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Polylactones and their preparation

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POLYLACTONES AND THEIR PREPARATION

This is a divisional patent (application) from parent patent application 87/15214 (publication No. 2 192 202 A).

The invention provides poly-α-hydroxyacrylic acid polylactones, the molecular weight of which is such that upon hydrolysis to the corresponding sodium poly-α-hydroxyacrylate the average molecular weight Mw of this sodium salt is 2000 to 10'000 and the process for their production.

Preferred poly-α-hydroxyacrylic acid polylactones are those which upon hydrolysis to the corresponding sodium poly-α-hydroxyacrylate have an average molecular weight Mw of the sodium poly-α-hydroxyacrylate from 3000 to 10'000, more preferably 4000 to 8000. By average is meant an average in the weight. The molecular weight of these polymers may be measured according to known methods, e.g. by means of gel permeation chromatography. The molecular weights indicated above are as determined by gel permeation chromatography using a 10% aqueous solution of sodium poly-α-hydroxyacrylate at a pH of 6.5-7. Preferably the sodium poly-α-hydroxyacrylate is obtained by hydrolysis of the corresponding polylactone with a buffer salt having a buffering action at pH 6.5 to 7.5, particularly a phosphate buffer.

The polylactones may be prepared by polymerization of α-chloroacrylic acid in an aqueous acidic medium.

The concentration of the α-chloroacrylic acid in the aqueous reaction medium may advantageously be from 5 to 70 % by weight, preferably from 5 to 40 % by weight. Polymerization is conveniently carried out at a temperature within the range of 40-150°C, preferably 60-98°C, more preferably 70-90°C, advantageously in the presence of a polymerization catalyst. Suitable catalysts are for example water-soluble azo-bis-compounds such as 4,4'-azo-bis-(4-cyanopentanoic acid) or 2,2'-azo-bis-(2-aminodipropane) dihydrochloride; a peroxy compound such as benzoyl hydroperoxide, cumene hydroperoxide, dibenzoyl peroxide, sodium perborate, hydrogen peroxide or potassium or ammonium peroxydisulphate. Preferred polymerisation catalysts are the peroxy compounds, particularly potassium and ammonium peroxydisulphate and hydrogen peroxide, the latter being especially preferred. Hydrogen peroxide may be added as such to the reaction medium or used as hydrogen peroxide-yielding compound, e.g. potassium peroxide. Preferably hydrogen peroxide is added directly to the reaction medium.

It may also be advantageous to carry out the polymerization in the presence of a chain transfer agent, e.g. a thiol compound such as mercaptoethanol, thiophenol or ethyl thioglycolate. Preferably, however, the polymerization is carried out in the absence of a chain transfer agent. To regulate the molecular weight within the desired range e.g. to keep it low, it is preferred to vary reaction parameters, for example the temperature or the amount of catalyst.

Hydrogen peroxide is advantageously used in an amount of from 3.5 to 11 g, preferably 7 - 10 g per mole of α-chloroacrylic acid.

When the catalyst is a peroxy compound of a higher molecular weight than hydrogen peroxide, it is used in a corresponding amount.

Polymerization is conveniently carried out at a pH value between 1 and 5. The reaction mixture may be acidified with an inorganic or organic acid, for example sulphuric, hydrochloric or phosphoric acid or an aromatic sulphonic acid such as p-toluene sulphonic acid. Hydrochloric acid is preferred.

The reaction steps to give the polymeric compound comprise a polymerization step to poly-α-chloroacrylic acid (optionally partially in the salt form when the α-chloroacrylic acid is used for example in an alkali metal salt form), the hydrolysis of the chlorine located in the α-position to the carboxylic acid and lactonization. Lactonization may be partial or full. The resulting polylactone is insoluble in water and is present as a solid in the aqueous reaction medium. It may be isolated and purified by any known method, e.g. filtration or centrifuging. If desired, the polylactone may be converted into the corresponding poly-α-hydroxyacrylic acid salts by reaction with an aqueous base, e.g. an alkali metal hydroxide, e.g. lithium, sodium or potassium hydroxide, ammonium hydroxide or an amine, e.g. a mono-, di- or tri-C_{1-4}alkyl or -C_{2-4}alkanolamine, particularly tri(C_{2-3}alkanol)amine, or a buffer salt derived from such a base and having a buffering action at pH 6 to 8 preferably at pH 6.5 to 7.5, the alkali metal hydroxides, especially sodium hydroxide, being preferred. The poly-α-hydroxyacrylic acid salts may also be obtained directly without any intermediary isolation of the polylactone, by addition of an aqueous base to the polylactone-containing reaction mixture.

The following Examples, in which the percentages are by weight and the temperatures are in degrees Centigrade, illustrate the invention.

