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3,448,087

MODIFIED POLYCARBONAMIDES

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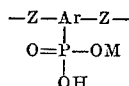
Int. Cl. C08g 20/20

U.S. Cl. 260—78

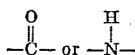
5 Claims

ABSTRACT OF THE DISCLOSURE

Polycarbonamides (nylon) having acid dye resistance are produced by incorporating into the polymer chain, from 0.1 to 2.0 weight percent of a compound of the formula



wherein Ar is an aromatic nucleus, Z is a



radical and M is an alkali metal. These polycarbonamides are particularly useful in the production of textile fibers.

Although textile fibers obtained from fiber-forming polycarbonamides heretofore known are of great value, they are deficient in dyeing properties inasmuch as they all possess the same acid dyeable characteristic and each type will dye to a single shade only. This is a distinct disadvantage since it eliminates the possibility of obtaining other dyeable color effects where some of the fibers do not absorb dye or absorb less dye. It is desirable therefore to produce polycarbonamides which have acid dye-resist characteristics so that by combining such polycarbonamides with standard polycarbonamides in varying amounts it would be possible to produce polycarbonamide articles which are dyeable to different tones of the same color.

It is an object of the present invention to provide novel and useful fiber-forming synthetic linear polycarbonamides.

Another object is to provide shaped articles such as textile fibers, produced from such polycarbonamides, the said articles having superior acid dye-resist properties. A further object is to provide a process for the production of polycarbonamides from which shaped articles having superior acid dye-resist properties can be prepared.

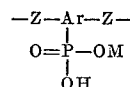
These and other objects will become apparent in the course of the following specification and claims.

The polycarbonamides of the present invention are useful in the production of shaped articles by extrusion, molding, or casting in the nature of yarns, fabrics, films, pellicals, bearings, ornaments, or the like. They are particularly useful in the production of textile fibers.

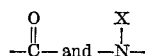
The present invention provides a novel polycarbonamide wherein recurring polycarbonamide linkages are an integral part of the polymer chain and containing as a component part of the polymer chain between about 0.1 and 2.0 weight percentage and preferably between about 0.5 and about 1.0 weight percentage, based on the weight

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of the polycarbonamide, of units represented by the formula:

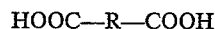


wherein Ar is an aromatic nucleus containing 6 to 12 carbon atoms, Z is a member of the class consisting of

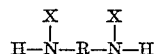


X is a member of the class consisting of hydrogen and lower alkyl radicals and M is an alkali metal.

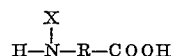
In a typical preparation the polycarbonamide is formed by interpolymerizing a polycarbonamide composition selected from the group consisting of (A) substantially equal molecular proportions of at least one dibasic carboxylic acid represented by the formula:



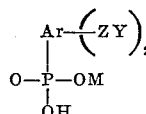
wherein R is a divalent hydrocarbon radical, and at least one diamine represented by the formula:



wherein X and R are as defined above, (B) a monoaminomonocarboxylic acid represented by the formula:



wherein X and R are as defined above, and (C) mixtures of (A) and (B), in the presence of an aryl alkali metal phosphonate represented by the formula:



wherein Ar, Z and M are as defined above and Y is —H, —OH, —Cl or R', R' being a lower alkyl such that R'—OH is volatile below the decomposition temperature of the polycarbonamide formed.

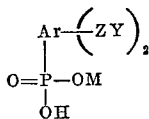
The nature of the radical —R— in the acid, the diamine, or the aminoacid is not critical. Preferably, it is a divalent hydrocarbon radical containing no more than that 20 carbon atoms. Acids of the class illustrated by the formula designated (b) are oxalic, adipic, suberic, pimelic, azelaic, sebacic, brassylic, octadecanedioic, undecanedioic, glutaric, tetradecanedioic, p-phenylenediacetic, isophthalic, terephthalic, hexahydroterephthalic, and the like, and mixtures thereof.

