Patented Oct. 10, 1944

2,359,867

UNITED STATES PATENT OFFICE

2,359,867

FIBER-FORMING INTERPOLYMERS

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No Drawing. Application November 26, 1941, Serial No. 420,591

14 Claims. (Cl. 260—78)

This invention relates to polymeric materials and more particularly to polyamide compositions of improved dyeing properties.

The polyamides with which this invention is concerned are synthetic, high molecular weight, fiber-forming polyamides of the general type described in U. S. Patents 2,071,250, 2,071,253 and 2,130,948. These polyamides are usually made by the self-polymerization of a monoaminomonocarboxylic acid, or by heating a diamine with a dibasic carboxylic acid until the product has polymerized to the fiber-forming stage, which stage is not generally reached until the polyamide has an intrinsic viscosity as defined in the last mentioned patent of at least 0.4. The polymers obtained from mixtures of diamine and dibasic carboxylic acid, or from amide-forming derivatives of these reactants, include a number of polyamides which are particularly valuable as textile fibers because of their high melting points and because filaments of these polyamides can be cold drawn to strong, highly oriented fibers. These fibers, however, are deficient in dyeing properties in that they have a low dye receptivity for dyestuffs of the acid, direct and vat classes, and in that the dyeing accentuates minor non-unformities in denier and elongation.

This invention has as an object the preparation of polyamides which, in addition to the desirable physical properties mentioned above, possess improved dyeing properties. A further object is the production of new and useful polyamide compositions. A still further object is the manufacture of improved dyed polyamide fibers and fabrics. Other objects will appear hereinafter.

These objects are accomplished by interpolymerizing in certain proportions two different polyamide-forming compositions one of which comprises essentially hexamethylenediamine and adipic acid in substantially equimolecular proportions, and the other of which comprises a bifunctional amide-forming reactant containing at least one oxygen atom in the chain separating its amide-forming groups. For convenience the reactant containing the said oxygen atom will be referred to as the "hetero oxygen-containing reactant."

I have discovered that when this mixture of polyamide-forming compositions is interpolymerized in the proportion by weight, based on the total weight of the named ingredients, of from 5% to 25% of the polyamide-forming composition containing the hetero oxygen-containing reactant, that the resulting interpolymer can be formed into strong oriented fibers which are markedly improved as compared to other diamine-dibasic acid polyamides in dye receptivity and which have high melting points, namely, above 220° C. I have discovered further that the hetero oxygen-containing polyamides, and particularly those obtained with the use of a diamine having at least two hetero oxygen atoms, have, in addition to improved dye receptivity, improved level dyeing characteristics, i. e., improved uniformity in dyeing. This is a very important property because the minor irregularities normally present in yarns and fabrics become evident on dyeing unless the yarns and fabrics have good level dyeing properties.

A diamine which contains at least 2 hetero oxygen atoms in the chain separating the amino groups and which gives outstanding results in the practice of this invention is triglycoldiamine (3,6-dioxa-1,8-octanediamine). This diamine has the formula

$$NH_2CH_2CH_2OCH_2CH_2OCH_2CH_2NH_2$$

Another useful diamine of this type is tetraglycoldiamine (3,6,9-trioxa-1,11-hendecanediamine) of formula

$$NH_2(CH_2)_2O(CH_2)_2O(CH_2)_2O(CH_2)_2NH_2$$

These hetero oxygen-containing diamines which are especially useful in the practice of this invention are primary diamines, that is, diamines in which each of the two functional amide-forming amino nitrogens bears two hydrogen atoms.

When the hetero oxygen-containing reactant is a diamine, a substantially equimolecular amount of dibasic carboxylic acid is added as complementary reactant. In this case either of the two pairs of reactants, one of which is the hexamethylenediamine and adipic acid and the other of which is the hetero oxygen-containing diamine and dibasic carboxylic acid, can be used as such in preparing the interpolyamides, but for convenience are preferably used in the form of the diamine-dibasic acid salt.

