

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number:

**0 000 832
B1**

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: **01.02.84**

(51) Int. Cl.³: **C 08 G 63/18,
C 08 G 63/30**

(21) Application number: **78300244.7**

(22) Date of filing: **03.08.78**

(54) **Melt processable resorcinol-phthalate polyesters and process for their preparation.**

(30) Priority: **08.08.77 US 822579**

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(43) Date of publication of application:
21.02.79 Bulletin 79/4

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(45) Publication of the grant of the patent:
01.02.84 Bulletin 84/5

(64) Designated Contracting States:
BE CH DE FR GB LU NL SE

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**BEILSTEINS HANDBUCH DER ORGANISCHEN
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EP 0 000 832 B1

Melt processable resorcinol-phthalate polyesters and process for their preparation

Technical field

The present invention relates to a melt polymerization process for preparing resorcinol phthalate polyesters, wherein an ester interchange reaction takes place and to the product prepared therefrom.

5 Background art

In the past, polyesters have been prepared by a variety of methods including ester interchange, direct esterification, interfacial polymerization and acidolysis (see U.S. Patent No. 4,011,199).

10 The stability of the reactants and the melt viscosity of the polyester prepared therefrom often play a dominant role in selecting a commercially acceptable manufacturing process. For example, polyesters of aliphatic and cycloaliphatic diols have viscosities that make these polyesters particularly suitable for commercial preparation using an ester interchange process. Polyesters prepared using aromatic diols, however, typically have such high melt viscosities that ester interchange cannot be used.

15 One particular method of achieving an ester interchange reaction is by a melt polymerization technique. This procedure is advantageous because it permits utilization of the free acid as opposed to the more expensive acid chloride required by certain other techniques. Further advantages of this technique lie in the ability to dispense with the solvent recovery and acid neutralization procedures which are necessary when the acid chloride route is used.

The melt polymerization procedures of the prior art, however, yield a commercially unacceptable product when applied to the preparation of a resorcinol phthalate polyester.

20 This results, in part, from the fact that resorcinol by itself does not react with phthalic acids in a melt process to yield a usable resorcinol phthalate polyester.

It has been observed that resorcinol phthalate polyesters in general are known as illustrated by W. Eareckson, *Interfacial Poly Condensation X Poly Phenyl Esters*, 40 J. Pol. Sci. 399—406 (1959); U.S. Patent Nos. 3,160,602; 2,595,343; and 2,035,578; and British Patent No. 863,704. The discussion of resorcinol-phthalate polyesters in the prior art, however, has typically centered on methods of making polyesters in general. Consequently, the description of specific resorcinol phthalate polyesters and the properties associated therewith have been of limited scope.

USP 3161710 describes the production of resorcinol phthalate polyesters using 100% isophthalic acid or 100% terephthalic acid or 25% isophthalic acid and 75% terephthalic acid.

30 German O.L.S. 2035846 describes the production of resorcinol phthalate polyesters using 100% isophthaloyl chloride or a 50/50 blend of isophthaloyl and terephthaloyl chlorides.

It has heretofore been unknown that only certain proportional isomer ranges of isophthalic and terephthalic acid are capable of yielding a melt processable polymer. It has also been unknown that the effective utilization of a melt polymerization process to prepare a resorcinol phthalate polyester is also contingent upon the employment of certain specified proportional acid isomer ranges.

35 It has been further observed that wholly aromatic polyesters may be prepared by an ester interchange reaction as illustrated by U.S. Patent Nos. 3,160,604; 3,036,992; and 2,595,343.

40 It has been still further observed that a wide variety of catalysts have been considered for use in preparing wholly aromatic polyesters in general by an ester interchange reaction as illustrated by U.S. Patent Nos. 3,824,213 and 3,651,014.

Disclosure of the invention

45 It is, therefore, an object of the present invention to provide a process for the preparation of a melt processable resorcinol phthalate polyester by the melt polymerization of resorcinol diacetate and mixtures of isophthalic acid and terephthalic acid.

It is a further object of the present invention to provide a melt processable resorcinol phthalate polyester.

50 In one aspect of the present invention, there is provided a process for preparing a melt processable resorcinol phthalate polyester capable of being made into shaped articles from the molten state which comprises (a) reacting resorcinol diacetate with a mixture of 95% to 70 mole % isophthalic acid and 5 to 30 mole % terephthalic acid, which reaction is conducted in the presence of a catalyst consisting of an alkali or alkaline earth metal acetate catalyst or a mixture of such catalysts at a temperature of 180 to 240°C for a period sufficient to form a non-volatile pre-polymer; and (b) polymerizing the non-volatile pre-polymer of step (a) at a temperature above the melting point of both the pre-polymer and the resulting polymerized product in the presence of an alkali or alkaline earth metal acetate catalyst or a mixture of such catalysts to yield a polyester having an inherent viscosity of 0.4 to 1.5; the resorcinol diacetate being reacted with the mixture of phthalic acids in step (a) in the presence of a heat transfer medium which is removed from the non-volatile pre-polymer prior to commencing the polymerization reaction of step (b); and in which the resorcinol diacetate is prepared by reacting resorcinol and an acetylating agent by heating said compounds to a temperature of 100 to 130°C and so as to yield resorcinol diacetate; and purifying the resulting resorcinol diacetate,

preferably by vacuum distillation to the extent sufficient to obtain at least 99.5% by weight resorcinol diacetate, the balance, if any being the dimerization product of resorcinol.

