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(21) International Application Number: PCT/GB94/02748 (22) International Filing Date: 16 December 1994 (16.12.94) (30) Priority Data: 9326511.4 29 December 1993 (29.12.93) GB (71) Applicant (for all designated States except US): SOLVAY INTEROX LIMITED [GB/GB]; Baronet Works, Baronet Road, Warrington, Cheshire WA4 6HB (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): WASSON, Robert, Craig [GB/GB]; 3 Speedwell Close, Barnston, Wirral L60 2TB (GB). (74) Agent: PEARCE, Timothy; Solvay Interlox Limited, Patent Dept., P.O. Box 51, Moorfield Road, Widnes WA8 0FE (GB).		(81) Designated States: AU, BR, JP, KR, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: MACROMONOMER PREPARATION (57) Abstract A process for the preparation of macromonomers by reaction between a lactone and a hydroxyalkylacrylate in the presence of > 200 ppm phosphoric acid catalyst is provided. The reaction takes place in the presence of a free radical inhibitor at a temperature of from 100 to 130 °C. Preferably, the lactone is ϵ -caprolactone and the hydroxyalkylacrylate is selected from the group consisting of 2-hydroxyethylacrylate and 2-hydroxyethylmethacrylate.		

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Macromonomer Preparation

This invention concerns a process for the preparation of macromonomers. More specifically, this invention concerns a process for preparing macromonomers by reaction of a lactone with a
5 hydroxyalkylacrylate.

Lactones have found wide applicability as monomers in the preparation of many different polymers, particularly polyesters and polyurethanes. In addition, lactones can be used in the preparation of monomers containing a plurality of reactive sites. Such monomers are often referred to as
10 macromonomers, and have found particular application in the preparation of cross-linked polymers and polymers where further chemical modification is desirable. Important examples of macromonomers result from the reaction between a lactone and a hydroxyalkylacrylate.

The reaction between a lactone and a hydroxyalkylacrylate requires the
15 presence of a catalyst in order to achieve a commercially acceptable rate of reaction at a moderate temperature. Use of a moderate temperature is important not only for economic reasons but also because use of too high a temperature can cause extreme discolourisation of the macromonomer product.

20 In US Patent 3,655,631, strong organic carboxylic or sulphonic acids are proposed as catalysts. There is some concern that when these acids remain in the subsequently-produced polymer they could result in reduced shelf life of the polymer.

In UK Patent Application 2,101,121, tin dihalides are taught for use as
25 catalysts for the reaction between lactones and a hydroxyalkylacrylates. Recently, there has been some concern over the toxicological properties of heavy metal compounds.

EP-A-0 108 372 teaches the use of a wide range of catalysts, including protonic acids at concentrations below 200 ppm in the reaction product
30 although only tin compounds are exemplified. A repeat of example 1 of this application produced a gelled product having a high yellow colouration. This indicates that the processes taught in this application can be difficult to control because gelling is commonly caused by cross-linking of the macromonomer during its manufacture. Gelling is also undesirable because it renders the
35 macromonomer intractable and unusable. Additionally, many of the applications in which macromonomers are employed, for example in the paints industry, require a substantially colourless product, so that the yellow colouration present would result in this product being unacceptable.

In Japanese patent application 61043623, perchloric acid is taught as a suitable catalyst. Perchloric acid, however, is extremely reactive and can readily form explosive mixtures with organic compounds, so it would be desirable to identify a catalyst that did not have such hazardous properties.

5 The processes of the prior art notwithstanding, it remains desirable to identify additional and further process for the production of macromonomers by the reaction of lactones with hydroxyalkylacrylates.

It is a first object of the present invention to provide a new or modified process for the production of macromonomers by the reaction of lactones with
10 hydroxyalkylacrylates.

It is a second object of some or further aspects of the present invention to provide a process for the production of macromonomers by the reaction of lactones with hydroxyalkylacrylates that avoids or ameliorates the problems associated with the processes of the prior art.

15 According to the present invention, there is provided a process for the preparation of macromonomers by the catalysed reaction between a lactone and a hydroxyalkylacrylate, characterised in that the catalyst comprises phosphoric acid at a concentration of greater than 200 mg/kg, preferably greater than 250 mg/kg, of reaction mixture, and that the process is carried
20 out at a temperature of from 100°C to 130°C.

Although EP-A-O 108 372 names a number of possible catalysts for the reaction between a lactone and a hydroxyalkylacrylate, it does not specify phosphoric acid.

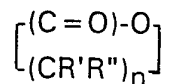
During the course of the studies leading to the present invention, it was
25 surprisingly found that when phosphoric acid was employed as a catalyst for the reaction between a lactone and a hydroxyalkylacrylate at a concentration greater than the range for protonic acids recommended in EP-A-O 108 373, an easily controllable reaction occurred that enabled the production of a product having a markedly reduced yellow colouration compared with that of Example
30 1 of EP-A-O 108 373.

Phosphoric acid catalyst is employed in the process according to the present invention at a concentration of greater than 200 mg/kg, preferably greater than 250 mg/kg, of reaction mixture. It will be recognised that the actual concentration employed can vary widely, and will in many
35 embodiments be selected considering other process factors, for example, the desired reaction rate and the desired reaction temperature. The concentration of phosphoric acid employed is unlikely to be greater than about 2000 mg/kg and is often preferably less than 1000 mg/kg of reaction

mixture. In certain embodiments of the present invention, good results have been achieved employing a phosphoric acid concentration in the range of from 300 mg/kg to 750 mg/kg, and particularly from 400 to 600 mg/kg.

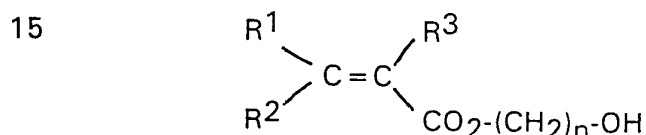
Lactones that can be employed in the process according to the

5 present invention have the general chemical formula:



wherein R' and R'' are independently hydrogen atoms or alkyl groups having up to 12 carbon atoms and n is from 3 to 7. Preferably the total number of
10 carbons in R' and R'' is 0 or 1 to 4. Particularly preferably, the lactone is ϵ -caprolactone.

Many hydroxyalkylacrylates that can be employed in the process according to the present invention have the general chemical formula:



where R¹, R² and R³ are independently hydrogen atoms, aryl groups or short
20 chain alkyl groups having up to 4 carbon atoms, and n is an integer from 1 to 6, preferably from 2 to 4. Examples of such hydroxyalkylacrylates include 2-hydroxyethylacrylate, 2-hydroxyethylmethacrylate, 3-hydroxypropylacrylate, 3-hydroxypropylmethacrylate, 4-hydroxybutylacrylate and 4-hydroxybutylmethacrylate. Further hydroxyalkylacrylates that can be
25 employed include those where the hydroxyl group is a secondary or tertiary hydroxyl group and/or the hydroxyalkyl group is substituted with one or more substituents including for example, additional hydroxyl groups, short chain alkyl groups and halogens. Examples of these further hydroxyalkylacrylates include 2-hydroxypropylacrylate, 2-hydroxypropylmethacrylate, 2-hydroxy-3-
30 chloropropylacrylate, 2-hydroxy-3-chloropropylmethacrylate, 2,3-dihydroxypropylacrylate and 2,3-dihydroxypropylmethacrylate. The most preferred hydroxyalkylacrylates are 2-hydroxyethylacrylate and 2-hydroxyethylmethacrylate.

The mole ratio of lactone to hydroxyalkylacrylate employed can be
35 selected from a wide range and is often determined by the nature and molecular weight of the macromonomer it is desired to produce. The mole ratio is usually at least 1 : 1, and is commonly less than 40 : 1, preferably from 1 : 1 to 20 : 1. The molecular weight of the macromonomer produced

is often in the range from about 250 to about 10,000 and preferably 300 to 3,000.

The process according to the present invention is carried out in the presence of a free radical inhibitor to prevent or reduce polymerisation of the hydroxyalkylacrylate double bond. Examples of such inhibitors are well known in the art and are commonly selected from substituted phenols such as 4-methoxyphenol or quinones such as hydroquinone, benzoquinone and monomethylhydroquinone. The inhibitor is usually present at a concentration of less than 2000 mg/kg, commonly from 100, preferably from 500 to 1500 mg/kg.

In certain embodiments of the present invention, a solvent is employed in order to facilitate handling of the reaction mixture. Where a solvent is employed, the solvent should not be reactive towards the lactone or the hydroxyalkylacrylate. Examples of suitable solvents include aromatic hydrocarbons such as toluene and xylene, and aliphatic hydrocarbons such as petroleum ethers. In many preferred embodiments, no solvent is employed.

The process according to the present invention is carried out at a temperature of at least 100°C, preferably at least 105°C, and particularly preferably at least 110°C. Preferably, the reaction temperature is not greater than 130°C.

The process according to the present invention is usually continued until substantially all of the lactone has reacted. This can be determined by regular sampling and analysis of the reaction mixture, for example by gas chromatography. In many embodiments, substantially all the lactone is considered to have reacted when the reaction mixture comprises less than 1% w/w of lactone. It will be recognised that the actual reaction time will depend on the conditions being employed, and particularly the reaction temperature and phosphoric acid concentration. Typical reaction times are greater than 3 hours and less than 20 hours, and commonly from 5 to 12 hours.

The process of the present invention can be carried out under an inert, eg a nitrogen atmosphere for at least a part of the time taken to heat the reaction mixture to the desired reaction temperature and reaction time. However, in many embodiments, the process employs an air atmosphere throughout.

The process according to the present invention can be carried out by charging the lactone, hydroxyalkylacrylate and catalyst, plus any free

radical inhibitor and/or solvent to a reaction vessel fitted with a heater and a stirrer. The reaction mixture is stirred, heated to the desired reaction temperature and maintained at that temperature until the reaction is complete. The product can be obtained by conventional means, for example in the case of a liquid product, pouring or running off into a suitable reception vessel. This can be effected after cooling, particularly when the product is fluid at room temperature or before cooling, for example when the product is not fluid at room temperature.

According to a preferred aspect of the present invention, there is provided a process for the preparation of macromonomers by the catalysed reaction between ϵ -caprolactone and a 2-hydroxyethylacrylate, characterised in that the catalyst comprises phosphoric acid at a concentration of 300 mg/kg to 750 mg/kg of reaction mixture and the reaction is carried out at a temperature is from 105 to 130°C in the presence of from 500 to 1500 mg/kg of a free radical inhibitor.

Having described the invention in general terms, specific embodiments thereof are described in greater detail by way of example only.

20 Example 1

2-hydroxyethylacrylate (371g), ϵ -caprolactone (628g), 4-methoxyphenol (1g) and phosphoric acid (98% w/w, 0.5g) were charged to a 1 litre reaction vessel fitted with a mechanical stirrer. The mixture was stirred and heated to 120°C. The reaction mixture was stirred at 120°C for 8 hours, at which point analysis by gas chromatography indicated that the concentration of ϵ -caprolactone was <1% w/w, and the reaction was deemed to be complete. The product obtained was a water white liquid having an OH value of 166.2 mg KOH/g and an H⁺ value of 1.95 mg KOH/g.

30

Comparison 2

The procedure of Example 1 of European Patent Application no 0 108 372 was repeated. The product obtained was an intractable gel having a strong yellow colouration.

35

Examples 3 and 4

The general method of Example 1 was followed, except that the weights of 2-hydroxyethylacrylate (HEA, g) and ϵ -caprolactone (LACT, g) were as detailed in

Table 1 below, and that the reaction was considered to be complete when the concentration of ϵ -caprolactone was less than 0.5% w/w. The OH value (mg/KOH/g), H^+ value (mg/KOH/g) and average molecular weight (MWT) of the products are given in Table 1 below. In each of these Examples, the product obtained was a water white liquid.

Table 1

Example No.	Weight HEA	Weight LACT	H+ value	OH value	MWT
3	2575	2525	1.76	233.8	240
10 4	1683	3317	1.95	166.7	339

Examples 5 to 9

The method of Examples 3 and 4 were followed, except that of 2-hydroxyethylmethacrylate (HEMA) was employed in place of the HEA, and the weights of HEMA (g) and ϵ -caprolactone were as detailed in Table 2 below. The OH value (mg/KOH/g), H^+ value (mg/KOH/g) and average molecular weight (MWT) of the products are given in Table 2 below. In each of these Examples, the product obtained was a water white liquid.

20 Table 2

Example No.	Weight HEMA	Weight LACT	H+ value	OH value	MWT
5	466.4	1634	1.55	91.9	611
6	2720	2380	1.28	223.4	251
7	1854	3246	1.13	150.8	372
25 8	1406	3694	1.25	121.5	462
9	1378	3622	2.85	117.1	479

The results of Examples 1 and 3 to 9 show that the process according to the present invention could successfully be employed to produce a range of different macromonomers having acceptable physical properties, whereas the process of Comparison 2, according to Example 1 of European Patent Application no 0 108 372, produced a product having unacceptable physical properties.

Claims

1. A process for the preparation of macromonomers by the catalysed reaction between a lactone and a hydroxyalkylacrylate, characterised in that the catalyst comprises phosphoric acid at a concentration of greater than 200 mg/kg, preferably greater than 250 mg/kg, of reaction mixture, and that the process is carried out at a temperature of from 100°C to 130°C.
2. A process according to claim 1, characterised in that the phosphoric acid concentration is from 300 mg/kg to 750 mg/kg.
3. A process according to claim 1, characterised in that the phosphoric acid concentration is from 400 mg/kg to 600 mg/kg.
4. A process according to any preceding claim, characterised in that the lactone is ϵ -caprolactone.
5. A process according to any preceding claim, characterised in that the hydroxyalkylacrylate is selected from the group consisting of 2-hydroxyethylacrylate and 2-hydroxyethylmethacrylate.
6. A process according to any preceding claim, characterised in that the reaction is carried out at a temperature of 105°C or greater.
7. A process according to claim 6, characterised in that the reaction is carried out at a temperature of 110°C or greater.
8. A process according to any preceding claim, characterised in that the reaction is carried out in the presence of a free radical inhibitor at a concentration of from 500 to 1500 mg/kg.
9. A process according to claim 8, characterised in that the free radical inhibitor is 4-methoxyphenol.
10. A process for the preparation of macromonomers by the catalysed reaction between ϵ -caprolactone and a 2-hydroxyethylacrylate, characterised in that the catalyst comprises phosphoric acid at a concentration of 300 mg/kg to 750 mg/kg of reaction mixture and the

reaction is carried out at a temperature is from 105 to 130°C in the presence of from 500 to 1500 mg/kg of a free radical inhibitor.

11. A process for the preparation of macromonomers by the catalysed reaction between a lactone and a hydroxyalkylacrylate substantially as described herein with reference to the Examples.
12. A process for the preparation of macromonomers by the catalysed reaction between a lactone and a hydroxyalkylacrylate substantially as described herein with reference to any novel feature or combination of features.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 94/02748

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G63/08 C08G63/82

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 108 372 (UNION CARBIDE CORPORATION) 23 November 1988 cited in the application see page 5, line 14 - line 22; claim 1 -----	1-12

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Decocker, L

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-0108372	16-05-84	CA-A- 1237239	24-05-88
		JP-B- 6015599	02-03-94
		JP-A- 59098118	06-06-84
		JP-A- 6107595	19-04-94
		US-A- 4683287	28-07-87
