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INTERPOLYAMIDES

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Our present invention relates to new polyamides and more particularly to easily soluble interpolyamides.

It has already been proposed to prepare polyamides by condensing two different diamines with two different dicarboxylic acids in substantially equimolecular amounts. The interpolyamides thus obtained are only partially soluble in methanol or other simple aliphatic alcohols. The solubility of these mixed condensates rarely amounts to above 10%.

It is also known to produce polyamides from two condensation reactants one of which contains a heteratom in the carbon chain, for instance a sulfur atom. Such simple polyamides are insoluble in methanol and simple aliphatic alcohols as attempts have shown.

An object of our present invention is to provide interpolyamides at least 20 per cent of which dissolve in alcohols or mixtures of alcohols and halogenated hydrocarbons.

Another object is the preparation of adhesives, artificial leather, and laminated articles from the new polyamides.

A further object is the manufacture of films, foils and coatings from said polyamides.

Other objects of our invention will become apparent as the description proceeds.

These objects are accomplished by condensing at least two α-ω-dicarboxylic acids with at least two α-ω-diamines, at least one of these reactants containing sulfur in the carbon chain. Instead of one of these diamine-dicarboxylic acid combinations an aminocarboxylic acid may be employed and in place of the dicarboxylic acids and diamines or the aminocarboxylic acids the amide-forming derivatives thereof, for instance esters, chlorides, anhydrides or lactams may be used in the preparation of the new soluble interpolyamides.

The solubility properties of our new interpolyamides surprise all the more so as a product which is insoluble in aliphatic alcohols is obtained by condensing two salts which have the same acid components and one salt of which is a diamine salt containing sulfur, for instance, such as $\beta\beta'$-diaminodiethylsulfide-adipic acid and hexamethylenediamine-adipic acid. The solubility behavior of interpolyamides of this kind is shown in the following Table wherein HA means hexamethylenediammonium adipate and DSA diaminodiethylsulfide adipate (the parts being by weight).

Parts of reactants HA	Parts of reactants DSA	Parts of interpolyamide per 100 parts of methanol	Solubility behavior
0	100	2	Undissolved.
10	90	2	Undissolved, slightly fragile.
25	75	1	Undissolved, fragile.
33.3	66.7	1	Do.
50	50	1	Undissolved, hard.
75	25	1	Do.
85	15	2	Undissolved, slightly fragile.
100	0	2	Undissolved, hard.

If, however, the diamine containing sulfur is heated together with another diamine and corresponding quantities of two different dicarboxylic acids, interpolyamides are obtained of which 20–40% are easily soluble in methanol or a mixture of methanol and halogenated hydrocarbons.

In using two polymethylenediamine-dicarboxylic acid salts the mixture thereof in equimolecular amounts or in the proportion by weight of 1:1 is generally very advantageous. For instance, an interpolyamide prepared from hexamethylenediammonium sebacate and diaminodiethylsulfide adipate has the best solubility behavior when the reactants are present in the ratio of 1:1.

The solubility in methanol of interpolyamides prepared from hexamethylenediammonium sebacate (HS) and diaminodiethylsulfide adipate (DSA) is shown in the following Table (the parts being by weight):

Parts of reactants HS	Parts of reactants DSA	Parts of interpolyamide per 100 parts of methanol	Solubility behavior
0	100	2	Undissolved.
25	75	2	Swelled, nearly undissolved, partially fragile.
33.3	66.7	2	Dissolved nearly without residue.
50	50	25	Dissolved without residue.
54.6	45.4	10	Do.
(Molecular proportion)			
66.7	33.3	2	Only a small part dissolved.
75	25	2	Nearly undissolved.
100	0	2	Undissolved.

When ethylenediammonium sebacate is substituted for half the amount of hexamethylenediammonium sebacate, i. e. when the interpolyamide is produced from 50 per cent of diaminodiethylsulfide adipate, 25 per cent of hexamethylenediammonium sebacate, and 25 per cent of ethylenediammonium sebacate, the solubility of the interpolyamide is essentially increased. It is possible to prepare solutions containing 30–50 per cent of this interpolyamide.

The interpolyamides are advantageously obtained by condensing together two salts consisting of different diamines and different dicarboxylic acids. It is known of course that the components may also be caused to react separately in their molecular proportions. Instead of the free dicarboxylic acids the corresponding esters, chlorides, diamides, and semiamides may be employed and diurmethanes, diammonium formates and diammonium carbonates may be substituted for the diamines. By adding amino acids or esters and anhydrides thereof such as ϵ-caprolactam to the compositions of the salts condensation products are formed which possess an increased solubility in methanol or mixtures of methanol and a halogenated hydrocarbon.

Interpolyamides prepared from ϵ-caprolactam or 6-aminohexanoic acid and a polymethylenediammonium salt also dissolve relatively easily (20 per cent thereof) in methanol. On the other hand the solubility of condensates derived from an ω-aminocarboxylic acid of high molecular weight, for instance such as 9-aminononanoic acid or 11-aminohendecanoic acid, and a polymethlenediaminoniumdicarboxylate is low (about 2–3 per cent) if the diamine used in the condensation does not contain at least one atom of sulfur in the carbon chain. Interpolyamides, however, produced by reacting an aminocarboxylic acid of high molecular weight with a diammonium salt containing sulfur comparatively easily (above 20 per cent) dissolve in methanol, ethyl alcohol, butanol, and mixtures of alcohols and halogenated hydrocarbons. By using a diamine containing sulfur the solubility of the interpolyamides which have ϵ-caprolactam as a reactant can likewise considerably be increased.