In another aspect of the present invention there is provided a melt processable resorcinol phthalate polyester capable of being made into shaped articles from the molten state characterised in that it comprises the reaction product of resorcinol diacetate and a mixture of from 95 to 80 mole percent isophthalic acid and correspondingly from 5 to 20 mole percent by weight terephthalic acid.

When terephthalic acid is present in an amount greater than 30 mole percent the melting point of the resulting polyester is greater than the temperature at which significant degradation occurs and it is not feasible to prepare the polymer by a melt polymerization procedure. (C.f. US—A—30 36 990, fig. 2 and 3). Moreover, a resorcinol phthalate polyester having a terephthalate content greater than 30% is not melt processable. A melt processable resorcinol phthalate polyester is one which is capable of being made into shaped articles from the molten state. One example of a method of making shaped articles from the molten state is melt extrusion (e.g. injection moulding) typically at temperatures of from 250 to 320°C at a pressure of 5,000 to 25,000 psi (34450 to 172250 Kilopascals).

Properties of the resorcinol phthalate polymer such as tensile strength, flexural strength, modulus, glass transition temperature (T_g) and heat distortion temperature may be varied by altering the isophthalic-terephthalic acid isomer ratio within the described ranges.

In general, the presence in limited amounts of the terephthalate moiety in the resulting polyester increases the strength and use temperature thereof while lowering the melting point and thereby improving melt processability.

Thus, although isophthalic and terephthalic acid may be present in the reaction mixture in any amounts within the defined limits it is preferred that the isophthalic acid be present in amounts which can vary from 95 to 80, or 90 to 85 mole percent (e.g., 90 mole percent) by weight of the total mixture, and correspondingly the terephthalic acid can be present in amounts which can vary from 5 to 20 mole percent, and most preferably from 10 to 15 mole percent (e.g., 10 mole percent) by weight of the total mixture.

The resorcinol diacetate utilized as a reactant in the melt polymerization process should not contain impurities which would adversely affect the resulting polymer product.

The melt polymerization reaction is generally conducted with the reactants present in amounts sufficient to fully transesterify the resorcinol diacetate. Generally, substantially stoichiometric amounts of each reactant are employed; typical molar amounts of from 1:0.9:0.1 to about 1:0.8:0.2 of resorcinol diacetate, isophthalic acid, and terephthalic acid, respectively, are utilized.

The melt polymerization reaction of the present invention has been found to be dependent on the utilization of certain specific catalysts and temperatures.

Conventional polytransesterification catalysts such as Sb_2O_3 , tetra alkyl titanates (e.g., tetrabutyl titanate), dialkyl tin oxides (e.g., dibutyl tin oxide), diaryl tin oxide, titanium dioxide, alkoxy titanium silicates, titanium alkoxides, and the gaseous acid catalysts such as Lewis acids, hydrogen halides (e.g., HCl) are unsuitable for the purposes of the presently claimed invention and yield only highly colored low molecular weight material. It is believed that the unacceptably poor results obtained by these catalysts are due to the tendency of the polymer and/or the resorcinol diacetate monomer to undergo Fries rearrangements or Friedel-Crafts type substitution on the resorcinol ring.

Condensation without a catalyst is very slow and leads to incomplete reactions.

In order to achieve the advantages of the presently claimed process it is necessary to conduct both the prepolymer forming reaction and the melt polymerization reaction in the presence of a catalyst consisting of a metal acetate catalyst wherein said metal is selected from cations of alkali and alkaline earth metals and mixtures thereof.

The relative reactivity of the catalysts varies depending on whether it is utilized in the first stage of pre-polymer formation or the second stage of polymerization, i.e., melt polymerization.

Thus, in the first stage the preferred metals utilized to provide the metal acetate catalysts include in order of descending reactivity, sodium, potassium, lithium and calcium while the preferred metal of the second stage includes in order of descending reactivity potassium, calcium, lithium and sodium.

The most preferred catalyst for both stages is a mixture of sodium acetate and potassium acetate wherein the components of said mixture are present at a molar ratio of about 1:1.

Although any effective amount of catalyst may be utilized in either the first (i.e., pre-polymer forming) stage or second (i.e., melt polymerization) stage, it is preferred that such amount constitute in the first stage from 1.0 to 0.1%, most preferably about 0.7% by weight based on the total monomer weight of resorcinol diacetate, and in the second stage from 1.0 to 0.1%, and most preferably about 0.5% by weight of the total weight of the non-volatile pre-polymer.

Utilization of the above described metal acetate catalyst enables two step polymerization times of about 3 to about 12 hours, preferably from about 3 to about 8 hours, and most preferably from about 3 to about 4 hours to be obtained in accordance with the present invention. The short polymerization times obtainable by the use of the metal acetate catalyst minimize the rearrangement of the polyester molecule chains and consequently a high molecular weight melt processable polymer can be obtained.

As described above, the process of the present invention is accomplished in two stages.

The first stage is conducted at temperatures below the boiling point of the resorcinol diacetate to

yield a non-volatile pre-polymer. It is not feasible to directly melt polymerize the above reactants since resorcinol diacetate exists as a liquid at room temperature and is volatilized at the temperature required for melt polymerization. To overcome this difficulty, the resorcinol diacetate monomer is reacted at low temperature to an extent sufficient to condense at least one of the acetate groups present thereon with a carboxyl group of the phthalic acid to form a pre-polymer comprising dimers, trimers and the like. The pre-polymer may be characterized as being non-volatile, in that it degrades under the influence of elevated temperatures before it vaporizes into the gaseous state. Thus the temperature is below the boiling point of the resorcinol diacetate but is sufficient to achieve the desired reaction and as indicated above is from 180 to 240°C, preferably from 200 to 240°C, and most preferably from 220 to 240°C.

