

1

3,438,949

POLYCARBONAMIDES RESISTANT TO ACID DYES AND CONTAINING TERMINAL NAPHTHYL DISULFONATED RADICALS

Lawrence W. Crovatt, Jr., Raleigh, N.C., assignor to Monsanto Company, a corporation of Delaware
No Drawing. Filed Oct. 21, 1965, Ser. No. 500,358
Int. Cl. C08g 20/20, 53/14
U.S. Cl. 260—78

4 Claims

ABSTRACT OF THE DISCLOSURE

Fiber-forming linear polycarbonamides modified to contain certain terminal naphthyl disulfonated radicals as an integral part of the polymer chain possess excellent acid dye-resistant properties. Fibers formed from these polycarbonamides may, for example, be combined with standard polycarbonamide fibers to provide a fabric which is dyeable in a single dye bath to different colors or color tones.

This invention relates to fiber-forming synthetic polymeric materials and the shaped articles produced therefrom. More particularly, this invention relates to novel fiber-forming synthetic linear polycarbonamides and the shaped articles produced therefrom which are particularly resistant to acid type dyes.

Although textile fibers obtained from fiber-forming polycarbonamides heretofore known are of great value, they are deficient in dyeing properties in that 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 desirable 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. Heretofore, additives employed for this purpose have not been found to be entirely satisfactory due to their ability to impart only a limited amount of acid dye-resistance to the fibers. For example, U.S. Patent 3,039,990 discloses fibers treated with alkali metal dicarboxybenzene monosulfonates. While these additives serve to make the fibers receptive to basic dyes, they do not impart a sufficient acid dye-resist character to the fibers to make them commercially acceptable for use with acid dyes in the production of a wide range of off-shade fabrics.

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.

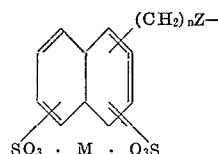
These and other objects will become apparent in the course of the following specification and claims.

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, fibers, pellicles, bearings, ornaments, or the like. They are particularly useful in the production of textile fibers.

The present invention provides a novel 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

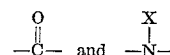
2

chain between about 0.05 and 2.0 mole percentage and preferably between about 0.1 and about 1.0 mole percentage, based on the molecular weight of the polycarbonamide, of units of the structure:



(a)

wherein Z is a member of the class consisting of

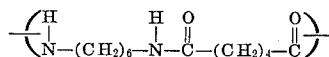


X is a member of the class consisting of hydrogen and lower alkyl, M is an alkaline earth metal and n is a number from zero to 6 inclusive with the proviso that when



then n is at least 1.

As used herein, the term "molecular weight of the polycarbonamide" refers to the molecular weight of one repeating unit of the polycarbonamide. Thus, the molecular weight of polyhexamethylene adipamide would be 226 which is the molecular weight of one repeating unit having the formula



In a typical preparation the polycarbonamide is formed by interpolymersing a polycarbonamide composition selected from the group consisting of (A) substantially equimolecular proportions of a dibasic carboxylic acid having the formula:

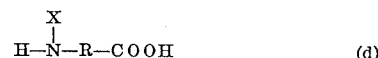


wherein R is a divalent hydrocarbon radical, and a diamine having the formula



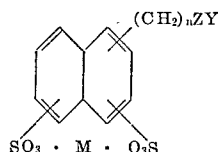
(c)

wherein X and R are as defined above and (B) a monoaminocarboxylic acid having the formula:



(d)

wherein X and R are as defined above, in the presence of a monofunctional disulfonated compound having the formula:



(e)

wherein n, Z and M are as defined above and Y is a member of the class consisting of hydrogen, —OH, —Cl, OR', R' being a monovalent hydrocarbon radical 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 amino acid is not critical. Preferably it is a divalent hydrocarbon radical containing no more than about 20 carbon atoms. Typical acids of the class illustrated by the formula designated (b) above are oxalic, adipic, suberic, pimelic, azelaic, sebacic, brassylic, octadecanedioic, undecanedioic, glutaric, tetradecanedioic, p-phenylene diacetic, isophthalic, terephthalic, hexahydroterephthalic, and the like, and mixtures thereof.

