

ALIEN PROPERTY CUSTODIAN

POLYESTERS

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The present invention relates to polyesters, and more particularly to polyesters containing amide groups.

It is known that highly polymerized products are in general readily obtained by condensing substances capable of forming linear polyamides in appropriate proportions, for instance, ω,ω' -diamines and ω,ω' -dicarboxylic acids and mixtures which contain functional derivatives thereof capable of forming polyamides in the presence of supplemental reactants (such derivatives are, for instance, esters, amides, nitriles, formyl compounds, urethanes, diamine salts of volatile acids, especially those of carbonic acid or formic acid, diisocyanates and compounds forming diisocyanates in the heat) instead of diamines or dicarboxylic acids or besides them, moreover ω' -aminocarboxylic acids and polyamide-forming functional derivatives thereof such as formyl compounds, urethanes, esters, amides lactams, nitriles (in the presence of water or water-forming substances) or mixtures of glycols and diisocyanates or substances forming such compounds. On the other hand one meets with considerable technical difficulties in producing highly polymerized polyesters, specially fiber-forming polyesters, so-called super-polyesters (confer G. V. Schulz, Zeitschrift für physikalische Chemie, 1938 A, volume 182, page 127) by simply condensing the reactants. The same is true in preparing polyesteramides containing in their molecule carboxylic acid ester groups as connecting links in addition to the amide groups. In these cases it is necessary to heat the reactants under a high vacuum for a very long duration (see, for instance, Journal of American Chemical Society, volume 54, pages 1557 et seq., 1566 et seq., and 1579 et seq.).

The present invention has as an object a process of easily preparing highly polymerized polyesters containing amide groups.

Further objects will be seen from the reading of the following description.

These objects are accomplished by first condensing reactants capable of forming polyesters, for instance, hydroxycarboxylic acids having at least five chain-forming atoms between the hydroxyl group and the carboxyl group, substantially equimolecular mixtures of glycols and dicarboxylic acids or aminoalcohols and dicarboxylic acids or mixtures of these compounds to form moderately highly polymerized polyesters or polyesteramides and then heating the obtained substances containing hydroxyl and/or carboxyl groups as reactive end groups with the

addition of a diisocyanate or a compound capable of splitting off a diisocyanate in the heat, until the desired high degree of polymerization is reached, the amount of the added diisocyanate being dependent on the number of the said end groups.

The diisocyanate may be added in one portion or by degrees, which latter step is more conveniently in most cases, for instance, by passing gaseous isocyanate into the liquid reaction mixture, if desired under pressure.

The following reactants can, for instance, be used for the production of the polyesters serving as the starting substance:

15 Hydroxycarboxylic acids such as 6-hydroxycaproic acid, 11-hydroxyhendecanoic acid, 12-hydroxystearic acid, ω -hydroxytetradecanoic acid, p-(ω -hydroxyethyl) benzoic acid.

20 Dicarboxylic acids such as carbonic acid, adipic acid, oxalic acid, succinic acid, maleic acid, glutaric acid, β -methyladipic acid, pimelic acid, sebacic acid, diglycolic acid, dipropylether- ω,ω' -dicarboxylic acid, dipropylsulfide- ω,ω' -dicarboxylic acid, phenylenedipropionic acid, isophthalic acid, 4,4'-diphenyloxydicarboxylic acid.

25 Glycols such as ethyleneglycol, trimethyleneglycol, $\beta\beta'$ -dimethyltrimethyleneglycol, β -methyl- β -n-butyl-trimethyleneglycol, tetramethyleneglycol, hexamethyleneglycol, a mixture of glycols produced by reducing the esters from the acid mixture obtained by the oxidation of technical hexahydroresol, decamethyleneglycol, triethyleneglycol, thiodiglycol.

30 Aminoalcohols such as aminoethanol, 3-amino-propanol, 6-aminohexanol.

The polyesters used as the starting compound are prepared according to the usual methods (see J. Am. Chem. Soc., volume 51, pages 2560 et seq., 2464 et seq., volume 52, page 314 et seq., and volume 55, page 4714).

The following diisocyanates and compounds splitting off diisocyanate on heating may, for instance, be employed for the reaction with the polyesters thus prepared:

45 Tetramethylenediisocyanate, pentamethylenediisocyanate, hexamethylenediisocyanate, octamethylenediisocyanate, decamethylenediisocyanate, m-phenylenediisocyanate, p-phenylenediisocyanate, 4,4'-diphenylenediisocyanate, diisocyanates from γ,γ' -diaminodipropylether, from ethyleneglycol-bis- ω -aminoethylether, from γ,γ' -diaminodipropylsulfide arylcarbamicester from diamines such as hexamethylenediaminebenzidine, di- δ -aminobutylmethylamine, the dicarbamic acid aryl ester from di- δ -aminobutylamine,

the addition products of diisocyanates as, for instance, hexamethylene-diisocyanate and compounds capable of being enolized such as acetoacetic acid ester and dihydroresorcinol.