To achieve the desired extent of the pre-polymer forming reaction it is possible to monitor the evolution of acetic acid. This can be accomplished by condensing the vapor as it is removed from the reaction vessel and measuring the weight or volume. The reaction is considered complete when about 90% by weight of the theoretical amount is collected.

Alternatively, the pre-polymer forming reaction can be conducted to provide a pre-polymer having an inherent viscosity (I.V.) measured in a 0.8% solution in pentafluorophenol of from 0.05 to 0.2 (e.g., 0.1).

Typical reaction times sufficient to obtain the non-volatile pre-polymer can vary from 1 to 4 hours, preferably from 1 to 3 hours, and most preferably from 1 to 2 hours.

The pressure at which the pre-polymer forming reaction can be conducted is typically atmospheric.

The pre-polymer forming reaction is desirably conducted under an inert atmosphere such as nitrogen.

The heat transfer medium should be capable of substantially dissolving the reactants and resulting pre-polymer and refluxing under the temperatures employed to prepare a pre-polymer. It should also be incapable of undergoing reaction with the reactants. Thus, the heat transfer medium serves to conduct heat uniformly to the reactants while at the same time washes the sides of the reaction vessel thereby keeping the reactants in contact with each other. Suitable heat transfer mediums include inert solvents having a boiling point of not lower than about 250°C.

Representative heat transfer mediums include diphenyl ether, terphenyls and mixtures thereof such as those composed of meta and para isomers commercially available from Monsanto Chemical Company under the trademark Therminol (e.g., Therminol 88, 77, or 66) chlorinated diphenyls, benzophenone, and chlorinated diphenyl ether.

A preferred heat transfer medium is diphenyl ether.

The heat transfer medium (e.g., diphenyl ether) is typically present at an amount which can vary from 10 to 50% by weight of the combined weight of reactants and heat transfer medium.

The heat transfer medium is removed from the reaction vessel prior to commencing the second stage of polymerization by any means known to those skilled in the art, such as by distillation.

The non-volatile pre-polymer prepared in accordance with the procedure described above is then polymerized at a temperature above the melting point of both the pre-polymer and the resulting polymerized product and in the presence of the above-described metal catalyst to yield a resorcinol phthalate polyester.

Although any temperature above the melting point of both the pre-polymer and the resulting product and below the decomposition temperature of the same may be utilized, it is preferred that the temperature is from 240 to 300°C, more preferably from 260 to 290°C, and most preferably from 270 to 280°C. Thus, the second stage polymerization is conducted with the reactants and products of reaction in the molten state and in the absence of solvent medium.

In a preferred form of the invention the melt polymerization reaction is conducted at the above-described temperatures for a period of 1 to 8 hours, more preferably from 2 to 6 hours, and most preferably from 2 to 4 hours and under a reduced pressure of 0.4 to 2 mm Hg, preferably from 0.1 to 1 mm Hg, and most preferably from 0.1 to 0.3 mm Hg.

It is also preferred to conduct the melt polymerization reaction under an inert atmosphere such as nitrogen or argon.

Generally, the melt polymerization reaction is conducted so as to obtain a resorcinol phthalate polyester having an inherent viscosity (I.V.) of from 0.4 to 1.5, and preferably from 0.5 to 1.0 (e.g., 0.5) decilitres/gram.

The I.V. is determined by measurement of the relative viscosity of a 0.1% solution of the polymer at 25°C in a suitable solvent, such as pentafluorophenol. The viscosity of the polymer solution is measured relative to that of the solvent alone and the inherent viscosity (I.V.) is determined from the following equation:

$$I.V. = \frac{I_n \frac{V_2}{V_1}}{C}$$

In the above formula, V_2 is the efflux time of the solution, V_1 is the efflux time of the solvent, and C is the concentration expressed in grams of polymer per 100 ml of solution. As is known in the polymer art, inherent viscosity is monotonically related to the molecular weight of the polymer.

Another aspect of the present invention is directed to a process for preparing a melt processable resorcinol phthalate polyester from resorcinol and acetic anhydride or other suitable acetylating agent. It has been found that it is not feasible to react resorcinol and an acetylating agent under elevated temperature and utilize the resulting resorcinol diacetate product directly in the preparation of resorcinol phthalate polyester. This results from the fact that resorcinol diacetate synthesis is accompanied by the formation of several undesirable side products which if present during resorcinol phthalate polyester synthesis will yield a dark brown low molecular weight polymer which is not melt processable. The side products are believed to be induced by Fries rearrangements and/or acylation of the active resorcinol ring. The undesirable side products must, therefore, be removed from the synthesized resorcinol diacetate prior to commencing the synthesis of a resorcinol phthalate polyester from a resorcinol diacetate.

Accordingly, resorcinol is reacted with a suitable acetylating agent.

Suitable acetylating agents include acetic anhydride and acetyl halides such as acetyl bromide and preferably acetyl chloride.

The acetylating reaction is conducted at temperatures from 100 to 130°C (e.g., 120°C) so as to yield resorcinol diacetate.

Temperatures in excess of the boiling point of the acetylating agent (e.g., 138°C for acetic anhydride) should not be utilized to avoid loss of the acetylating agent.

