ten.	E	Mi	d.p.f.	I.V.
a	none	100/0	16	50	4.0	21	6.8	430	2.3	4.5
b	none	100/0	20	60	3.5	21	4.7	600	4.1	5.1
c	none	100/0	20	60	4.1	26	5.6	440	2.9	5.2
d	none	100/0	20	86	6.4	27	4.3	640	2.3	5.0
e	hydrofluoric acid	80/20	22	37	1.3	17	3.7	460	6.6	5.0
f	trifluoromethanesulfonic acid	50/50	20	80	7.7	22	3.9	630	1.5	4.3
g	1,1,2,2-tetrafluoroethane- sulfonic acid	80/20	20	102	12.2	21	2.8	810	1.3	4.7
h	p-chlorobenzenesulfonic acid	80/20	20	114	5.8	19	2.9	740	1.1	4.5
i	trifluoroacetic acid	80/20	17	77	4.7	25	5.2	470	3.0	4.5
j	dichloroacetic acid	80/20	20	99	4.1	17	3.9	560	3.2	4.0
k	2,2,3,3-tetrafluoropropanol-1	80/20	17	80	4.3	14	4.7	430	2.5	4.1
l	hexafluoroisopropyl alcohol	80/20	17	110	4.4	18	4.4	520	3.4	5.0
m	2,2,2-trichloroethanal	82/18	17	80	5.0	15	3.7	570	3.5	4.4
n	nitrobenzene	88/12	18	80	3.6	15	4.3	390	3.3	4.2

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TABLE II

Item	Diamine — Diacid Chloride	Polymer	Polymer Code
a.	chloro-p-phenylenediamine — TC1	poly(chloro-p-phenylene terephthalamide)	Cl PPD-T
a ₁ .	chloro-p-phenylenediamine/PPD — TC1	copoly(chloro-p-phenylene/p-phenylene terephthalamide)	Cl PPD/PPD-T
b.	1,2-bis(p-aminophenyl)ethane/PPD — TC1	copoly(4,4'-bibenzylene/p-phenylene terephthalamide)	DDE/PPD-T
c.	3,3'-dimethylbenzidine/PPD — TC1	copoly(3,3'-dimethyl-4,4'-biphenylene/p-phenylene terephthalamide)	DiMePP/PPD-T
d.	m-phenylenediamine/PPD — TC1	copoly(m-phenylene/p-phenylene terephthalamide)	MPD/PPD-T
e.	PPD — 4,4'-bibenzoyl chloride/TC1	copoly(p-phenylene 4,4'-biphenylene-dicarboxamide/terephthalamide)	PPD-BB/T
f.	PPD — fumaryl chloride/TC1	copoly(p-phenylene fumaramide/terephthalamide)	PPD-Δ4/T
g.	PPD — 4,4'-azobenzenedicarbonyl chloride/TC1	copoly(p-phenylene 4,4'-azobenzene-dicarboxamide/terephthalamide)	PPD-BN ₂ B/T
h.	PPD — chloroterephthaloyl chloride/TC1	copoly(p-phenylene chloroterephthalamide/terephthalamide)	PPD-Cl T/T
i.	PPD — isophthaloyl chloride/TC1	copoly(p-phenylene isophthalamide/terephthalamide)	PPD-IT
j.	PPD — chloroterephthaloyl chloride	poly(p-phenylene chloroterephthalamide)	PPD-ClT
k.	PPD — <i>trans</i> -hexahydroterephthaloyl chloride/TC1	copoly(p-phenylene <i>trans</i> -hexahydroterephthalamide/terephthalamide)	PPD-HT/T

EXAMPLE IV.

This example shows the use of various polyamides made from diamines and diacid halides.

- 5 The polymers are made by dissolving the amine in the solvent, cooling the amine solution to about 5 to 10°C., then rapidly adding the diacid chloride with stirring and continuing the stirring, when possible, for at least about 1 hour. The polymer is recovered from the crumbs or gel by pulverizing it in water in a Waring Blendor type mixer, collecting on a filter and repeated washings with water and then drying. The usual precautions in forming high molecular weight polymers are observed.

