

Nov. 22, 1966

W. SWEENY

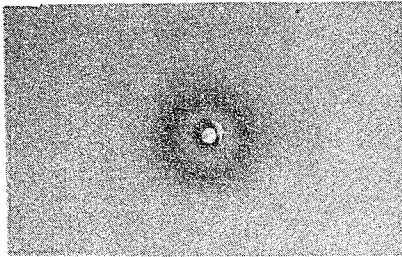
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POLY-META-PHENYLENE ISO-PHTHALAMIDES

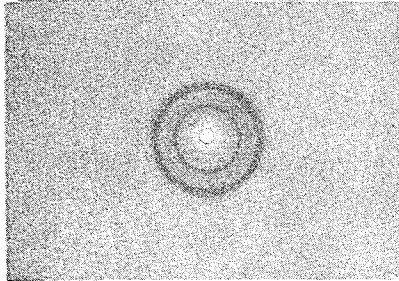
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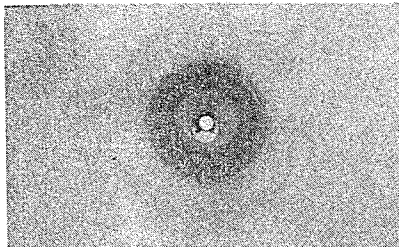
**FIG. I**



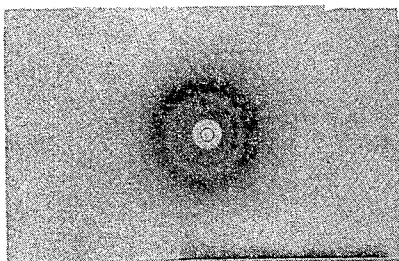
**FIG. II**



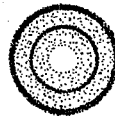
**FIG. III**



**FIG. IV**



**FIG. IIa**



**FIG. IIIa**



**FIG. IVa**



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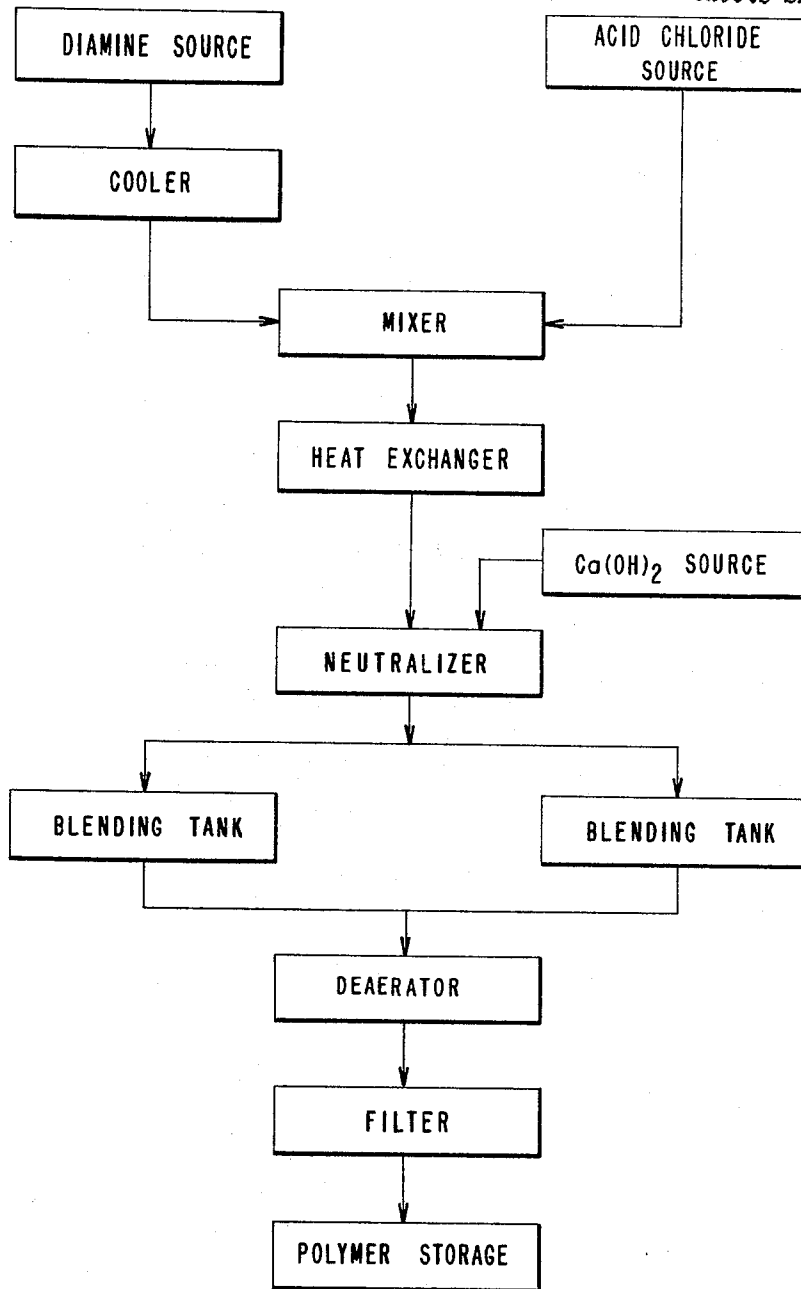


FIG. V

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**POLY-META-PHENYLENE ISOPHTHALAMIDES**  
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Filed May 7, 1965, Ser. No. 454,086

9 Claims. (Cl. 260-78)

This application is a continuation-in-part of application Serial No. 171,755 filed February 19, 1962, which is a continuation-in-part of Serial No. 774,156, filed November 17, 1958 (now Patent No. 3,094,511 dated June 18, 1963), which in turn is a continuation-in-part of Serial No. 642,928, filed February 28, 1957, and now abandoned.

This invention relates to a novel and useful synthetic textile fiber and fabrics produced therefrom. More specifically it relates to a textile fiber from poly(m-phenyleneisophthalamide) and ring substituted derivatives thereof, hereinafter referred to as MPD-I polymers.

Textile fibers from synthetic polymers are conventionally prepared by extrusion of a melt (melt spinning) or a solution (dry spinning) of the polymer. A relatively low melting point or high solubility of polymer is therefore conducive to ease of fiber formation. These same properties, i.e., low melting point and high solubility, are however highly undesirable in a textile material for obvious reasons. The present invention provides a class of synthetic, fiber-forming polymers which are capable of existing in two forms, one form, referred to hereinafter as the "alpha" form (i.e.,  $\alpha$ -MPD-I polymers), having high solubility, the other, referred to hereinafter as the "beta" form (i.e.,  $\beta$ -MPD-I polymers), possessing low solubility.