The reactants are present at substantially stoichiometric molar ratio of about 1:2 of resorcinol and acetylating agent, respectively, although an excess, i.e., up to 50 mole % of the acetylating agent may be utilized to increase the reaction rate and then recycled. The resorcinol diacetate is then purified to eliminate the undesirable side products, such as, by vacuum distillation or low temperature recrystallization.

The purification procedure is conducted to the extent sufficient to obtain a purity of about 99.5% and to eliminate any monoacetate, and products resulting from Fries rearrangement or ring acylation which produce a chain stopping action if present during the pre-polymer formation and particularly during the melt polymerization step.

The only impurity whose presence is acceptable in trace amounts is the dimerization product of resorcinol, and only less than 0.5% of this can be present.

The purified resorcinol diacetate is then utilized in accordance with the processes described above.

Generally, the above-described process is conducted in a batch-type manner, however, any other suitable manner known to those skilled in the art may be employed if so desired.

When it is intended that the resorcinol phthalate polyester be utilized in molding applications, one or more solid fillers or reinforcing agents optionally may be incorporated in the same via a melt admixture technique to form a filled and/or reinforced injection molding compound.

Such fillers and/or reinforcing agents may be included in a total concentration of about 0 to 40% by weight of the resulting molding compound.

Representative fibers which may serve as reinforcing media include glass fibers, asbestos, graphitic carbon fibers, amorphous carbon fibers, synthetic polymeric fibers, aluminium fibers, aluminium silicate fibers, oxide of aluminium fibres, titanium fibers, magnesium fibers, rock wool fibers, steel fibers, tungsten fibers, cotton wool, and wood cellulose fibers. If desired the fibrous reinforcement may be preliminarily treated to improve its adhesion ability to the resorcinol phthalate polyester which ultimately serves as a continuous matrix phase. Representative filler materials include calcium silicate, silica, clays, talc, mica, polytetrafluoroethylene, graphite, alumina trihydrate, sodium aluminium carbonate and barium ferrite. Colorants optionally may be included.

Molded shaped articles formed from the resorcinol phthalate polyester of the present invention generally exhibit a superior tensile strength, flex strength, and impact strength. Also, the appearance of the resulting molded articles is commonly clear and exhibits a light yellow to amber color and an attractive smooth surface.

Best mode of carrying out the invention

The invention may be put into practice in various ways and certain specific embodiments will be given to illustrate it with reference to the accompanying Examples.

Unless otherwise indicated, all percentages or proportions of materials mentioned in the specification and appended claims are by weight.

Example 1

29.9 gm (0.18 mole) isophthalic acid, 3.3 gm (0.02 mole) terephthalic acid, 39.4 gm (0.20 mole), (1.5% excess) resorcinol diacetate, 10 ml diphenylether, 1 ml acetic anhydride and 0.27 gm (0.002 mole) sodium acetate trihydrate catalyst are weighed into a dry three neck 300 ml flask. The acetic anhydride is used as a water scavenger and acetylating agent for any unreacted or partially acetylated

resorcinol. The diphenyl ether solvent is not required for the reaction but is used for convenience to wash the sides of the vessel during the early stages of the condensation. The flask is fitted with a nitrogen inlet, Servodyne™ mechanical stirrer with RPM and torque read outs, condenser, fifty ml graduated receiver and vacuum adaptor. The flask is purged with dry, oxygen free nitrogen and brought to 240°C over 0.5 hr, with stirring. The reaction is held at 240°C for 3 hr while a theoretical amount of acetic acid is collected. At this point, vacuum is applied to remove the diphenyl ether, and the reaction temperature is brought to 280°C. The mixture is held at 280°C and 1.0 mm Hg pressure for three hours and the increase in viscosity is monitored by observing the stirring torque. The reaction is then cooled under nitrogen, the flask broken and polymer ground to approximately 5 mesh.

Examples 2—5

The same general procedure outlined in Example 1 is repeated with the exception that identity of the catalyst and/or reaction temperatures are varied. The catalyst and reaction conditions are summarized in Tables IA and IB.

TABLE IA
Thermal synthesis of poly(resorcinol phthalate)
Heating profile

Example No.	Catalyst	1st Stage		2nd Stage	
		Temp.	Time	Temp.	Time
2	Na OAc	240°C	2 hr	280°C	2.5 hr
3	KOAc	240°C	2.5 hr	280°C	1 hr
4	Mg(OAc) ₂	240°C	3.5 hr	280°C	2 hr
5	KOAc+Na OAc	240°C	2 hr	280°C	1.5 hr

TABLE IB

Example No.	Relative rate ^a	I.V. ^b	Comments
2	1st—fast 2nd fast	0.83	light amber, tough flexible
3	1st—fast 2nd—very fast	0.83	light amber, tough flexible
4	1st—moderate 2nd—fast	0.66	light amber, tough flexible
5	1st—fast 2nd—very fast	0.69	light amber, tough flexible

^a 1st Stage—rate of HOAc distillation
2nd Stage—rate of torque increase

^b 0.1% in pentafluorophenol.

Example 6

A 6 lb (2.72 kgs) resorcinol phthalate sample is prepared in accordance with the procedure outlined in Example 1 utilizing a sodium acetate catalyst with the exception that a longer reaction time for the second stage is utilized (i.e., 10 hrs under vacuum in melt). The resulting product is pelletized by a Warner-Pfleider ZSK twin screw extruder, dried and injection molded. Molding conditions and polymer physical properties are summarized in Table II.

