OPIC
Office de la propriété intellectuelle du Canada

CIPO
Canadian Intellectual Property Office

(12) (19) (CA) **Demande-Application**

(21) (A1) **2,293,745**
(86) 1998/06/17
(87) 1998/12/23

(72) HSU, CHIH-PIN, US
(72) CRUMP, L. SCOTT, US
(72) ZHAO, MING-YANG, US
(71) COOK COMPOSITES AND POLYMERS COMPANY, US

(51) Int.Cl.[7] C08G 63/42, C08G 63/87, C08G 63/58
(30) 1997/06/18 (08/878,282) US

(54) **SYNTHESE DE POLYESTERS A L'AIDE DE CATALYSEURS A BASSE TEMPERATURE DE DECOMPOSITION**

(54) **POLYESTER SYNTHESIS USING CATALYSTS HAVING LOW DECOMPOSITION TEMPERATURES**

(57) Procédé amélioré en deux phases destiné à la préparation de résines de polyester, qui comporte une réaction initiale d'un acide dicarboxylique tel que de l'acide isophtalique avec un oxyde d'alkylène tel que de l'oxyde d'éthylène ou de propylène en présence d'un catalyseur pour former un mélange de réaction oligoester, suivie par une réaction de seconde étape entre le mélange de réaction oligoester et un acide ou anhydride dibasique. Le catalyseur de première étape présente une température de décomposition thermique égale ou inférieure à la température de réaction de seconde phase. Le catalyseur idéal pour la première phase est le chlorure de benzyltriéthylammonium.

(57) An improved two-stage process for the preparation of polyester resins is provided which involves an initial reaction of a dicarboxylic acid such as isophthalic acid with an alkylene oxide such as ethylene or propylene oxide in the presence of a catalyst to form an oligoester reaction mixture, followed by a second stage reaction between the oligoester reaction mixture and a dibasic acid or anhydride; a first-stage catalyst is employed which has a thermal decomposition temperature substantially at or below the second-stage reaction temperature. The most preferred first-stage catalyst is benzyltriethylammonium chloride.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C08G 63/42, 63/87, 63/58	A1	(11) International Publication Number: WO 98/58009
		(43) International Publication Date: 23 December 1998 (23.12.98)

(21) International Application Number: PCT/EP98/03728

(22) International Filing Date: 17 June 1998 (17.06.98)

(30) Priority Data:
08/878,282 18 June 1997 (18.06.97) US

(71) Applicant *(for all designated States except PL)*: COOK COMPOSITES AND POLYMERS COMPANY [US/US]; 919 East 14th Avenue, North Kansas City, MO 64116 (US).

(71) Applicant *(for PL only)*: CRAY VALLEY S.A. [FR/FR]; Tour Total, 24, cours Michelet, F–92800 Puteaux (FR).

(72) Inventors: HSU, Chih–Pin; 10512 North Cherry Drive, North Kansas City, MO 64116 (US). CRUMP, L., Scott; 7404 North Park Avenue, Gladstone, MO 64118 (US). ZHAO, Ming–Yang; 6410 N. Fisk Court, Kansas City, MO 64151 (US).

(74) Agent: CHAILLOT, Geneviève; Cabinet Chaillot, 16–20, avenue de l'Agent Sarre, Boîte postale 74, F–92703 Colombes Cedex (FR).

(81) Designated States: BR, CA, JP, MX, PL, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: POLYESTER SYNTHESIS USING CATALYSTS HAVING LOW DECOMPOSITION TEMPERATURES

(57) Abstract

An improved two–stage process for the preparation of polyester resins is provided which involves an initial reaction of a dicarboxylic acid such as isophthalic acid with an alkylene oxide such as ethylene or propylene oxide in the presence of a catalyst to form an oligoester reaction mixture, followed by a second stage reaction between the oligoester reaction mixture and a dibasic acid or anhydride; a first–stage catalyst is employed which has a thermal decomposition temperature substantially at or below the second–stage reaction temperature. The most preferred first–stage catalyst is benzyltriethylammonium chloride.

POLYESTER SYNTHESIS USING CATALYSTS HAVING LOW DECOMPOSITION TEMPERATURES.

