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POLYAMIDES

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Our present invention relates to polyamides, and in particular to a new method for preparing hydrophilic superpolyamides.

In our co-pending application Ser. No.—
(corresponding with the German application 1 66 310 IVd/120) it has been disclosed that hydrophilic polyamides may be produced by condensing \(\omega \)—monoaminomonocarboxylic acids having at least four carbon atoms between the amino group and the carboxyl group or the derivatives 10 thereof as, for instance, lactams, esters, or amides in the presence of an inorganic acid. According to the acid content one obtains polymeric substances which are water-swellable or yield a colloidal aqueous solution or are transformed from 15 the sol-state of the warm aqueous solution into the gel-state on cooling.

This invention is based on the observation that under similar conditions the reactants of the superpolyamides, i. e. diamines and dicarboxylic 20 acids having long chains or the derivatives thereof, likewise yield hydrophilic, water-soluble condensation products in the presence of inorganic acids.

While polymers stable on boiling and insoluble in water and in usual solvents are obtained by the condensation of the diamines and dicarboxylic acids having long carbon chains, a content of more than 0.1 mol of inorganic acid anion in the polymer effects that the condensation 30 products are capable of strongly swelling in water, alcohols or other hydrophilic solvents or dissolving therein.

As reactants with a long carbon chain mixtures of diamines or derivatives thereof having 35 at least five carbon atoms between the amino groups and dicarboxylic acids or derivatives thereof (if desired substituted by aliphatic or cyclic radicals) having at least four carbon atoms between the carboxyl groups.

As inorganic acids the halogen hydracids are preferably employed. The process of the invention may also be accomplished with other monobasic mineral acids as, for instance, nitric acid or with polybasic inorganic acids.

The condensation or polymerization is conveniently carried out by heating at 200-250°C in the absence of air. It is not necessary to use a special catalyst since the mineral acid already effects a sufficient acceleration of the condensation procedure. The acid is preferably added in the form of the salt of the diamine to be condensed or a derivative thereof.

It is also possible to prepare interpolyamides in which case the choice of the reactants 55 depends on the intended use and may be made regardless of the desired sensitivity to water since

this factor is solely controlled by the mineral acid used.

The new polyamides are used in various forms and for many purposes as, for instance, for gelatin substitutes binding agents, sizing and finishing agents, and thickening agents for printing pastes.

The more detailed practice of the invention is illustrated by the following examples. There, are, of course, many forms of the invention other than these specific embodiments:

Example I

80 g of hexamethylenedlamine adipate and 20 cc of concentrated hydrochloric acid (37.8%) are intimately mixed and heated together in an atmosphere of carbon dioxide at 211-222° C during 20 hours after the air is carefully removed by carbon dioxide. The product thus obtained is yellowish brown and soluble in water and methanol.

If the amount of hydrochloric acid is decreased, water-insoluble polymers are obtained.

Example II

75 g of hexamethylenediamine adipate and 23 g of ϵ -aminocaproic-acid-hydrochloride are intimately mixed and condensed in the same way as described in Example I. The thus resulting product is yellowish brown and soluble in water and hot alcohols.

If the amount of ϵ -aminocaproic-acid-hydrochloride is decreased, products are formed which have a small solubility in water.

Example III

60 g of hexamethylenediamine adipate, 40 g of ϵ -caprolactam and 50 g of ϵ -aminocaproicacid-hydrochloride are polymerized in the manner as described in Example I. The polymer thus prepared is a tenacious transparent yeliow product soluble in water and aqueous alcohols.

If the amount of ϵ -aminocaproic-acid-hydrochloride is lowered to 6.5g, a milky water-insoluble polymer is produced.

Example IV

A mixture of 60.6 g of sebacic acid, 25.9 g of hexamethylenediamine and 23.4 g of hexamethylenediamine hydrobromide is melted and heated at 225° C for 15 hours in absence of air. The polymerization product is a slightly yellow and very tenacious mass soluble in water and warm methanol and can be worked up into transparent films.

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