TABLE II
Mechanical properties of poly(resorcinol phthalate)

I.V.	0.49
Tensile strength (psi)	11,400 (78546 kilopascals)
Flex strength (psi)	16,400 (112996 kilopascals)
Flex modulus (psi × 10 ⁵)	4.00 (27.56 kilopascals)
Notched izod (ft-lb/in)	0.95 (0.051 joules/cm)
Heat distortion temp.	119°C
—(264 psi (1819 kilopascals))	
Rockwell hardness M. scale	91

TABLE II (contd.)

Molding conditions	
Cylinder temp.	560°F (293°C)
Mold temp.	175°F (79°C)
Cycle time (cycle times/sec)	Inj.—10, cooling—20, delay—2
Injection press (psi)	15,000 (103350 kilopascals)
Molding temp.	590°F (319°C)

Example 7

Preparation of resorcinol diacetate

110 gm (1.0 mole) of resorcinol and 255 gm (2.5 mole) of acetic anhydride are added to a reaction vessel fitted with a distillation head, condenser, thermometer, and receiving vessel and heated to a temperature of 100°C for a period of about 1 hr under an atmosphere of nitrogen. The temperature is then raised to 130°C to distill off acetic acid and finally to 140°C to distill off the excess acetic anhydride.

The resulting product is purified by vacuum distillation under a pressure of about 10 mm Hg. The yield of purified resorcinol diacetate is about 85 to 90% by weight.

The resulting purified resorcinol diacetate is reacted with isophthalic and terephthalic acid in accordance with the procedure outlined in Example 1. The resulting polymer possesses substantially the same physical and chemical properties as the polymer of Example 1.

Examples 8—11

These are comparative examples to illustrate that many of the catalysts typically employed in an ester interchange reaction, utilized to prepare other wholly aromatic polyesters, are unsuitable for use in the present invention. Several different catalysts are utilized in place of the metal acetate catalysts of the present invention in accordance with the procedure outlined in Example 1. The catalysts and reaction conditions are summarized in Tables IIIA and IIIB. The effect of the absence of a catalyst is also illustrated in Tables IIIA and IIIB.

As may be seen from a review of Tables IIIA and IIIB conventional ester interchange catalysts yield very slow reaction rates and inferior end products.

TABLE IIIA
Thermal synthesis of poly(resorcinol phthalate)
Heating profile

Example No.	Catalyst	1st Stage		2nd Stage	
		Temp.	Time	Temp.	Time
8	none	240°C	3 hr	—	—
9	(C ₄ H ₉) ₂ SnO	240°C	6.5 hr	275°C	4 hr
10	Na OAc+Sb ₂ O ₃	240°C	5.5 hr	280°C	4.5 hr
11	Ni (OAc) ₂ +Ni (ClO ₄) ₂	240°C	4 hr	280°C	3 hr

Example No.	Relative rate ^a	I.V. ^b	Comments
8	1st—very slow	—	only 20% reaction
9	1st—very slow	—	dark brown—brittle
10	2nd—no apparent reaction	—	amber, glassy, brittle
11	1st—slow	—	amber, glassy, brittle
	2nd—slow	—	
	1st—moderate	0.16	amber, glassy, brittle
	2nd—no apparent reaction		

^a 1st Stage—rate of HOAC distillation

2nd Stage—rate of torque increase

^b 0.1% in pentafluorophenol

Example 12

This is a comparative example to illustrate the effect on melt polymerizability of utilizing an isophthalic:terephthalic isomer ratio wherein the terephthalic acid is in excess of 30 mole percent of the total isomer mixture.

Thus, a resorcinol phthalate polyester is prepared in accordance with the procedure outlined in Example 1 except that 19.9 gm (0.12 mole) isophthalic acid, and 13.3 gm (0.08 mole) terephthalic acid

are reacted with 39.4 gm of resorcinol diacetate. This corresponds to a molar ratio of isophthalic acid to terephthalic acid of 60:40.

Upon removal of the diphenyl ether as described in Example 1, the pre-polymer solidifies at 240°C and although it melts at temperatures of about 300°C or higher the temperature must be increased to about or above the degradation temperature of the polymer to obtain a melt viscosity suitable to achieve successful melt polymerization.

Example 13

This is a comparative example to illustrate the effect of utilizing an isophthalic:terephthalic acid isomer ratio, wherein the terephthalic acid component is in excess of 30 mole percent, i.e. 60:40 isophthalic:terephthalic, on the melt processability of a resorcinol phthalate polyester.

Since the preparation of a resorcinol phthalate polyester having an acid isomer ratio of about 60:40 isophthalic:terephthalic, respectively, by the melt polymerization described herein is not feasible, it is necessary to prepare such polymer by the solution polymerization technique.

Thus, 27.5 gm (0.25 mole) of resorcinol are added to a reaction vessel containing 400 ml of methylene chloride. 115 gm of triethylamine in 300 ml of methylene chloride is then added to the reaction vessel. A second solution containing 61.6 gm (0.25 mole) of a mixture of isophthaloyl chloride and terephthaloyl chloride wherein the components of said mixture are present therein at a molar ratio of about 0.6:0.4, respectively, is dissolved in 150 ml of methylene chloride and added to the reaction vessel containing the resorcinol at about room temperature. The resulting resorcinol phthalate polyester is then washed several times in HCl and water and attempted to be injection moulded at the conditions utilized in Example 1. It is found that the polymer does not injection mould at the conditions employed.

