

ALIEN PROPERTY CUSTODIAN

PROCESS FOR THE PRODUCTION OF HIGH POLYMERIC CONDENSATION PRODUCTS

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This invention relates to the production of high polymeric condensation products.

It is an object of this invention to produce high polymeric products by condensation.

Another object is the provision of high polymeric products of various properties.

These and other objects will be apparent from the following description.

It has been found that aromatic acids being substituted at least by two, if necessary substituted amino groups, may be condensed with aliphatic carboxylic acids or aromatic substituted aliphatic amino carboxylic acids. The condensation products thus obtained have a high softening point and good film-forming properties. The moulded products obtained therefrom show also good mechanical properties. The mixing proportion of the components leads to high polymeric compounds of a very wide range. If polyamino carboxylic acids are used as starting material in excess, preferably resinous glass-clear products are obtained. If the aliphatic amino carboxylic acid is in excess, preferably polymers of the so called superpolyamide type are obtained. Such condensates are not pure chain-polymerisates, but show also net- and bridge-formation.

The chemical and physical character of the high polymeric reaction products is extensively defined by the kind of aromatic polyamino carboxylic acids used in this reaction. The influence of the aliphatic amino carboxylic acids on the properties of the final product is within the scope of the facts known about superpolyamide resins. The application of the symmetrical 3,5-diamino benzoic acid for instance leads to very hard condensates, whereas the application of the 2,5-diamino benzoic acid results in softer high polymers.

As aliphatic amino carboxylic acids in principle all known compounds of this constitution may be used, preferably, however, ω -aminocarboxylic acids, containing 5 and more carbon atoms between the amino and the carboxyl group. Instead of the free aliphatic amino carboxylic acids just as well its condensable derivatives, like anhydrides, esters, nitriles, halides and the like may be employed. Instead of the purely aliphatic amino carboxylic acids also aromatic substituted ones may be applied. Care has to be taken, however, that the substitution does not occur on the primary amino group, as amino carboxylic acids with a secondary amino group react much slower.

It is also possible to use instead of the amino carboxylic acid mixtures of dicarboxylic acids and terminal diamines, which simultaneously are condensed amongst themselves into acid amides,

which afterwards react with the polyamino carboxylic acids.

Amongst the aromatic polyamino carboxylic acids preferably may be mentioned the various diamino benzoic acids, diamino naphthoic acids and the corresponding triamino carboxylic acids, in which still other places of the rings or an amino group may be substituted.

Also such aromatic polyamides may be applied according to our invention which contain more than one carboxyl group, e. g. the 4,4'-diaminodiphenyl-3,3'-dicarboxylic acid or diamino-diphenylmethane - 4,4'-dicarboxylic-acid-p-amino-diphenyl-aspartic acid.

The union of the various amino carboxylic acids is accomplished in the simplest form by melting, which may be done in the presence or absence of an indifferent solvent or non-solvent for the starting components or for the reaction product. The reaction temperature lies at an average within 175-250° C. If polymerization of the reactants into high molecular reaction products occurs already below that temperature range, this takes place very slowly and often without to obtain the maximal chain-length.

High purity of the starting materials and also the exclusion of atmospheric oxygen during the reaction is most important for the quality of the high molecular final product. The pressure in the reaction vessel is far less important. One may work at the normal atmospheric pressure, but also in a vacuum or with excess pressure, according to the steam- and sublimation pressure of the reactants and the kind of reaction-polymerization and/or condensation, whereby water is split off.

Generally it is not necessary to add special catalysts accelerating the polymerization. Most probably the polycarboxylic acid is already enough reaction accelerating. However, if the speed of the reaction is slow, it may be increased by catalysts. The number of catalytically effective substances is great corresponding to the variety of the reaction possibilities. Catalysts of an acid nature are most effective. There may be mentioned inorganic acids i. e. hydrochloric acid, aliphatic and aromatic carboxylic acids, phenols, sulfo acids, hydrohalides of amines or amino carboxylic acids, generally speaking compounds reacting under formation of organic acids. Secondary in this respect are indifferent neutral compounds like diatomaceous earth, active carbon, fuller's earth which essentially are surface active and basic compounds, preferably organic amines.

The field of application of the high polymers is very wide. Besides their usefulness for textile

purposes in the form of filaments they are well suited for the production of films (for photographic and other purposes), plates (as substitutes for glass), sheets or foils (for electric insulation, coating foils for cigarette tips, wrapping foils, adhesive foils, light filters, patterns, stencils, supports for prints or the like), sound records (either those in which the sound track is cut mechanically into the support or is impressed therein without removal of material. (The Edison or the Berliner method)), masses for the reproduction and printing arts, masses for dye-casting and moulding by pressure (production of camera parts and casings for rollfilm or film-packs by pressing or rolling, production of spools or parts thereof for photographic rollfilms by the moulding method), as adhesive or intermediate layers for composite glass. The sheets or foils made from the materials according to this invention may be provided with a metallic coating according to a known process.