- 10 Monomers used and the polymers formed are shown in Table II where the abbreviations "PPD" and "TCI" are used for p-phenylenediamine and terephthaloyl chloride respectively. Some specific details of the polymerization are given in Table III. When 2 monomers of the same type are used for copolymers the molar ratio of the monomers is given.

- 25 Mixtures of 2 solvents, hexamethylphosphoramide (A) and N-methylpyrrolidone (B) are used for all items except item a where 100% N,N-dimethylacetamide (DMAc) was used and item j, where equal volumes of B and DMAc were employed. The weight ratio of the 2 solvents is given in the table as is the weight ratio of the solvent to the total monomers.

Dopes are prepared using sulfuric acid (99.7 to 100.0% H_2SO_4) (a mixture of sulfuric and fluorosulfuric acids in a weight ratio of 1:1 for items j, l and n and 1.15:1 for item b₁) to give 46 grams of polymer/100 ml. of acid (20 weight %). In some cases the polymer used is a blend of several polymerizations.

The dopes are extruded at temperatures (spinneret blocks) between 51 and 100°C. (except item j, 35°C.) using the apparatus and technique of Example I from spinnerets containing 2 or 3 mil (0.051 or 0.076 mm.) diameter holes through a layer of air (0.5 to 1.9 cm.) into water (0 to 4°C.) and the filaments wound up at speeds ranging from 230 f.p.m. (71 m.p.m.) for item j to 1430 f.p.m. (438 m.p.m.) for item p. The fibers are thoroughly washed in water and dried on the bobbins.

S.S.F. and filament properties are given in Table III. The I.V. on item e and e₁ is measured at a concentration of 0.1%.

A 20/80 copolymer of item q, a 5/95 copolymer of items c, d, m and a and the homopolymer of n and p, all of Table II. can be spun by the above procedure into fibers.

Dope containing 56 g. of polymer per 100 ml. of sulfuric acid (23.4 weight %) is made from poly(chloro-p-phenylene terephthalamide) of 4.1 I.V. and satisfactorily spun by the above procedure into fibers with filament tenacity of 17 gpd.

TABLE II (Cont'd)

Item	Diamine — Diacid Chloride	Polymer	Polymer Code
l.	4,4'-diamino diphenyl ether/PPD — TCl	copoly(4,4'-oxydiphenylene/p-phenylene terephthalamide)	PCP/PPD-T
m.	PPD — sebacyl chloride/TCl	copoly(p-phenylene sebacamide/terephthalamide)	PPD-10/T
n.	PPD — 2,6-naphthalene dicarboxylic acid chloride	poly(p-phenylene 2,6-naphthalene dicarboxamide)	PPD-2,6N
o.	4,4'-diaminodiphenylmethane/PPD — TCl	copoly(4,4'-methylene diphenylene/p-phenylene-terephthalamide)	DDM/PPD-T
p.	2-methyl-p-phenylenediamine dihydrochloride — TCl	poly(2-methyl-p-phenylene terephthalamide)	MePPD-T
q	PPD — oxalyl chloride/TCl	copoly(p-phenylene oxamide/terephthalamide)	PPD-2/T
r.	PPD — 2,5-pyridinedicarboxylic acid chloride	poly(p-phenylene 2,5-pyridinedicarboxamide)	PPD-2,5-Pyr

