

[54] METHOD OF INCREASING THE INITIAL
MODULUS AND REDUCING THE
ORIENTATION ANGLE OF UNDRAWN
POLY (PARA-BENZAMIDE) FIBERS

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1970, abandoned, which is a continuation of Ser. No.
644,851, June 9, 1967, abandoned, which is a
continuation-in-part of Ser. No. 556,934, June 13,
1966, abandoned.

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264/346

[51] Int. Cl. B29c 25/00

[58] Field of Search 264/184, 205, 235, 346,
264/210 F, 290 N, 342 RE; 161/172

[56]

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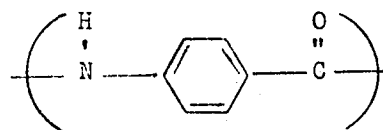
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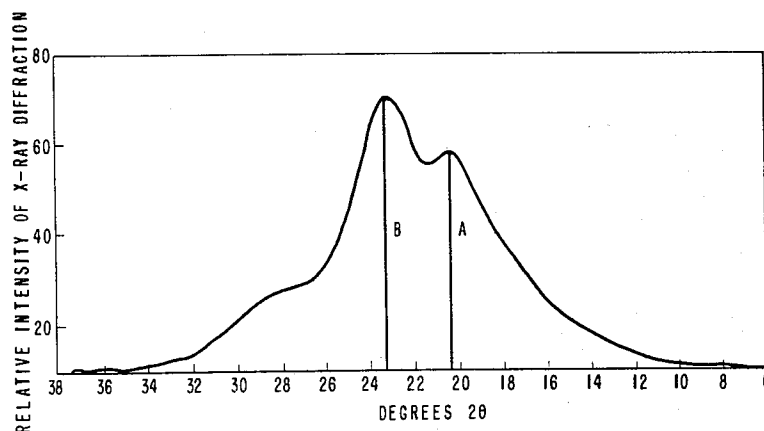
ABSTRACT

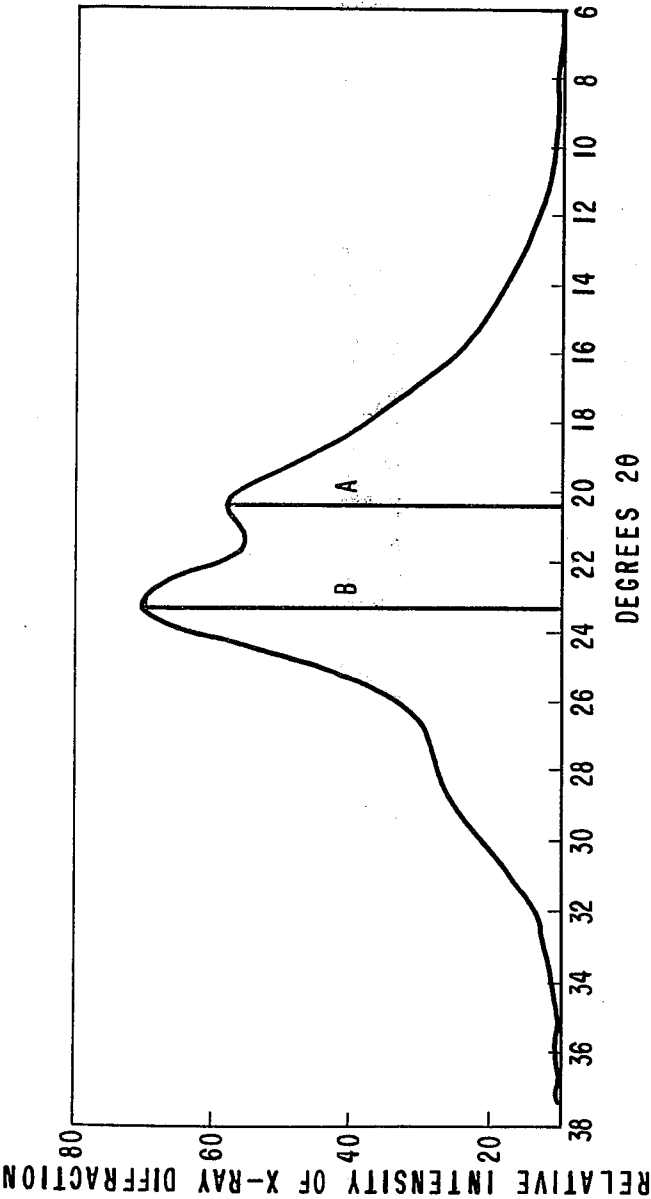
High molecular weight polymers consisting essentially
of recurring units of the formula



are useful for the production of fibers having a high
initial modulus. The initial modulus is increased and
the orientation angle is reduced in the undrawn fibers
by heating the fibers at a temperature of at least
350°C while under tension, or while relaxed.

1 Claim, 1 Drawing Figure





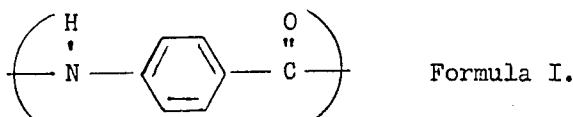
METHOD OF INCREASING THE INITIAL MODULUS AND REDUCING THE ORIENTATION ANGLE OF UNDRAWN POLY (PARA-BENZAMIDE) FIBERS

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my co-pending application Ser. No. 30,089, filed Apr. 20, 1970, which in turn is a continuation of my application Ser. No. 644,851, filed June 9, 1967, now abandoned which in turn is a continuation-in-part of my application Ser. No. 556,934, filed June 13, 1966, now abandoned.

DETAILED DESCRIPTION

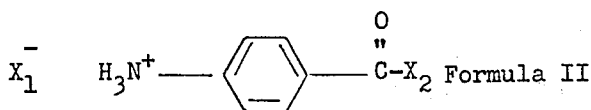
In accordance with this invention, there is provided a process for treating high molecular weight substantially homopolymeric poly(p-benzamide) fibers consisting essentially of recurring units of the formula



In the inherent viscosity range of from about 0.8 to about 2.5 (measured as described hereinafter) this polymer is useful for the production of fibers. At values of inherent viscosity as low as about 0.7, it is useful for the production of films, fibrils, and coatings. These uses require the polymer to be preliminarily in the form of a dope.

The most stable dopes to be used for extrusion of the homopolyamide referred to above into filaments contain, on a weight basis, between 4 and 30% of polymer, preferably 5 to 15%, from 3 to 22% lithium chloride (LiCl), and the remainder tetramethylurea (TMU). At least 0.5 mol of LiCl should be present per repeating unit of polymer. However, the presence of LiCl is not necessary if the dope is used within a reasonable period after preparation. Thus, to assure that the dope is in proper condition for dry- or wet-spinning, either the polymer is prepared in TMU or in TMU-LiCl optionally followed by complete or partial neutralization of the by-product acid, and spun directly (coupled process). It is not necessary that the by-product acid be neutralized, except that it is found to be corrosive to the spinning equipment. In an alternate procedure, the polymer is first prepared and isolated, then combined with TMU-LiCl all as indicated below.