It is an object of the present invention to provide polymers of  $\alpha$ -MPD-I and  $\beta$ -MPD-I of fiber-forming molecular weight.

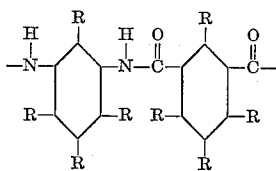
Another object is to provide a useful shaped structure from  $\alpha$ - and  $\beta$ -MPD-I polymers.

Another object is to provide a process for forming a synthetic textile of  $\beta$ -MPD-I polymers from a textile of  $\alpha$ -MPD-I polymers.

A further object is to provide a synthetic textile fiber having a high flame resistance.

These and other objects will become apparent in the following specification and claims.

The present invention provides the novel and useful polymers of  $\alpha$ -MPD-I and  $\beta$ -MPD-I, shaped structures thereof and processes for their production. In accordance with the present invention, polycarbonamide is provided having an inherent viscosity of at least 0.8 in sulfuric acid at 30° C. at a concentration of 0.5 gram of polymer per 100 cc. of solution, the polycarbonamide of the class consisting of (a) an alpha polymetaphenylene isophthalamide characterized by relatively high solubility and (b) a beta polymetaphenylene isophthalamide characterized by relatively low solubility, the polycarbonamide consisting of repeating units of which at least about 85% are of the formula



wherein the hexagon represents the benzene nucleus, R is a non-amide forming substituent on nuclear carbon. Preferably at least two or three of the "R" groups are hydrogen, and copolymeric units, when present, are carbonamidic.

By a "non-amide forming substituent" is meant a substituent which is non-amide forming at room temperature

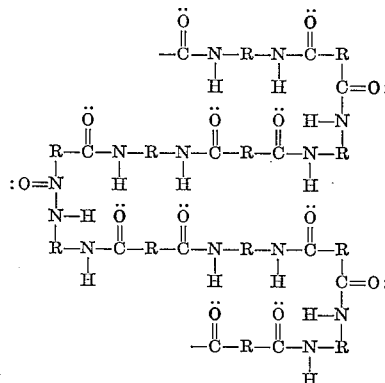
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via reaction with a member from the class consisting of amino hydrogen and carbonyl halide.

The invention will be more readily understood by reference to the illustrations.

FIGURE I is an X-ray diffraction pattern of the amorphous form of an MPD-I polymer. FIGURES II, III and IV are X-ray diffraction patterns of the crystalline form of MPD-I polymers in the  $\alpha$ ,  $\beta$  and salt complex forms respectively. FIGURES IIa, IIIa and IVa being artist's representations of each of the respective corresponding photographic images. FIGURE V is a flow sheet of the continuous process referred to in Example 16.

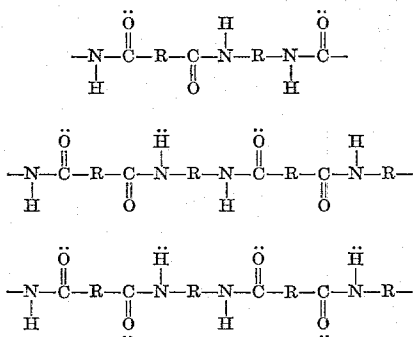
MPD-I polymers, as defined above, are characterized by the existence of two linear forms which will be referred to hereinafter as an "alpha" (soluble in selected organic solvents) form and a "beta" (insoluble in organic solvents) form. As will be further explained hereinafter, each of the  $\alpha$ - and  $\beta$ -forms may be complexed using selected salts as described hereinafter to render the  $\beta$ -form soluble in organic solvents and to increase the solubility of the  $\alpha$ -form. MPD-I polymer may also exist in the cross-linked form, i.e., intractable and insoluble in concentrated sulfuric acid as well as organic solvents. In each of the alpha form and the beta form the polymer or shaped structure formed therefrom may exist in the amorphous or the crystalline state. The alpha form of polymer can be formed by low temperature polymerization. Attempts to obtain fiber-forming molecular weight by high temperature polymerization as taught in U.S. 2,244,192 always lead to formation of cross-linked polymer which cannot be employed to form shaped articles. The alpha form is highly soluble in conventional dry spinning solvents such as dimethylformamide and dimethyl acetamide, whether in the amorphous or crystalline state. The beta form is insoluble in such solvents whether in the amorphous or crystalline state. While applicants do not wish to be bound by any theory of operation, it is believed that a network of interchain hydrogen bonding, which may be ordered enough to be crystalline, between the carbonyl oxygens and weakly acidic —NH groups of adjacent chains, is characteristic of the beta form. On the other hand, the alpha form of the polymer is largely free of such bondings due to intrachain hydrogen bonding between carbonyl oxygens and weakly acidic —NH groups of another recurring unit in the same chain. Thus the alpha form of the polymer is characterized by a hydrogen bonding which may be represented by a folded or coiled structure as follows:



the paired dots in the formula indicating hydrogen bonding and the symbol —R— representing phenylene or substituted phenylene upon which the carbonyl and amine substituent groups shown are meta oriented. The high degree of intrachain hydrogen bonding obtained is believed possible due to the short distance between adjacent carbonyl and imine groups peculiar to the meta orienta-

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tion of each group. This bonding permits a high degree of solubility as compared with structures having a significant amount of the beta form which beta form may be represented as follows:



The alpha form may be converted to the beta form by (a) increasing the chain mobility with heat, suitable plasticizers or solvents so that the chain can rearrange to the more stable  $\beta$ -structure (this is accelerated by the presence of H-bond active material such as water, alcohol or carboxylic acids) and (b) by ordering the chain molecules by some process of orientation, as in the shearing of a solution, casting of a film, spinning a fiber or drawing a yarn. The alpha form in solution is converted to the beta form slowly at room temperatures but more rapidly at higher temperatures. Such conversion in solution is normally undesirable since the solutions gel to immobility. It is therefore convenient to convert the alpha to the beta form during the spinning or casting operation in the formation of shaped objects such as fibers or films. The temperature at which conversion from the  $\alpha$  to the  $\beta$  form occurs in solution will vary depending upon the nature of the solvent (due to differences in solvent power). Thus the  $\alpha$  form is relatively stable in dimethylformamide at from about  $-10^\circ\text{C}$ . to about  $+15^\circ\text{C}$ ., whereas in dimethylacetamide the range of solution stability shifts to from about  $0^\circ\text{C}$ . to about  $35^\circ\text{C}$ . In dry N-methylpyrrolidone, the  $\alpha$  form is relatively stable from room temperature to about  $80^\circ\text{C}$ . Conversion from the  $\alpha$  to the  $\beta$  form can occur rapidly as will be demonstrated below where a film of soluble  $\alpha$  polymer is rendered insoluble by being plunged into the same solvent at elevated temperature.