The present invention is broadly concerned with an improved two-step process for the preparation of polyesters wherein use is made of a first-stage catalyst having a relatively low decomposition temperature allowing substantially complete thermal decomposition of the catalyst prior to the second-stage reaction. More particularly, the invention pertains to such an improved process involving an initial catalyzed reaction between a carboxylic acid (e.g., isophthalic acid or terephthalic acid) and an alkylene oxide (e.g., propylene or ethylene oxide) in the presence of a low-degradation temperature catalyst such as benzyltriethylammonium chloride in order to form an oligoester mixture ; in preferred practice, the reaction product is heated to essentially completely decompose the first-stage catalyst, whereupon the oligoester reaction product is reacted with a dibasic acid or anhydride. Advantageously, the first-stage catalyst has a thermal degradation temperature at or below the second-stage reaction temperature.

A well-known route for the production of polyester resins involves an initial reaction between a carboxylic acid and an alkylene oxide in the presence of a catalyst to form an oligoester (typically hydroxyalkyl ester) reaction product. This first-stage addition reaction is generally carried out at an elevated temperature on the order of 100-230°C and at a superatmospheric pressure of up to about 1.47 MPa (15 kg/cm^2). A variety of catalysts have been proposed for use in this context, such as simple amines (U.S. Patent No. 4,306,056) and alkyl quaternary amine compounds (U.S. Patent No. 4,560,788).

After the first-stage reaction is completed, it is conventional to heat the reaction mixture in the presence of an inert gas such as nitrogen in order to remove the first stage catalyst. At this point, the catalyst-stripped first-stage reaction product may be mixed with a glycol such

as dipropylene glycol and the mixture is reacted with a diacid or anhydride, especially maleic anhydride at elevated temperatures and pressures. This yields the desired unsaturated polyester product.

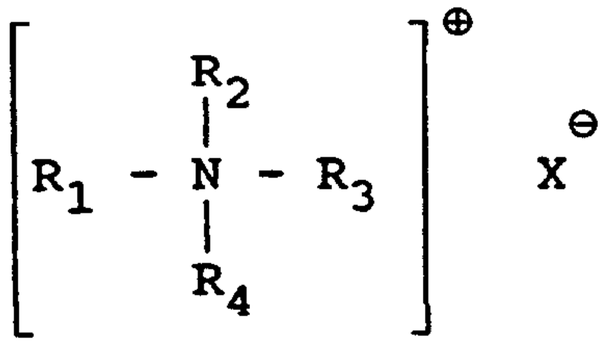
A significant problem with prior two-stage processes for polyester resin production stems from the fact that residual first-stage catalysts remaining in the second-stage reaction mixture tends to significantly discolor the final polyester resin products. Moreover, the attempted thermal degradation of the first-stage catalysts represents a material energy input to the process, thus raising costs.

There is accordingly a real and unsatisfied need in the art for an improved two-stage polyester resin process which ameliorates the problems of resin discoloration and excess energy usage.

The present invention overcomes the problems outlined above, and provides a greatly improved two-stage polyester preparation process yielding final products having very low Gardner color numbers. Broadly speaking, the process of the invention includes the conventional steps of reacting a carboxylic acid with an alkylene oxide in the presence of a catalyst to form an oligoester reaction mixture, and thereafter reacting the oligoester reaction mixture with a dibasic acid or anhydride at an elevated second-stage reaction temperature to form a polyester. However, the invention makes use of a catalyst in the first-stage carboxylic acid-alkylene oxide reaction which will thermally decompose at a temperature substantially at or below the elevated second-stage reaction temperature. Accordingly, the catalyst may be readily removed at relatively low temperatures prior to the second-stage reaction. Moreover, any residual amounts of catalyst remaining at the outset of the second-stage reaction are thermally decomposed during the course of the reaction, so that the catalyst does not adversely affect the color of the final polyester resin.

Aryl groups, C_1-C_{18} alkyl-substituted aryl groups,

In preferred forms, the catalyst is selected from the group consisting of aryl alkyl quaternary amines and derivatives thereof. Preferred compounds of this type are selected from the formula



wherein R_1 is an aryl or C_1-C_{18} alkyl-substituted aryl group and R_2, R_3 and R_4 may be the same or different and are independently selected from the group consisting of aryl groups, C_1-C_{18} alkyl-substituted aryl groups, C_1-C_4 hydrocarbons and C_1-C_4 hydroxy-substituted hydrocarbons, and X is selected from the group consisting of a hydroxyl group, the halogens, and moieties of carbonic, bicarbonic, mono- and di-carboxylic acids. A more preferred group is where R_2, R_3 and R_4 are the same or different and more independently selected from the group consisting of C_1-C_4 alkyl groups and C_1-C_4 hydroxy-substituted groups, and R_1 is a benzyl group. The single most preferred class of catalysts are the benzyl lower trialkylammonium halogen salts, where the lower trialkyl groups are independently selected from the group consisting of the C_1-C_4 alkyls. The decomposition temperature of the catalyst of the invention should preferably be in the range of from about 100-240°C and more preferably from about 150-220°C. In addition, the first-stage catalyst, when heated to a temperature greater than 50°C, has a half-life of at least 10 hours.

The carboxylic acid used in the first-stage reaction is preferably an alkyl or aryl dicarboxylic acid, with the benzene-dicarboxylic acids being the most preferred. Isophthalic and terephthalic acids and mixtures thereof are the most commonly used acids in this context. The alkylene oxide reactant is preferably selected from the C_2-C_8 alkylene oxides with propylene oxide, ethylene oxide

such as dipropylene glycol

and mixtures thereof generally being used. The molar ratio of the first-stage alkylene oxide to carboxylic acid should preferably be in the range of from about 0.1:1 to 10:1 and more preferably from about 0.5:1 to 5:1. The first-stage reaction is normally carried out at a temperature of from about 50-200°C, and more preferably from about 75-150°C ; reaction pressures normally vary from about 0.0689-2.76 MPa (10-400 psi), more preferably 0.137-0.689 MPa (20-100 psi). Reaction times are also variable but generally range from about 20 min. to about 20 hours, more preferably from about 30 min. to about 10 hours.

The second stage reaction involves reaction of the oligoesters derived from the first stage (and generally after an intermediate thermal catalyst degradation / removal step) with an unsaturated dibasic acid or its anhydride. Glycol may be added to the first-stage oligoesters at this stage, and a mixture of unsaturated and saturated dibasic acids or anhydrides can be used ; in the latter case, the saturated dibasic acid or anhydride can consitute up to 80 mole percent (more preferably up to 40 mole percent) of the mixture. The preferred dibasic acids are the C_2-C_{10} acids, for example, maleic, fumaric, citraconic, mesaconic and itaconic acids ; the corresponding anhydrides can also be employed. Where saturated dicarboxylic acids or anhydrides are used in conjonction with the unsaturated acids or anhydrides, typical saturated acids or anhydrides would be phthalic, succinic, adipic, sebacic and/or dimerized fatty acids and their corresponding anhydrides.

The second-stage reaction conditions generally involve a reaction temperature of from about 150 to 250°C, a pressure of from about 0 to 2.07 MPa (0 to 300 psi) and a reaction time of from about 2 to 50 hours. The unsaturated polyesters obtained in the second-stage reaction are normally blended with one or more monomers capable of crosslinking with the vinyl groups in the resins. Examples of such monomers include styrene, vinyl toluene, p-methyl styrene, chlorostyrene, t-butyl styrene, diallyl phthalate,

mono- or multifunctional lower alkyl esters of the acrylic or methacrylic acids such as methyl methacrylate and glycol diacrylate and the like. The amount of monomer in the resin ranges between about 30 to about 70% by weight. Styrene is the reactive monomer of choice. Such final resin products have very good color characteristics, typically having a Gardner color scale of less than 4 and more preferably less than 2.

The following examples are provided by way of illustration only and nothing therein should be taken as a limitation upon the overall scope of the invention.

EXAMPLE 1

In this example, a hydroxy alkyl oligoester was produced for use as a solvent in subsequent examples. The following ingredients were introduced into a two-gallon stainless steel autoclave : 15 g benzyltriethylammonium chloride (TEBAC), 1800 g xylene, and 2000 g of isophthalic acid. The air in the autoclave was completely replaced by the introduction of nitrogen gas and the mixture was heated to 125°C. 1400 g of propylene oxide was then continuously added over 160 min. at a stirring rate of 200 rpm while maintaining a reaction temperature in the autoclave of 125°C and a reactor pressure below 0,345 MPa (50 psi). After completion of the propylene oxide addition, the reaction was continued at 125°C for an additional 60 min. at a pressure below 0,345 MPa (50 psi). The reaction product was then purged with nitrogen and subjected to a vacuum for 2 hours to remove the xylene. 3390 g of the oligoester A reaction product having an acid value of 15 (mg KOH/g) was obtained.

EXAMPLES 2-6

In this example, two additional hydroxy alkyl oligoesters are prepared under the conditions set in Table 1

below and as described in Example 1 using the oligoester A as a solvent. The properties of the resulting oligoesters are also given in Table 1.

Table 1

	Example 2	Example 3	Example 4	Example 5	Example 6
Oligoester A (g)	1800	1800	1800	1800	1800
Isophthalic acid (g)	2000	--	1000	2000	2000
Terephthalic acid (g)	--	2000	1000	--	--
Propylene oxide (g)	1400	1400	1400	1400	1400
Catalyst (g)	15 A[1]	15 A	15 A	15 B	15 C
Temperature (°C)	130	125	125	125	125
Maximum pressure in MPa (psi)	0,345 (50)	0,345 (50)	0,345 (50)	0,345 (50)	0,345 (50)
PO addition time (min.)	200	200	200	240	150
Holding time (min.)	60	60	60	60	60
Yield (g)	5060	5030	5100	4950	5910
Ether compound (% by weight)	8	5	8	6	5
Acid value	12	5	12	11	9
Gardner color scale	< 1	< 1	< 1	< 1	< 1

1 A is benzyltriethylammonium chloride ;
B is triethylamine ;
C is tetramethylammonium chloride.

EXAMPLE 7

In this example, an unsaturated polyester is prepared. In the first step, 1910 g of the Example 2 hydroxy alkyl oligoester is placed in a reactor equipped with an agitator, thermometer, nitrogen purge apparatus and a partial reflux condensor. The oligoester is heated to 215°C for 30 min. under vacuum 0.0675 MPa (20 in Hg) in order to decompose and remove the catalyst. The reactor is then cooled to 180°C and 510 g of maleic anhydride is added thereto. The mixture is heated to 215°C and maintained at

that temperature for about 8 hours to complete the reaction. 2010 g of unsaturated polyester resin having an acid value of 12, Gardner viscosity of S-T, and a Gardner color scale of less than 2 (viscosity and color scale measured in a 50% solution in styrene) is obtained. Styrene and hydroquinone (1080 and 1 g, respectively) are added to the unsaturated polyester resin to form a liquid resin product.

EXAMPLES 8-10

Additional polyester products are prepared using the oligoesters prepared in Examples 4-6, using the techniques described in Example 7. The polyester made using the Example 4 oligoester have a Gardner scale color of less than 2, whereas the polyesters made using the Example 5 and 6 oligoesters (i.e., those prepared using prior art catalysts) have Gardner scale colors of 5-6.

It will be appreciated that a wide variety of ingredients and reaction conditions can be followed in carrying the present invention. The following Table 2 sets forth broad and preferred approximate ranges for these reaction parameters.

Table 2

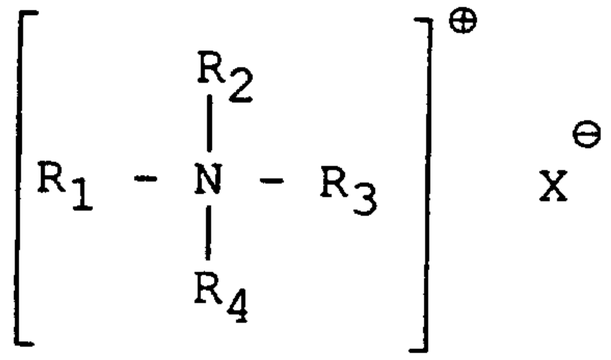
Reaction parameter	Broad Range	Preferred Range
First-stage Reaction		
Carboxylic Acid Type	alkyl or aryl dicarboxylic	benzene-dicarboxylic
Alkylene Oxide Type	C_2-C_8 alkylene oxides	C_2-C_4 alkylene oxides
Catalyst	aryl alkyl quaternary amines and derivatives	benzyl lower trialkylammonium halogen salts
Reaction Temperature (°C)	50-200	75-150
Reaction Pressure MPa (psi)	0.0689-2.76 (10-400)	0.137-0.689 (20-100)
Reaction Time	20 min. to 20 hrs.	30 min. to 10 hrs
Alkylene Oxide : Carboxylic Acid Molar Ratio	0.1:1 to 10:1	0.5:1 to 5:1
Catalyst Removal		
Decomposition Temperature (°C)	at or below second-stage reaction temperature	150-220
Pressure in MPa (psi)	0 to 1.38 (0 to 200)	0 to 0.345 (0 to 50)
Reaction Time	10 min. to 3 hrs.	15 min. to 1 hr.

Tableau 2 (continued)

Reaction Parameter	Broad Range	Preferred Range
Second-Stage Reaction		
Dibasic Acid / Anhydride	C_2-C_{10} dibasic acids/ anhydrides	C_2-C_6 dibasic acids/ anhydrides
Reaction Temperature	150 to 250	180 to 240
Reaction Pressure in MPa (psi)	0 to 2.07 (0 to 300)	0 to 0.689 (0 to 100)
Reaction time	2 to 50 hours	5 to 20 hours
Dibasic Acid/Anhydride : oligoester Molar Ratio	1:4 to 4:1	1:2 to 2:1
Polyester Final Product		
Gardner Color	< 4	< 2

CLAIMS

1 - In a process for preparing a polyester including the steps of initially reacting a carboxylic diacid with an alkylene oxide in the presence of a catalyst to form an oligoester reaction mixture, and thereafter reacting the oligoester reaction mixture with an unsaturated dibasic acid or anhydride or with a mixture of unsaturated and saturated dibasic acids or anhydrides, in a second reaction at an elevated second reaction temperature to form the polyester, the improvement which comprises the step of employing a catalyst in said initial reaction which will thermally decompose at a temperature substantially at or below said elevated second reaction temperature, said catalyst being selected from the group consisting of compounds of the formula



wherein R_1 is an aryl or C_1-C_{18} alkyl-substituted aryl group and R_2, R_3 and R_4 may be the same or different and are independently selected from the group consisting of aryl groups, C_1-C_{18} alkyl-substituted aryl groups, C_1-C_4 hydrocarbons and C_1-C_4 hydroxy-substituted hydrocarbons, and X is selected from the group consisting of a hydroxyl group, the halogens, and moieties of carbonic, bicarbonic, mono- and di-carboxylic acids.

2 - The process of claim 1, wherein R_2, R_3 and R_4 are the same or different and are independently selected from the group consisting of aryl groups, C_1-C_{18} alkyl-substituted aryl groups, C_1-C_4 alkyl groups and C_1-C_4 hydroxy-substituted groups, and R_1 is a benzyl group.

3 - The process of anyone of claims 1 or 2, said catalyst having a decomposition temperature of up to about 240°C.

4 - The process of anyone of claims 1 to 3, said decomposition temperature being from about 150-220°C.

5 - The process of anyone of claims 1 to 4, said catalyst, when heated to a temperature greater than 50°C, having a half life of a least 10 hrs.

6 - The process of anyone of claims 1 to 5, said catalyst being benzyltriethyl-ammonium chloride.

7 - The process of anyone of claims 1 to 6, said carboxylic diacid being selected from the group consisting of isophthalic, terephthalic acid and mixtures thereof.

8 - The process of anyone of claims 1 to 7, said alkylene oxide being selected from the group consisting of propylene oxide, ethylene oxide and mixtures thereof.

9 - The process of anyone of claims 1 to 8, including the step of carrying out said initial reaction at a temperature of from about 50-200°C, a pressure of from about 0.0689-2.76 MPa (10-400 psi) and for a time of from about 20 min. to 20 hrs.

10 - The process of anyone of claims 1 to 9, the molar ratio of said alkylene oxide to said carboxylic diacid in said initial reaction being from about 0.1:1 to about 10:1.

11 - The process of claim 10, said molar ratio being from about 0.5:1 to about 5:1.

12 - The process of anyone of claims 1 to 11, including the step of heating said oligoester reaction mixture to a temperature sufficient to decompose said catalyst, prior to said reaction between said oligoester reaction mixture and said dibasic acid or anhydride.

14 - The process of claims 12 or 13, said temperature sufficient to decompose said catalyst being from about 100 to 240°C.

15 - The process of anyone of claims 1 to 14, including the step of carrying out said second reaction at a temperature of from about 150-250°C, a pressure of from about 0-2.07 MPa (0-300 psi) and for a time of from about 2 to 50 hrs.

16 - The process of anyone of claims 1 to 15, including the step of adding a glycol to said oligoester reaction mixture prior to said reaction between said oligoester mixture and said dibasic acid or anhydride.

17 - The process of claim 16, said glycol being dipropylene glycol.

18 - The process of anyone of claims 1 to 17, which leads to a final resin having a Gardner color scale of less than 4 and more preferably less than 2.