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PROCESS FOR THE PRODUCTION OF A HIGHLY ORIENTABLE, CRYSTALLIZABLE, FILAMENT-FORMING POLYAMIDE

Stephanie Louise Kwolek, Wilmington, Del., and Paul Winthrop Morgan, West Chester, Pa., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

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1 Claim. (Cl. 260—78)

This invention relates to a novel class of crystalline, linear condensation polyamides and to a manufacturing process therefor.

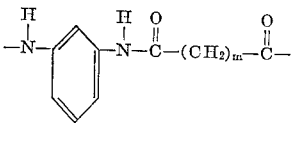
Among the numerous combinations of bifunctional complementary reactants heretofore suggested for the manufacture of linear condensation polyamides, those of wholly aliphatic reactants, e.g. adipic acid and hexamethylene diamine which yield nylon 66, have been most frequently employed in commercial practice since crystalline products have been readily obtained. Such crystalline products have been particularly attractive since, in comparison with non-crystalline or amorphous forms, they possess higher softening points, distinct melting points, greater light stability and opacity as well as improved tenacity and elongation values.

Although the use of aromatic polyamide reactants is also known, i.e. to achieve other desired benefits, certain combinations which include such reactants have not previously produced suitable crystalline polymers. Illustrative of such combinations are those of meta-phenylene diamine and either adipic, suberic or sebacic acid, as described for example in Flory U.S. Patent 2,244,192. Rather than exhibiting the properties of crystalline polymers, the products of those materials are amber colored resinous materials which soften at temperatures considerably below their melting point.

In accordance with the present invention, a novel class of crystalline polyamides is provided by means of a unique series of critical processing steps. In contrast to prior art polyamides prepared to contain the same recurring units, the products of the invention exhibit the desirable features which are generally characteristic of crystalline polymers and in addition afford outstandingly higher modulus values. As a consequence of these properties, fabrics produced of the novel polymers in filament form exhibit improved fabric aesthetics.

More particularly the invention provides a linear polyamide selected from the group consisting of polymetaphenylene adipamide, polymetaphenylene suberamide, and polymetaphenylene sebacamide, said polyamide having an inherent viscosity of at least 0.8 and a crystallinity index above 50.

The novel crystalline polyamides of the invention consist of recurring structural units of the formula:



wherein m is an even number integer from 4 through 8. In filament form, the polyamides have excellent light stability and improved tensile properties, particularly in terms of higher modulus and tenacity values.

The method of the invention involves the following series of critical steps to obtain a polyamide in a highly orientable, crystallizable form:

(1) Forming an anhydrous condensation mixture consisting of (a) a diacid chloride of an acid selected from the group consisting of adipic acid, suberic acid, and sebacic acid, together with (b) a stoichiometric equivalent, based on the said diacid chloride, of meta-phenylene diamine, and (c) an organic, acid accepting diluent which is a solvent for said diamine and said polyamide and which is present in such an amount to provide a final concentration of 5–35% by weight of polyamide therein, by addition of said diacid chloride to a solution of said diamine in said diluent while maintaining the said condensation mixture under continuous agitation in the absence of water at a temperature between —20 and 25° C., preferably 0–25° C., until completion of said addition,

(2) Continuing said agitation at a temperature not above 30° C. until a polyamide is formed having an inherent viscosity of at least 0.8, and

(3) Separating the polyamide thusly formed.

Strict adherence to the foregoing process variables is necessary to obtain the particular polyamides in such form that they be capable of crystallization to a crystallinity index of 50 or more. The reactants and diluent should be highly purified such that water and other extraneous materials are essentially excluded. The water content of the reaction mixture, in particular, should not exceed 0.02% by weight. For purposes of excluding moisture and other reactive vapors, the reaction should be conducted under an inert atmosphere such as nitrogen, dry air or the like. The stoichiometric equivalent of diacid chloride in undiluted form should be added to the diluent solution of diamine as rapidly as possible but without permitting the temperature to exceed 25° C. during the addition. For this purpose it is normally desirable to initially cool the diamine solution to a temperature between 0 and 10° C. Even after completion of the addition, the reaction mixture should not be heated above 30° C.

Following complete addition of the diacid chloride to the amine solution it is desirable to allow the reaction mixture to warm up to between 10° and 25° C. while continuing the agitation for at least 20 minutes. Subsequently the polycondensate can be precipitated by pouring the reaction mixture into water under conditions of agitation. The recovered, washed and dried polymer is then desirably dry spun from dimethylacetamide or dimethylsulfoxide to give fibers with excellent tenacity and elongation properties.

Suitable organic, acid accepting diluents in which to conduct the polymerization include alkyl substituted amides such as N-methylpyrrolidone, dimethylacetamide and hexamethyl phosphoramide.

The manner in which the prepared polyamides are crystallized is not a critical feature of the invention. Although steam setting of drawn fibers, as performed in the examples, is a preferred technique, others are also suitable. Typical among such other methods are those involving dry-heat setting, hot-wet treatment, or the use of hydroxyl-containing organic non-solvent swelling agents, such as described in U.S. Patents 2,307,846 and 2,289,377.

It is to be understood that once the polymers have been prepared in a highly purified crystallizable form, they can be suitably modified as by the inclusion of dyes, fillers, delusterants, anti-static agents and the like.

The crystalline polyamides can be employed in the form of filaments, sheets, rods, tubes, coatings and the like. In the form of filaments they are particularly useful in the fabrication of tire cords, carpets, wearing apparel, etc.

Examples I through III hereinafter illustrate the preparation of polyamides according to the process of the invention. Example IV illustrates the crystallization of those polyamides in the form of filaments. Example V demonstrates comparative properties of polymetaphenylene adipamide versus polyhexamethylene adipamide. In the examples, all parts are by weight unless otherwise stated.