The essentially homopolymeric poly(p-benzamide) in this invention may readily be obtained by certain polymerization techniques from suitable monomers. For example, it may be obtained by the low temperature solution polymerization of p-aminobenzoyl halide salts of the formula



wherein X₁ represents a member selected from the group consisting of arylsulfonate, alkylsulfonate, acid

sulfate, and halogen radicals, preferably bromide or chloride radicals, and X₂ represents a halogen radical, preferably bromide or chloride. p-Aminobenzoyl chloride hydrochloride is the monomer preferred. Other monomers suitable for this purpose are p-aminobenzoyl bromide hydrobromide, p-aminobenzoyl chloride hydrobromide, p-aminobenzoyl chloride methanesulfonate, p-aminobenzoyl chloride benzenesulfonate, p-aminobenzoyl chloride toluenesulfonate, p-aminobenzoyl bromide ethanesulfonate, and p-aminobenzoyl chloride sulfate. The preferred p-aminobenzoyl chloride hydrochloride may be prepared in high yield from an ethereal solution of p-thionylaminobenzoyl chloride by the general procedure of Graf and Langer, J. prakt. Chem. 148, 161 (1937) under anhydrous conditions. The drying and anhydrous storage of this monomer are preferably performed under room temperature conditions because of the tendency for the compound to polymerize at higher temperatures.

POLYMERIZATION CONDITIONS

The low temperature, i.e., under 60°C. and preferably from 0°-20°C., solution polymerizations which provide the polyamide useful in this invention preferably employ a solvent selected from the group consisting of TMU, hexamethylphosphoramide, N,N-dimethylacetamide, and N-methylpyrrolidone. Other useful polymerization media are N-methylpiperidone, N,N-dimethyl ethylene urea, N,N,N',N'-tetramethylmalonamide, N-methylcaprolactam, N-acetylpyrrolidine, N,N-diethylacetamide, N-ethylpyrrolidone, N,N-dimethylpropionamide, N,N-dimethylbutyramide and N,N-dimethylisobutyramide.

The above-mentioned polymerizations may be carried out by dissolving the desired monomer in the amide solvent and vigorously stirring the resulting solution, externally cooled, until it becomes very viscous. The polyamide may then be isolated by the addition of water. Alternatively, the monomer may first be slurried in a small quantity of an inert organic liquid prior to the addition of the amide solvent. In a variation of the former method, the solvent may be frozen and mixed, while frozen, with the desired monomer. The solvent is permitted to thaw and the resulting slush stirred until a gel-like mass forms. A suitable chain-terminating agent may be used in these reactions in order to limit the molecular weight of the polymeric product. For the attainment of the highest molecular weights, these polymerizations are performed under strictly anhydrous conditions. The reaction vessel and auxiliary equipment, solvents, and reactants are carefully dried prior to use and the reaction vessel is continuously swept with a stream of dry, inert gas, e.g., nitrogen, during the polymerization.

One such polymerization may be accomplished by first adding, with stirring, a quantity of an anhydrous organic liquid, such as tetrahydrofuran, dioxane, benzene, or acetonitrile, to a quantity of the desired monomer in the gas-swept polymerization apparatus. This liquid also contains the calculated amount of the desired chain-terminating agent, e.g., benzoyl chloride, whenever this agent is to be used. The resulting mixture is stirred at an increased rate and a relatively large volume of anhydrous amide solvent, e.g., TMU, N,N-dimethylacetamide, hexamethylphosphoramide, or N-methylpyrrolidone, is then rapidly added to the flask.

The resulting solution, externally cooled, is stirred continuously until there is a substantial increase in the viscosity of the composition. The latter may, if desired, stand overnight or longer at room temperature. When the polymer is to be isolated in bulk form, the polymerization mixture is combined with water in a suitable blender and then is converted to a fine powder. The powdered polymer, after being washed with both water and alcohol, is dried overnight in a vacuum oven at about 80°–90°C. before being stored or dissolved for subsequent processing.

As indicated above, chain terminators may be used in these polymerizations. By assisting in the control of the molecular weight of the polyamide, the use of chain terminators contributes to the ease by which subsequent dissolution of the polymer occurs and enhances the stability of the polymer dope for application in the coupled polymerization spinning process. Among the suitable chain terminators are monofunctional compounds which can react with the acid chloride ends of these polyamides such as ammonia, monoamines (e.g., methylamine, dimethylamine, ethylamine, butylamine, dibutylamine, cyclohexylamine, aniline, etc.), compounds containing a single amide-forming group, such as N,N-diethylethylenediamine, hydroxylic compounds such as methyl alcohol, ethyl alcohol, isopropyl alcohol, phenol, water, etc., and monofunctional compounds which can react with the amine ends of the polyamides such as other acid chlorides (e.g., acetyl chloride), acid anhydrides (e.g., acetic anhydride, phthalic anhydride, etc.), and isocyanates (e.g., phenyl isocyanate, m-tolyl isocyanate, ethyl isocyanate, etc.).

All useful terminators are especially effective and uniformly distributed if added at the beginning of the polymerization or prior to the addition of any acid-neutralizing agent (e.g., lithium hydroxide).

The essentially homopolymeric poly(p-benzamide) possesses a peak height ratio of below 0.86 and, moreover, no sediment is seen in the tube when the polymer is subjected to the sedimentation test, all as described below. It has been found that polymer of inherent viscosity > 0.80 and meeting these two requirements can be spun into yarns having an extremely high modulus and a low orientation angle. It will be understood, however, that the peak height ratio as measured on polymer that has been spun or heated at elevated temperatures may exceed 0.86. Sedimentation properties may also change on heating or spinning.

DOPE PREPARATION

The polyamide which has been prepared by the previously described methods and which has been isolated from the polymer preparation system are then incorporated into dopes for spinning, etc. One such method is as follows: a mixture of homopolyamide, TMU, and lithium chloride in proportions earlier defined is placed in a suitable vessel equipped for stirring. The mixture is stirred and heated at about 130°–150°C. for at least 1 hour. While the stirred mixture is maintained at this temperature, it generally becomes an extremely viscous, gelatinous mass completely unsuitable for spinning. This material is then cooled to about 0°C. or below in a bath of solid carbon dioxide, or by other spinnable dope.

The amount of heating and cooling required to form by this method a dope with the flow characteristics needed for smooth spinning varies with the inherent

viscosity, the crystallinity, and the particle size of the polyamide sample employed, as well as with the quality of the stirring action. In the formation of these dopes care must be taken to avoid overheating the dope locally and thus forming a "dry" or gelled spot. Such portions of polymer do not readily redissolve.