It will be obvious from the above discussion that useful shaped structures such as fibers and films cannot be made from cross-linked MPD-I due to its intractable and insoluble nature. On the other hand, the  $\alpha$  form is readily extruded or cast into fibers and films due to its soluble nature. The structures formed are particularly valuable since they may be converted after shaping into the  $\beta$  or even the intractable cross-linked form. It will also be obvious, as is demonstrated below, that preparation of the  $\alpha$  form of polymer must be by a low temperature technique, since melt polymerization leads to the cross-linked variety, when attempt is made to polymerize to a fiber-forming molecular weight.

The following examples are intended to illustrate the invention. They are not intended to limit it in any manner. All parts and percentages are by weight unless otherwise indicated. Values of inherent viscosity are determined in sulfuric acid (sp. gr. 1.841 at  $60^\circ\text{F}$ .), at  $30^\circ\text{C}$ . at a concentration of 0.5 gram polymer per 100 cc. of solution. All polymers of this invention have an inherent viscosity of at least about 0.8 on this basis (i.e., they are of fiber-forming molecular weight) and a polymer melt temperature of at least about  $300^\circ\text{C}$ . (When a powdered, high-melting-point polymer is placed at the proper point on a melting bar which is heated at one end only so as to provide a suitable gradient in temperature along its length, the polymer will generally be observed to soften to a plastic, deformable mass which may stick to the bar.

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This softening point is what is intended by the expression "polymer melt temperature." Measurement of surface temperature of the bar at the point of softening and sticking provides a reasonably reproducible indication of melting point. The higher this temperature the greater the error in the measurement and the more subjective it becomes.) Unsymmetrical substituents such as that disclosed in Example 10 reduce the polymer melt temperature somewhat, but not below  $300^\circ\text{C}$ . Some ring substitutions, as for example, that disclosed in Example 11 actually increase the polymer melt temperature over that of the polymers made from aromatic diamines and diacyl halides without ring substituents.

#### Example 1

A solution of 10.3 grams of isophthaloyl chloride and one drop of sulfuric acid in 175 ml. of tetrahydrofuran is added at room temperature to a rapidly stirred solution of 5.4 grams of m-phenylene diamine and 10.6 grams of sodium carbonate in 150 ml. of water. After stirring for five minutes, the polymer formed is collected on a filter, washed in a blender twice with water and twice with acetone and thereafter dried at room temperature under vacuum. The inherent viscosity of the product is 2.1. This is the  $\alpha$  form of polymer as is evidenced by its solubility in dimethylformamide at  $0^\circ\text{C}$ . and in either dimethylacetamide or N-methylpyrrolidone at room temperature to the extent of at least about 5%. The product has a polymer melt temperature of  $360^\circ\text{C}$ .

#### Example 2

A shaped amorphous structure of the  $\alpha$  MPD-I is prepared by casting a film of a solution of two grams of the above prepared polymer in 13.4 grams N-methylpyrrolidone under cyclohexane, carefully excluding moisture. After hardening under the liquid for 20 minutes the film is dried for 18 hours in a vacuum oven at  $50^\circ\text{C}$ . with a stream of dry nitrogen blowing through it. The dried film can be redissolved in dimethylformamide at  $0^\circ\text{C}$ . and in either dimethylacetamide or N-methylpyrrolidone at room temperature. An X-ray diffraction pattern of the amorphous film is shown in FIGURE I. When ether is substituted for cyclohexane in the above procedure, the resulting film is also soluble in dimethylformamide, dimethylacetamide and N-methylpyrrolidone, as expressed in Example 1, but shows a trace of  $\alpha$  crystallinity in its X-ray pattern.

#### Example 3

A shaped highly crystalline structure of the  $\alpha$  MPD-I is prepared by casting a 6 in. by 2 in. film from a solution as employed in Example 2, in air and at room temperature and with exclusion of moisture. The resulting film is immediately placed in a vacuum oven and is dried at room temperature with a gentle stream of dry nitrogen passing over it for 60 hours. The resulting film is opaque, tough and soluble in dimethylformamide at  $0^\circ\text{C}$ ., dimethylacetamide at  $25^\circ\text{C}$ . and N-methylpyrrolidone at  $80^\circ\text{C}$ . Its X-ray diffraction pattern, FIGURE II, demonstrates that it is highly crystalline.

#### Example 4

A shaped structure having medium crystallinity of the  $\beta$  MPD-I is prepared by modifying the procedure of Example 3 above by drying the film at room temperature in air. This film is insoluble in all of the solvents listed under Example 3 except the N-methylpyrrolidone at  $80^\circ\text{C}$ .

#### Example 5

A portion of the shaped highly crystalline structure of  $\alpha$  MPD-I prepared in Example 3 is converted to a highly crystalline  $\beta$  MPD-I by plunging the film in dimethylformamide heated to about  $90^\circ\text{C}$ . and keeping it at this temperature for about 2 hours. Transformation from the  $\alpha$  to the  $\beta$  form is so rapid that no visible solution of the  $\alpha$  form occurs. The resulting film is there-

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after insoluble in both dimethylformamide and dimethylacetamide whether cold or hot. X-ray analysis shows the structure to be highly crystalline.

Transformation of the same highly crystalline structure of  $\alpha$  MPD-I to the highly crystalline  $\beta$  form is also accomplished by subjecting the film of Example 3 to a stream of steam for about one hour.

#### Example 6

In addition to the techniques illustrated in Example 5, shaped structures of  $\alpha$  MPD-I can be converted to  $\beta$  MPD-I by heat alone. This is illustrated in Table I. Films prepared in accordance with Example 3 are placed at different positions on a hot bar for one minute, each sample being exposed to the temperature indicated. Solubility characteristics of the resulting heat treated films indicated each to be in the  $\beta$  form. The amount of perfection of crystallinity is also indicated in the table. The solubility was determined in dimethylformamide at 0° C.

TABLE I

Sample	Temp., ° C.	Solubility	Crystallinity	
			Amount	Perfection
A-----	180	Swells-----	Medium-----	Medium-----
B-----	214	Insoluble-----	do-----	Do-----
C-----	254	do-----	do-----	Do-----
D-----	284	do-----	High-----	High-----
E-----	360	do-----	do-----	Do-----

While Examples 1-6 above show the preparation of films for illustrative purposes, it will be obvious to those skilled in the art that other shaped structures such as fibers, coated and molded articles and the like may also be formed from the  $\alpha$  form of the polymer by conventional techniques, due to the solubility of this form of polymer. Because the alpha-form is rapidly converted to the beta-form by heat, spinning of fibers from the alpha-form may best be accomplished in a wet-spinning process wherein low solution temperatures are consistent with practical spinning rates. Thereafter the structure in the shape desired may be transformed into the  $\beta$  form to render it insoluble in solvents such as dimethylformamide, dimethylacetamide and N-methylpyrrolidone. More conveniently the transformation from  $\alpha$  to  $\beta$  form may take place during or in conjunction with the shaping operation. For instance, in the formation of fiber, the  $\alpha$  form may be wet spun and converted to the  $\beta$  form in a subsequent wet extraction-heating treatment.