The process of this invention is not limited to starting substances which are only prepared by condensing compounds of the above-mentioned kind. Such mixed products are likewise useful as in addition to substances adapted to form polyesters contain in their molecule reactants forming polyamides on heating, for instance monoaminomonocarboxylic acids having at least five carbon atoms between the amino and carboxyl groups or combinations of diamines and dicarboxylic acids or are decomposed into three compounds on hydrolysis. Starting materials of this kind are, for instance products obtained by condensing any mixture of ϵ -aminocaproic acid or the lactam thereof and 11-hydroxyhendecanoic acid, the substance prepared by condensing 1 mol of hexamethylenediamine, 2 mols of adipic acid and 1 mol of tetramethyleneglycol, the mixed condensate produces from 1 mol of sebacic acid, 0.8 mol of tetramethylenediamine, and 0.2 mol decamethyleneglycol, and the mixed condensate prepared from 1 mol of adipic acid, 0.5 mol of ω,ω' -dihydroxy di-*n*-butylether, and 0.5 mol of hexamethylenediamine.

Moreover, products containing compounds having basic nitrogen atoms can be used, for example, polyamides containing *N*-methyldiethanolamine or *N*-di- ω,ω' -diaminodibutylamine (prepared from γ -bromobutylbenzamide and methylamine) as the component.

In addition to carboxylic acids linear polyurethanes may also be employed the chain ends of which are alcoholic hydroxyl groups. Such products are obtained according to a known process by reacting diisocyanates with glycols in excess, conveniently in the presence of a solvent.

The starting substances can be heated together with the diisocyanate or compounds forming diisocyanates on heating to form the products of the invention. It is, however, often of advantage to use solvents as, for instance, ethylene chloride, chlorobenzene, dioxane, diethylformamide, or pyridine, as the reaction can thus be carried out especially easily and uniformly. It is convenient to stir the mixture during the reaction in order to distribute the diisocyanate sufficiently. Instead of stirring a boiling solvent can be employed for mixing. It is not necessary that the process of the invention is carried out directly subsequent to the primary condensation; the after-condensation, if desired, for obtaining the superpolymeric condition can also be accomplished later and in another stage. The after-condensation can, for instance, be effected together with a procedure in which the mixture is molded into fibers, foils, coating layers, or shaped articles. Accordingly, the pre-condensate can be cautiously melted together with the necessary amount of diisocyanate and the obtained mass not readily condensed can be stored until it is worked up, for example, into die cast articles. Hard powdered products pre-condensed can also be mixed with a powdered reactant as, for instance, hexamethylene-bis-2-hydroxydiphenylcarbamic acid ester (prepared by reacting the chloroformic acid ester of phenol with hexamethylenediamine or hexamethylene-diisocyanate with the corresponding phenol). The dry, if required, stored mixture is then heated to reaction temperature in the working up.

It is without difficulty to ascertain the amount

of diisocyanate or diisocyanate-forming substance necessary for preparing a polymer as highly polymerized as possible. It is merely necessary to vary the amount of the diisocyanate with respect to the starting material and ascertain the change in viscosity corresponding with the added amount. In order to regulate the relations of the reaction, it is also possible to determine the number of the reactive and groups (carboxyl and/or hydroxyl groups) with the acid of the hydroxyl and acid values or the movable hydrogen (Zerewitinoff) and calculate the amount to be added by means of the equivalent values found. If low-viscous products are required, the optimum amount of the substance to be added is to be reduced or increased as the case may be. The relations are most favorable if the two end groups are carboxyl. Therefore, starting substances are preferred which are prepared with an excess of the carboxyl reactant. It is, however, evident, that products can also be worked up which preferably have hydroxyl end groups. Such products are conveniently used if the formation of gaseous by-products, for instance, CO₂ is to be avoided, for example in after-condensing the reactants in conjunction with a spinning procedure or the like. For controlling the chain length monofunctional substances can be added in a manner known per se, especially compounds slightly volatile as, for instance, carboxylic acids such as stearic acid, *p*-chlorobenzoic acid, and benzaminocaproic acid, alcohols such as naphthylmethylalcohol, octadecylalcohol, and phthalylaminoethynol, or amines such as cyclohexylamine and octadecylamine.

The products highly polymerized of the invention can be worked up into fibers, foils and shaped articles in the same manner as the known highly polymerized polyesters and polyesteramides. They are especially suitable for preparing pliable foils and coatings for paper, fabrics etc. Some products of the invention are also valuable as sizing and finishing agents and the like.

The products of the invention cannot only be worked up into fibers and the like from the melt but in many cases from solutions thereof, for instance in esters, halogenated hydrocarbons or mixtures thereof with alcohols. Some products are also soluble in saturated or unsaturated alcohols and water, especially if the atom chains of the starting substances contain amide-, ether-, or sulfamide groups. The solubility is particularly increased of radicals of amino acids having a relatively short chain as, for instance, of α -aminocaproic acid are present.

Polyesters having incorporated therein a sufficient number of basic amino groups by condensation are soluble in diluted acids such as acetic acid and can be applied from these solutions on fabrics, paper etc.

