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3,328,352

**FLUORINE CONTAINING AROMATIC  
POLYCARBONAMIDES**

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No Drawing. Filed June 17, 1963, Ser. No. 288,473  
8 Claims. (Cl. 260-47)

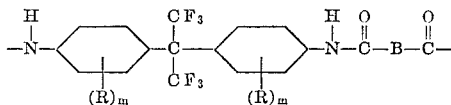
This invention relates to a novel and useful composition of matter. More specifically it concerns a novel and useful class of polyamides.

It is an object of the present invention to provide an aromatic polyamide having a melting point above about 350° C. and sufficient solubility in organic solvents to permit spinning of fibers and forming of films therefrom.

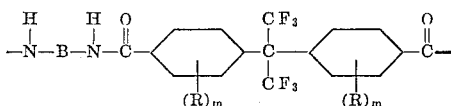
Another object is to provide a high melting aromatic polyamide which may be draw-oriented at relatively low temperatures.

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

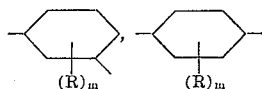
In accordance with the present invention there is provided a linear, fiber-forming, synthetic polycarbonamide wherein recurring carbonamide linkages are an integral part of the polymer chain from the class consisting of a homopolymer and a copolymer, the said homopolymer and copolymer consisting essentially of recurring units of the class consisting of



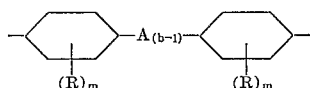
and



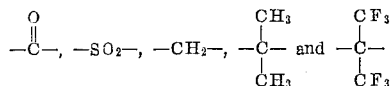
wherein B is a divalent radical from the class consisting of



and



A is a divalent radical from the class consisting of  $\text{---CH}_2\text{---}$ ,



R is a monovalent replacement for hydrogen on nuclear carbon from the class consisting of  $\text{---Cl}$ ,  $\text{---lower alkyl}$  and  $\text{---lower alkoxy}$ ;  
m is a number from 0 to 2 inclusive;  
b is a number from 1 to 2 inclusive;  
and the hexagon represents the benzene nucleus;

other copolymeric units whenever present constituting no more than about 10% of the recurring polycarbonamide units, the said polycarbonamide having a melting point of at least about 350° C. and an inherent viscosity of at least about 0.6 in sulfuric acid at 30° C. at a concentration of 0.5 gram of polymer per 100 cc. of solution.

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 on

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each ring, at low temperatures (below 100° C.). These processes are described in detail in U.S. 2,831,834 to Magat (Apr. 22, 1958) and U.S. 3,063,966 to Kwolek, Morgan and Sorenson (Nov. 13, 1962).

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*

Ditolylperfluoropropane is prepared by condensing 37 grams of toluene (0.4 mole) with 32 gm. (0.2 mole) of perfluoroacetone (prepared by the oxidation of perfluoroisobutylene as described by Brice et al., J. Am. Chem. Soc. 75, 2698 (1953)) in 66 grams of anhydrous hydrogen fluoride in a sealed bomb under autogeneous pressure for 10 hours at 140° C. After venting off the hydrogen chloride, the ditolylperfluoropropane is recovered. It is then oxidized by incremental addition of 115 gm. of potassium permanganate to a solution of 33 gm. dissolved in 185 cc. of 2/1, pyridine/water mixture, the addition of a solid permanganate being regulated to maintain the solution under gentle reflux. Excess potassium permanganate is then destroyed by adding a small amount of methanol. The brown suspension is then filtered to remove solid manganese dioxide and an excess of hydrochloric acid is added. The product, 2,2-bis(4-carboxyphenyl)hexafluoropropane, precipitates in an essentially pure form. It is dried under vacuum at 100° C. and then converted to the diacid chloride by refluxing in 150 cc. thionyl chloride containing a few drops of dimethylformamide as catalyst until the acid dissolves completely. The thionyl chloride is then distilled off over the steam bath first at atmospheric pressure and then under a slight vacuum. The solid 2,2-bis(4-chlorocarbonylphenyl)hexafluoropropane is thereafter crystallized from hexane.

In a small round-bottomed flask equipped with mechanical stirrer, as well as a stoppered opening for admitting reactants, are placed 2.483 g. (0.01 mole) of bis(4-aminophenyl) sulfone, 3.20 ml. of N,N-diethylaniline, and 30 ml. of 2,4-dimethyltetramethylene sulfone. The solution is cooled with ice and water and there is added all at once 4.292 g. (0.01 mole) of the solid 2,2-bis(4-chlorocarbonylphenyl) hexafluoropropane. The acid chloride slowly dissolves over a period of 2 hrs. during which time the mixture is stirred. There is a gradual increase in viscosity. As a matter of convenience, the system is stirred for an additional 22 hrs. at about 27° C.

The polymer is isolated by precipitation in vigorously stirred water, collection on a filter, and thorough washing with 50% aqueous ethanol and water. The polymer is dried at 70° C. under vacuum. The yield is 7.8 g. The product has an inherent viscosity of 0.70 (H<sub>2</sub>SO<sub>4</sub>) and does not melt below 350° C.

The procedure is repeated using equimolecular weights of 2,2-bis(4-chlorocarbonyl-phenyl)hexafluoropropane and the diamines of Table I. The polymers have the properties indicated in the table.

TABLE I

Diamine	Inherent Viscosity	Polymer Melt Temp. (° C.)
4-methyl-m-phenylenediamine.....	0.81	Above 350.
3,3'-dimethoxydiamiline.....	1.1	Above 375.