The preferred method of forming structures of  $\beta$  polymer from the  $\alpha$  polymer involves the use of a salt complex which renders the polymer more soluble and stabilize the solution by inhibiting or retarding the  $\alpha$  to  $\beta$  transformation by preventing the inter-chain hydrogen bonding which is responsible for the beta form. Solutions using such complexes are described and claimed in Beste and Stephens, United States Patent 3,068,188 issued 12/11/62. While applicants do not wish to be bound by any particular theory, it is postulated that the selected salts have greater attraction for the amide groups than the amide groups possess for each other. Thus when the hydrogen bonding of the  $\alpha$  form is disturbed, for instance, by increased chain mobility or ordering of the chain molecules, formation of the salt complex is favored over interchain bonding which would lead to the  $\beta$  form, thus maintaining the polymer in a non-hydrogen bonded condition. The salt complex intermediate technique permits the polymer to be handled at a higher temperature

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than is possible without complexing. The salt is conveniently removed from the shaped structure by aqueous boil-off, which also serves to transform the shaped structure into the  $\beta$  form. Obviously prolonged heating or heating at a high temperature may be employed to transform the shaped structure into the truly cross-linked condition. The examples below illustrate the technique of forming a shaped structure wherein the intermediate salt complex form is involved.

#### Example 7

(A) Meta-phenylenediamine dihydrochloride in the amount of 5.4 parts is placed in a reaction vessel fitted with a high speed stirrer and a solution of 12.1 parts of triethylamine in 200 parts methylene chloride is added rapidly. The mixture is stirred for one minute to dissolve the diamine salt. Triethylamine hydrochloride is formed in situ. 6.1 parts of isophthaloyl chloride in 200 parts of methylene chloride are then added. Polymerization is completed and  $\alpha$  MPD-I is precipitated by addition of a volume of hexane about equal to the volume of the reaction mass. The product is water-white and has an inherent viscosity of 1.71. It is obtained in 91% yield.

A blend of several polymers in the  $\alpha$  form prepared by the procedure outlined above is dissolved to a concentration of 17% in a mixture of 95 parts dimethylformamide and 5 parts lithium chloride. This solution at 128° C. is spun through a 5-hole spinneret, in which each orifice has a diameter of 0.10 mm., into an air column maintained at 225° C. Fiber, wound up at the rate of 92 yards per minute is thereafter drawn to 4.00 times its original length and boiled off in water to remove the salt. The final fiber,  $\beta$  MPD-I, has a tenacity of 3.8 grams per denier, with a 39% elongation at the break.

(B) Another sample of the same polymer is dissolved in a mixture of 95% dimethylformamide and 5% lithium chloride to give a 15% polymer solution. This solution is cast into a film. The solvent is flashed off in an oven at 160° C. The resulting film is leached in water at 65° C. for 24 hours to remove residual dimethylformamide and salt. Test strips of the wet film of  $\beta$  MPD-I so formed are clamped in frames prior to drying in a vacuum at 90° C. Physical properties of the films at various temperatures are reported in the table below:

TABLE II

Temperature, ° C.	Tensile Strength (p.s.i.)	Modulus (p.s.i.)	Percent Elongation
20-----	12,000	500,000	4-5
150-----	7,500	350,000	2-9
200-----	7,000	350,000	4-15

The film is also noted to have a high dielectric constant which drops off only fractionally at temperatures as high as 200° C., while commercially available insulating materials such as polyethylene or rubber are either completely destroyed or become molten at such temperatures.

(C) In order to illustrate the non-flammable nature of the polymers, another sample of fiber similar to that prepared in paragraph (A) of this example (differing only in that it was drawn  $\times$  4.75 and had 4.9 gms. per denier tenacity and 30% elongation at the break) is subjected to a standard flammability test (A.A.T.C.C. 45° angle test, American Handbook of Synthetic Textiles, 1st Ed. (1952), Textile Book Publishers Inc., N.Y.) along with a cotton fiber control. Both fibers are knit into tubes and exposed to an open flame until ignited, at which time the

flame is removed. Test results are shown in the table below:

wherein the hexagon represents the benzene nucleus, R are the same or different non-amide-forming substituents,

TABLE III.—FLAMMABILITY OF KNIT FABRICS

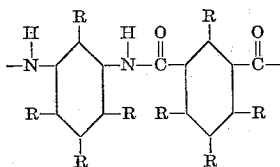
Sample	Ignition Time, sec.	Total Time to Burn	Dimensions Char Zone (inches)	Type of Burning	Type of Residue
Test Fiber (five samples)-----	3.8	Went out (5.4 sec.)-----	0.35 x 0.30-----	Slow ignition, negligible burning period....	Crusty hard. Feather.
Cotton fiber (five samples)-----	2	13 to 430 secs.-----	1.5 x 6, sample burned completely.	Rapid ignition, quick flaming, glowing char slowly disintegrates.	

As can be seen, the fiber of this invention is outstandingly superior to cotton in flame resistance. In similar tests, the fibers of this invention are compared to other commercial synthetic fibers, and proved more difficult to ignite and in addition were self-extinguishing. A sample of a fabric from poly(hexamethylene adipamide) yarn is burned to the extent of  $\frac{3}{8}$  of the fabric area, while the fabric prepared from fibers of this example is charred for less than  $\frac{1}{40}$  of its area.

(D) In another typical preparation of MPD-I, a solution of 2.0 grams of isophthaloyl chloride in 2.00 cc. of methylene chloride is added to a stirred and cooled (ice) solution of 1.8 grams of m-phenylenediamine dihydrochloride and 4.1 grams triethylamine in 50 cc. of methylene chloride. The polymer precipitates immediately. Stirring is continued for 10 minutes after which the polymer is filtered, washed with warm water and dried at 60° C. under vacuum. A yield of 1.5 grams of polymer having a polymer melt temperature estimated at about 360° C. and an inherent viscosity in dimethylformamide of 1.06 is obtained. A film is cast from a solution of the polymer in dimethylformamide. After the film is dried at 90° C. it is observed to be no longer soluble in dimethylformamide.