TABLE III

Item	Polymer	Solvents A/B	Solvent		I.V. Yarn	Filament Properties						PACS Å	O.A. °
			Monomers	S.S.F.		Ten	E	Mi	dpf	ten.			
a	Cl PPD-T		11.3	3.3	3.9	18	6.5	370	3.9	0.61	17	27.0	
a ₁	Cl PPD/PPD-T 25/75	1.0	8.3	3.0	5.7	22	6.9	350	4.3	0.74	0	23.8	
b	DDE/PPD-T 7.5/92.5	1.0	5.6	3.1	3.4	21	3.8	730	2.1	0.43	38		
e	PPD-BB/T 55/45	1.0	9.7	2.1	5.3	21	5.5	690	3.4	0.64	<20	19.6	
f	PPD-Δ4/T 40/60	1.0	15.3	4.4	3.3	18	5.7	560	1.6	0.55	<20	20.2	
g	PPD-BN ₂ B/T 5/95	9.0	4.9	2.1	3.4	19	4.6	500	3.1	0.45	40		
h	PPD-Cl T/T 5/95	1.0	8.5	3.3	5.5	23	4.2	580	4.2	0.46	43	18.7	
i	PPD-I/T 5/95	9.0	4.7	3.3	3.9	20	4.6	580	1.5	0.49	34		
j	PPD-CIT		7.8	1.7	3.7	21	4.8	640	1.9	0.54	<20	21.8	
h ₁	PPD-Cl T/T 50/50	0.96	8.0	2.8	5.0	21	4.5	630	1.9	0.50	<20		
k	PPD-HT/T 25/75	1.0	9.2	6.0	4.3	22	4.5	540	1.4	0.51	24	14.0	
k ₁	PPD-HT/T 50/50	1.0	9.2	5.5	3.4	18	4.9	490	2.1	0.47	31		
l	POP/PPD-T 5/95	1.0	5.5	2.6	4.3	24	6.2	520	2.6	0.78	26	16.6	
r	PPD-2,5Py _r	9.0	19.8	4.9	5.3	18	5.8	470	3.5	0.57	22	16.4	
s	PPD-2,6N/I 50/50	1.4	12.7	5.3		19	5.6	580	1.3	0.56	0	20.3	
e ₁	PPD-BB/T 10/90	1.0	10.7	3.5	6.5	26	6.4	620	4.1	0.88	15	15.1	
f ₁	PPD-Δ4/T 20/80	1.0	14.7	3.9	4.3	24	5.7	680	1.6	0.76	22	14.8	
b ₁	DDE/PPD-T 10/90	0.7	5.7	4.6	3.2	22	3.6	730	1.4	0.41	37		

EXAMPLE V.

This example shows polyamides made from A—B monomers.

A random copolymer (item a) (p-benzamide/p-phenylene terephthalamide 25/75) is made by adding p-aminobenzoyl chloride hydrochloride to a cooled (about 6°C.) solution of p-phenylenediamine in a mixture of 10.4 parts by weight of hexamethylphosphoramide and 10 parts by weight of N-methylpyrrolidone. After about 5 minutes and with continued cooling to about 6°C., terephthaloyl chloride is rapidly added with stirring. Stirring is continued for about 5 minutes. The polymer is recovered as above. The mole ratio of the three monomers used is 1:3:3 respectively.

A random copolymer (item b) (p-benzamide/chloro-p-phenylene terephthalamide 75/25) is made by dissolving p-aminobenzoyl chloride hydrochloride and chloro-p-phenylenediamine in N,N-dimethylacetamide, cooling to about 11°C., rapidly adding terephthaloyl chloride with stirring and recovering the polymer as above after standing overnight. The mole ratio of the monomers is 3:1:1 respectively.

A homopolymer (item c) [poly(p-benzamide)] is made by cooling N,N-dimethylacetamide to -10°C. and rapidly adding 4-(p-aminobenzamido)-benzoyl chloride hydrochloride (solvent/monomer weight ratio=6.5) with stirring. After 2.75 hours of stirring, the mixture is neutralized with lithium carbonate and stirring is continued another 1.5 hours. The polymer is recovered as above.

The polymer I.V. range from 4.0 (item b) to 5.9 (item a). Dopes are prepared using sulfuric acid (99 to 100% H₂SO₄) to give about 46 grams of polymer/100 ml of acid (20 weight %) for all items except c (40 g/100 ml or 18 weight %).