When the low-temperature-solution polymerization is conducted in TMU with p-aminobenzoyl chloride hydrochloride as the monomer the polymer formed usually attains a useful molecular weight after the polymerization has proceeded for about 15 minutes to an hour or even longer and the mixture is useful as a dope that can be spun or cast. Gelling may begin to occur in from about 0.5 to 2 hours reaction time, depending in part at least upon the degree of polymerization attained. The stability of such dopes may be extended to periods of many days by the addition of chain-terminating agents described earlier. A directly extrudable dope may be obtained where polymerization is continued in TMU for a time in excess of about 0.5 hour or more by adding a quantity of lithium chloride to the TMU medium prior to the polymerization or by adding to the half hour-old reaction system a quantity (up to 2 equivalents of lithium per mole of monomer charged when an acid chloride hydrochloride is employed) of an inorganic salt or salt-forming reagent such as lithium chloride, lithium acetate, lithium hydroxide, lithium carbonate, or lithium oxide; in addition, external heat may be subsequently applied to the contents of the reaction vessel to assist in forming or maintaining the extrudable dope. The above-cited basic materials each react with the hydrogen chloride formed during the polymerization to generate lithium chloride in situ. It is preferred that lithium hydroxide, lithium oxide and like bases be used in amounts not in excess of that required to neutralize the hydrogen chloride or other acids formed in the reaction. In spinning those TMU dopes described above, spinnerets of platinum-gold construction and reservoirs, filters, conduits, and the like, prepared from, for example, corrosion-resistant stainless steel, are particularly suitable. Metals coated with Teflon polyfluorocarbon and glass-lined equipment, as well as acid-, heat-, and solvent-resistant plastic parts may be used.

SHAPED ARTICLES AND THEIR PREPARATION

Conventional wet- and dry-spinning techniques and equipment can be used to prepare the polyamide filaments from the previously described dopes. In wet spinning, an appropriately prepared TMU (or other suitable solvent) dope of the polyamide, whose temperature may vary from room temperature to about 150°C., is extruded into a suitable coagulating bath, e.g., a water bath maintained at 65°–90°C. Other useful coagulants include ethylene glycol, glycerol, mixtures of TMU and water, mixtures of alcohol and water, and aqueous salt baths. These are preferably maintained at a temperature of 40°–45°C. or above. Formation of good fibers (i.e., those with enhanced tensile properties) is assisted by keeping the filaments taut while they are in the coagulating bath. This may be accomplished, for example, by passing the filaments around guides placed in the coagulating bath.

Dry spinning may be accomplished by extruding filaments from a polyamide. TMU-LiCl dope, preferably maintained at 50°–150°C., into a heated column whereby the TMU is evaporated.

After being formed, the filaments are passed over a finish-application roll and wound up on bobbins at high speeds. They can be readily back-wound. Development of maximum levels of filament and yarn properties is assisted by soaking the bobbins in water or in mixtures of water and water-miscible inert organic liquids (e.g., TMU, DMAc, acetone, ethyl alcohol, glycerol) to remove residual solvent and salt. The removal of salt and any residual solvent may also be accomplished by passing the yarn through aqueous baths on the run, by flushing the bobbins with water as the yarn is formed, and by washing or soaking skeins, rather than bobbins, or yarn. The yarn is strengthened by washing with even a minor amount of water.

The fibers possess high tenacity and a very high initial modulus, i.e., above 200 gpd. and often exceeding 300 gpd., which is necessary for many reinforced plastic applications. They are crystalline and possess an orientation angle of less than about 35°. In general, as shown in the examples which follow, homopolymeric poly(p-benzamide) filaments prepared and treated as described above, possess these unusual and unanticipated tensile properties without being drawn. The freshly extruded filaments are usually of low void content. Use of spin stretch factors (defined below) approaching one in dry spinning or, on occasion, in wet spinning with such polymers will yield as-spun fibers having an orientation angle of above 35° and a modulus below 200. In that event, the fiber may be heated taut at about 400°C. for about 2-5 seconds in nitrogen to bring the orientation angle down and the modulus up.

As used herein the term "as-spun" or "undrawn" describes the filament condition at the wind-up or first roll following extrusion. Spin stretch, which is not considered as draw, may occur in the zone preceding the first roll depending on the yarn velocity at the first roll as compared to the velocity of the dope as it passes through the spinneret holes. The yarn may be drawn after it leaves the first roll.

Heat treatments of the as-spun filaments under tension or with only a slight amount of drawing produce a significant increase in their tenacity and modulus values. The tensile properties of these filaments can also be enhanced by subjecting the unknown fibers to a heat treatment in the relaxed state. Hot air ovens, hot pins, hot slots, hot plates and liquid heating baths are useful for such treatments. Heating is generally carried out above 350°C. while drawing said fibers less than about 25%. It will be understood that the selection of heating time and temperature will be such as to avoid undue polymer degradation.

The chemical and thermal stabilities of filaments and yarns prepared from poly(p-benzamide) by the processes of this invention are excellent. The fibers retain their tensile properties after being heated at the boil for 0.5 hour in aqueous hydrochloric acid (1%) and caustic (1%) solutions. The fibers are essentially unaffected after being soaked for one hour at 60°C. in commercially-used dry cleaning solvents such as "Perclene" perchlorethylene and "Triclene" trichlorethylene. The fibers display excellent retention of tensile properties during and after heating in air at 300°C. for a prolonged period. The fibers are self-extinguishing when removed from an open flame.

It will be understood that the usual additives such as dyes, fillers, UV stabilizers, antioxidants, etc. can be

incorporated in with the polymer for the purposes intended prior to fiber preparation.

MEASUREMENTS AND TESTS

Orientation Angle: The orientation angle of the fiber is determined by the general method described in Krimm and Tobolsky, *Textile Research Journal*, Vol. 21, pp. 805-22 (1951). A wide angle X-ray diffraction pattern (transmission pattern) of the fiber is made, using nickle-filtered Cu radiation, a fiber-sample thickness of 20 mils (0.05 cm.), a sample-to-film distance of 5 cm., and an exposure time of 45 minutes. The arc length in degrees at the half-maximum intensity of the first equatorial diffraction spot, which is located at 20.3°, 2θ, is measured and taken as the orientation angle of the sample. Since the intensity trace is an essentially Gaussian curve and the measurement is made at half-maximum intensity, the physical meaning of the orientation angle given by the determination is that approximately 77% of the crystallinities are aligned within this angle about the fiber axis.