Example 1

1120 g demineralized water, 175.5 g sodium chloride and 385.5 g sodium α-chloroacrylate are introduced at room temperature in a 2.5 l flask equipped with stirrer and thermometer. 180 g of a 30 % hydrochloric acid solution are then added dropwise within 30 minutes at such a rate that the temperature does not exceed 40° (pH = 2.5). Thereafter 75 g of 35 % hydrogen peroxide are added in the course of 5 minutes, the reaction mixture is heated within one hour from 40° to 75° and stirred for three hours at 75°. After cooling to room temperature, the resulting polylactone is filtered and then washed with 9000 g demineralized water. There is obtained a beige filtration cake having a dry content of 27 %. The filtration cake is dried at 110°.

Example 2

632 g of the wet filtration cake as obtained in Example 1 are suspended with stirring in 1606 g demineralized water. 201 g of a 30% sodium hydroxide are then added dropwise within 10 minutes, the temperature rising to 30-32°. The resulting mixture is further stirred at 30-32° and at a pH of 6.5-7 for 50 minutes. Thereafter 7 g of 35 % hydrogen peroxide are added and the mixture is stirred for 30 minutes. The resulting yellowish solution can be either evaporated to dryness, or used directly as such. The resulting sodium poly-α-hydroxyacrylate has a molecular weight of 5260 and the polydispersity Mw/Mn obtained by gel permeation chromatography (measured by using standard polyacrylic acid) is 3.17.

Example 3

The procedure of Example 1 is repeated to the production of the polylactone suspension. The resulting polylactone suspension is not filtered but reacted directly with 450 g of a 30 % sodium hydroxide solution at 50-60°. To the resulting slightly turbid, brown red solution there is added 7 g of 35 % hydrogen peroxide and the whole mixture is stirred at 60° for 30 minutes.

The resulting sodium poly-α-acrylate has a molecular weight Mw of 4865 and a polydispersity Mw/Mn of 5.41 (measured as disclosed in Example 1).

Example 4

The procedure of Examples 1 and 2 is repeated but using 60 g of 35 % hydrogen peroxide instead of 75 g as polymerization catalyst. The resulting sodium poly-α-hydroxyacrylate has a molecular weight Mw of 6200.

Example 5

The procedure of Examples 1 and 2 is repeated but using 45 g of 35 % hydrogen peroxide instead of 75 g. The resulting sodium poly-α-hydroxyacrylate has a molecular weight Mw of 7000.

Example 6

The procedure of Examples 1 and 2 is repeated but using 30 g of 35 % hydrogen peroxide instead of 75 g. The resulting sodium poly-α-hydroxyacrylate has a molecular weight Mw of 10'000.

Example 7

75 g of a 12 % hydrochloric acid solution are introduced in a 1.5 l flask and heated to 70°. From two separated dropping funnels, there added simultaneously within one hour 64 g of sodium α-chloroacrylate dissolved in 233 g water and 25 g ammonium peroxydisulphate dissolved in 35 g water. The temperature is kept

constant at 70-72°. The resulting polylactone percipitates. When the reaction is complete, the polylactone is filtered, washed with water and dried. Yield: 35 g polylactone having after hydrolysis with a sodium dihydrogeno phosphate / disodium hydrogeno phosphate buffer into the sodium salt a molecular weight Mw of 10,000.

Example 8

The procedure of Example 7 is repeated but the temperature is kept constant at 80-82° instead of 70-72°. Yield: 35 g polylactone having after hydrolysis with a sodium dihydrogeno phosphate/disodium hydrogeno phosphate buffer into the sodium salt a molecular weight Mw of 6000.

Example 9

The procedure of Example 7 is repeated but the temperature is kept constant at 90-92° instead of 70-72°. Yield: 34 g polylactone having after hydrolysis with a sodium dihydrogeno phosphate/disodium hydrogeno phosphate buffer into the sodium salt a molecular weight Mw of 3500.

Claims: -

1. A poly-α-hydroxyacrylic acid polylactone, the molecular weight of which is such that upon hydrolysis to the corresponding sodium poly-α-hydroxyacrylate the average molecular weight Mw of this sodium salt is 2000 to 10'000.

2. A process for the production of a polylactone according to Claim 1, comprising polymerizing α-chloroacrylic acid in an aqueous acidic medium.

3. A process according to Claim 2, in which the polymerization is carried out in the presence of a peroxy compound as polymerization catalyst.

4. A process according to Claim 2 or 3 in which α-chloroacrylic acid is polymerized in an aqueous acidic medium using from 3.5 to 11g hydrogen peroxide or an equivalent amount of a peroxy compound of a higher molecular weight per mole of α-chloroacrylic acid as polymerization catalyst.

5. A polylactone as obtained by a process according to any one of Claims 2 to 4.

6. A process for the production of a water-soluble poly-α-hydroxyacrylic acid salt (a) comprising reacting a polylactone according to Claim 1 or 5 with an aqueous base or a buffer salt thereof.

7. A process for the production of a poly-α-hydroxyacrylic acid polylactone substantially as herein described with reference to Examples 1 and 3 to 9.

8. A poly-α-hydroxyacrylic acid polylactone substantially as herein described with reference to Examples 1 and 3 to 9.

9. A process for the production of a water-soluble poly-α-hydroxyacrylic acid salt, substantially as herein described with reference to Examples 2 to 9.

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