Example 14

This is a comparative example to illustrate the effect of failing to purify the resorcinol diacetate prior to reacting it with a phthalic acid or mixture thereof.

Thus, example 7 is repeated with the exception that the resulting resorcinol diacetate is not purified prior to forming the resorcinol phthalate polyester.

The resulting impure resorcinol diacetate when attempted to be melt polymerized in accordance with Example 1 does not yield a polymer which gradually increases to the desired molecular weight. Instead, the presence of the impurities changes the stoichiometry of the reaction thereby prohibiting formation of a high molecular weight polymer. The resulting product is dark amber, brittle, glossy and has a low molecular weight which is insufficient for use in typical injection molding techniques.

Industrial applicability

Thus resorcinol phthalate polyesters of the type described herein have a high char, low flammability and good injection molding properties, i.e. they are easily melt processable.

In general, decreased flammability will lead to incomplete combustion which is typically accompanied by the production of large amounts of smoke. Resorcinol phthalate polyesters are exceptions to this rule.

The ability of this polymer to form a char upon combustion contributes to the unexpectedly low level of flammability by retaining the less oxidizable aromatic moieties in the bulk phase via cross linking and thereby removes them from involvement in the combustion as combustible gaseous fuel. Moreover, the carbonaceous char also acts as a thermal (e.g., heat sink) and gas diffusion barrier thereby inducing a cooling effect at the polymer surface while simultaneously disrupting diffusion of oxygen to the polymer surface and small combustible molecules to the flame front.

The resorcinol phthalate polyester of the present invention can be readily melt processed to form a variety of shaped articles, e.g. molded three dimensional articles, fibers, or films. The polyester of the present invention is particularly suited for molding applications and may be molded via standard injection molding techniques commonly utilized when forming molded articles unlike resorcinol phthalates having an acid isomer ratio outside the claimed ranges. Fibers or films may be melt extruded.

Claims

1. A process for preparing a melt processable resorcinol phthalate polyester capable of being made into shaped articles from the molten state which comprises:
 - (a) reacting resorcinol diacetate with a mixture of 95 to 70 mole % isophthalic acid and 5 to 30 mole % terephthalic acid, which reaction is conducted in the presence of a catalyst consisting of an alkali or alkaline earth metal acetate catalyst or a mixture of such catalysts and at a temperature of 180 to 240°C for a period sufficient to form a non-volatile pre-polymer; and
 - (b) polymerizing the non-volatile pre-polymer of step (a) at a temperature above the melting point of both the pre-polymer and the resulting polymerized product in the presence of an alkali or alkaline earth metal acetate catalyst or a mixture of such catalysts to yield a polyester having an inherent

viscosity of 0.4 to 1.5 decilitres/gram; the resorcinol diacetate being reacted with the mixture of phthalic acids in step (a) in the presence of a heat transfer medium which is removed from the non-volatile pre-polymer prior to commencing the polymerization reaction of step (b); and in which the resorcinol diacetate is prepared by reacting resorcinol and an acetylating agent by heating the

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2. A process as claimed in Claim 1 in which the said metal acetate catalyst is a mixture of sodium acetate and potassium acetate in a molar ratio of about 1:1.

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3. A process as claimed in Claim 1 or 2 in which the said metal acetate catalyst is present during steps (a) and (b) in an amount of 1.0 to 0.1% by weight based on the total monomer weight of resorcinol diacetate.

4. A process as claimed in any one of Claims 1 to 3 in which the melt polymerization of the said non-volatile pre-polymer in step (b) is conducted at a temperature of 260 to 290°C.

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5. A process as claimed in any one of Claims 1 to 4 in which the heat transfer medium is diphenyl ether which is present in an amount of from 10 to 50% by weight of the combined weight of reactants and heat transfer medium.

6. A process for preparing a melt processable resorcinol phthalate polyester capable of being made into shaped articles from the molten state which comprises:

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(a) reacting resorcinol diacetate with a mixture of isophthalic acid and terephthalic acid wherein the isophthalic acid is present in said mixture in an amount of 90 mole percent and terephthalic acid is present therein in an amount of 10 mole percent of said mixture which reaction is conducted in the presence of from 1.0 to 0.1% by weight based on the total monomer weight of resorcinol diacetate of a metal acetate catalyst consisting of a mixture of sodium acetate and potassium acetate wherein the components of said catalyst mixture are present at a molar ratio of about 1:1 and at a temperature of 220 to 240°C for a period sufficient to form a non-volatile pre-polymer; and

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(b) polymerizing a melt of the pre-polymer of step (a) at a temperature of 260 to 290°C in the presence of from 1.0 to 0.1% by weight of said metal catalyst mixture of step (a) to yield a polyester having an inherent viscosity of 0.4 to 1.5 decilitres/gram; the resorcinol diacetate being reacted with the mixture of phthalic acids in step (a) in the presence of a heat transfer medium which is removed from the non-volatile pre-polymer prior to commencing the polymerization reaction of step (b); and in which the resorcinol diacetate is prepared by reacting resorcinol and an acetylating agent by heating the said compounds to a temperature of 100 to 130°C and so as to yield resorcinol diacetate and purifying the resulting resorcinol diacetate to the extent sufficient to obtain at least 99.5% by weight resorcinol diacetate, the balance, if any, being the dimerization product of resorcinol.

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7. A process as claimed in Claim 6 in which the acetylating agent is acetic anhydride or an acetyl halide.