The present interpolymers are prepared by heating the polymer-forming compositions at polyamide-forming temperatures. In the usual practice substantially chemical equivalent amounts of diamine and dibasic acid, or amide-forming derivatives thereof, are heated in the presence or absence of solvent or catalyst, and preferably in the absence of air, at temperatures of from 180°–300° C., and preferably from 200°–290° C., until a fiber-forming polymer of the desired properties is formed. The reaction

is carried out under conditions which permit the removal of water or other by-product, at least during the last stages of the reaction. As previously indicated, it is desirable to use the two polyamide-forming compositions in the form of their preformed diamine-dibasic acid salts since the salts are easily obtained in pure form and contain substantially equivalent amounts of the diamine and dibasic acid reactants. Thus from 75% to 95%, and preferably from 85% to 95%, of the salt of hexamethylenediamine and adipic acid, namely, hexamethylenediammonium adipate, is reacted with from 5% to 25%, and preferably from 5% to 15%, of the salt of the hetero oxygen-containing diamine. The hetero oxygen-containing diamines preferably have the formula H_2NRNH_2 and the dibasic carboxylic acid or acids used therewith preferably have the formula HOOC—R'—COOH, in which R and R' are divalent organic radicals free from reactive groups and in which R contains at least two hetero atoms of the oxygen family in the chain separating the amino groups. Hydrolysis with hydrochloric acid converts the interpolymers of this invention into the dibasic acid or acids and the hydrochlorides of the diamines from which they were derived. Thus in the case of the preferred interpolyamides the hydrolysis products will contain adipic acid, hexamethylenediamine hydrochloride, and the hydrochloride of a diamine containing two hetero oxygen atoms.

The invention is further illustrated by the following examples in which the parts are by weight:

Example I

Hexamethylenediammonium adipate, referred to in the tables below as salt B, and triglycoldiammonium adipate, referred to as salt A, mixed in the proportions indicated in Table I, are heated in sealed reactors for two hours at 180° to 220° C., one hour at 287° C. under an atmosphere of nitrogen, and finally for three hours at 287° C. under reduced pressure.

Table I

Salt A	Salt B	M. P. (in air) of polymer	Intrinsic viscosity	Manual spinnability	Cold drawing
Parts	*Parts*	°C.			
5	95	243	1.04	Good	Good.
5	95	243	0.75	do	Do.
20	80	235	0.71	do	Do.

The molecular weight can be controlled by stabilization which consists in introducing a reactant, e. g., a mono-functional amide-forming reactant which halts polymerization at a given stage in the reaction, as described in U. S. Patent 2,174,527. Thus, the second and third compositions in the table were stabilized with 1% of hexamethylenediammonium acetate. The intrinsic viscosities are consequently lower than that of the unstabilized polymer.

Example II

Hexamethylenediammonium adipate and triglycoldiammonium adipate in the proportions indicated in Table II are intimately mixed and polymerized in a closed autoclave in the presence of water and under an atmosphere of nitrogen at 285° C. for three hours. The steam is gradually bled off until atmospheric pressure is reached and the heating is continued for an additional hour. The polymers are then dried and melt spun into 148 denier-13 filament yarns at a speed of 3000 ft. per minute. The yarns are subsequently drawn at draw ratios also recorded in Table II. Draw ratio corresponds to the ratio of the drawn yarn to the undrawn yarn. For example a foot of undrawn yarn drawn to 4.5 feet would then have a draw ratio of 4.5.

Table II

Salt A	Salt B	M. P. (absence of air)	Draw ratio	Denier	Elongation
		°C.			
50	950	263	3.76	37.7	15.2
100	900	258	3.39	35.0	16.5
150	850	254	4.10	29.2	16.5

Each polymer was stabilized with 0.5 mol per cent of acetic acid.