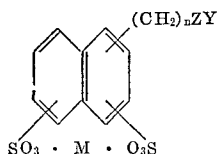
Typical suitable diamines of the class illustrated above

by the formula designated (c) above are ethylenediamine, propylenediamine, tetramethylenediamine, pentamethylenediamine, hexamethylenediamine, octamethylenediamine, decamethylenediamine, p-xylylenediamine, p-phenylenediamine, hexahydro-p-phenylenediamine, bis(4-aminocyclohexyl)methane, piperazine, dimethylpiperazine, tetramethylpiperazine, the N,N'-dimethyl, the N,N'-diethyl and the N,N'-diisopropyl derivatives of the above, and the like, as well as mixtures thereof.

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

In place of the above dibasic carboxylic acids, diamines, and amino acids, the amide-forming derivatives thereof can be employed to form fiber-forming polymers. Amide-forming derivatives of the dibasic carboxylic acids comprise the mono- and di-ester, the anhydride, the mono- and di-amide, and the acid halide. Amide-forming derivatives of the diamines include the carbamate and the 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 two sulfonate groups and one amide-forming group attached to a naphthalene ring and are represented by the formula:



wherein, n , M , Z and Y are as defined above.

The compounds which are represented by this formula are the mono-alkaline earth metal salts of carboxyl- or aminonaphthalene disulfonate. The term alkaline earth metal is intended to include calcium, barium, magnesium, and strontium. It is to be understood that the amide-forming group, that is, the amino or carboxyl group may be attached to either the 1 or 2 position of the naphthalene ring. Illustrative compounds are, when Z is



calcium -1-carboxy-naphthalene disulfonate, barium-2-carboxy-naphthalene disulfonate, magnesium-2-carboxy-naphthalene disulfonate, strontium-1-carboxy - naphthalene disulfonate, and the like, when Z is



calcium-1-methylamino-naphthalene disulfonate, barium-2-ethylamino-naphthalene disulfonate, magnesium-1-methylamino-naphthalene disulfonate, strontium-2-ethylamino-naphthylene disulfonate, and the like.

The polycarbonamides of this 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 as employed herein is defined as

$$C \xrightarrow{\text{Lim.}} \frac{\log_e N_r}{C}$$

in which N_r is the relative viscosity of a dilute solution of the polymer in m-cresol in the same units 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 between about 0.05 and 2.0 mole percentage based on the molecular weight of the polycarbonamide. At least 0.05 mole 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 between about 0.1 and about 1.0 mole percentage of additive based on the molecular weight of the polycarbonamide are employed. Amounts greater than 2.0 mole percentage have an adverse effect on the viscosity of the polycarbonamide produced. Since the additives employed in this invention contain only one functional group, i.e. one carboxyl or one amino group, it can be seen that they react in such a manner as to terminate the polymer chain of the polycarbonamide. This type of reaction is similar to the reaction which occurs upon the addition of additives which are termed by the art as chain terminators or viscosity stabilizers. Thus, the greater amount of additive which is employed in the present invention, the shorter will be the polymer chain of the polycarbonamide and the lower will be the viscosity of the polycarbonamide. As noted above, it has been found preferable to employ amounts of additives between about 0.1 and 1.0 mole percentage since when employing such amounts 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 examples are given, it is to be understood that they are intended to be only illustrative and not limitative. Parts are given by weight unless otherwise indicated.

EXAMPLE I

This example illustrates the preparation of a conventional polycarbonamide, namely, polyhexamethylenedipamide. This polymer and the fiber produced therefrom are to be used as a standard comparison with the modified polycarbonamides of the present invention.