Peak Height Ratio: A measure of the relative intensity of the two major equatorial diffraction peaks is given by the peak height ratio (PHR). A suitable method for determining the PHR involves the use of a reflection technique to record the intensity trace of the X-ray diffraction pattern with an X-ray diffractometer. Approximately 0.5 gram of water- and TMU-free polymer is pressed into a Phillips sample holder under an applied pressure of 3,125 lb./in.² (219.7 × 10³ g/cm.²). Using nickle-filtered Cu radiation, a Philips diffractometer with 0.5° slits, and a pulse height analyzer, a trace of intensity is recorded from 6° to 40°, 2θ, at a scanning speed of 1°, 2θ, per minute, a chart speed of 1 inch per minute (2.54 cm./min.), and a time constant of 2; 2θ being the angle between the undiffracted beam and the diffracted beam. The full scale deflection of the recorder is set so that the peak with maximum intensity is at least 50% of the scale, which is a linear scale. To calculate the PHR, a base line is first established on the diffractometer scan by drawing a straight line between the points on the curve at 8° and 38°, 2θ. Vertical lines (at constant 2θ values) are drawn from the peaks in the vicinity of 20.3° and 23.4°, 2θ, to the base line, and the height of the peaks, in chart divisions, above the base line is ascertained. The PHR is then calculated from the equation

$$\text{PHR} = A/B$$

where A = height of the peak, approximately located at 20.3°, 2θ, above the base line in chart divisions, B = height of the peak, approximately located at 23.4°, 2θ, above the base line in chart divisions.

A typical trace appears in the figure. A smooth line was drawn as indicated to compensate for instrument noise and the measurements are made therefrom.

SEDIMENTATION TEST

Polymer powder (0.10 g.), as prepared, is dried, comminuted to pass through a 20-mesh screen, and placed in a dry test tube. To this added 10.0 ml. of a solution of lithium chloride (6.9% by weight) in tetramethylurea. The tube is stoppered and its contents subjected to mechanical agitation (the tube is rotated at 110 rpm about a diametrical axis through its mid-point for 24 hours at 21°C.). The tube is then allowed to stand upright for a further 24 hours. After this time no

polymer residue lies settled on the bottom of the tube.

SPIN STRETCH FACTOR

$$S.S.F. = \frac{\text{Velocity of yarn at wind-up (ft./min.)}}{\text{Velocity of dope through spinneret (ft./min.)}}$$

where

$$\text{Vel. of dope through spinneret} = \frac{\text{Rate of pumping (cu. ft./min.)}}{\text{No. of spinneret holes} \times \text{cross-sectional area of one hole (sq. ft.)}}$$

INHERENT VISCOSITY

Inherent viscosity (η_{inh}) is defined by the following equation:

$$\eta_{inh} = \ln (\eta_{rel})/C$$

wherein (η_{rel}) represents the relative viscosity and (C) represents a concentration of 0.5 gram of the polymer in 100 ml. of solution. The relative viscosity (η_{rel}) is determined by dividing the flow time in a capillary viscometer of a dilute solution of the polymer by the flow time for the pure solvent. The dilute solutions used herein for determining (η_{rel}) are of the concentration expressed by (C), above; flow times are determined at 30°C., using concentrated (95–98%) sulfuric acid as a solvent.

Fiber properties of tenacity, elongation, and initial modulus are coded as T/E/Mi and are reported in their conventional units. Denier is coded as Den. The boiling off treatment of fibers prior to physical testing consists of boiling the fibers 30 minutes in 0.1% aqueous sodium lauryl sulfate, rinsing, drying at 40°C. for 1 hour, and conditioning at 21°C. and 65% r.h. for 16 hours.

Tensile properties were determined on yarn samples which measured one inch (2.54 cm.) in length between the jaws of an Instron tester (product of the Instron Engineering Corp., Canton, Mass.) and which are subjected therein to a load sufficient to cause elongation to occur at the rate of 10% per minute measured at 21°C. and 65% r.h.

The following nonlimiting examples are illustrative of the practice of the invention.

EXAMPLE I

Polymer Preparation: A two-liter resin-making kettle equipped with a stirrer, nitrogen-inlet tube and calcium chloride drying tube is flamed with a Bunsen burner and simultaneously flushed with nitrogen. The kettle is sealed and placed in a dry-box, i.e., a chamber maintained under anhydrous conditions. Hexamethylphosphoramide (520 ml., distilled from calcium hydride through a spinning band column at reduced pressure and stored over calcium hydride) is filtered in the dry-box into a Erlenmeyer flask which is then sealed and cooled in ice. Tetrahydrofuran (75 ml., distilled and stored over sodium metal, water content less than 0.0001%) is filtered in the dry-box into an Erlenmeyer flask which is then sealed and cooled in ice. p-Aminobenzoyl chloride hydrochloride (124.0 g., 0.646 mole) is weighed out in the dry-box and transferred to the "resin-kettle". The kettle is removed from the dry-box, reconnected with the stirring motor and nitrogen line, and cooled in an ice bath. Just prior to the poly-

merization, 1.20 ml. of benzoyl chloride (distilled) is added to the above-mentioned tetrahydrofuran.

15 The benzoyl chloride-tetrahydrofuran solution is poured, with moderate stirring, into the p-aminobenzoyl chloride hydrochloride and the mixture is stirred for about 1 minute. The stirring rate is increased and the hexamethylphosphoramide is rapidly added. The resulting mixture is stirred for about 1 hour while being cooled in an ice bath. The mixture gradually gels as a result of this treatment. The cooling bath is removed and the polymeric mass is allowed to stand overnight at room temperature. The solid gel is then combined with water and stirred at high speeds in a gallon-size (3.785 liter) blender wherein it is converted to a fine, white powder. The polymer is washed 3 times with water and once with alcohol by means of stirring in a blender and filtration on a sintered-glass medium-pore Buchner funnel. The polymer is dried overnight in a vacuum oven at 80°–90°C. The yield of poly(p-benzamide) is 92.3% ($\eta_{inh} = 1.35$). The polymer had a peak height ratio of 0.78. When subjected to the sedimentation test, no solid residue remained at the bottom of the tube.

Dope Preparation: Into a 700 ml. bottle equipped with an air-driven stirrer are placed 20 g. of the polymer and 180 g. of TMU/lithium chloride solution containing 6.5% by weight of the salt. The resulting mixture is stirred and heated to 150°C. by means of an oil bath. There is obtained an extremely viscous gelatinous mass. This mixture is cooled in solid carbon dioxide for 1 hour. the mixture is then heated at 150°C. for 4 hours with stirring, to produce a fluid, somewhat gelatinous hazy dope. The latter is cooled for 1 hour in solid carbon dioxide. The mixture is then stirred and heated for 4 hours at a temperature of 130°C. to produce a readily-spinnable haze dope which is subsequently cooled in solid carbon dioxide for 1 hour. This smooth, hazy dope flows slowly at room temperature and reflects light upon being stirred.