The dopes are extruded at temperatures between 37 (item b) and 68°C. (item c) using the apparatus and technique of Example I from spinnerets containing 2 or 3 mil (0.051 or 0.076 mm) diameter holes through a layer of air (0.5 to 1.2 cm) into water (1 to 3°C.) and the filaments wound up at speeds ranging from 600 f.p.m. (184 m.p.m.) for item b to 1060 f.p.m. (325 m.p.m.) for item c. The fibers are thoroughly washed in water and dried on the bobbins.

Properties are given in Table IV.

TABLE IV

Item	S.S.F.	I.V. Yarn	Filament Properties					P.A.C.S. Å	O.A. °
			Ten	E	Mi	dpf	Tou.		
a	4.7	5.4	32	5.4	800	1.9	0.90	32	11.9
b	4.5	3.9	23	4.8	680	3.3	—	14	
c	5.7	3.7	19	4.0	570	1.0	0.41	11	15.8

EXAMPLE VI.

This example shows some variables in the spinning process. Dopes of PPD—T in sulfuric acid (99.7—100% H₂SO₄) are made and spun using the apparatus and general technique of Example I. Some specific conditions and results are given in Table V. All dopes contain 46 g. polymer/100 ml solvent (20 weight %) except item e which uses 38 g/100 ml (17 weight %).

All dopes are extruded at about 95°C. (spinneret block) except items e, i and j (73, 85 and 80°C. respectively) from a spinneret with 2 mil (0.051 mm) diameter holes except items c, d, and j [10, 8 and 3 mil (0.25, 0.20 and 0.076 mm) diameter respectively] through a layer of air of from 0.5 to 1.5 cm thick into a coagulating bath.

The coagulating bath is water for all items except f, g and h which use 47.5, 54 and 70% H₂SO₄ respectively. For the latter 3 items the yarn coming from the coagulating tube is

passed under a rod and into a second bath (water 15°C.), under a rod and thence to the windup. Windup speeds of from 650 to 1450 f.p.m. (198 to 440 m.p.m.) are used.

All fibers are thoroughly washed and dried on the bobbin. Filament tenacities are given in Table V. All items have filament (a) elongation of 3.5 to 4.8%, (b) moduli of 420 (item e) to 850 g.p.d. (item f), (c) deniers per filament of 1.1 to 2.7 except items c and d (12.4 and 10.5 respectively) and all have toughness values of 0.22 to 0.69 gpd.

When the procedure of item e is changed by placing the face of the spinneret under the surface of the water the maximum windup speed that can be used is only 90 f.p.m. (27 p.m.) at a spin stretch factor of 0.6 to give 9.2 d.p.f. filaments with a tenacity of 3.7 gpd.

Using the procedure of item a with a SSF of 3, filaments with tenacities of 23, 22 and 21 gpd are obtained when spinning tube

- lengths of 8.5, 4 and 0.5 inches (21.6, 10. and 1.27 cm.) are used. The variation in spinning tube length varies the velocity of the water and hence the tension on the thread-line.
- 5 The spinning conditions of item a are modified by extruding the dope at about 90°C. (from 4.6 I.V. polymer) through a 1 cm. layer of air vertically into a bath of 4°C. water, under a guide and out of the bath to a windup at 480 f.p.m. (147 m.p.m.) with a SSF of 3.0. The washed and dried fibers have a filament tenacity of 17 gpd. This process was essentially repeated with the layer of air replaced by a 1 cm. layer of toluene so that the spinneret face is immersed in toluene.

TABLE V

Item	Inherent Viscosity polymer/yarn	Extrusion Temperature °C.	Coag. Bath Temp. °C.	Spin Stretch Factor	Filament Tenacity	Variable
a	4.7/4.2	ca 95	5.5	3.9	25	bath temperature
b	„	„	27	„	22	bath temperature
c	4.7/4.5	„	4	12.1	17	large denier
d	„	„	„	10.5	17	large denier
e	4.7/- -	73	23	6.0	16	polymer con.
f	5.4/- -	ca 95	3	4.1	23	acid bath
g	„	ca 98	5	3.1	21	acid bath
h	„	ca 95	4	4.4	20	acid bath
i	6.9/5.4	ca 85	3	5.8	30	inherent viscosity
j	2.8/2.8	ca 80	3	4.0	16	inherent viscosity

EXAMPLE VII.

- 20 This example shows the effect of extrusion temperature on the process.
- 25 A dope containing 46 g. polymer/100 ml. of sulfuric acid (99+ % H_2SO_4) made from PPD—T of 5.2 I.V. is extruded—using the general procedure of Example II—from a spinneret having 100 holes of 0.05 mm. diameter, through about a 4.8 mm. layer of air into 5°C. water. The fiber was wound up at about 500 f.p.m. (153 m.p.m.) with a SSF of about 4.7 to 5.5. The dope in the kettle is kept at about 85°C. The temperatures of the transfer line, spinning block and spinneret are adjusted to about the extrusion temperature for each spin. The estimated temperature of the dope—as extruded—the I.V. of the fiber and the filament properties are given below.

item	a	b	c
Extrusion Temperature °C.	85	100	110–115
I.V.	4.8	4.5	3.9
Ten.	24	22	19
E	5.0	4.6	4.5
Mi	484	458	414
dpf	1.3	1.3	1.3

EXAMPLE VIII.

5 Fibers of poly(*p*-phenylene terephthal-
amide) (PPD—T) are prepared using the
general spinning conditions of Example IIA
with the exceptions noted below. Fiber
10 properties are shown in Table VI for items
d to *i*.

Extrusion temperatures are about 85°C
except for item *i* which is 95°C. The co-
agulating bath is 1—4°C water except *i* which
15 is 20°C water. Items *d*, *e*, *f*, and *h* use a
roller after the spin tube; items *g* and *i* use a
ceramic pin. Items *e* and *h* are extruded from
spinnerets with 570 and 285 holes, respec-
tively. All spinnerets contain 2 mil (0.05
20 mm) diameter holes except item *f* (20 holes
of 6 mil, 0.15 mm diameter). Jet velocities
range from 68 (item *f*) to 200 (item *i*) feet
minute (ca. 21 to 58 meters/min.). Spin-
stretch factors range from 3.5 (item *i*) to 5.2
25 (item *d*). Item *g* is prepared from granules
of solidified dope by remelting in a screw
melter.

Items *e* and *h* use a feed wheel sprayed
with NaHCO₃ before the windup which is
30 sprayed with water; *e* and *h* store the bobbins
in water and then in dilute aqueous NaOH
when feeding the extracting device. Items *e*

and *h* are dried on hot rolls at 120°C.

Items *f* and *i* are washed on the bobbin
with water and for 12 hours standing in
35 water and then dried in air at room tem-
perature.

Items *d* and *g* are washed with aqueous
sodium bicarbonate solution on the windup
and in the bath before the extracting device. 40
Item *d* is dried at 40°C and item *g* is dried
at 75°C.

The yarns of items *d*, *g* and *h* are 6 ply, 4
ply and 2 ply respectively.

The filament properties on items *d*, *e* and
h are made on 5, 5 and 4 breaks respectively. 45

The yarns of this example are particularly
useful for preparing tire cords. Such yarns
should have an I.V. of at least 4.0, and
have yarn properties (ten/E) of at least 18
50 gpd and 3%. Preferably, yarns for use in tire
cords should have an I.V. of 4.5 and ten/E/tou
(on yarn) of 20/3.5/0.35. The filaments of
preferred yarns will have a dpf of less than
2.5 and preferably <2.0 since a greater
55 conversion of yarn strength to tire cord
strength is obtained than with larger dpf. Pre-
ferred yarns have a tenacity/elongation/
toughness as measured at 150°C that is at
least 70% of the value measured at 24°C. 60