Yarns of the three compositions are dyed with a vat color, an acid color, and a direct color. The receptivities recorded in Table III, where PTGA refers to polytriglycol adipamide, and PHMA to polyhexamethylene adipamide, show the improvement over that of polyhexamethylene adipamide. The percentages represent the extent to which the dye bath was exhausted. These percentages are based on the results obtained by dyeing one gram of yarn in 40 cc. of dye solution. Values for silk are included for comparison.

Table III

Composition	Vat color having colour index No. 1113 5% bath	Acid color having colour index No. 114 2% bath	Direct color having colour index No. 518 2% bath
Polyhexamethylene adipamide	*Per cent* 40	*Per cent* 25	*Per cent* 10
5% PTGA 95% PHMA	60	60	20
10% PTGA 90% PHMA	80	90	60
15% PTGA 85% PHMA	95	90	90
Silk		75	90

Yarns of each of the interpolymers derived from hexamethylenediammonium adipate with 5, 10, and 15% triglycoldiammonium adipate are drawn so that certain samples differ by 4% in draw ratio. For example, a portion of the yarn of the last interpolymer in the table is drawn to 4.28 times its original length, and another portion is drawn to 4.10 times its original length. The yarn of 4.28 draw is fed into a single thread circular-knitting machine, and after approximately a two inch section has been knit, the thread is broken and tied to the fiber drawn to 4.10 its original length and the knitting continued. Such sections are used in level dyeing studies. The interpolymer yarns show vast improvement in level dyeing properties when compared to polyhexamethylene adipamide yarns differing similarly in draw ratios. This is particularly marked for acid colors but is also evident for vat and direct colors.

Example IV

Following the general procedure described in Example I an interpolymer is made from 85 parts of hexamethylenediammonium adipate and 15% of the salt derived from hexamethylenediamine and diglycolic acid. The polymer is spun into yarn. One portion of the yarn is cold drawn to a draw ratio of 4.73 and another portion to a draw ratio of 4.94, the denier of the drawn yarns being 52.2 and 50 respectively. The two portions of yarn are knitted into a fabric as described in Example III and dyed with an acid dye of colour

index No. 430. No color difference is apparent at the junction of the two yarns. This is true also when the acid dye is one of colour index No. 1088. Only a slight color difference is noticeable when the dye is a direct color of colour index No. 375. On the other hand, a fabric knit from two polyhexamethylene adipamide yarns exhibiting the same difference in draw ratios as the interpolymer yarns showed a marked difference in color at the juncture of the two yarns. Furthermore, the interpolymer shows a higher receptivity for acid, direct, and vat dyes than does polyhexamethylene adipamide.

Further examples of diamines which contain at least two hetero oxygen atoms in the chain separating the amino groups and which are suitable for use in the practice of this invention include bis-aminopropoxyhexane

$$[NH_2(CH_2)_3O(CH_2)_6O(CH_2)_3NH_2]$$

3,7-dioxa-1,9-nonanediamine, 3,8-dioxa-1,10-decanediamine, 3,9 - dioxa-1,11-hendecanediamine, 3,10-dioxa - 1,12 - dodecanediamine, 3,11-dioxa-1,13-tridecanediamine, 4,7,10-trioxa-1,13-tridecanediamine, 3,12 - dioxa - 1,14 - tetradecanediamine, 3,13-dioxa-1,15-pentadecanediamine, and higher homologs, 4,7-dioxa-1,10-decanediamine, 5,8-dioxa-1,12-dodecanediamine, 4,8-dioxa-1,11-hendecanediamine, and 5,9-dioxa-1,13-tridecanediamine. It is also possible to use diamines containing two oxygen hetero atoms in the chain which contain aromatic or hydroaromatic rings. Examples of such are diphenylolpropane-di-beta-aminoethyl ether and 1,4-di-hydroxybenzene-di-beta-aminoethyl ether. However, triglycoldiamine is outstanding.