Fiber Preparation by Dry Spinning: The dope prepared as above is heated to 130°C. and extruded at the rate of about 0.9 ml./min., under a pressure of 70 lb./in.² (4,921 g.cm.²), through a heated (140°–144°C.) protrusion-type spinneret having 4 holes of 0.004 inch (0.01 cm.) diameter and a capillary length of 0.008 inch (0.02 cm.), into a drying column whose walls are kept within the range of 202°–210°C. The column is swept with a cocurrent flow (5 ft.³/min.; 0.142 m.³/min.) of dry nitrogen which enters the column at 265°–270°C. The emerging filaments, each of approximately 2 denier and having an oval cross-section, are passed over a small guide roll bearing a finish solution and are wound up on a bobbin at the rate of about 200 yd./min. (183 m./min.). This constitutes a spin stretch

factor of 6.58. The filaments do not stick and are readily back-wound. These opaque extruded filaments become lustrous white upon being soaked in changes of water (25°C.) to remove residual solvent and salt. The inherent viscosity of the polymer in the filaments is 1.32. The water-leached, air-dried (70°F. 65(193)% r.h.) filaments exhibit crystallinity and an orientation angle of 21°. A yarn prepared from these filaments exhibits the following T/E/Mi/Den. values (32 filaments; non-boiled-off): 6.02/2.17/431/58.5. Filaments that have been boiled off display the following T/E/Mi/Den. values: 4.75/1.38/429/1.72.

Heat Treatment of Fibers: The filaments or yarn prepared as above are passed taut over a 3-inch (7.62 cm.) plate maintained at 438°C. in a single stage operation so as to increase their length by 0–1%. Residence time over the hot plate was about 5 seconds. The resulting fibers exhibit crystallinity and have an orientation angle of 13°. Filaments have the following T/E/Mi/Den. properties (boiled off fiber): 7.66/1.2/599/1.87.

Other filaments prepared as above were subjected to heat treatments in both the relaxed and taut states. It was noted that the tensile properties of the filaments were improved.

The following Table I summarized improvements obtained in the tensile properties of water-leached, air-dried undrawn poly(p-benzamide) fibers prepared similarly but not exactly as above. The fibers are given the indicated heat treatments in both the relaxed and taut stages for a 1 hour period. Contrasting data is shown for a control sample. All values shown are for boiling off filaments and are obtained after the filaments are returned to room conditions (70°F., 65% r.h.).

TABLE I

Sample	Treatment Conditions	Post-treatment Tensile Properties Observed					
		Relaxed Fiber			Taut Fiber		
		T	B	Mi	T	E	Mi
A	200°C. hot air oven	6.88	1.75	476	7.34	1.92	473
B	250°C. hot air oven	7.38	1.67	491	7.45	1.72	456
C	198°–210°C. glycerol bath	6.79	1.79	457	6.17	1.62	443
D	235°–268°C. *Silicone-550** oil bath	6.61	1.48	506	7.50	1.74	503
E	Control	T/F/Mi:			5.85/1.69/426		

*Designation for a fluid, heat-stable silicone product of the Dow-Corning Corporation.

EXAMPLE II

This example illustrates the preparation of the poly(p-benzamide) fibers of the invention wherein a coupled process of polymer production and filament spinning is employed. It will be noted that the fiber properties are significantly enhanced after heat treatment.

In a 250 ml. round bottom flask (dried by flaming, filled with dry nitrogen, equipped with a stirrer, drying tube, and nitrogen inlet, and immersed in an ice-water bath) are combined 11.5 g. of p-aminobenzoyl chloride hydrochloride and 61 ml. of cold TMU. Immediately solution results. The mixture is stirred for 2 hours at approximately 0°C. and for 16 hours at 26°C. During this time the polymer separates as a swollen precipitate. Lithium hydroxide (2.87 g.) is added as an anhydrous powder and stirred in. There is considerable heat of neutralization and shortly thereafter a nearly clear, viscous dope of polymer containing now LiCl results, which at 100°–120°C., has the required consistency for facile dry-spinning. (The inherent viscosity of an isolated polymer sample is 1.12. It has a peak height ratio of 0.73 and passes the sedimentation test.)

The above-described dope is dry-spun under the following conditions: spinneret adapter temperature, 120°C.; pressure on dope 100 psi (7,031 g./cm.²); spinneret, 3 holes of 0.004 inch (0.01 cm.) diameter, each; spinneret temperature, 135°–140°C.; column-wall temperature, 195°–203°C.; wind-up speed, 200 yd./min. (183 m./min.). the speed stretch factor was 6.13. The yarn on bobbins is soaked in repeated changes of water at room temperature until essentially free of TMU and lithium chloride.

The T/E/Mi/Den. values of the washed and boiled-off fiber are 7.16/2.16/486/2.80, respectively. The fibers are crystalline and have an orientation angle of 16°.

After passing the washed, dry fiber over a hot plate at 438°C., the T/E/Mi/Den. values for a boiled-off sample of filaments are 10.7/1.7/695/2.82, respectively. The filaments are highly crystalline and exhibit an orientation angle of 12°.

EXAMPLE III

Into a 2-liter resin kettle are placed 153.6 g. (0.8 mole) of p-aminobenzoyl chloride hydrochloride with stirring under nitrogen. A 2% solution of lithium chloride in distilled TMU is prepared, heated at 60°C. and topped under vacuum to remove any water which might be present. About 800 g. of this solution are added rapidly to the monomer powder in the resin kettle at 30°C. while stirring. After about three-fourths of an hour, the first of three 4 ml. additions of diethylamine is made to stop the polymerization. The second 4 ml. are added 5 minutes later and the final 4 ml. are added 30 minutes after that. About 70 g. (0.946 mole) of lithium carbonate are added 18 minutes later. The

resulting viscous mix is then heated in an oil bath at 115°–120°C., diluted with 150 ml. of TMU and stirred under vacuum to distill off water formed in the neutralization and excess solvent. Final polymer concentration is about 9%.

One portion of the mix is diluted in dimethylformamide/lithium chloride 95/5 and coagulated in water. The precipitated polymer is washed in distilled water three times and finally in acetone. It was then dried at 60°C. under vacuum. It has an inherent viscosity of 0.97, a peak height ratio of 0.80, and when subjected to the sedimentation test, leaves no solid polymer residue at the bottom of the tube.

Fiber Preparation by Wet Spinning: The 9% dope as prepared above is pre-filtered through a 200-mesh stainless steel screen to remove excess Li₂CO₃ powder. Approximately 300 g. of the dope are then placed in a spinning cell, then filtered through a sand and screen filter pack before reaching the spinneret. The spinneret has 100 holes, each having a diameter of 0.003 inch (0.076 mm.). They are arranged in three circles within a half-inch (1.27 cm.) diameter overall. The spinneret

jets into a 65°C. bath of distilled water which is continuously recirculated and filtered. The bath is also continuously diluted with fresh water to prevent excessive build-up of salt and solvent in the bath. The yarn is drawn through a 135 cm. bath and over a 3.75 inch (9.53 cm.) diameter bobbin and wound up on a second 3.75 inch (9.53 cm.) bobbin. The spin stretch is controlled by varying the wind-up speed of the first bobbin. The minimum wind-up speed possible without yarn build-up in the bath is 32 ft./min. or 384 in./min. (16.26 cm./sec.). The calculated unextracted polymer solution jet velocity is 605 in./min. (25.61 cm./sec.). This indicates a lengthwise extraction shrinkage of 36.5% before wind-up. The optimum wind-up speed is found to be 540 in./min. (22.86 cm./sec.) and the maximum wind-up speed at which continuous spinning was possible was 635 in./min. (26.88 cm./sec.). These values correspond to spin stretch values of 1.4 and 1.65, respectively, based on the normalized value of 384 in./min. (16.26 cm./sec.) at spin stretch of 1.0. Based on jet velocity they are 0.893 and 1.05, respectively.

The as-spun yarn is soaked for 2 hours in water, then allowed to dry on the bobbins. The as-spun yarn has an orientation angle of 27° as determined by X-ray analysis. T/E/Mi/Den values for the as-spun yarn are 5.9/4.8/354/3.1 (after boil-off).

The yarn is subsequently heat treated by drawing it over a 12-inch (0.03 m.) long grooved hot shoe at 30 ft./min. (15.24 cm./sec.) to give a 2 second contact time. A nitrogen blanket is maintained over the hot zone.

The wet-spun sample after various heat treatments has the following properties (boiled-off):

	T/E/Mi (g.p.d./%g.p.d.)	dpf	Orientation 23.4°2θ
400°C.	7.0/1.7/596	2.9	16°
450°C.	8.9/1.4/773	2.9	15°
500°C.	8.4/1.0/990	2.9	14°
550°C.	6.9/0.8/937	2.8	12°

EXAMPLE IV

This example illustrates the effect of heat treatment on the tenacity and modulus of fibers of poly(1,4-benzamide) and preparation of a laminate from such fibers.

A 2-liter resin-making kettle is dried by flaming and allowing to cool in a nitrogen atmosphere. The kettle is fitted with an egg-beater-type aluminum stirrer and nitrogen inlet and outlet devices. While a slow current of dry nitrogen is passed through the kettle, it is charged with 150 g. of p-aminobenzoyl chloride hydrochloride. To this are added rapidly with vigorous stirring, 770 ml. of TMU, precooled to about -10°C. (This solvent had previously been dried to a water content of less than 150 parts per million by distillation over calcium hydride). Considerable heat is evolved initially; this is absorbed by surrounding the kettle with an ice-bath for the initial 15 minutes after reaction was started. After stirring the kettle's contents for about 2 hours at about 21°C., 38.0 g. of powdered, anhydrous lithium hydroxide is added and the stirred mixture is raised to a temperature of 120°C. by external heating. The highly viscous, rubbery mixture becomes a more free-flowing spin dope as stirring at 120°C. is continued for about 30 minutes. By distilling off about 50 ml. of solvent under a vacuum of about 20 cm. of mercury, most of the water, introduced by reaction of lithium hydroxide, is removed. The spin dope contains 10.2% polymer content.

Approximately 5 g. of spin dope are added to 200 ml.

water in a Waring blender. After stirring this for 5 minutes, the aqueous liquid is decanted from the recipitated polymer. A further 200 ml. water are added and stirring continued for a further 5 minutes. The treatment is repeated, using 200 ml. ethanol in place of the water. The polymer is filtered and dried for 15 hours at 70°-80°C. in a vacuum oven (20-40 cm. of mercury) fitted with a nitrogen bleed. The polymer has an inherent viscosity of 1.38, a peak height ration of 0.76, and, under the conditions of the sedimentation test, leaves no polymeric residue on the bottom of the test tube after 48 hours.

Spinning: The above spin dope is dry spun as follows. From the spinning vessel, in which it was kept at 155°C., the dope is expressed by a piston under a pressure of 68 lb./in.² (4,780 g./cm.²) through a spinneret adapter (at 125°C.), then through a spinneret (at 160°C.). The spinneret is of the protrusion type, consisting of nine effective holes, each of 0.004 in. (0.01 cm.) diameter. In the adapter the dope passes through a filter consisting of one 50 mesh screen, three 200 mesh screens, one cotton cloth of 2.4 oz./yd.² (81.5 g./m.²) woven in a plain weave with 148 pics per inch and 160 ends per inch, and one table felt pad of 2.8 oz./yd.² (95 g./m.²) and a density of 7.8 lbs./ft.³ (0.125 g./cm.³) at atmospheric pressure. The dope jets through the spinneret at a rate of 2.92 ml./min. into a cocurrent stream of nitrogen at a temperature of 235°C., flowing at 5 ft.³/min. (0.142 m.³/min.), in a spinning cell with walls heated at 200°C. The fibers issuing from the cell are passed through water and wound up at a rate of 135 yd./min. (123.5 m./min.), (spin stretch factor is 3.2). The fiber is wound up at this rate for 1 hour. The yarn cake is then immersed in a large excess of distilled water at 21°C. for 15 hours to extract salt and solvent. The wet cake is stored in a polyethylene bag. The as-spun and extracted yarn exhibits T/E/Mi/Den. = 8.22/3.1/509/3.06, after being dried.

Extracted and dried yarn of the preceding preparation is passed through a hot stainless steel tube, 0.286 inch (7.26 mm.) inside diameter and 32 inches (81.3 cm.) in length, at 12 ft./min. (3.66 m./min.) under a nitrogen atmosphere without significantly changing its length. The nitrogen is passed through the tube from the yarn entry end at such a rate as to change the atmosphere in the tube once every minute. The tube is heated externally by a 12 inch (0.3 m.) long furnace which was controlled by a thermocouple braised to the external central surface of the pipe and connected to a Minneapolis-Honeywell "Pyrovane" controller. The nominal heat-treating temperature of the tube given in Table III is the temperature indicated by a thermocouple braised to the center of the inside of the tube. A profile of the temperature in the tube for a "nominal" temperature of 536°C. obtained by varying the position of a test thermocouple is given in Table II.

TABLE II

TEMPERATURE PROFILE OF HEAT-TREATING TUBE

Distance from Entrance In. (Multiply × 2.54 for distance in cm.)	Temperature, °C.
0	135
6	179
10	336
12	452
14	515
15	532
16	537

TABLE II-Continued

TEMPERATURE PROFILE OF HEAT-TREATING TUBE	
Distance from Entrance In. (Multiply $\times 2.54$ for distance in cm.)	Temperature, $^{\circ}\text{C}$.
17	536
18	527
20	474
22	368
24	270
28	213
32	184

Properties of yarns treated at different temperatures are given in Table III.