Typical suitable diamines of the class illustrated by the formula designated (c) above are ethylene diamine, enediamine, hexamethylenediamine, octamethylenediamine, decamethylenediamine, p-xylylenediamine, p-phenylenediamine, hexahydro-p-phenylenediamine, bis(4-aminocyclohexyl)methane, piperazine, dimethylpiperazine, tetramethylpiperazine, the N,N'-dimethyl, N,N'-diethyl and N,N'-diisopropyl derivatives of the above, and the like, as well as mixtures thereof.

Typical suitable amino acids of the class illustrated by the formula (d) above are 6-aminocaproic acid, 9-aminononanoic acid, 11-aminoundecanoic acid, and 17-aminoheptadecanoic acid, and the like.

In place of the above noted dibasic dicarboxylic acids, diamines, and amino acids, the amide forming derivatives thereof can be employed to form fiber-forming polymers. Amide forming derivatives of the dibasic dicarboxylic acids comprise the mono- and di-ester anhydride, and mono- and di-amide in the acid halide. Amide forming derivatives of the diamines include the carbamate and N-formyl derivatives. Amide forming derivatives of the amino acids include the ester, the anhydride, amide, lactam, acid halide, N-formyl derivative, carbamate, and in the presence of water, the nitrile.

As indicated above, the compounds found useful in the practice of this invention are characterized by an alkali metal phosphonate group and two amide-forming groups attached to aryl nucleus and are represented by the formula:



wherein Ar, Z, M, and Y are as defined above. Illustrative of such compounds are potassium-dicarboxy benzenephosphonate, sodium-dicarboxybenzenephosphonate, sodium-carboxyaminobenzenephosphonate, lithium-carboxyaminobenzene-phosphonate, lithium-diaminobenzenephosphonate, potassium-dicarboxyl-naphthalene phosphonate, sodium-dicarboxynaphthalenephosphonate, sodium-diaminonaphthalenephosphonate, lithium-carboxyaminonaphthalene phosphonate, and the like. The preferred additive compound is potassium-dicarboxybenzene phosphonate.

The polycarbonamides of the invention are prepared by procedures well known in the art, and commonly employed in the manufacture of simple polyamides. That is, the reactants are heated at a temperature of from 180° C. to 300° C. and preferably from 200° C. to 295° C. until the product has a sufficiently high molecular weight to exhibit fiber-forming properties, which properties are reached when the polyamide has an intrinsic viscosity of at least 0.4. The reaction can be conducted at super-atmospheric, atmospheric, or sub-atmospheric pressure. Often it is desirable, especially in the last stage of the reaction, to employ conditions, e.g., reduced pressure, which will aid in the removal of the reaction by products. Preferably, the reaction is carried out in the absence of oxygen, for example, in an atmosphere of nitrogen.

Intrinsic viscosity is employed herein as defined as

$$C \xrightarrow{\text{Lim.}} \text{O} \left(\frac{\log_e N_r}{C} \right)$$

in which N_r is the relative viscosity of a dilute solution of the polymer in m-cresol in the same units and at the same temperature, and C is the concentration in grams of polymer per 100 cc. of solution.

The amount of additive which may be present as a component part of the polymer chain of the polycarbonamides of this invention may vary depending upon the type of polymer desired and the particular shaped article in which it is to find its end use. It has been found necessary to employ about 0.1 and 2.0 weight percentage based on the weight of the polycarbonamide. At least 0.1 weight percentage of additive is required in order that a significant level of acid dye-resist properties be obtained. It has been found that the best results are obtained when about 0.5 and about 1.0 weight percentage of additive based on the weight of the polycarbonamide are employed. Amounts greater than 2.0 weight percentage do not show improvement significant enough to justify the additional amount of additive. It has been found that when the additives of the present invention are employed within amounts of 0.05 and 1.5 weight percentage based on the weight of the polycarbonamide, and especially from about 0.1 to 0.5 weight percentage, the polycarbonamide produced has

been found to possess excellent acid dye-resist properties and to have a viscosity in the fiber-forming range.

In order to illustrate the invention and the advantages thereof with greater particularity, the following specific example is given. It is to be understood that it is intended to be only illustrative and not limitative. Parts are given by weight unless otherwise indicated.