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 1

A mixture of 1 mol of 9-aminononanoic acid, 1 mol of adipic acid, and 1 mol of decamethyleneglycol is heated at 225° C in an autoclave and an atmosphere of nitrogen for 4 hours. The water formed during the reaction is then cautiously blown off whereupon the mass is heated at 230° C in vacuo for 4 hours. The product obtained on cooling is waxy and hardly capable of being

drawn into useful fibers. A highly polymerized product adapted to form filaments from the melt is prepared by melting the mass with $\frac{1}{20}$ mol of octamethylenediisocyanate for each mol of bi-functional starting substance in the original mixture.

Example 2

A mixture of 1 mol of adipic acid and 1 mol of aminopropanol is heated in an autoclave from 150 to 200° C during 4 hours and kept at 200° C for 1 hour. After the formed water is blown off, the mass is heated at 220° C for 3 hours. $\frac{1}{50}$ mol of hexamethylenediisocyanate in the form of vapor is then passed into the melt whereupon the mixture is heated at 200° for a further hour. The product thus obtained can be worked up into fibers and foils.

Example 3

A completely dry polyurethane prepared by reacting 1 mol of 1,4-butyleneglycol with 0.95 mol of hexamethylenediisocyanate is mixed with 0.045 mol of octamethylenediisocyanate. The mass is then heated in fused condition for 1 hour. The polyurethane above-mentioned can also be mixed with an equivalent amount of diphenyl-4,4-diisocyanate whereupon the mass is melted together and subsequently molded. As the fused substance is low-viscous in the beginning, it can be worked up easily.

Example 4

A mixture of 11 mols of adipic acid and 10 mols of 1,4-butanediol is gradually heated to 180° C, the water splitted off being removed by distilling. After the pressure has been reduced to 10 mm/Hg, the temperature is raised to 200° C and the mass then heated at 200-210° C for 5 hours. On cooling the mass becomes hard and waxy (melting point 49° C, acid number 79). 40 parts (by weight) of this polyester are heated by degrees with 10.5 parts (by weight) of hexamethylene-bis-carbamic acid diphenyl-ester to 200° C whereby a great amount of CO₂ is splitted off, and maintained at this temperature for 1 hour. The phenol formed during this reaction is finally distilled off by heating the mixture in vacuo (water jet pump) at 200° C for 2½ hours. The light brown condensation product obtained on cooling is tenacious and elastic and soluble in methylenechloride, ethylenechlorohydrin and m-cresol. Melting point is 105° C; viscosity (sh/c) of a m-cresolic solution of 0.5 per cent strength is 0.63.

Example 5

A mixture of 10 mols of pentamethyleneglycol and 9 mols of adipic acid is condensed in boiling chlorobenzene until the splitting off of water is finished whereupon the solvent is distilled off and the mass is heated in vacuo at 180° C for 2 hours. The reaction product is then dissolved in methyl-

ene-chloride whereupon an equivalent amount of hexamethylenediisocyanate ascertained according to the method of Zerewitnoff and calculated from the number of the reactive hydrogen atoms is added. Sheets of paper are then impregnated with the solution thus obtained. A tenacious and homogenous impregnation is attained by subsequently heating the paper to 120° C.

Example 6

A mixture of 10 mols of adipic acid and 9 mols of pentamethyleneglycol is condensed in vacuo at 180° C until the splitting off of water is finished. The percentage of carboxyl groups is then determined by titrating a test portion dissolved in alcohol whereupon 1 mol of hexamethylenediisocyanate is added for two carboxyl groups. The mass is then after-condensed under normal pressure at 200-230° C until the viscosity does not increase any longer and the splitting off of CO₂ has ceased. The melt is especially suitable for forming filaments. With a glass rod filaments 10 m and more long can be drawn from the melt. The filaments are elastic like gum and can therefore be used as rubber substitute. They have the advantage over threads of rubber that they are resistant to aging. Foils produced from material after-condensed may be employed for the manufacture of protecting jackets and coverings.

The resistance to heat of the polymers can be increased by using suitable reactants as, for instance, fumaric acid, p-phenylenedipropionic acid, and high-melting glycols.

A specially elastic polymer is obtained by substituting β,β -dimethyltromethyleneglycol for pentamethyleneglycol.

Example 7

A mixture of 1 mol of maleic anhydride and 0.9 mol of 1,4-butanediol is heated to 180° C in an atmosphere of nitrogen and the presence of 0.18 gram of hydroquinone during 4 hours. After the pressure has been reduced to 10 m/Hg the temperature is kept additional 2 hours. The product obtained on cooling is yellowish white, soft and waxy. If this product is heated with 5.2% of its weight of hexamethylenediisocyanate from 100 to 180° C during 2 hours, a polymer is produced which is tenacious, foamy, rubber-like, soluble in warm ethylenechlorohydrin, and moldable by rolling.

If the mixture of the reactants is heated at 150° C instead of 180° in the first and second stage, a polymer more soluble than that above-mentioned is produced from the melt of which filaments elastic like rubber can be drawn. On heating in open air this polyester becomes insoluble in the solvents in the same manner as the known maleic acid polyesters.

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