TABLE III

Sample	Nominal Heat Treat. Temp. $^{\circ}\text{C}$.	Den. Fil.	Ten. g/d	Elong. $\%$	Mod. g/d	Fiber Den. g/cm. ³	Fiber Inh. Vis.	Orient. Angle $^{\circ}$	Peak Height Ratio
1	Room Temp.	3.060	8.22	3.1	509	1.4183	1.67	18	.63
2	100 $^{\circ}\text{C}$.	3.231	8.04	2.8	486	1.4180	1.69	17	.65
3	200 $^{\circ}\text{C}$.	2.769	9.38	2.5	545	1.4270	1.74	15	.67
4	304 $^{\circ}\text{C}$.	3.033	10.25	2.4	604	1.4363	1.78	13	.72
5	400 $^{\circ}\text{C}$.	2.804	13.18	2.5	671	1.4622	1.92	15	.71
6	500 $^{\circ}\text{C}$.	2.691	15.96	2.1	861	1.4643	2.32	13	.90
7	525 $^{\circ}\text{C}$.	2.649	16.87	1.9		1.4655	2.40	10	1.19
8	536 $^{\circ}\text{C}$.	2.785	15.69	1.7	040	1.4639	2.61	10	1.15
9	550 $^{\circ}\text{C}$.	2.885	15.48	1.6	029	1.4643	2.75	10	1.10
					030				

Preparation of a Laminate: Yarn from the preceding spin is heat-treated by passing the yarn through a hot tube at a nominal temperature of 536 $^{\circ}\text{C}$. and a speed of 11.58 ft./min. (3.53 m./min.). It is wound up on a bobbin of 4.13 in. (10.5 cm.) diameter as a thin cake approximately 1.5 in. (3.81 cm.) wide. The traversing rate at the wind-up is 1 stroke/11 revolutions; the yarn filaments in the cake are nearly parallel. A test specimen of the yarn has Denier/T/E/Mi values of 2.967/16.17/1.7/1096.

A laminate is prepared from the above fiber as follows. A mixture consisting of 10 g. "Epon 815" (Shell's epoxy resin), 9 g. or "Nadic" (methyl anhydride curing agent Allied Chemical Corporation), and 0.1 g. of benzyl dimethylamine is poured into a mold having a cavity with the following dimensions: length, 5.95 in.; width, 0.5 in.; depth, 0.9 in. (15.2 $\times$ 1.27 $\times$ 2.29 cm.). The mold and its contents are placed in a vacuum chamber for 1 hour to remove gases. The mold is then removed from the vacuum chamber. The fiber is cut from the bobbin and divided into ribbons (5.95 in. (15.2 cm.) long) which are arranged in a stack with the fibers substantially parallel to the long axis to the ribbon. The fiber weighs 4.84 g. The fiber is placed on top of the resin and gently pressed in, care being taken to preserve the parallel orientation of the fibers. The mold and its contents are returned to the vacuum chamber for a further 30 minutes for removal of unwanted gases. The mold is then taken from the vacuum chamber and a flanged plug, having dimensions of 5.75 $\times$ 0.5 $\times$ 1.0 in. (14.6 $\times$ 1.27 $\times$ 2.54 cm.), is pushed into the cavity and pressed slowly down upon the resin-fiber mix in order to allow bubbles and excess resin to find their way to the open spaces between the plug ends and

cavity ends without disarranging the fibers. The plug flange rests upon shims which are sized to leave a gap of 0.1 in. (0.254 cm.) between the plug and the bottom surface of the mold. The mold and its contents are placed in a Pasadena press, the platens of which have been heated to 150 $^{\circ}\text{C}$. The press is closed and a total pressure of 1.5 tons (1.36 metric tons) is applied to the mold. The mold is left in the press for 2.75 hr. before being taken out and cooled to room temperature.

- 10 The ends of the laminate sample are cut off and hand sanded. The sample measures 5.32 $\times$ 0.502 $\times$ 0.095 in. (13.5 $\times$ 1.27 $\times$ 0.24 cm.). The tangent modulus of elasticity in flexure (i.e., flex modulus) of the sample is measured having a 4 in. (10.16 cm.) long portion
- 15 chosen in the middle of the laminate as the test section.

- 35 The sample is mounted as a supported beam with load applied in the center in an "Instron" testing machine. The load member is deflected at the rate of 0.02 in./min. (0.508 mm./min.) until a load of 20 lb. (9.07 kg.) is applied. The flex modulus is found to be 14.41 $\times 10^6$ lb./in.² (10.13 $\times 10^8$ g./cm.²). By comparison, commercial aluminum with a modulus of 10 to 20 $\times 10^6$ lb./in.² (70.3 to 140.6 $\times 10^7$ g./cm.²) has a density of 2.56 g./cm.³. Laminates of "E" glass have a theoretical
- 40 modulus limit of 8 $\times 10^6$ lb./in.² (56.2 $\times 10^7$ g./cm.²) at a density of 2.22 g./cm.³.

EXAMPLE V

- 50 Polymer Preparation: A 250-ml. round-bottomed flask equipped with a stirrer, nitrogen inlet tube, and calcium chloride drying tube is flamed with a Bunsen burner and simultaneously flushed with nitrogen. The dry flask with its attachments is placed in a dry-box and 11.52 g. of p-aminobenzoyl chloride hydrochloride is added. The flask is then attached to a stirring motor and nitrogen source and stirring and slow nitrogen flow started while the flask is cooled in an ice bath. Cold TMU (58.7 ml.) is added quickly in a single portion.
- 55 The monomer immediately dissolves and polymerization starts. Stirring is continued for 2 hours with ice cooling and for 2 hours without cooling. The forming polymer yields a viscous, somewhat hazy dope. Polymer is isolated from a sample of the dope at 4 hours by precipitation in water and is found to have an inherent viscosity of 1.38.

Fiber Preparation: A sample of polymer dope, prepared as described above but from a duplicate reaction mixture, is charged into a 15-ml., syringe-type cell hav-

ing a mechanically-driven plunger and being constructed of stainless steel. A 20-hole spinneret, having 0.003 in. (0.076 mm.) holes and constructed of a platinum alloy, is attached to the syringe by a ring-nut over a simple filter pack consisting of a 200-mesh stainless steel screen, a thin layer of fine glass wool and then 50-mesh, 200-mesh, and 50-mesh screens in succession. The dope is extruded at a slow rate into a water bath kept at about 50°C. and the fibers are collected on a bobbin at a speed of 61 ft./min. (18.6 m./min.) after traveling in the bath for about 3 ft. (0.91 m.). The fibers have the following properties:

TABLE IV

Treatment	Den.	T	E	Mi
Washed and air-dried	5.67	3.8	4.1	221
Heated at 440°C., 4 sec.	4.86	5.8	1.0	619
under N ₂				
Heated at 530°C., 2 sec.	5.05	6.7	1.2	577
under N ₁				

The polymer of the as-spun fiber has an η_{inh} of 1.12 and a peak height ratio of 0.78.

Some of the dopes used in this invention may be further characterized by their microscopic birefringent qualities which are manifested by their effect on plane-polarized light. Such an observation may be made by the following method. A drop taken from the interior of a dope sample of this invention is put on a dry, clean strain-free glass slide; a square cover of glass, supported on one edge by a glass tube or wire of known thickness (1.3 mm. diameter is convenient) is pressed down on the drop so as to form the roof of a liquid wedge. The edges are sealed with a fast-drying binder avoiding actual contact with the dope. The sharp edge of the wedge is sealed by excess dope which is squeezed out. In the operation, common care should be taken to avoid evaporation, moisture uptake, excessive shearing actions, dirt, and any suspended solid particles.