EXAMPLE I

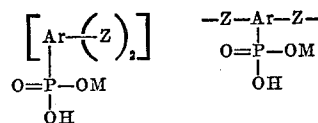
A solution of 147 grams of hexamethylene diammonium adipate salt was dissolved in 153 grams of water and added to a stainless steel evaporator which had previously been purged with nitrogen. The solution was heated under a nitrogen blanket at a pressure of 13 p.s.i.g. with the continuous removal of steam until the condensate and salt solution reached the temperature of 137° C. At this point the salt solution was charged to a stainless steel high pressure autoclave which contained 1.27 grams (0.1 weight percent) of potassium-dicarboxybenzene phosphonate. The temperature and pressure were slowly raised to 243° C. and 250 p.s.i.g. during which time there was a continuous removal of steam. Thereafter the pressure was gradually reduced to atmospheric pressure over a 25 minute period and the polymer melt was allowed to equilibrate for 30 minutes at 278° C. The finish polymer was then melt spun through a 13 hole spinneret yielding white multifilament yarns. These yarns were drawn over hot pins at a draw ratio of 4.8 times the original length.

Dyeing of these yarns was carried out by immersing in an acid dye bath containing 3 percent, based on the weight of the yarn, of Scarlet 4 RA Conc. CF(C. I. Acid Red 18) and 1.2 percent formic acid. The weight ratio of dye bath: fiber was maintained at 40:1 and dyeing was conducted for 2 hours at 100° C. and at a pH of 3.1. Spectrophotometric measurement showed these yarns absorbed 0.5 percent of the dye whereas dye absorption for unmodified polyhexamethylene adipamide yarns which were prepared and dyed in an identical manner as above was 1.06 percent.

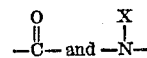
As can be seen from the above results, fibers made from the polycarbonamides of the present invention all possess a resistance to acid type dyes. This enables manufacturers to produce fibers having the same basic polycarbonamide molecular structure as conventional polycarbonamides but different affinities for acid dyes. This in turn offers dyeing diversification for fabric color-on-white effects and tone-on-tone effects heretofore not readily obtainable.

What is claimed is:

1. A fiber-forming synthetic linear polycarbonamide wherein recurring carbonamide linkages are an integral part of the polymer chain and containing as a component part of the polymer chain between about 0.05 and 1.5 weight percentage, based on the weight of the polycarbonamide of units represented by the formula:



wherein Ar is a carbocyclic aromatic nucleus containing 6 to 12 carbon atoms, Z is a member of the class consisting of



X is a member of the class consisting of hydrogen and lower alkyl radicals and M is an alkali metal.

2. The fiber-forming synthetic linear polycarbonamide as set forth in claim 1 wherein the polycarbonamide is poly-hexamethylene adipamide.

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3. A fiber-forming synthetic linear polycarbonamide wherein recurring polycarbonamide linkages are an integral part of the polymer chain and containing as a component part of the polymer chain between about 0.05 and 1.5 weight percentage based on the weight of the polycarbonamide of potassium-dicarboxybenzene phosphonate.

4. Poly-hexamethylene adipamide containing as a component part of the polymer chain between about 0.05 and 1.5 weight percentage based on the weight of the poly-hexamethylene adipamide of potassium-dicarboxybenzene phosphonate.

5. A textile fiber of the polycarbonamide as defined in claim 1.

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10 HAROLD D. ANDERSON, *Primary Examiner*.

U.S. Cl. X.R.

8—55; 57—140

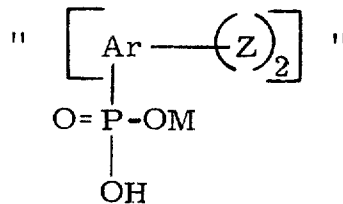
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,448,087 Dated June 3, 1969

Inventor(s) James B. Ballentine and Lawrence W. Crovatt, Jr.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 2, line 46, "that" should read --about--;
line 55, "enediamine"
should read --propylene diamine-- and before "hexamethylenediamine"
--tetramethylenediamine, pentamethylenediamine, -- should be
inserted. Claim 1, the formula



should be deleted.

**SIGNED AND
SEALED
AUG 11 1970**

(SEAL)

Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents