

PROCESS FOR THE PRODUCTION OF POLYLACTONES OF POLY-[α -HYDROXY-(ACRYLIC AND/OR CROTONIC) ACID]

The present invention relates to the production of polylactones of poly-[α -hydroxy-(acrylic and/or crotonic)acid] and of the corresponding poly-(α -hydroxy-acrylates and/or -crotonates).

According to the invention there is provided a process for the production of polylactone of poly-[α -hydroxy(acrylic and/or crotonic)-acid] comprising the steps of chlorinating an alkyl acrylate or an alkyl crotonate or a mixture thereof to the corresponding 2,3-dichloropropionic acid alkylester or 2,3-dichlorobutanoic acid alkylester or mixture thereof and treating the so produced 2,3-dichloropropionic acid alkylester or 2,3-dichlorobutanoic acid alkylester or mixture thereof with an aqueous base to dehydrochlorinate it and convert it into the corresponding salt followed by acidification and polymerisation and conversion into the polylactone of poly-[α -hydroxy-(acrylic and/or crotonic)acid] under acidic conditions, provided that the process is carried out without isolation of the intermediate products.

Any alkyl ester residue is preferably C_{1-4} -alkyl, more preferably linear C_{1-4} -alkyl, particularly n-butyl, n-propyl, ethyl or methyl, ethyl and methyl being most preferred.

The chlorination of the starting acrylic and/or crotonic acid ester is conveniently carried out in the absence of a solvent (also of water). The addition reaction of chlorine is effected by direct addition of chlorine in gas form, advantageously in the presence of a chlorination catalyst. Preferably the catalyst is a N-substituted amide of a carboxylic acid, advantageously of a C_{1-9} -aliphatic carboxylic acid, preferably a C_{1-4} -aliphatic carboxylic acid, espe-

cially acetic or formic acid. The amide residue may bear one or two C_{1-12} -hydrocarbon residues, preferably one or two C_{1-4} -hydrocarbon residues, especially methyl or ethyl. Particularly preferred as a catalyst is dimethylformamide. The chlorination catalyst is conveniently used in a concentration of from 0.01 to 5%, preferably from 0.5 to 5% by weight based on the weight of the ester. The chlorination is conveniently carried out in the absence of light, at a temperature from 0 to 70°C, preferably from 15 to 50°C. An excess of chlorine may be used, e.g. up to 10 mol %; however, a stoichiometric amount of chlorine may be sufficient to obtain an optimal chlorination degree in a closed vessel.

Directly thereafter, without isolating, the resulting 2,3-dichloropropionic and/or -butanoic acid alkylester is dehydrochlorinated and saponified in the presence of an aqueous base. Suitable bases include an alkali metal hydroxide such as NaOH, KOH or LiOH or ammonium hydroxide, ammonium hydroxide and especially sodium hydroxide being preferred. Dehydrochlorination and saponification are carried out almost simultaneously, advantageously at a temperature from -10°C to +60°C, preferably from 0° to 60°C, particularly from 20° to 40°C. The base is conveniently added in such an amount and at such a rate that the alkaline conditions are maintained during the whole dehydrochlorination and saponification. The base may be added either at a stoichiometric amount or in excess, e.g. up to 70 mol % per one mole ester, in a single portion, portionwise or continuously. Dehydrochlorination and saponification may be carried out in an aqueous medium containing an inert salt. When ammonium hydroxide is used as a base, it may be advantageous to add an alkali metal halogenide to the reaction mixture, preferably sodium chloride; preferably a concentrated brine such as a 20-30% sodium chloride solution is added to the reaction mixture. The concentration of the 2,3-dichloro-ester in the aqueous reaction mixture may advantageously be from 5 to 70% by weight, preferably from 5 to 20%, particularly from 7 to 15% by weight.

After dehydrochlorination and saponification are complete, the reaction mixture is acidified to a pH < 7, preferably to a pH from 1 to 5, advantageously by addition of a strong organic or inorganic acid, for example sulphuric acid, hydrochloric acid, phosphoric acid, or an aromatic sulphonic acid such as p-toluene-sulphonic acid; hydrochloric acid is preferred. The temperature may be within the range of -10° to +60°C, preferably 0°C to 40°C. For the further polymerisation step it may be advantageous to acidify only to the extent that a mixture of free acid and the corresponding alkali metal or ammonium salt is obtained. The acid should be added in an amount sufficient to neutralize the excess of base and to convert only a part of the α -chloroacrylic and/or α -chlorocrotonic acid salt into the corresponding free acid form. In general 0.4 to 2 moles, preferably 0.4 to 1 mol acid (preferably hydrochloric acid) are added per mol alkylester.

The α -chloroacrylic acid and/or α -chlorocrotonic acid may be obtained either in the free acid form or admixed with the salt form depending on the pH conditions.

If it is desired to store temporarily the monomeric acid or acid salt in solution without polymerising, it may be advantageous to add a polymerisation inhibitor, conveniently hydroquinone or hydroquinone monomethyl ether. The inhibitor is conveniently added in an amount from 30 to 100 ppm based on the weight of the monomer.

The polymerisation of α -chloroacrylic acid or α -chlorocrotonic acid (or copolymerisation in the case of a mixture of both acids) is conveniently carried out under acidic conditions, preferably at a pH in the range of 1-5, more preferably 1-3.5, in the same aqueous medium in which the monomeric acid was produced. A catalyst as commonly used for a polymerisation reaction is added to the reaction medium, e.g. an azo compound, particularly 4,4'-azo-bis-(4-cyanopentanoic acid) or azo-bis-iso-butyronitril, a peroxy compound such as, cumene hydroperoxide, sodium perborate, hydrogen peroxide or

potassium peroxodisulphate, or a redox system comprising as oxidant a peroxy compound as indicated above, and a reducing agent, for example sodium dithionite or sodium bisulphite. Of the above catalysts the per-compounds are preferred, in particular hydrogen peroxide; the hydrogen peroxide may be used as such or in the form of an H_2O_2 -yielding compound, e.g. potassium peroxide, the direct use of hydrogen peroxide being preferred. The catalyst may be used in the usual amounts, e.g. in an amount of at least 0,0001 mole of catalyst per mole of monomer. If the catalyst is an azo compound it is preferably used in amounts of 0.0001 to 0.005 moles, more preferably 0.0002 to 0.003 moles per mole of monomer. If the catalyst is a per-compound (in particular H_2O_2) it is preferably used in amounts of 0.005 to 3.25 moles per mole of monomer. For the production of polymers with an average molecular weight M_w of the sodium salts in the range of 2000 to 10'000 (preferably 3000-10'000, more preferably 4000-8000) the per-catalyst is preferably used in amounts of 0.1 to 3.25, more preferably 0.2 to 3 moles per mole of monomer. Polymerisation (or copolymerisation) is conveniently carried out at a temperature $\geq$ room temperature and $\leq 150^\circ C$, depending on the catalyst used. When a redox system is used as a catalyst, polymerisation may be carried out at a temperature of at least $20^\circ C$; in the presence of a peroxy compound, polymerisation may be effected at a temperature of at least $40^\circ C$, preferably of at least $50^\circ C$; when azo compounds are used as catalysts, polymerisation may conveniently be carried out at a temperature of at least $60^\circ C$, preferably of at least $70^\circ C$. If desired, polymerisation may be carried out in an autoclave. Preferred temperature ranges are 80 to $105^\circ C$ when an azo compound is used as a polymerisation catalyst, and 70 to $90^\circ C$, in particular $< 80^\circ C$ when a peroxy compound is employed as a polymerisation catalyst.

Depending on the desired molecular weight, it may be advantageous to add, before polymerisation, a chain transfer agent, e.g. thioglycolic acid, methyl thioglycolate, SH_2 , nC_{2-4} mercaptans or a water-soluble alcohol, in catalytic amounts.

5 The exchange of the α -chlorine atom by a hydroxy radical in the polymer may conveniently be carried out within the same temperature range and under analogous pH-conditions as disclosed above for the polymerisation. Preferably the chlorohydrolysis is effected almost simultaneously with the polymerisation. As soon as the α -chlorine atom is replaced by hydroxy, lactonization takes place and the polylactone is produced almost simultaneously. Lactonization may be partial or full.

10 The resulting polylactones are insoluble in water and are present as a solid in the aqueous reaction medium. They may be isolated and purified by any known method, e.g. filtration or centrifuging and rinsing with water. If desired, the polylactone may be converted into the corresponding poly-(α -hydroxy-carboxylic acid) salts by reaction with an aqueous base, e.g. an alkali metal hydroxide, e.g.
15 LiOH, NaOH or KOH, ammonium hydroxide or an amine e.g. tri-(β -hydroxy- C_{2-3} -alkyl)amine, preferably sodium hydroxide. The poly-(α -hydroxy-carboxylic acid) salts may also be obtained directly without an intermediary isolation of the polylactone, by addition of an aqueous base to the polylactone-containing reaction mixture.

20 The molecular weight of the resulting polymers whether in lactone or salt form may vary. Advantageously they have an average molecular weight of from 1,000 to 1,000,000, preferably from 1,000 to 500,000, particularly from 2000 to 140,000 (referred to the sodium salt).

25 The polylactones and the corresponding poly-(α -hydroxy-carboxylic acid) salts, particularly poly-(α -hydroxy-acrylic acid) salts are known compounds. They are used e.g. as sequestering agents, auxiliaries in alkaline peroxy bleaching liquors or as dispersing agents.

30 The process of the invention is particularly advantageous in that a

polylactone is produced directly from alkyl acrylate and/or crotonate with a high yield and without any intermediary isolation step, and may be carried out in one vessel (as a one-pot process).

5 According to a preferred embodiment of the invention, the poly-
lactone of a poly-(α -hydroxy-acrylic acid), or an alkali metal poly-
(α -hydroxy-acrylate) are prepared.

The following Examples illustrate the invention. So far as not otherwise indicated, all percentages are by weight and all temperatures in degrees Celsius.

10 Example 1

86g (1 Mole) methyl acrylate and 2.58g dimethylformamide are introduced at room temperature in a three-necked flask. After purging the flask with nitrogen, 71g chlorine are passed into the mixture in the absence of light at room temperature, at such a rate that
15 the temperature does not exceed 30°. Methyl 2,3-dichloropropionate is obtained with purity degree $\geq$ 94%.

A solution of 50g sodium hydroxide in 285ml water is added dropwise to the resulting methyl 2,3-dichloropropionate over two and a half hours at such a rate that the temperature is kept between -5 and
20 0°. After a further 2.5 hour period, a solution of 50g sodium hydroxide in 70ml water is added dropwise to the reaction mixture at such a rate that the temperature does not exceed 0°. The resulting mixture is then stirred at 0° for 5 hours and afterwards let to stand overnight at 0-15°. The resulting sodium α -chloro-acrylate
25 is converted at 0° by the addition of 100g 36% HCl into α -chloro-acrylic acid, the reaction mixture having a pH of 2.5.

Without isolating the α -chloroacrylic acid, the reaction mixture is heated to 95-98° and a solution of 0.34g 4,4'-azo-bis-(4-cyanopentanoic acid) in 60ml water is added thereto dropwise with stirring

over 15 hours together with a few drops of 2N sodium hydroxide, whereby a solid is precipitating. The reaction mixture is then further heated at the boil with reflux for 3 hours. After cooling, the reaction mixture is filtered, the filtration cake is washed with water and then dried. 81.4g Polylactone of the poly-(α -hydroxy-acrylic acid) are thus obtained with a yield of 90% according to microanalysis.

Example 2

The procedure of Example 1 is repeated with the following modification:

440g of a 26% sodium chloride brine are added to the resulting methyl 2,3-dichloro-propionate. After cooling to 0°, 163.2g of a 25% solution of ammonium hydroxide (calculated as NH_3) are added dropwise over one hour at such a rate that the temperature remains below 0°. Thereafter the reaction mixture is stirred at 0° for five hours and then let to stand overnight at 0-15°. The mixture is then further treated as disclosed above in Example 1 to yield the polylactone.

Example 3

258g Methyl acrylate are introduced in a 750ml 4-necked flask and mixed with 7.7g dimethylformamide. After purging the flask with nitrogen, 213g chlorine are passed through the mixture in the absence of light. The temperature raises from 20° to 40-45° but should not exceed 45°. When the chlorine addition is complete, the mixture is further stirred at 45° for 30 minutes to complete the reaction; thereafter it is heated to 50° and evacuated until no further chlorine escapes from the medium. 477g methyl 2,3-dichloro-propionate with a purity of $\geq 97\%$ and corresponding to 99.6% of the theoretical yield are thus obtained.

159g of the resulting methyl 2,3-dichloro-propionate and 239g water are introduced into a four-necked flask. While stirring 266g of a 30% sodium hydroxide solution are added dropwise during three hours at a temperature not exceeding 40°. Thereafter a clear solution of sodium α -chloroacrylate is obtained to which there are further added dropwise 50g of a 38% HCl solution during about 60 minutes at a temperature not exceeding 40°. The resulting pH is 2.5. The reaction mixture is heated to 95° and then a solution of 0.113g 4,4'-azo-bis-(4-cyanopentanoic acid) in 20ml water is added thereto dropwise over one hour. When the addition of the catalyst is complete, the reaction mixture is heated to 95° for a further one hour period and, after cooling to room temperature, the resulting precipitate is filtered, washed free from chlorine and dried at 50° under vacuo. During the addition of the catalyst, the ester is submitted successively to polymerisation, chlorohydrolysis and lactonization. At the end of the reaction, the precipitation of the polylactone of the poly(α -hydroxy-acrylic acid) is substantially complete.

Yield: 73.5f of a white powder having a carbon atom content of about 45%.

Example 4

The procedure of Example 3 is repeated but replacing the 0.113g 4,4'-azo-bis-(4-cyanopentanoic acid) as catalyst by 1g 37% hydrogen peroxide. The yield, the C-analysis and the aspect of the resulting polylactone correspond to that of the polymer of Example 3.

Example 5

The procedure of Example 4 is repeated but the polymerisation is effected at 75° in the presence of 5g of 40 vol.% hydrogen peroxide instead of 95° and the reaction mixture is further treated at 75° for one hour to complete the reaction. The yield, the C-analysis

and the aspect of the resulting polylactone are similar to those of the polymer of Example 4.

Example 6

5 The procedure of Example 5 is repeated but 0.003g thioglycolic acid are added to the reaction mixture before adding the hydrogen peroxide. The yield, the C-analysis and the aspect of the resulting polylactone are similar to those of the polymer of Example 5.

Example 7

10 258g of methyl acrylate are introduced in a 2.5 l flask equipped with a stirrer and a thermometer and 7.7g of dimethylformamide are added. 213g of chlorine are then passed in the absence of light into the mixture at such a rate that the temperature of the mixture does not exceed 40°. When the chlorination reaction is completed, the chlorine in excess is eliminated with vacuo. The obtained product is stirred with 503g of demineralized water until a good distribution of the organic phase in water is obtained. 800g of a 30% sodium hydroxide solution are then added dropwise. The temperature rises from 20° to 40° and is then maintained at 40°C by cooling. After 2½ hours the dropwise addition is complete. The mixture is maintained at 40° for further 30 minutes, after which 180g of a 30% hydrochloric acid solution are added dropwise within 30 minutes at this temperature to the obtained sodium α-chloroacrylate solution. After the acid addition the pH of the reaction solution is ca. 2.5. 75g of 35% hydrogen peroxide are then added within 5 minutes by which the reaction mixture becomes turbid. The reaction mixture is then heated continuously within one hour from 40 to 75°, stirred for further 3 hours at 75° and then cooled to room temperature. The obtained polylactone suspension is suction-filtered and washed with 9000 g of demineralized water. There is obtained a beige filtration cake having a dry content of 27%. The filtration cake is dried at 110°.

15
20
25
30

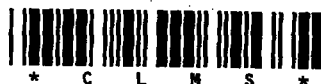
Example 8

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

The resulting sodium poly(α -hydroxy-acrylate) has a molecular weight Mw of 4865.

CLAIMS:

1. A process for the production of polylactone of poly-[α -hydroxy-(acrylic and/or crotonic)acid] comprising the steps of chlorinating an alkyl acrylate or an alkyl crotonate or a mixture thereof to the corresponding 2,3-dichloropropionic acid alkylester or 2,3-dichlorobutanoic acid alkylester or mixture thereof and treating the so produced 2,3-dichloropropionic acid alkylester or 2,3-dichlorobutanoic acid alkylester or mixture thereof with an aqueous base to dehydrochlorinate it and convert it into the corresponding salt followed by acidification and polymerisation and conversion into the polylactone of poly-[α -hydroxy(acrylic and/or crotonic)acid] under acidic conditions, provided that the process is carried out without isolation of the intermediate products.
2. A process according to Claim 1, in which an acrylic acid alkylester or a crotonic acid alkylester or a mixture thereof is chlorinated in the presence of an N-substituted carboxylic acid amide used as a chlorination catalyst.
3. A process according to Claim 1, in which the dehydrochlorination and the conversion into the salt form are carried out in the presence of an aqueous solution of an alkali metal hydroxide or ammonium hydroxide.
4. A process according to Claim 1, in which the acidification is carried out by addition of a strong organic or inorganic acid to obtain a pH from 1 to 5.
5. A process according to any of Claims 1 to 4, wherein the obtained polylactone is hydrolyzed with an aqueous base to the corresponding poly-(α -hydroxy-carboxylate).



6. A process according to Claim 5, wherein the polylactone is hydrolyzed without isolating it from the mother liquor.

7. A process according to any of Claims 1 to 4 as hereinbefore described, with particular reference to any one of Examples 1 to 7.

5

8. A process according to Claim 5 or 6 as hereinbefore described, with particular reference to Example 8.



* C L M S *