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CROSS-LINKED POLYCARBONAMIDE

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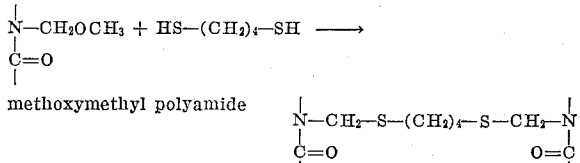
This invention relates to improved synthetic polymeric fibers and more particularly to modified synthetic polyamide fibers and fabrics having improved properties.

It is known that polycarbonamides may be modified by introducing crosslinks between adjacent polymer chains. This may be accomplished, for instance, by reaction with formaldehyde to introduce methylene bridges between the amide nitrogens of adjacent polymer chains. While this procedure, if properly applied, leads to fibers of improved properties, these fibers are not altogether satisfactory since fabrics produced from them are more difficult to dye than fabrics from unmodified nylon.

It is accordingly an object of this invention to provide a crosslinked polycarbonamide fiber of improved dyeability. Further objects will become apparent from the example and discussion to follow.

These and other objects are accomplished by an oriented crystalline synthetic polycarbonamide fiber in which a limited number of the amide nitrogens on adjacent polymer chains are crosslinked by groups of the class —R—S—R_1—S—R_2— wherein R and R_2 are methylene or ethylene groups and R_1 is an alkylene group having up to 8 carbon atoms. The crosslinks should be located predominantly in the amorphous areas of the fiber and the number of crosslinks is preferably in the range of 15 to 600 gram equivalents of crosslinks per 10^6 grams of fiber.

The fibers of this invention may be prepared by first reacting a drawn polycarbonamide fiber with formaldehyde in the presence of methanol to form methoxymethyl nylon. The methoxymethyl nylon is then reacted with a dithiol such as butane dithiol to form alkylene sulfide crosslinks as illustrated below.



methoxymethyl polyamide

butane dithiol

Alternatively, the methoxymethyl nylon may be reacted with a monothiol such as thiourea to form mercaptomethyl nylon, which is then reacted with an alkylene dihalide such as ethylenedichloride to form crosslinks having the structure —CH_2—S—$(CH_2)_2$—S—CH_2—. This type of reaction is not only useful for the formation of crosslinks, but may be used to introduce other functional groups into the amorphous areas of nylon fibers, e.g., thioglycolic acid may be reacted with the methoxymethyl polyamide to introduce a large number of carboxyl groups which enhance the heat resistance of the fiber when converted to metallic salts such as the sodium or calcium salts.

Example

A solution for methoxymethylating nylon is prepared by dissolving 1000 grams of paraformaldehyde in 1 liter of methanol at 50–60° C. In order to aid the hydrolysis of the paraformaldehyde, two pellets of sodium hydroxide are added. The solution is then treated with activated charcoal and filtered. The filtrate is adjusted to a pH

of 0.6 by adding oxalic acid. A plain weave nylon fabric woven from conventional drawn 70-denier, 34-filament 66 nylon yarn is soaked in the above solution at room temperature in a closed container for a period of 16 hours. The fabric is then removed from the solution, and excess solution is removed by padding with paper towels. The air dried methoxymethyl nylon fabric is then refluxed with 1,4-butanedithiol for 4 hours. The fabric is then removed and extensively extracted with methanol. After drying the fabric is found to be insoluble in formic acid and resistant to hole melting, indicating the presence of crosslinks. Sulfur analysis shows 1.61% by weight of sulfur indicating the presence of 252 gram equivalents of crosslinks per 10^6 grams of fiber. The number of gram equivalents of crosslinks per 10^6 grams fiber=percent sulfur×10,000/64. X-ray examination of the fiber indicates that the crystalline areas of the fiber are not substantially changed by the introduction of the crosslinks, thus indicating that the crosslinks are predominantly in the amorphous areas. When the fabric is dyed in the conventional manner using Celanthrene Blue (Disperse Blue 7; Color Index No. 62,500 in the Colour Index by the American Association of Textile Chemists and Colorists) dye it is observed to dye to a deeper shade in a given length of time than comparable fabrics crosslinked to the same degree with formaldehyde. The fabric is also found to be much more resilient than similar fabrics from untreated nylon.

The foregoing example illustrates the advantage of the alkylene sulfide crosslinked polyamide fibers of this invention in the preparation of fabrics which not only have improved resilience, but retain a large measure of their dyeability. By restricting the reaction to the amorphous area of the already-formed fiber, the improvement in resilience is obtained, whereas, a random distribution of crosslinks as obtained in reactions carried out in the solution, prevents the formation of crystalline areas in the fiber and produces a non-resilient fiber of low strength which is not suitable for apparel fabrics.

In order to obtain an appreciable improvement in fiber properties the fiber should contain at least about 15 gram equivalents of crosslinks per 10^6 grams fiber. Preferably, the number of crosslinks should not exceed about 600 gram equivalents.

The introduction of the alkylene sulfide crosslinks of this invention into the amorphous areas of polyamide fibers may be practiced to advantage with any polyamide having reactive —NH groups. Crosslinks of this type have the advantage that they are longer than the crosslinks usually employed and thus the reaction may be carried out successfully with polyamides which normally do not react due to inability of the chains to be brought sufficiently close together. In addition to the 66 nylon set forth in the example, other suitable polyamide fibers are those prepared from polymers disclosed in U.S. Patents 2,071,253, 2,130,523, and 2,130,948. Interpolyamides prepared from mixtures of diamines, dibasic acids, and amino acids can also be used for the practice of this invention. Likewise, melt blends of two or more polyamides can be used, if desired. Specific examples of other polyamides which may be employed include 6 nylon fibers, fibers from polyhexamethylene sebacamide, polyhexamethylene isophthalamide, poly-4,4′-dicyclohexylmethane azelamide, poly-p-xylylene azelamide, poly-2-methyl hexamethylene terephthalamide, poly-4,4′-dicyclohexylpropane-2 azelamide, and interpolymers thereof.

It will be apparent that many widely different embodiments of this invention may be made without departing from the spirit and scope thereof, and therefore

it is not intended to be limited except as indicated in the appended claim.

I claim:

A synthetic polycarbonamide fiber having 15 to 600 gram equivalents of crosslinks per 10^6 grams of fiber, across amide nitrogens on adjacent polymer chains, said cross-links being located predominantly in the amorphous areas of the fiber and having the formula

$$—CH_2—S—(CH_2)_n—S—CH_2—$$

wherein n is 2 or 4.

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