Examples of dicarboxylic acids which can be used with the hetero oxygen-containing diamines in the reaction with the polyhexamethylene adipamide forming reactants in forming the present interpolymers include such compositions as oxalic acid, malonic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, di-glycolic acid, N-methyliminodiacetic acid, piperazine diacetic acid, diphenic acid, and p-phenylenediacetic acid. It is preferred, however, to use adipic acid and particularly to react hexamethylenediammonium adipate with triglycoldiammonium adipate.

While the preferred hetero atom reactants are diamines containing at least two oxygen atoms, reactants containing only one oxygen atom, or containing the hetero oxygen atom or atoms in the dibasic carboxylic acid can be used in obtaining interpolyamides having improved dye receptivity as compared with polyhexamethylene adipamide. Interpolyamides prepared from hexamethylenediamine, adipic acid, a hetero oxygen-containing diamine and a hetero oxygen-containing di-basic acid also fall within the scope of the invention. Additional examples of hetero oxygen-containing reactants are 2,2'-diamino diethyl ether, 3,3'-diamino dipropyl ether, 5-oxazelaic acid and phenylene dioxyacetic acid. Polymerizable amino acids containing a hetero oxygen atom, e. g., p-aminophenoxy acetic acid, can be used as the hetero oxygen-containing polyamide composition which is reacted with hexamethylenediamine and adipic acid.

The amide-forming derivatives which can be used in place of the dibasic carboxylic acids and diamines mentioned herein include a number of available compounds. Amide-forming derivatives of the dibasic carboxylic acids comprise the mono- and di-esters, the anhydrides, the mono- and di-amides, the acid halides, and the following compounds in the presence of water: Nitriles, cyanocarboxylic acids, cyanoamides, and cyclic imides. Amide-forming derivatives of the diamines include the carbamates, N-formyl derivatives, and the N,N'-diformyl derivatives. It is to be understood that reference to a diamine or dibasic carboxylic acid in the claims includes also the amide-forming derivatives thereof.

The interpolymers of this invention have surprisingly greater receptivity for acid, vat, direct, and basic colors than do polyhexamethylene adipamide or similar diamine-dibasic acid polymers. They also have high receptivity for dyestuffs of the cellulose acetate class, e. g., those disclosed in U. S. Patent 2,220,129. The dye receptivity of the present polymers, particularly those prepared with the use of a diamine containing at least two oxygen atoms, approaches, and in some cases exceeds, that of rayon and silk. Furthermore, dyeings on oriented fibers of the interpolymers prepared with the use of diamines containing at least two oxygen atoms are greatly improved in uniformity and levelness, and minor non-uniformities in denier and elongation of the fibers are not accentuated as is the case with polyhexamethylene adipamide, which heretofore has been one of the most desirable fiber-forming polyamides. The most valuable of the new interpolyamides described herein are those melting above 225° C. When the percentage of hetero oxygen-containing polyamide composition, e. g., triglycoldiammonium adipate, is substantially above 25% there is an objectionable sacrifice in melting point, and the light stability and weathering properties of the polymers decrease rapidly. The presence of substantially less than 5% of hetero oxygen-containing composition does not result in the desired increase of dye receptivity or level dyeing properties.

The polyamides of this invention are of primary interest in the preparation of yarns and fabrics. However, they can also be used in the applications to which synthetic linear polyamides have been put, e. g., bristles, films, and coating, adhesive and molding compositions. They are of particular value in uses where high dye receptivity is desired.

The polyamides of this invention can be used in conjunction with other polyamides and/or in conjunction with resins, cellulosic materials, pigments, delusterants, plasticizers, antioxidants, and other modifying agents.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that I do not limit myself to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. A polymer having higher receptivity for acid dyes than polyhexamethylene adipamide, said polymer comprising the reaction product of 75 to 95 parts by weight of a mixture of hexamethylenediamine and adipic acid in substantially equimolecular proportions and 5 to 25 parts by weight of a polyamide-forming composition comprising a bifunctional polyamide-forming reactant containing at least one oxygen atom in the chain of atoms separating its amide-forming groups, said polyamide-forming composition being selected from the class consisting of (*a*) mixtures of diamine and dibasic carboxylic acid in substantially equimolecular proportions, and (*b*) monoaminomonocarboxylic acids.