The wedge is positioned in a light beam, on a microscope stage between crossed polarizer and analyzer, so that the thickness of the center of the layer of dope through which the light beam passes is 80 μ in thickness. The intensity is measured with polarizer and analyzer crossed (I_+^s) (superscript s to denote sample present in wedge) and with analyzer removed (I_-^s) and the difference $I_-^s - I_+^s$ is obtained. The transmitted light may be measured by conventional light sensitive detectors (e.g. by photo multipliers, selenium or cadmium light meters, bolometers, etc.). The same measurements are then made on a similarly constructed wedge containing air, and the difference $I_-^c - I_+^c$ (superscript c for control) is recorded. When these dopes of this invention are placed in the wedge, the expression $(I_-^c - I_+^c) - (I_-^s - I_+^s)$ will be greater than zero, and greater than can be accounted for by experimental error. It represents the increase in light transmittance through the analyzer due to the presence of the sample. The magnitude of $(I_-^c - I_+^c) - (I_-^s - I_+^s)$ will vary with the solvent being used, polymer concentration, and concentration of dissolved salt, and the units in which light intensity is measured.

EXAMPLE VI

The results presented in the following Table V illustrate the effects of using various chain terminators, with and without added lithium hydroxide monohy-

drate, in preparing the poly(p-benzamide) used in this invention. Data for two control runs are also presented.

In each of these polymerizations, 200 ml. of TMU are placed in an ice-cooled glass reaction vessel and 0.0025 mole of the designated terminator is added thereto. To these ingredients are added 32 g. (0.17 mole) of p-aminobenzoyl chloride hydrochloride. The contents of the reaction vessel are stirred for 15 minutes, after which the cooling bath is removed and the contents stirred for another 1.75 hour. Lithium hydroxide monohydrate (12.8 g., 0.31 mole) is added to the vessel and the contents are stirred for 30-60 minutes at autogenous temperature. The reaction mixture is then permitted to stand for 20 hours at autogenous temperature before being agitated with water in a blender to precipitate the polymer. The latter is collected, washed three times with water and once with 2B alcohol (all done in a blender), and dried in a vacuum oven. The particular terminator employed, the polymer's viscosity, and presence or absence of lithium hydroxide monohydrate are indicated in appropriate columns of Table V.

TABLE V

Item	Terminator	LiOH.H ₂ O	η_{inh} of Poly (p-benzamide)
1	None	Yes	1.9
2	None	Yes*	1.67
3	Butylamine	No	1.68
4	Butylamine	Yes	1.56
5	Piperidine	No	1.57
6	Piperidine	Yes	1.52
7	p-Phenylenediamine	Yes	1.67
8	Terephthalic hydrazide	Yes	1.88
9	Terephthalic hydrazide	Yes*	1.49
10	Cyclohexylamine	Yes	1.67
11	Cyclohexylamine	No	2.07

*Added 1 hr. after monomer addition instead of 2 hr. later.

EXAMPLE VII

This example illustrates that some dopes used in this invention cause an increase in the transmittance of light through crossed polarizers.

In this example, the apparatus by which the anisotropic character of these dopes is determined consists essentially of an A. O. Spencer Orthoscope Illuminator which contains a tungsten overvoltage microscope lamp (color temperature 3800°K.), an optical wedge containing the sample, an optical wedge containing air, a Bausch and Lomb Polarizing Microscope having a Leitz 10 $\times$ objective and a Leitz 10 $\times$ ocular Periplan, a Polaroid M 3 Industrial Land Camera and a Gossen "Sinarsix" exposure meter. The wedge containing the sample is prepared as previously described and is positioned on the microscope stage (i.e., between the polarizer and the analyzer) to provide a sample layer of 80 μ thickness in the path of any light which reaches the analyzer and the light meter. The polarizer and the analyzer are adjusted to provide 90° crossed polarization planes. Light from the lamp which passes the analyzer by the route previously described is projected into the camera and is measured in the image plane (at the ground glass level) by the exposure meter (I_+^s). The same measurement is made with the analyzer removed (I_-^s). This is repeated with the control wedge of air 80 μ thick to give I_+^c and I_-^c . The light readings from the Sinarsix exposure meter may be converted to light intensities by multiplying them by 0.301 (i.e. by log 2) and then determining the antilog of this product. These

values are designated $I_{+}^{s'}$, $I_{-}^{s'}$, $I_{+}^{c'}$, and $I_{-}^{c'}$. The expression $I_{+}^{s'}/I_{-}^{s'}$ is the ratio of light intensities transmitted by the dope being examined. The ratio $I_{+}^{c'}/I_{-}^{c'}$ is the ratio of light transmitted by the control wedge. The difference $(I_{+}^{s'}/I_{-}^{s'}) - (I_{+}^{c'}/I_{-}^{c'})$ represents the increase in intensity of light transmitted due to the presence in the wedge of the dope being examined.

Since the theoretical maximum value of $I_{+}^{s'}/I_{-}^{s'} - I_{+}^{c'}/I_{-}^{c'} = 0.5$, an index of the increase of light transmittance may be conveniently taken as $2(I_{+}^{s'}/I_{-}^{s'} - I_{+}^{c'}/I_{-}^{c'}) \times 100$ since in this way, the maximum value is 100. When measured according to the foregoing procedures, dopes having values greater than two are considered herein to be anisotropic in nature.

Shown in the following Table VI are data determined by the above described procedure on typical dopes of this invention. The symbol T is used for the value obtained from the expression $2(I_{+}^{s'}/I_{-}^{s'} - I_{+}^{c'}/I_{-}^{c'}) \times 100$. All dopes are in TMU. Each dope sample shown in Table VI contains lithium chloride.

End Uses: The fibers are excellent for reinforced plastic laminates because of their high modulus, low density, high dimensional stability, high strength, high thermal stability and high flexural rigidity at a given laminate weight. Specific end-uses may include spiral

TABLE VI

LIGHT DEPOLARIZATION BY POLY(p-BENZAMIDE DOPES)				
Item	Poly(p-benzamide weight Percent		Wgt. % Salt	T
	η_{inh}	In Dope		
1	0.7	10%	5.9	30
2	1.4	5%	3	47
3	1.14	5%	3.2	53

wound pressure vessels, skis, bows, fishing rods, and golf club shafts.

The high modulus, high strength, fatigue resistance and impact strength of the fibers render them useful in mechanical rubber goods such as belts.

The fibers are useful in sewing thread and in uses such as protective clothing, laundry press covers, filtration fabrics, industrial hose, dryer felts, all of which utilize the high thermal stability of the fiber.

What is claimed is:

1. A method for increasing the initial modulus and reducing the orientation angle of undrawn fibers consisting essentially of poly(p-benzamide having an orientation angle of up to about 55° comprising heating the undrawn fibers at a temperature of at least 350°C. While under tension or, while relaxed.

* * * * *