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3,322,728
SULFONYL AROMATIC POLYAMIDES
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This invention relates to novel polymers and to shaped structures prepared therefrom. More specifically, it relates to high molecular weight aromatic polyamides having unusually high melting points. This application is a continuation in part of our copending application Ser. No. 774,156, filed Nov. 17, 1958, now Patent No. 3,094,511.

Polyamides have found wide commercial acceptance, because they can be formed into strong abrasion-resistant fibers and films. As discussed in the aforementioned application, several desirable properties notably high temperature softening point and resistance to high tempera- 20 ture degradation had not been achieved in polyamides prior to our invention. For example, polyamides disclosed in U.S. 2,130,948 have relatively low melting points, and degrade rapidly in the presence of air at temperatures as low as 200° C. More important, they lose a substantial 25 portion of their strength at temperatures much lower than their melting points. Polyamides disclosed in U.S. 2,244,-192 show little tendency to crystallize to a dimensionallystable structure, soften at temperatures considerably below their melting points and exhibit an undesirable amber 30 color which renders them unsuitable for many purposes. Cold-drawn filaments prepared from these polyamides tend to retract or shrink at temperatures considerably below their melting points due, in part, to lack of crystallinity, and degrade rapidly at their melting temperatures. There had been a need for high molecular weight polyamides which are strong and stable at high temperatures and suitable for forming into filaments and films having waterwhite clarity. Polymetaphenylene isophthalamide of high molecular weight, disclosed in the aforementioned application along with several of its homologues, provided highly desirable properties, but these products are often so intractable that expensive procedures and materials are required to shape them into fibers and films.

It is an object of this invention to produce a new and useful class of high molecular weight aromatic polyamides formable into films and filaments by economical processes.

Another object is to provid an aromatic polyamide having inherent viscosity of at least 0.6 which has relatively high solubility in commercial solvents.

A still further object is to provide high molecular weight, wholly aromatic polyamides having a high melting point and good solubility.

These and other objects will become apparent from 55 the following specification and claims.

In accordance with the present invention there is provided a high molecular weight polymer containing a recurring structural unit from the class consisting of

and

wherein B is a member of the class consisting of

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and

B' is a member of the class consisting of

High molecular weight polymers of this invention are prepared by interfacial or solvent polymerization by reacting an aromatic diacid chloride with an aromatic diamine, the acid groups of the diacid chloride and the amine groups of the diamine being meta or para oriented relative to each other, at low temperatures (below 100° C.). These processes are described in United States Patent No. 2,831,834 to Magat (Apr. 22, 1958) and United States Patent No. 3,063,966 to Kwolek, Morgan and Sorenson (Nov. 13, 1962).

Polymers of this invention are characterized by an exceptionally high melting point. Whereas known polyamides melt at temperatures below about 270° C., generally the polyamides of this invention have melting points in excess of 350° C. and in many instances above 400° C. Moreover, filaments of polyamides of this invention retain their filament form at temperatures of about 350° C. Polymers of this invention are also distinguished from known polyamides in having water-white color, excellent resistance to corrosive atmospheres, substantially no flammability, and outstanding resistance to degradation by high energy particle and gamma ray radiation. These polymers resist melting upon exposure to 300° C. for extended periods while retaining hitherto unrealized high proportion of room temperature physical properties. Flash exposure for 20 seconds to temperatures as high as 700° C. does not destroy these fiber properties. Because of their solubility, these polymers may be processed into shaped structures such as films and filaments by conventional techniques. These polymers have high tenacity, good work recovery, high flex life at elevated temperatures, and are readily crystallizable.

The following examples illustrate the invention. All parts and percentages are by weight unless otherwise indicated. Unless otherwise indicated inherent viscosity reported in the examples is determined in sulfuric acid (sp. gr. 1.841 at 60° F.), at 30° C. at a concentration of 0.5 gram polymer per 100 cc. of solution. All polymers of this invention have an inherent viscosity of at least about 0.6 on this basis and a melting point of at least about 350° C.

## Example 1

m-Phenylenediamine (2.163 g.) is dissolved in 30 ml. of dimethylacetamide and the solution is cooled in a pack of solid carbon dioxide. Bis(4-chlorocarbonylphenyl) sulfone (6.864 g.) is added and the mixture is stirred for 3 hr. while surrounded by an ice-water bath.

The polymer is isolated by pouring the solution into rapidly stirred water. The washed and dried product is obtained in 100% yield and has an inherent viscosity of 1.03 (H<sub>2</sub>SO<sub>4</sub>). The polymer does not melt below 400° C.

It forms a heat-stable 20% solution in hot dimethylformamide.

## Example 2

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Bis(4-aminophenyl) methane (2.48 g.) and 2.53 g. of triethylamine are dissolved in 50 ml. of anhydrous, alcohol-free chloroform. With vigorous stirring is added a solution of 4.29 g. of bis(4-chlorocarbonylphenyl) sulfone in 250 ml. of chloroform.

Stirring is continued 5 min. and the mixture stands over-