2. A fiber-forming interpolyamide melting above 220° C. which has a receptivity for acid dyes substantially greater than that of polyhexamethylene adipamide and approaching that of silk and which comprises the reaction product of a mixture of hexamethylenediamine, a primary diamine containing at least two oxygen atoms in the chain of atoms separating the amino groups, and dibasic carboxylic acid which is present in equimolecular proportion to said diamines and which comprises adipic acid in amount which is at least in equimolecular proportion to the hexamethylenediamine, the hexamethylenediamine and adipic acid in substantially equimolecular proportion therewith being from 75 to 95 parts by weight of said mixture, and said primary diamine and dibasic carboxylic acid in substantially equimolecular proportions therewith being from 5 to 25 parts by weight of said mixture.

3. A fiber-forming polymer which comprises the interpolymerization product of reactants comprising essentially substantially equimolecular proportions of hexamethylenediamine and adipic acid, substantially equimolecular proportions, in amount of from 5% to 25% by weight of the total reactants forming said polymer, of a dibasic carboxylic acid and a primary diamine containing at least two oxygen atoms in the chain separating the amino groups.

4. The polymer set forth in claim 3 in which said dibasic carboxylic acid and primary diamine consists of from 5% to 15% of the total weight of said two polyamide-forming compositions.

5. A fiber-forming polymer which comprises the interpolymerization product of reactants comprising essentially substantially equimolecular proportions of hexamethylenediamine and adipic acid, and substantially equimolecular proportions, in amount of from 5% to 25% by weight of the total reactants forming said polymer, of a dibasic carboxylic acid and triglycoldiamine.

6. The polymer set forth in claim 5 in which said dibasic carboxylic acid and triglycoldamine consists of from 5% to 15% of the total weight of said two polyamide-forming compositions.

7. A fiber-forming polymer which comprises the interpolymerization product of reactants comprising essentially substantially equimolecular proportions of hexamethylenediamine and adipic acid, and substantially equimolecular proportions, in amount of from 5% to 25% by weight of the total reactants forming said polymer, of adipic acid and triglycoldiamine.

8. A dyed fiber composed of the interpolyamide defined in claim 1.

9. A dyed textile fabric composed of the interpolyamide defined in claim 3.

10. A dyed textile fiber composed of the interpolyamide defined in claim 7.

11. A process for making polymers of improved dyeing properties which comprises heating at polyamide-forming temperatures 75 to 95 parts by weight of a composition comprising essentially equimolecular proportions of hexamethylenediamine and adipic acid and 5 to 25 parts by weight of a polyamide-forming composition comprising a bifunctional polyamide-forming reactant containing at least one oxygen atom in the chain separating its amide-forming groups, and continuing the interpolymerization reaction until a fiber-forming polymer is obtained, said polyamide-forming composition being selected from the class consisting of (*a*) mixtures of diamine and dibasic carboxylic acid in substantially equimolecular proportions, and (*b*) monoaminomonocarboxylic acids.

12. A process for making fiber-forming polymers of improved dyeing properties which comprises heating at polyamide-forming temperatures reactants comprising essentially equimolecular proportions of hexamethylenediamine and adipic acid, and substantially equimolecular proportions, in amount of from 5% to 25% by weight of the total reactants forming said polymer, of a dibasic carboxylic acid and a primary diamine containing at least two oxygen atoms in the chain separating the amino groups, and continuing the polymerization reaction until a fiber-forming polymer is obtained.

13. A process which comprises heating at polyamide-forming temperatures a mixture of two diamine-dibasic acid salts one of which is hexamethylenediammonium adipate and the other of which is the salt of a dibasic carboxylic acid and a primary diamine containing at least two oxygen atoms in the chain separating the amino groups, said last mentioned salt being from 5% to 25% by weight of said two salts.

14. The process set forth in claim 11 in which said diamine is triglycoldiamine.

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