The  $\alpha$  form of the polymer from which the fiber or other shaped structure is produced is formed by a low temperature, solvent polymerization technique as illustrated in the specific examples. The process is described in greater detail and claimed in copending U.S.P. 3,063,966, issued 11/11/62 to Kwolek, Morgan and Sorenson filed February 5, 1958. In general the process comprises combining the diacid halide of isophthalic acid with m-phenylenediamine in the presence of an acid acceptor in a liquid reaction medium which is a solvent for each reactant such as chloroform, methylene chloride, 1,1,2-trichloroethane, 1,2-dichloroethane, methyl ethyl ketone, acetonitrile, tetramethylene sulfone, 2,4-dimethyltetramethylene sulfone, diethylcyanamide, dimethylcyanamide, chlorobromomethane, symtetrachloroethane, cis-1,2-dichloroethane, propionitrile, N-methyl pyrrolidone and the like. Suitable acid acceptors include trimethylamine, triethylamine, ethylpiperidine, diethylbenzylamine, dimethylbenzylamine, ethylmorpholine, methylmorpholine, N,N,N',N'-tetramethylhexamethylenediamine and the like as well as amide type materials which may also serve simultaneously as a liquid reaction medium.

The MPD-I polymers of the present invention consist of at least about 85% repeating polycarbonamide units of the formula



preferably members of the class consisting of lower alkyl, lower alkoxy, halogen, nitro, cyano, sulfonyl, lower carbalkoxy and hydrogen. Other aromatic as well as aliphatic cycloaliphatic and heterocyclic diamines may be employed as copolymeric components within the limits set forth above. Typical copolymer forming reactants include single, multiple and fused ring aromatic diamines, in which the amino groups are oriented ortho, meta or para with respect to each other as 4,4'-oxydiphenyldiamine, 4,4'-sulfonyldiphenyldiamine, 4,4'-diphenyldiamine, 3,3'-diphenyldiamine; aliphatic, cycloaliphatic and heterocyclic diamines as ethylene diamine, hexamethylene diamine, diaminocyclohexane, piperazine and the like; and the compounds corresponding to any of the above in which one or more hydrogens are replaced by lower alkyl, lower alkoxy halogen, nitro, sulfonyl and low carbalkoxy groups as well as meta- and paraphenylene diamines bearing such substituents for hydrogen. Copolymers may also be formed wherein the diacid compound is other than isophthalic acid. Suitable acids for use in preparing such copolymers include aromatic, aliphatic, cycloaliphatic and heterocyclic compounds. Specific typical acids are single and multiple and fused ring aromatic acids, in which the acid groups are oriented ortho, meta or para with respect to each other such as terephthalic acid, 4,4'-oxydibenzoic acid, 4,4'-sulfonyldibenzoic acid, 4,4'-dibenzoic acid, 3,3'-oxydibenzoic acid, 3,3'-sulfonyldibenzoic acid and 3,3'-dibenzoic acid; aliphatic acids such as adipic, sebacic, azelaic and the like, and compounds corresponding to any of the above in which one or more hydrogens are replaced by one or a combination of lower alkyl, lower alkoxy, halogen, nitro, sulfo, lower carbalkoxy groups. Such copolymeric units are particularly valuable in rendering the fiber sensitive to particular dyes. Examples 8 to 12 below illustrate various substituted MPD-I polymers and also copolymers.

#### Example 8

Fiber-forming poly(meta-phenylene chloroisophthalamide) of high polymer melt temperature is prepared using methylene chloride as the reaction medium, in the presence of triethylamine as acid acceptor and in the presence of 100% excess of triethylamine hydrochloride. In preparing the polymer, 7.12 parts of 4-chloroisophthaloyl chloride in 143 parts of methylene chloride is added to a Waring Blendor containing 5.43 parts of metaphenylene diamine dihydrochloride, 12.14 parts of triethylamine and 143 parts of methylene chloride. After stirring for 10 minutes, the alpha polymer having an inherent viscosity of 0.84 is obtained.

#### Example 9

A nuclear substituted aromatic polyamide of high molecular weight and high polymer melt temperature, the nuclear substituents being lower alkyl or lower alkoxy, can be prepared in the same reaction medium and under the same conditions as the unsubstituted polymer. For instance, methylene chloride using triethylamine as an

acid acceptor and in the presence of 50% excess triethylamine hydrochloride is suitable for the preparation of poly(4-methyl meta-phenylene isophthalamide), since the same system is suitable for poly(meta-phenylene isophthalamide). Polymer is prepared in a 2-liter flask equipped with stirrer, condenser and dropping funnel. A charge of 7.32 parts of 4-methyl meta-phenylene diamine, 11.1 parts of triethylamine hydrochloride, 12.3 parts of triethylamine and 430 parts of methylene chloride is placed in the flask. A solution of 12.2 parts of isophthaloyl chloride in 500 parts of methylene chloride is added over a period of about 10 seconds. Moderate stirring is continued for three minutes after which additional portions of each reactant, i.e., (a) 7.32 parts of the diamine and 12.3 parts of triethylamine in 322 parts of methylene chloride and (b) 12.2 parts of the acid chloride in 322 parts of methylene chloride, are added simultaneously over a period of about 30 seconds. After 10 minutes, alpha polymer having an inherent viscosity of 2.03 is obtained. In a similar preparation of the same polymer, the product, with an inherent viscosity of 1.38, is observed to have a polymer melt temperature of 330° C.

#### Example 10

A solution of 6.1 parts of isophthaloyl chloride in 200 parts of methylene chloride is added to a Waring Blendor simultaneously with a solution of 6.33 parts of 4-methoxyphenylenediamine monohydrochloride and 12.1 parts of triethylamine in 200 parts of methylene chloride. After 10 minutes, polymer having an inherent viscosity of 0.84 is recovered. It is soluble in dimethylformamide from which strong, transparent, flexible films are formed by casting.

The polymers of this invention may also be prepared by a polymerization procedure wherein one or both of the reactants is a mixture of diamines or diacid chlorides.

#### Example 11

2.554 parts of 4,6-diamino meta-xylene and 3.975 parts of sodium carbonate are dissolved in 100 parts of water. A separate solution of 3.807 parts of isophthaloyl chloride in 136 parts of 2,4-dimethyl tetramethylene sulfone is prepared. The diamine solution is placed in a Waring Blendor and is agitated rapidly. The acid chloride solution is then added and stirring is continued for 5 minutes. The reaction takes place at room temperature, and at the end of the reaction time the  $\alpha$  polymer is precipitated by the addition of water. Filtered and washed polymer is obtained in a yield which is 100% of theoretical, and the polymer has an inherent viscosity of 0.81. In a similar preparation of the same polymer, the product, with an inherent viscosity of 0.92 is observed to have a polymer melt temperature of at least 375° C. since it neither softened nor stuck to the heated bar at or below that temperature.

