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3,063,966

PROCESS OF MAKING WHOLLY AROMATIC POLYAMIDES

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This invention is concerned with a chemical process for preparing polymers and more particularly with a low temperature process for preparing high molecular weight polyamides.

Among the most important synthetic polymers are polyamides. These polymers offer a wide range of desirable physical and chemical properties. Because of their high degree of usefulness, many different methods for preparing polyamides have been studied and several methods have been developed in some detail. Commercially, most polyamides are prepared by melt polymerization techniques involving high temperatures up to 300° C. This process is useful but suffers from certain handicaps. High molecular weight wholly aromatic polyamides having water-white color cannot be prepared by melt polymerization techniques because the high temperatures required for melt polymerizations foster reactant condensations other than the desired amide formation so that only highly colored low molecular weight or cross-linked products are obtained.

Low temperature reactions below 100° C. and preferably below 50° C. are desirable for economy and to reduced by-product formation and promote linear polyamide formation. However, when high temperatures are not employed, the reactants, themselves must be very reactive in the absence of added heat and use of very reactive materials again produces the problem of side reactions and by-product formation. For example, diamines and acid halides are the fastest reacting intermediates in the preparation of polyamides but are likewise the most susceptible to hydrolysis and to interaction with a solvent medium. In addition, mobility of both the growing polymer and the reactants is reduced as high polymer forms which serves to limit the molecular weight which can be obtained. This is particularly true if polymerization is attempted without any solvent. Even when solvents are used, by-product formation usually interferes with the formation of high molecular weight products.

The process of U.S. 2,708,617 provides one solution to the general problem of low-temperature polyamidation. In this process, acid halide solution encounters the coreactive phase at the moment when polymer is formed at an interface of controlled shape and then the contact is only momentary because the polymer is immediately withdrawn. Thus, opportunities for side-reactions are minimized. The system works well with aliphatic intermediates which give polymers sufficiently swollen by the solvents employed to permit rapid formation of high molecular weight polymer, but is unsuitable for producing high molecular weight polyamides from aromatic diamines and aromatic diacid chlorides.

It would be desirable to utilize a low-temperature polyamidation reaction in which other reactions do not impede the formation of a high molecular weight product. Such a process would be particularly desirable for the preparation of polyamides from aromatic intermediates. Aromatic diamines react more slowly with aromatic diacid chlorides and, therefore, the side-reaction problem is accentuated. Moreover, aromatic polyamides are less soluble and less mobile during polymerization and low tem-

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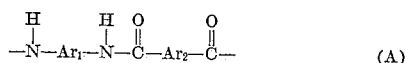
perature polymerizations cannot always be prolonged until high molecular weight polymers are obtained.

It is an object of this invention to provide a process for preparing wholly aromatic polyamides having properties not heretofore realized.

It is a still further object to provide solutions of wholly aromatic polyamides suitable for further processing into fibers, films and similar shaped structures.

It is another object to prepare high molecular weight wholly aromatic water-white film- and fiber-forming polyamides in a solution process at room temperatures.

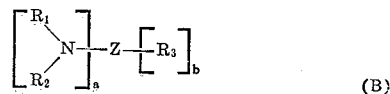
In accordance with the process of this invention, an aromatic diamine is reacted with an aromatic diacid halide in solution in a selected liquid medium to produce a high molecular weight film- and fiber-forming wholly aromatic polyamide characterized by the recurring structural unit



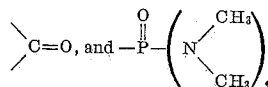
wherein Ar₁ and Ar₂ may be the same or different and may be an unsubstituted divalent aromatic radical or a substituted divalent aromatic radical, the chain-extending bonds of these divalent aromatic radicals being oriented meta or para to one another and the substituents attached to any aromatic nucleus being one or more or a mixture of lower alkyl, lower alkoxy, halogen, sulfonyl, nitro, lower carbalkoxy, or other groups which do not condense with the reactants during polymerization.

In a preferred embodiment of this invention, the reaction of aromatic diamine and aromatic diacid halide is carried out in a liquid medium comprising a halogenated non-aromatic hydrocarbon which contains at least one hydrogen on a carbon attached to the halogen, or a cyclic methylene sulfone, and an organic tertiary amine as acid acceptor.

In another preferred embodiment, the liquid reaction medium is an amide-type organic compound of the formula:

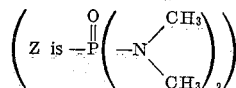


where R₁, R₂, and R₃ may be the same or different and are lower alkyl or alkylene radicals so chosen that the total number of carbon atoms in all of R₁, R₂, and R₃ is not more than 6 "a" is 1 or 2, "b" is 0 or 1, Z is an acidic radical such as



(where P is phosphorus) and the sum of a+b is such as to satisfy the above-indicated valences of the radical Z, While R₁, R₂, and R₃ as indicated can be separate alkyl groups, any two of these groups can be present in combination as an alkylene group, thus forming a heterocyclic ring structure. When such a heterocyclic ring is present, the ring must contain 5 or 6 nuclear atoms in all.

Typical amide-type solvents corresponding to the above structural formula are dimethyl acetamide (Z is >C=O); N,N,N',N'-tetramethyl urea (Z is >C=O); N-acetyl pyrrolidine (Z is >C=O); N-methyl-α-pyrrolidone (Z is >C=O) and hexamethylphosphoramide



Other solvents include N-dimethyl propionamide, N,N-diethyl acetamide, N-ethyl pyrrolidone, and dimethyl butyramide. These amide-type solvents act as their own acid