The application of the products in form of films, filaments and the like takes place according to known processes: dye-casting, casting from the melt or from solutions, drawing from the molten mass or under pressure below the softening point, warm- and cold stretching, rolling, in order to effect an orientation of the molecules in one or several directions, etc.

Example I

ϵ -aminocapro lactam and 3,5 diamino benzoic acid, both purified by repeated crystallization, are well mixed and heated 20 hours at 200°C in a glass tube in a pure CO₂ atmosphere under quicksilver cover allowing an excess pressure of about 50 mm Hg.

The following variations may be mentioned:

- (a) 3 parts ϵ -aminocapro lactam + 17 parts 3,5-diamino benzoic acid, a resin, stringy in liquid state, red-brown, clear transparent.
- (b) 9 parts ϵ -aminocapro lactam + 11 parts 3,5-diamino benzoic acid, a resin, stringy in liquid state, red-brown, clear transparent.
- (c) 13 parts ϵ -aminocapro lactam + 7 parts 3,5-diamino benzoic acid, a resin, stringy in liquid state, red-brown, clear transparent.
- (d) 15 parts ϵ -aminocapro lactam + 5 parts 3,5-diamino benzoic acid, a resin, stringy in liquid state, of honey-like color, transparent till opaque.
- (e) 19 parts ϵ -aminocapro lactam + 1 part 3,5-diamino benzoic acid, a resin, stringy in liquid state, opaque.

The hardness and the melting point increase from a-e, the latter being capable of being moulded at temperatures above 300°C only. a is capable of swelling in formic acid, b to d are dissolved therein and yield films from this solution, which are brittle except e. a is not soluble in 25 per cent hydrochloric acid, b to e are soluble therein, partly also in acids of lower concentration.

Example II

ϵ -aminocapro lactam is condensed with 1,2-phenylene-diamine-4-carboxylic acid according to Example I as dihydrochloride at 190°C for 24 hours.

The following variations may be mentioned:

- (a) 8 parts ϵ -aminocapro lactam + 12 parts 1,2-

phenylenediamine-4-carboxylic acid, a resin, slightly sticky, bluish, clear transparent.

- (b) 12 parts ϵ -aminocapro lactam + 8 parts 1,2-phenylenediamine-4-carboxylic acid, a resin, slightly sticky, bluish, clear transparent.
- (c) 15 parts ϵ -aminocapro lactam + 5 parts 1,2-phenylene, diamine-4-carboxylic acid, a violet resin.
- (d) 19 parts ϵ -aminocapro lactam + 1 part 1,2-phenylenediamine-4-carboxylic acid.

a and b dissolved in formic acid yield a soft, slightly sticky film, the film from c is somewhat harder, the film from d is still harder.

Example III

ϵ -aminocapro lactam and 2,5-diaminobenzoic-acid-dihydrochloride are mixed and heated as in Example 1 and 2 at 190-210°C for 24 hours.

The following variations may be mentioned:

- (a) 8 parts ϵ -aminocapro lactam + 12 parts 2,5-diaminobenzoic-acid-dihydrochloride, a black-green, sticky condensate.
- (b) 12 parts ϵ -aminocapro lactam + 8 parts 2,5-diaminobenzoic-acid-dihydrochloride, a green, transparent resin, soluble in methanol.
- (c) 15 parts ϵ -aminocapro lactam + 5 parts 2,5-diaminobenzoic-acid-dihydrochloride, a green, transparent, sticky resin, soluble in methanol.
- (d) 19 parts ϵ -aminocapro lactam + 1 part, 2,5-diaminobenzoic-acid-dihydrochloride, opaque, milky brownish resin of great hardness. It is insoluble in methanol, but dissolves readily in formic acid, m-cresol and concentrated sulfuric acid.

Example IV

4.5 grams ϵ -amino caproic acid, several times recrystallized are mixed with 0.5 gram 2,5-diaminobenzoic-acid-hydrochloride and heated at 200-205°C for 24 hours in a glass tube in pure CO₂ atmosphere under quicksilver cover allowing an excess pressure of about 50 mm Hg. A melt is obtained which is stringy in the liquid state, soluble in formic acid and which can be worked up from this solution into a mat brittle film.

If the reactants are mixed in the proportion 3.5:1.5 after heating for 48 hours, a dark colored melt is obtained soluble not only in formic acid, but also in hot water. The film from formic acid is transparent and brittle. If the reactants are mixed in the proportion 4:1 and a catalyst, e. g. ϵ -amino-caproic-acid-hydrochloride is added and the reaction mixture heated under the above mentioned conditions for 24 hours at 200-205°C, a dark-lustrous melt is obtained soluble in methanol and formic acid. After casting of this solution a sticky film is obtained.

Example V

3 parts hexamethylenediammonium adipate and 2 parts pure 3,5-diamino benzoic acid are caused to react at 200°C for 24 hours under conditions as mentioned in the preceding examples. A transparent, red color resin is obtained, not soluble in any solvent.

If the reactants are applied in the proportion 3:2, a transparent resin is obtained less red in color and capable of swelling in formic acid.

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