#### Example 12

A copolymer of  $\alpha$  MPD-I having an inherent viscosity of 1.45 and soluble in dimethylformamide, dimethylacetamide, and in N-methyl pyrrolidone is prepared by simultaneously adding to a Waring Blendor a solution of 6.1 parts of isophthaloyl chloride in 150 parts of methylene chloride as one solution and 5.16 parts of metaphenylene diamine dihydrochloride, 0.27 part of para-phenylene diamine dihydrochloride, and 6.10 parts of triethylamine dissolved in 150 parts of methylene chloride as the other solution. Additional methylene chloride is used for rinse purposes and added to the reaction mass. After 10 minutes the  $\alpha$  polymer is formed.

#### Example 13

A copolymer of  $\alpha$  MPD-I having an inherent viscosity of 2.08 is prepared following the technique of Example

12 using as one reactant solution 4.05 parts of meta-phenylene diamine and 7.95 parts of sodium carbonate in 113 parts of water and as the other reactant solution 6.53 parts of isophthaloyl chloride and 1.15 parts of terephthaloyl chloride in 135 parts of tetrahydrofuran as the other solution. The  $\alpha$  MPD-I product contains 15% by weight of the copolymeric terephthaloyl repeating unit.

An  $\alpha$  MPD-I containing 10% by weight copolymeric terephthaloyl repeating unit is formed by employing as the second reactant solution in the above process 6.91 parts of isophthaloyl chloride and 0.77 part terephthaloyl chloride in 135 part of tetrahydrofuran. The product has an inherent viscosity of 1.73.

In the preparation of spinning solutions, it is sometimes found that carbon dioxide gas is dissolved in the solution. This condition may be due to the use of a carbonate salt as an acid acceptor during polymerization treatment, such as described in U.S. Patent No. 3,063,966, by Kwolek, Morga and Sorenson, dated November 13, 1962, disclosing polymerization of wholly aromatic polyamides or, for example, may be a contaminant picked up by contact with the air. The presence of dissolved carbon dioxide in solutions to be spun into filaments and the like is undesirable because it frequently tends to cause formation of voids in the solid filaments. This situation can be remedied by the addition of a small amount of calcium oxide to the spinning solution. The calcium oxide reacts with carbon dioxide to form calcium carbonate which in the small quantities usually encountered is not detrimental in any way to the spinning solution. Other equivalent chemicals, such as barium oxide or magnesium oxide, as well as bases such as calcium hydroxide, can also be used. If desired, the spinning solution which has been so treated with excess calcium oxide can then be carefully neutralized with hydrochloric acid to form soluble calcium chloride.

In the preparation of spinning solutions as discussed above, it is sometimes desirable to remove a by-product halogen acid with an hydrous ammonia. This process results in the formation of ammonium chloride which is then removed by filtration. However, the filtration step sometimes leaves a turbid solution because of the presence of small amounts of very finely divided insoluble ammonium chloride. This turbidity can be removed by treating the spinning solution with an excess of propylene oxide which reacts with the ammonium chloride and converts it to soluble products. The exact nature of these products has not been observed, but the reaction occurs rapidly and leads to greater ease in the subsequent spinning operations.

As previously discussed and exemplified, after formation of an organic solvent solution of the  $\alpha$  form of polymer, the shaped form must be provided by spinning, extrusion, casting or the like, prior to transformation to the  $\beta$  form. Care must be taken to avoid increasing the chain mobility or ordering the chain molecules before shaping is complete in those cases where no complexing salt is used to solubilize the beta form. Most conveniently, the transformation to the beta form is accomplished by application of heat in the presence of air. The period necessary for this transformation will vary to some extent depending upon substituents which may be upon either the meta-phenylene diamine component or the isophthaloyl component of the repeating unit and upon the liquid in which the shaped structure of polymer is boiled. Table IV shows typical periods of time on the steam bath required to transform various  $\alpha$  derivatives to the  $\beta$  form in dimethylformamide (except as noted). Several examples also include water as indicated. Every item was originally soluble in the solvent in which it was heated. The  $\beta$  form of polymer which precipitated in the period indicated could in each instance be redissolved in the original solvent on addition of lithium chloride as a complexing salt.

TABLE IV

Item	MPD	Substituents I	Amount Water, Percent	Period (min.)
a	None	None	None	10
b <sup>1</sup>	2-methyl	do	None	60
c	4-methyl	do	10	5
d	2,4-dimethyl	do	10	120
e	4,6-dimethyl	do	None	1,440
f	2,4,6-trimethyl	do	None	45
g	None	5-methyl	None	60
h	do	5-tert. butyl	5	120
i	Dichloro	None	None	120
j	Methoxy	do	5	240
k	Hydroxy	do	5	240
l	Carboxy	do	None	240
m <sup>1</sup>	None	5-nitro	None	10
n	do	N-dimethylsulfonamide	None	120

<sup>1</sup> Dimethylacetamide used as solvent.

Rapid transformation frequently occurs at the boiling point of water as seen, and thus the step of transformation to the  $\beta$  form may be combined with aqueous purification to remove impurities such as salt formed in the polymerization reaction and/or complexing salt where such was used. The period of the boil-off may vary and while transformation to the  $\beta$  form occurs substantially instantaneously, a more extended washing is preferred in order to remove residual salts. Generally it is desirable that the final structure contain no more than about 0.5 to 0.7% by weight of the salt employed in complexing and/or formed in the reaction. Preferably the salt is reduced to a level which analyzes less than about 0.0028 gram atoms anion per 100 grams of fiber, using a boiling solution of equal parts of water and dimethylformamide or a flowing stream of deionized water at a temperature approaching the boiling point.

Prolonged heating of the  $\beta$  form of polymer at temperatures above 300° C. (approaching the fusion temperature of the polymer) will cause transformation to the truly cross-linked type of polymer which is insoluble in concentrated sulfuric acid and which will not form a soluble salt complex in the organic solvents as taught previously. Attempts to form the polymer in a fiber-forming molecular weight range by melt polymerization leads to the production of the truly cross-linked form. Example 14 illustrates such a procedure.