As solvents such liquids may advantageously be employed as have a high evaporation velocity, for instance, methanol, ethyl alcohol, propanol, butanol, and mixtures thereof. Moreover, mixtures of alcohols with halogenated hydrocarbons such as chloroform, carbon tetrachloride, and methylene chloride are solvents suitable for polyamides containing sulfur. Solutions of these polyamides in mixtures of alcohols and halogenated hydrocarbons also remain clear on cooling in super-cooled condition for a long time. They are, therefore, useful as ingredients in impregnating and coating compositions and as clear lacquers. When dissolved in an alcohol the polyamide tends to precipitate in most cases after some time. By adding 5–50 per cent of chloroform, chlorobenzene, cresols or other substances suitable as stabilizers the solutions can be kept in the clear condition for some days.

The solutions of polyamides of our invention are especially useful in making adhesives, laminated layers, and leather substitute. Furthermore, they are applicable when desired with additions of dyestuffs, pigments, and plasticizers in the preparation of smooth and pliable films, foils, and coats having a high tensile strength and tenacity. The following Examples in which quantities of reagents are parts by weight illustrate our invention.

Example I

Equal parts of hexamethylenediammonium sebacate and $\beta\beta'$-diaminodiethylsulfide were condensed together at 210° and 760 mm for 12 hours in an atmosphere of nitrogen. To the interpolyamide thus obtained a sufficient amount of methanol was added and the mixture was heated for three hours. 25 per cent of the interpolyamide were clearly dissolved in methanol by this heating treatment. On cooling the solution became turbid after some time. The precipitated interpolyamide could again readily be dissolved by heating. When 20–30 per cent of chloroform were added the solution remained clear for several days. By evaporating the solvent clear and pliable films were obtained.

Example II

Equal parts of ethylenediammonium sebacate and the salt prepared from $\beta\beta'$-diaminodiethylsulfide and adipic acid were condensed together at 210° and 760 mm for 15 hours in an atmosphere of steam. To the interpolyamide thus formed was added a sufficient amount of methanol and the mixture was heated under reflux for several hours. 20 per cent of the interpolyamide were clearly dissolved in methanol by this heating treatment. The solution is useful as an ingredient in coating compositions and making laminated articles.

Example III

50 parts of $\beta\beta'$-diaminodiethylsulfide adipate, 25 parts of hexamethylenediammonium sebacate, and 25 parts of ethylenediammonium sebacate were condensed together at 210° and 760 mm for 12 hours in an atmosphere of nitrogen.

To 100 grams of the interpolyamide thus obtained were added 400 cc. of methanol and the mixture was heated under reflux for several hours. The interpolyamide completely dissolved in the methanol. The solution may be used as an ingredient in impregnating compositions and making smooth and pliable foils.

Example IV

40 parts of hexamethylenediammonium sebacate, 40 parts of $\beta\beta'$-diaminodiethylsulfide adipate and 20 parts of ethylenediammonium adipate were condensed together at 210° C and 760 mm for 24 hours in an atmosphere of nitrogen. To 300 grams of the interpolyamide thus obtained were added 600 cc. of methanol and 400 cc. of butanol and the mixture was heated under reflux for 2–3 hours until the interpolyamide was completely dissolved. The solution became turbid on cooling. By adding chloroform the solution could be kept clear for many days. Solutions containing 5–10 per cent of the interpolyamide also remained clear as supercooled solutions for some time without any stabilizer.

Example V

50 parts of hexamethylenediamine sebacate, 25 parts of ethylenediamine adipate, and 25 parts of $\beta\beta'$-diaminodiethylsulfide adipate were condensed together at 210° C and 760 mm for 20 hours in an atmosphere of nitrogen. To 400 grams of the interpolyamide thus formed were added 1000 cc. of methanol and the mixture was heated under reflux for three hours. The solution which tended to become turbid on cooling could be kept clear for several days by adding a stabilizer.

Example VI

Equal parts of ε-caprolactam and ββ′-diaminodiethylsulfide adipate were condensed together at 180° C and 760 mm for 12 hours in an atmosphere of steam. To 100 grams of the interpolyamide thus prepared were added 200 cc. of methanol and the mixture was heated under reflux until the interpolyamide was completely dissolved. The light-colored methanolic solution was a viscous liquid.

Example VII

50 parts of ε-caprolactam, 25 parts of hexamethylenediammonium sebacate, and 25 parts of ββ′-diaminodiethylsulfide adipate were condensed together at 180°C and 760 mm for 12 hours in an atmosphere of nitrogen. To 100 grams of the interpolyamide thus prepared were added 100 cc. of methanol and the mixture was heated under reflux for several hours. The resulting solution was clear and very viscous and is useful in the making of films and foils.

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