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WHOLLY AROMATIC POLYAMIDES

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This invention relates to a novel polymer and shaped structures prepared therefrom. More specifically, it relates to a high molecular weight aromatic polyamide having an unusually high melting point.

It is known that diamines may be reacted with dibasic acids to form polyamides. These polymers have found wide commercial acceptance because they can be formed into strong abrasion-resistant fibers and films. Known polyamides, however, are deficient in several desirable properties. For example, polyamides disclosed in U.S. Patent 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, these polyamides lose a substantial portion of their strength at temperatures much lower than their melting points. Similarly, polyamides disclosed in U.S. Patent 2,244,192 show little tendency to crystallize and also soften at temperatures considerably below their melting points besides exhibiting an undesirable amber color rendering them unsuitable for many purposes. Cold-drawn filaments prepared from these polyamides tend to contract at temperatures considerably below their melting points and degrade rapidly at their melting temperatures. There has been a need for a high molecular weight polyamide which is strong and stable at high temperatures and suitable for forming into filaments and films having water-white clarity.

It is an object of this invention to produce a new high molecular weight aromatic polyamide formable into films and filaments. Another object is to provide a high molecular weight aromatic polyamide having an inherent viscosity of at least 0.6. Another object of this invention is to provide a high molecular weight wholly aromatic polyamide having an inherent viscosity of at least 0.6 and characterized by water-white clarity and a melting point above about 300° C. These and other objects will become apparent from the following specification and claims.

In accordance with the present invention, there is provided a high molecular weight polymer characterized predominantly by the recurring structural unit

$$-\overset{R_1}{\overset{|}{N}}-Ar_1-\overset{R_1}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-Ar_2-\overset{O}{\overset{\|}{C}}-$$

wherein R_1 is hydrogen or lower alkyl and wherein Ar_1 and Ar_2 may be the same or different and may be an unsubstituted divalent aromatic radical or a substituted divalent aromatic radical, the chain-extending bonds of these divalent aromatic radicals being oriented meta or para to one another and the substituents attached to any aromatic nucleus being one or more or a mixture of lower alkyl, lower alkoxy, halogen, nitro, lower carbalkoxy, or other groups which do not from a polyamide during polymerization.

The high molecular weight polymer of this invention is termed "an aromatic polyamide." This term refers to a polymer wherein repeating units are linked by a carbonamide group, i.e., the

$$-\overset{O}{\overset{\|}{C}}-\overset{R_1}{\overset{|}{N}}-$$

radical (R_1 being the same as above indicated), the nitrogen and carbonyl of each repeating carbonamide radical

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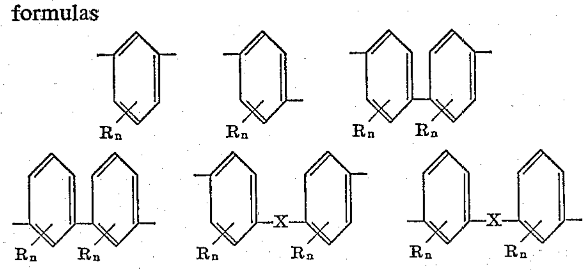
being directly attached to a carbon atom in the ring of an aromatic radical; that is, the nitrogen and carbonyl of each repeating carbonamide group each replaces a hydrogen of an aromatic ring. The term "aromatic ring" means a carbocyclic ring possessing resonance. Exemplary aromatic radicals have the following structural formulas



in which R is preferably a lower alkyl, lower alkoxy, or halogen group, *n* is a number from 0–4, inclusive, and X is preferably one of the groups of

$$-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-,\quad -\overset{Y}{\underset{Y}{\overset{|}{\underset{|}{C}}}}-$$

and —O—, in which Y is a hydrogen or a lower alkyl group. X may also be a lower alkylene or lower alkylene dioxy group although these are somewhat less desirable. R may also be a nitro, lower carbalkoxy, or other non-polyamide-forming group. All of these aromatic radicals are divalent and meta or para oriented, i.e., the unsatisfied bonds of the radicals (the "chain-extending bonds" when the radical is viewed in the repeating unit of the structural formula of the polymer) are meta or para oriented with respect to each other. One or more of the aromatic radicals may contain substituent groups as indicated and any aromatic ring may contain two or more of the same or different substituent groups. Preferable, however, are high molecular weight polymers in which the aromatic radicals are unsubstituted or contain only lower alkyl groups attached to any one ring. The term "non-polyamide-forming groups" refers to groups which do not form polyamides during the polymerization reaction herein disclosed. The term "chain-extending bond" refers to any bond in the polyamide which, if broken, would decrease the length of the polymer chain.

High molecular weight polymers of this invention are prepared 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.).

The diacid chloride of the dibasic aromatic acid useful as a reactant in the polymerization of the present invention includes compounds of the formula

$$\text{Hal-}\overset{O}{\overset{\|}{C}}-Ar_2-\overset{O}{\overset{\|}{C}}\text{-Hal}$$

wherein Ar_2 is a divalent aromatic radical, i.e., it contains resonant unsaturation, and Hal is a halogen atom from the class consisting of chlorine, bromine, and fluorine. The aromatic radical may have a single, multiple, or fused ring structure. One or more hydrogens of the aromatic nucleus may be replaced by non-polyamide-forming groups such as lower alkyl, lower alkoxy, halogen, nitro, sulfonyl, lower carbalkoxy, and the like. The terms "lower alkyl" and "lower alkoxy" and "lower carbalkoxy" refer to groups containing less then five carbon atoms.

Diacid chlorides which may be utilized to prepare the polyamides of this invention include isophthaloyl chloride and lower alkyl isophthaloyl chlorides, such as methyl-, ethyl-, propyl-, etc., isophthaloyl chlorides. There may