#### Example 14

A mixture of 5.45 grams of metaphenylene diamine, 8.27 grams of isophthalic acid and 0.046 gram of p-toluene sulfonic acid are added to a 55 ml. polymer tube following the technique of Example 6 of U.S. Patent 2,244,192 to P. J. Flory. The tube is evacuated three times and filled with dry nitrogen each time. It is then sealed under nitrogen pressure and heated for one hour at 226° C. During this heating period the mixture becomes a semi-solid and flows to the bottom of the tube, then slowly changes color from white to yellow to reddish-brown. Little further change is observable after the first half hour of heating. At the end of this time the tube is cooled, the seal is broken, and the distillation head is sealed on. Nitrogen is passed above the polymer while it is heated in turn for one hour at 218° C. (using a naphthalene vapor bath), 255° C. (using a diphenyl vapor bath), and 287° C. (using a diphenylene oxide vapor bath). The polymer does not undergo any visible change and remains solid during these heating periods. About 1-2 cc. of a liquid, presumably water, distills from the reaction mixture. Finally, the reaction mixture is heated at 287° C. for three hours at a pressure of 1 mm., then cooled. The contents consist of a red-brown, brittle polymeric mass, weight 11.95 g.—theory for complete amidation to poly-m-phenyleneisophthalamide 11.94 g. The polymer is ground in a mortar and characterized as to solubility, X-ray diffraction pattern, and infrared spectrum. Both the infrared spectrum and the X-ray diffraction pattern show that this polymer is essentially poly-

(m-phenyleneisophthalamide). There are slight differences in the infrared spectrum which may be due to more end groups in a lower molecular weight polymer and to groups contributing to cross-linking. The X-ray diffraction pattern shows that this polymer is very highly crystalline with very good perfection, resembling the beta form of the uncross-linked polymer. The polymer is insoluble in both lithium chloride-dimethylformamide mixtures (5/95) and in concentrated sulfuric acid, thus distinguishing it from the polymers of this invention.

The  $\beta$  form of polymer of the present invention is not a cross-linked structure since it is possible to convert the  $\beta$  (relatively insoluble) form, to the  $\alpha$  (relatively soluble) form. Such conversion is demonstrated in Example 15 below.

#### Example 15

Drawn  $\beta$  MPD-I yarn spun from a dimethylformamide solution essentially as taught in Example 7a is crystallized at high temperature by the procedure of U.S.P. 3,133,138 and cut to 1/4" staple. Five grams of the staple is added to 95 grams of dimethyl acetamide and the mixture is maintained at 75° C. for three days without effecting solution. Another five-gram sample of the same fiber is added to 95 grams of dimethyl acetamide containing 4% by weight lithium chloride. The fiber dissolves completely in three hours, at 75°C., without stirring, due to formation of the salt complex.

The salt complex is then destroyed by rapidly adding the solution to a large volume of water while stirring rapidly in a high-shear blender. Polymer in the  $\alpha$  form precipitates. The polymer crumbs so formed are then washed several times in the blender with additional quantities of water and dried at 50°C. under vacuum. When five grams of this polymer is added to 95 gms. dimethyl acetamide at room temperature, complete solution is effected within 15 minutes without stirring.

#### Example 16

This example illustrates the continuous polymerization of metaphenylene diamine and isophthaloyl chloride.

Referring to FIGURE V, a solution of 1 part metaphenylene diamine in 9.71 parts dimethylacetamide from the diamine source is metered through a cooler to a mixer, into which 1.88 parts of molten isophthaloyl chloride from the acid chloride source is simultaneously metered. The mixer is so proportioned and the combined flow of reagents is so selected as to result in turbulent mixing. The molten isophthaloyl chloride is fed at 60° C. and the metaphenylene diamine is cooled to -15° C. Heat of reaction results in a temperature of 74° C. in the mixer effluent which is introduced directly into jacketed, scraped-wall heat exchanger. The heat exchanger has a length to diameter ratio of 32 and is proportioned to have a hold-up of 9.3 minutes. During passage through the heat exchanger, the solution temperature is reduced to 29° C. by use of jacket cooling, and continuing polymerization results in an increase in solution viscosity from



about 2 poises, as measured at the mixer effluent, to about 1500 poises, as measured at the heat exchanger effluent. Heat exchanger effluent flows continuously to the neutralizer, to which is added continuously 0.311 lb. of calcium hydroxide for each pound of polymer in the solution. The neutralized solution is then blended, deaerated, filtered and stored for use in spinning. The final solution contains about 20% polymer of 1.65 inherent viscosity and about 9.3% calcium chloride.

Polymers of this invention are characterized by an exceptionally high melting point. Whereas known polyamides melt at temperatures below about 270° C., generally the polyamides of this invention in the  $\beta$  form have melting points in excess of 300° C. and in many instances above 350° C. Moreover, filaments of polyamides of this invention retain their filament form at temperatures of about 300° C. Polymers of this invention are also distinguished from known polyamides in having water-white color, excellent resistance to corrosive atmospheres, substantially no flammability. These polymers resist melting upon exposure to 300° C. for extended periods while retaining hitherto unrealized high proportion of room temperature physical properties. Flash exposure for 20 seconds to temperatures as high as 700° C. does not destroy these fiber properties. Because of their solubility, these polymers may be processed into shaped structures such as films and filaments by conventional techniques. These polymers have high tenacity, good work recovery, high flex life at elevated temperatures, and are readily crystallizable.

The polymers of this invention find application in a wide variety of physical shapes and forms. Among the most significant of these forms are fibers and films. The useful combination of desirable physical and chemical characteristics of these polymers are unique. Fibers and films of these polymers not only possess excellent physical properties at room temperatures, but retain their strength and excellent response to work-loading at elevated temperatures for prolonged periods of time.

For many end uses it is satisfactory to employ either amorphous or crystalline fibers or films. This is particularly true when the end use in mind takes chief advantage of the high melting point and chemical stability of these polymers. Some end uses require high tenacity at normal temperatures and resistance to melting under exposure to high temperatures for short periods of time or even extended periods of time, followed by additional tensioning at lower temperatures. For these, it is found that both amorphous and crystalline fibers are suitable. However, under circumstances which require retention of outstanding physical properties such as high tenacity and high work recovery while the material is subjected to temperatures close to the melting point and dimensional stability under conditions of cyclic change in moisture or temperature or both in the environment, it is found to be preferable that the fibers and films of the present invention be in a crystalline state. Crystalline fibers and films of the polymers of the present invention are outstanding in their retention of tenacity at elevated temperatures and in their constancy of elongation-to-break under extremely high temperatures. Crystalline fibers, films, and fabrics made from crystalline fibers are also more resistant to dimensional shrinkage under conditions of cyclic wet and hot dry treatment.

The fibers and films of the present invention as normally produced are oriented by drawing or stretching. Fibers are oriented in one direction. Films can be oriented in one or two directions. Following the orientation process, it is possible and sometimes highly desirable, depending upon the end use for which the shaped article is to be employed, to crystallize the material and to increase thereby its stability under certain ambient conditions. Of course, as already indicated, the polymer can be crystallized prior to forming into fibers, films and the like, but it is difficult to retain this crystallinity in the polymer

through the process of spinning a fiber or casting a film. Therefore, it is normally desired to retain the polymer in the amorphous condition until it has been shaped into a fiber, film, or similar article and then, as needed, to orient this article and follow the orientation treatment with a crystallization step. There are several crystallization treatments known by which the shaped article can be crystallized while retaining the shape and orientation of the product, as shown in some of the examples.