To a stainless steel evaporator there was added 8.47 moles of water containing 0.562 mole of hexamethylene diammonium adipate salt dissolved therein. The unit was purged with nitrogen and then pressurized to 13 pounds per square inch gauge. The salt solution was then heated to 137° C. with continuous removal of steam condensate. At this point the salt concentrate was piped under pressure into a stainless steel high pressure autoclave which had been purged previously with nitrogen. In this reactor, which contained a stirrer for agitation, the pressure was immediately raised to 250 pounds per square inch gauge and the temperature raised to 22° C. The steam was removed until the polymer melt temperature reached 243° C. At this point the reactor pressure was gradually reduced over a 25 minute period to atmospheric pressure and the polymer melt allowed to equilibrate for 30 minutes at 278° C.

The finished polymer so produced was melt spun at 280° C. through a 13 hole spinnerette yielding white multifilament yarn. These yarns were drawn over hot pins (90° C.) at maximum draw ratio of 5.65 times their original length.

Dyeing of these yarns was carried out by immersing in an acid dye bath containing 3 percent based on the

5

weight of the yarn of Scarlet 4RA conc. CF (C.I. acid red 18) and 1.2 percent formic acid. The weight ratio of dye bath to fiber was maintained at 40:1 and dyeing was conducted for 2 hours at 100° C. and at a pH of 3.1. These yarns absorbed 1.25 percent dyestuff.

EXAMPLE II

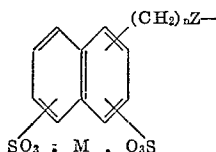
Barium - 2 - carboxy-naphthalenedisulfonate was prepared by treating an aqueous solution of di(potassium sulfonate)-naphthalene-2-carboxylic acid with saturating quantities of barium chloride. Precipitation of barium salt occurred and was isolated by filtration.

The procedure of Example I was repeated with the exception that the above prepared barium-2-carboxy-naphthalene disulfonate, in an amount sufficient to provide a finished poly-hexamethylene adipamide containing 0.56 mole percent additive was added along with the salt into the autoclave. This modified polymer thus produced was melt spun at 280° C. in the form of a 13 multifilament white yarn. These yarns were drawn over hot pins (90° C.) at a maximum draw ratio of 5.35 times their original length. These yarns were found to absorb 0.64 percent Scarlet 4RA Conc. CF (C.I. acid red 18) acid dyestuff when dyed under the identical procedure and with the same dye bath composition as outlined in Example I. This dye absorption represents very nearly 48.7 percent dye-resist character over the standard poly-hexamethylene adipamide.

As can be seen from the above results, fibers made from the polycarbonamides of the present invention 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 dye. This in turn offers dyeing diversification for fabric color-on-white effects and tone-on-tone effects heretofore not readily obtainable.

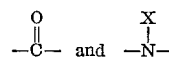
I claim:

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 2.0 mole percentage, based on the molecular weight of the polycarbonamide of units of the structure:



6

wherein Z is a member of the class consisting of



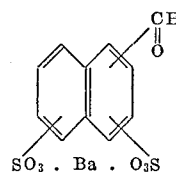
X is a member of the class consisting of hydrogen and lower alkyl, M is an alkaline earth metal and n is a number from zero to 6 inclusive with the proviso that when Z is



then n is at least 1.

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

3. Polyhexamethylene adipamide containing as a component part of the polymer chain between about 0.05 and 2.0 mole percentage based on the molecular weight of the polyhexamethylene adipamide of units of the structure:



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

References Cited

UNITED STATES PATENTS

3,039,990	6/1962	Huffman	260—78
3,142,662	7/1964	Huffman	260—78
3,184,436	5/1965	Magat	260—78
3,296,204	1/1967	Caldwell	260—78
3,328,484	6/1967	Lugaz et al.	260—78

45 WILLIAM H. SHORT, *Primary Examiner*.
H. D. ANDERSON, *Assistant Examiner*.

U.S. Cl. X.R.

50 260—78, 33.4; 8—55