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8. A melt processable resorcinol phthalate polyester capable of being made into shaped articles from the molten state characterised in that it comprises the reaction product of resorcinol diacetate and a mixture of from 95 to 80 mole percent isophthalic acid and correspondingly from 5 to 20 mole percent terephthalic acid.

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Patentansprüche

1. Verfahren zur Herstellung eines aus der Schmelze verarbeitbaren Resorcinphthalat-Polyesters, der aus dem Schmelzzustand zu Formgegenständen verarbeitet werden kann, dadurch gekennzeichnet, daß

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(a) Resorcindiacetat mit einem Gemisch aus 95 bis 70 Mol-% Isophthalsäure und 5 bis 30 Mol-% Terephthalsäure umgesetzt wird, wobei die Umsetzung in Gegenwart eines Katalysators aus einem Alkaliacetat oder Erdalkaliacetat oder eines Gemisches derartiger Katalysatoren und bei einer Temperatur von 180° bis 240°C eine hinreichende Zeit lang ausgeführt wird, um ein nichtflüchtiges Prepolymere zu bilden; und

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(b) das nichtflüchtige Prepolymere aus Schritt (a) bei einer Temperatur oberhalb des Schmelzpunktes sowohl des Prepolymeren als auch des erhaltenen Polymerisationsproduktes in Gegenwart eines Alkaliacetat- oder Erdalkaliacetat-Katalysators oder eines Gemisches derartiger Katalysatoren zu einem Polyester mit einer Eigenviskosität von 0,4 bis 1,5 dl/g polymerisiert wird;

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wobei das Resorcindiacetat mit dem Phthalsäuregemisch in Schritt (a) in Gegenwart eines Wärmeübertragungsmediums umgesetzt wird, das man aus dem nichtflüchtigen Prepolymeren vor Beginn der Polymerisationsumsetzung nach Schritt (b) entfernt; und wobei das Resorcindiacetate hergestellt wird durch Umsetzen von Resorcin mit einem Acetylierungsmittel unter Erwärmen dieser Verbindungen auf

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eine Temperatur von 100° bis 130°C, so daß sich Resorcindiacetat ergibt, und das entstehende Resorcindiacetat genügend gereinigt wird, um mindestens 99,5 Gew.-% Resorcindiacetat zu erhalten, während der Rest, falls vorhanden, das Dimerisierungsprodukt des Resorcins ist.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß der Metallacetat-Katalysator ein Gemisch aus Natriumacetat und Kaliumacetat in einem Molverhältnis von etwa 1:1 ist.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der Metallacetat-Katalysator während der Schritte (a) und (b) in einer Menge von 1,0 bis 0,1 Gew.-%, bezogen auf das Gesamtmonomeren-Gewicht des Resorcindiacetats, enthalten ist.

4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Schmelzpolymerisation des nichtflüchtigen Prepolymeren in Schritt (b) bei einer Temperatur von 260° bis 290°C ausgeführt wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, daß das Wärmeübertragungsmedium Diphenylether ist, der in einer Menge von 10 bis 50 Gew.-% des kombinierten Gewichtes aus Reaktanten und Wärmeübertragungsmedium enthalten ist.

6. Verfahren zur Herstellung eines aus der Schmelze verarbeitbaren Resorcinsphthalat-Polyesters, der aus dem Schmelzzustand zu Formgegenständen verarbeitet werden kann, dadurch gekennzeichnet, daß

(a) Resorcindiacetat mit einem Gemisch aus Isophthalsäure und Terephthalsäure umgesetzt wird, in dem die Isophthalsäure in einer Menge von 90 Mol-% und Terephthalsäure in einer Menge von 10 Mol-% vorliegt, die Umsetzung in Gegenwart von 1,0 bis 0,1 Gew.-%, bezogen auf das Gesamtmonomeren-Gewicht des Resorcindiacetats, eines Metallacetat-Katalysators, der aus einem Gemisch aus Natriumacetat und Kaliumacetat besteht, bei einer Temperatur von 220° bis 240°C eine hinreichende Zeit lang ausgeführt wird, wobei die Komponenten des Katalysatorgemisches mit einem Molverhältnis von etwa 1:1 zugegen sind, um ein nichtflüchtiges Prepolymeres zu bilden; und

(b) eine Schmelze des Prepolymeren aus Schritt (a) bei einer Temperatur von 260° bis 290°C in Gegenwart von 1,0 bis 0,1 Gew.-% dieses Metallkatalysatorgemisches aus Schritt (a) polymerisiert wird, um einen Polyester mit einer Eigenviskosität von 0,4 bis 1,5 dl/g zu erhalten;

wobei das Resorcindiacetat in Schritt (a) mit dem Phthalsäuregemisch in Gegenwart eines Wärmeübertragungsmediums umgesetzt wird, das man aus dem nichtflüchtigen Prepolymeren vor Beginn der Polymerisationsumsetzung des Schritt (b) entfernt; und das Resorcindiacetat hergestellt wird durch Umsetzen von Resorcin mit einem Acetylierungsmittel unter Erwärmen dieser Verbindungen bei einer Temperatur von 100 bis 130°C, so daß sich Resorcindiacetate ergibt, und das entstehende Resorcindiacetat genügend gereinigt wird, um mindestens 99,5 Gew.-% Resorcindiacetat zu erhalten, während der Rest, falls vorhanden, das Dimerisierungsprodukt des Resorcins ist.

7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Acetylierungsmittel Acetanhydrid oder ein Acetylhalogenid ist.