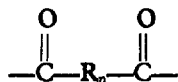
TABLE VI

Item	I.V. Yarn	P.A.C.S. Å	YARN PROPERTIES					Yarn		Filament Properties			
			O.A. °	Ten.	E.	Mi	Tou	D.P.F.	Denier	Ten.	E	Mi	Tou.
a	5.2	45	20.0	21.2	3.9	547	0.39	3.7	415	26	5.6	570	0.73
b	5.2	49	13.9	22.8	3.2	727	0.35	1.9	190	27	4.8	680	0.67
c	5.2	49	11.5	24.8	2.8	948	0.34	1.4	135	27	4.3	680	0.62
d	5.2	38	22.4	21.9	4.1	459	0.41	1.3	774	22	4.2	510	0.46
e	4.7	48	16.0	23.2	3.6	575	0.53	1.2	710	24	4.5	520	0.
f	5.4	39	14.6	21.5	3.5	629	0.35	12.5	253	21	4.7	600	0.50
g	4.7	49	15.8	21.1	3.4	556	0.34	2.0	780	24	4.6	630	0.57
h	4.8	51	17.2	25.0	4.1	529	0.52	1.2	702	28	4.8	580	0.67
i	5.2	47	15.3	18.2	3.0	586	0.26	1.8	176	21	4.1	510	0.43

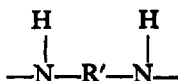
WHAT WE CLAIM IS:—

1. A fiber or a film of a polyamide having an inherent viscosity of at least 2.5 and consisting essentially of recurring units I and II, or III, or I and II and III, wherein:

I is



II is



and III is



and when units I and II are present in the polymer they are present in substantially equimolar amounts, R, R' and R'' groups, which may be the same or different, are divalent radicals, n is zero or the integer one, and at least 95 mol % of the total R, R' and R'' radicals in the polymer consist of single rigid radicals (as hereinbefore defined) with extended bonds (as hereinbefore defined) or a series of such rigid radicals linked together directly by extended bonds, with the proviso that rigid ring radicals may be linked by azo or azoxy groups, said fiber or film having a filament or film tenacity of 18 to 40 gpd., a filament or film breaking elongation of 3.5 to 8.0%, and crystalline regions with a primary apparent crystallite size of 0 to 52 Å.

2. A fiber or a film according to claim 1 wherein R, R' and R'' are selected from the following radicals which may be substituted: 1,4-phenylene, 4,4'-biphenylene, 1,5-naphthylene, 2,5-naphthylene, *trans*-1,4-cyclohexylene, 2,5-pyridylene, *trans*-, *trans*-4,4'-bicyclohexylene, and 1,4-phenylene groups linked by *trans*-vinylene, ethynylene, azo or azoxy; R may also be selected from *trans*-vinylene, ethynylene, *trans*-, *trans*-1,4-butadienylene or 2,4'-*trans*-vinylene-phenylene and R'' may be 2,4'-*trans*-vinylene-phenylene.

3. A fiber or a film according to claim 1 wherein R and R' are selected from 1,4-phenylene, 4,4'-biphenylene, 2,6-naphthylene, 1,5-naphthylene and *trans*-1,4-cyclohexylene; R may also be selected from 2,5-pyridylene and *trans*-vinylene; and R'' is 1,4-phenylene with the proviso that at least 50 mole % of the total R and R' groups are wholly aromatic.

4. A fiber or a film according to any of claims 1 to 3 wherein the filament or film breaking elongation is at least 4.5% and the polyamide inherent viscosity is at least 3.0.

5. A fiber or a film according to any of

claims 1 to 4 wherein the fiber or film has radical orientation as shown by an LCO value of at least 10.

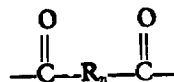
6. A fiber or a film according to claim 5 wherein the LCO value is at least 20.

7. A fiber or a film according to any of claims 1 to 6 wherein the fiber or film consists of poly(*p*-phenylene terephthalamide).

8. A fiber or a film of a polyamide substantially as hereinbefore described in any one of the Examples.

9. A method of preparing a polyamide fiber or film which comprises extruding a dope through an orifice through a layer of inert non-coagulating fluid and then into a coagulating bath, the dope comprising a polyamide and a solvent consisting essentially of sulfuric acid of at least 98% concentration, chlorosulfuric acid or fluorosulfuric acid and mixtures thereof at a concentration (C) of at least 30 grams of polymer per 100 ml. of solvent, the polyamide having an inherent viscosity of at least 2.0 but not less than 2.8—0.05(C—30) and consisting essentially of recurring units I and II, or III, or I and II and III, wherein:

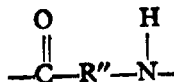
I is:



II is



and III is



and when units I and II are present in the polyamide they are present in substantially equimolar amounts, R, R' and R'' which may be the same or different, are divalent radicals, n is zero or the integer one, and at least 95 mol % of the total R, R' and R'' radicals in the polyamide consist of single rigid radicals (as hereinbefore defined) with extended bonds (as hereinbefore defined) or a series of such rigid radicals which are linked together directly by extended bonds with the proviso that rigid ring radicals may be linked by azo or azoxy groups.

10. A method according to claim 9 wherein the acid is sulfuric acid of at least 98% concentration.

11. A method according to claim 9 or 10 wherein the dope is solid at 25°C. and is extruded at 40—120°C.

12. A method according to claim 11 wherein the dope is extruded at 70—90°C.

13. A method according to any of claims 9 to 12 wherein the polyamide has an inherent viscosity of at least 3.0 and is present at a



concentration of at least 40 grams per 100 ml. of solvent.

14. A method according to any of claims 9 to 13 wherein there is between 40 and 56 grams of polymer per 100 ml. of solvent in the spinning dope.

15. A method according to any of claims 9 to 14 wherein the layer of fluid is between 0.1 and 10 cm. thick.

16. A method according to any of claims 9 to 15 wherein the layer of fluid is a gas.

17. A method according to any of claims 9 to 16 wherein the coagulating bath is at a temperature of under 50°C.

18. A method according to claims 16 and 17 wherein the fluid layer is air and the coagulating bath is water at a temperature of under 50°C.

19. A method according to any of claims 9 to 18 wherein the R, R' and R'' radicals in the polymer are selected from *trans*-1,4-cyclohexylene, 1,4-phenylene, 1,5-naphthylene, 2,6-naphthylene, 2,5-pyridylene, 4,4'-biphenylene, *trans,trans*-4,4'-bicyclohexylene radicals and 1,4-phenylene groups linked by *trans*-vinylene, ethynylene, azo or azoxy with the proviso that R may also be selected from *trans*-vinylene, ethynylene, *trans,trans*-1,4-butadienylene and 2,4'-*trans*-vinylene-phenylene.

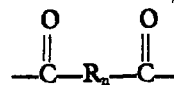
20. A method according to claim 19 wherein the polyamide is poly(*p*-phenylene terephthalamide).

21. A method of preparing a polyamide fiber or film substantially as hereinbefore described in any one of the Examples.

22. A polyamide fiber or film when prepared by the method claimed in any one of claims 9 to 21.

23. A spinning dope comprising a polyamide and a solvent consisting essentially of sulfuric acid of at least 98% concentration, chlorosulfuric acid or fluorosulfuric acid and mixtures thereof, said polyamide having an inherent viscosity of at least 4.0 and consisting essentially of recurring units I and II, or III, or I and II and III, wherein:

I is



II is



and III is



and when units I and II are present in the polymer they are present in substantially equimolar amounts, R, R' and R'' which may be the same or different, are divalent radicals, n is zero or the integer one, and at least 95 mol % of the total, R, R' and R'' radicals in the polymer consist of single rigid radicals (as hereinbefore defined) with extended bonds (as hereinbefore defined) or a series of such rigid radicals which are linked together directly by extended bonds, with the proviso that rigid ring radicals may be linked by azo or azoxy groups, the concentration of said polymer in the solvent being at least 30 grams of polymer per 100 ml. of solvent.

24. A spinning dope according to claim 23 wherein the polyamide is poly(*p*-phenylene terephthalamide).

25. A spinning dope substantially as hereinbefore described in any one of the Examples.

26. A tire cord which comprises a fiber as claimed in any of claims 1 to 8 or 22.

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