In fiber form the polymers of this invention may be used for high temperature heat and electrical insulation, protective clothing and curtains, filtration media, packing and gasketing materials, brake linings and clutch facings. In the aircraft industry these materials can be used in parachutes, fuel cells, tires, ducts, hoses and insulation. Cordage for tires and conveyor belts, particularly where such materials would be subject to prolonged high temperature exposure is another application. Press cloths in the dry cleaning industry prepared from such fibers have extreme hydrolytic stability. In the form of films, these polymers may be used in automotive and aviation interior head lining materials, decorative trim, high temperature heat and electrical insulation, such as for slot liners, use in dry transformers, capacitors, cable wrappings, etc., packaging of items to be exposed to high temperature while within the package, corrosion resistant pipe, hot water pipe, duct work, hot air ventilation, aircraft body skins, aircraft radomes, embossing roll covers, containers and container linings, printed circuits, tape for hot pipe overwrapping, laminated structures where the films are bonded to metal sheets or foils, mold liners or self-sustaining containers for casting low-melting (below 300° C.) fusible materials, including metals, and a variety of other similar and related uses. Valuable flexible materials similar in function to putty with outstanding high temperature stability can be made by combining fibers prepared from polymers of the present invention with flexible high-temperature polymers such as plasticized chlorotrifluoroethylene polymers.

Films formed from polymers of this invention may be stretched or otherwise oriented according to conventional procedures. Films may be oriented biaxially by stretching or rolling in both directions or by rolling in one direction and stretching in the other.

Because they retain fiber properties at elevated temperatures, fibers from the polymers of this invention can be used in high temperature applications along with heat-resistant resins and elastomers, such as polytetrafluoroethylene, fluoroethylene, fluoro-rubbers and silicone resins. Fabrics from aromatic polyamide fibers form a base material to which resins can be applied as a coating or impregnant, also, staple fibers can be mixed into a matrice of the resin to give a reinforced plastic material. Since these fibers melt at temperatures higher than some resins do, resins can be applied to them in molten form, or can be sintered after application as a solid powder, without damage to the fibers. Moreover, since the fibers retain good tensile properties at high temperatures, resins can be applied to the fabric in a continuous manner, its high strength permitting the fabric to be processed, e.g., run through a sintering furnace, without any need for supporting members. The products so obtained can be used at much higher temperatures than is possible with conventional fibers which decompose or melt below 300° C.

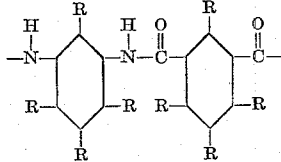
Solutions of polymers of this invention are valuable as varnishes, adhesives, wire-coatings, fabric-coatings, and similar products. Fabrics suitable as a substrate for the coatings of this invention include woven and non-woven fabrics made from fibers of glass, asbestos, polyethylene terephthalate, polyacrylonitrile, polyhexamethylene adipamide, and other nylons, cotton, wool, polytetrafluoroethylene and mixtures thereof. When applied to wood, metal, and ceramics, these solutions form strong, heat-resistant films which can withstand repeated flexing, hammer-blows and chemical attack.

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Many equivalent modifications will be apparent to those skilled in the art without a departure from the inventive concept.

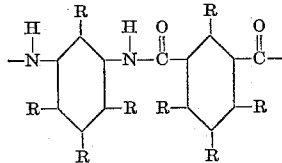
What is claimed is:

1. Polycarbonamide having an inherent viscosity of at least 0.8 in sulfuric acid at 30° C. at a concentration of 0.5 gram of polymer per 100 cc. of solution, the said polycarbonamide being of the class consisting of (a) an alpha polymetaphenylene isophthalamide characterized by relatively high solubility and (b) a beta polymetaphenylene isophthalamide characterized by relatively low solubility, the said polycarbonamide consisting of repeating units of which at least about 85% are of the formula



wherein the hexagon represents the benzene nucleus, R is a substituent which is non-amide forming at room temperature via reaction with a member from the class consisting of amino hydrogen and carbonyl halide.

2. Polycarbonamide having an inherent viscosity of at least 0.8 in sulfuric acid at 30° C. at a concentration of 0.5 gram of polymer per 100 cc. of solution, the said polycarbonamide being of the class consisting of (a) an alpha polymetaphenylene isophthalamide characterized by relatively high solubility and (b) a beta polymetaphenylene isophthalamide characterized by relatively low solubility, the said polycarbonamide consisting of repeating units of which at least about 85% are of the formula



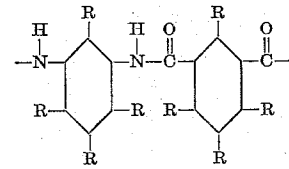
wherein the hexagon represents the benzene nucleus, R is a substituent on nuclear carbon from the class consisting of hydrogen, lower alkyl, lower alkoxy, halogen, nitro, cyano, sulfo and lower carbalkoxy.

3. The polycarbonamide of claim 2 wherein at least two R substituents are hydrogen and copolymeric units when present are carbonamidic.

4. Polycarbonamide having an inherent viscosity of at least 0.8 in sulfuric acid of 30° C. at a concentration of 0.5 gram of polymer per 100 cc., the said polycarbon-

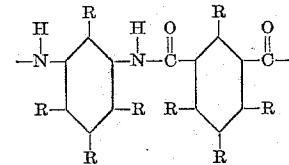
16

amide being an alpha polymetaphenylene isophthalamide characterized by relatively high solubility and consisting of repeating units of which at least about 85% are of the formula



wherein the hexagon represents the benzene nucleus, R is a substituent on nuclear carbon from the class consisting of hydrogen, lower alkyl, lower alkoxy, halogen, nitro, cyano, sulfo and lower carbalkoxy, at least three of the said R substituents being hydrogen.

5. Polycarbonamide having an inherent viscosity of at least 0.8 in sulfuric acid at 30° C. at a concentration of 0.5 gram of polymer per 100 cc. of solution, the said polycarbonamide being a beta polymetaphenylene isophthalamide characterized by relatively low solubility and consisting of repeating units of which at least about 85% are of the formula



wherein the hexagon represents the benzene nucleus, R is a substituent on nuclear carbon from the class consisting of hydrogen, lower alkyl, lower alkoxy, halogen, nitro, cyano, sulfo and lower carbalkoxy, at least three of the said R substituents being hydrogen.

6. A fiber of the polymer of claim 2.

7. A film of the polymer of claim 2.

8. A fiber of polymetaphenylene isophthalamide.

9. A film of polymetaphenylene isophthalamide.

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