8. Aus der Schmelze verarbeitbarer Resorcinsphthalat-Polyester, der aus dem Schmelzzustand zu Formgegenständen verarbeitet werden kann, dadurch gekennzeichnet, daß der Polyester das Reaktionsprodukt aus Resorcindiacetat und einem Gemisch aus 95 bis 80 Mol-% Isophthalsäure und entsprechend 5 bis 20 Mol-% Terephthalsäure aufweist.

45 Revendications

1. Un procédé de préparation d'un polyester phtalate de résorcinol se prêtant au façonnage à l'état fondu, capable d'être mis sous forme d'articles formés à partir de l'état fondu, qui comprend les étapes de:

(a) réaction de diacétate de résorcinol avec un mélange de 95 à 70% en moles d'acide isophtalique et de 5 à 30% en moles d'acide téréphtalique, cette réaction étant conduit en présence d'un catalyseur constitué d'un catalyseur acétate de métal alcalin ou alcalino-terreux ou d'un mélange de tels catalyseurs et à une température de 180 à 240°C pendant une durée suffisante pour former un pré-polymère non volatil; et

(b) polymérisation du pré-polymère non volatil de l'étape (a) à une température supérieure au point de fusion du pré-polymère et du produit polymérisé résultant en présence d'un catalyseur acétate de métal alcalin ou alcalino-terreux ou d'un mélange de tels catalyseurs pour donner un polyester ayant une viscosité intrinsèque de 0,4 à 1,5 décilitre/gramme; le diacétate de résorcinol ayant réagi avec le mélange d'acides phtaliques dans l'étape (a) en présence d'un milieu de transfert de chaleur qui est enlevé du pré-polymère non volatil avant de commencer la réaction de polymérisation de l'étape (b); et dans lequel le diacétate de résorcinol est préparé par réaction de résorcinol et d'un agent acétylant en chauffant les dits composés à une température de 100 à 130°C et de façon à donner du diacétate de résorcinol, et purification du diacétate de résorcinol résultant jusqu'à un point suffisant pour obtenir au moins 99,5% en poids de diacétate de résorcinol, le reste, s'il y en a, étant le produit de dimérisation du résorcinol.

2. Un procédé selon la revendication 1 dans lequel le dit catalyseur acétate de métal est un mélange d'acétate de sodium et d'acétate de potassium dans un rapport molaire d'environ 1/1.

3. Un procédé selon la revendication 1 ou 2 dans lequel le dit catalyseur acétate de métal est présent pendant les étapes (a) et (b) dans une quantité de 1,0 à 0,1% en poids par rapport au poids total de monomère de diacétate de résorcinol.

4. Un procédé selon l'une des revendications 1 à 3 dans lequel la polymérisation à l'état fondu du dit pré-polymère non volatil dans l'étape (b) est conduite à une température de 260 à 290°C.

5. Un procédé selon n'importe laquelle des revendications 1 à 4 dans lequel le milieu de transfert de chaleur est du diphenyl éther qui est présent dans une quantité comprise entre 10 et 50% en poids du poids combiné des réactifs et du milieu de transfert de chaleur.

6. Un procédé de préparation d'un polyester phtalate de résorcinol se prêtant au façonnage à l'état fondu, capable d'être mis sous forme d'articles formés à partir de l'état fondu, qui comprend les étapes de:

(a) réaction de diacétate de résorcinol avec un mélange d'acide isophtalique et d'acide téréphtalique où l'acide isophtalique est présent dans le dit mélange dans une quantité de 90 pourcent en moles et l'acide téréphtalique est présent dedans dans une quantité de 10 pourcent en moles du dit mélange, cette réaction étant conduite en présence de 1,0 à 0,1% en poids, basé sur le poids total de monomères de diacétate de résorcinol, d'un catalyseur acétate de métal constitué d'un mélange d'acétate de sodium et d'acétate de potassium où les composants du dit mélange catalyseur sont présents dans un rapport molaire d'environ 1/1 et à une température de 220 à 240°C pendant une durée suffisante pour former un pré-polymère non volatil; et

(b) polymérisation d'une masse fondue du pré-polymère de l'étape (a) à une température de 260 à 290°C en présence de 1,0 à 0,1% en poids du dit mélange catalyseur métallique de l'étape (a) pour donner un polyester ayant une viscosité intrinsèque de 0,4 à 1,5 décilitre/gramme; le diacétate de résorcinol ayant réagi avec le mélange d'acides phtaliques dans l'étape (a) en présence d'un milieu de transfert de chaleur qui est enlevé du pré-polymère non volatil avant de commencer la réaction de polymérisation de l'étape (b); et dans lequel le diacétate de résorcinol est préparé par réaction de résorcinol et d'un agent acétylant en chauffant les dits composés à une température de 100 à 130°C et de façon à donner du diacétate de résorcinol et purification du diacétate de résorcinol résultant jusqu'à un point suffisant pour obtenir au moins 99,5% en poids de diacétate de résorcinol, le reste, s'il y en a, étant le produit de dimérisation du résorcinol.

7. Un procédé selon la revendication 6 dans lequel l'agent acétylant est l'anhydride acétique ou un halogénure d'acétyle.

8. Un polyester phtalate de résorcinol se prêtant au façonnage à l'état fondu, capable d'être mis sous forme d'articles formés à partir de l'état fondu, caractérisé en ce qu'il comprend le produit de réaction de diacétate de résorcinol et d'un mélange de 95 à 80 pourcent en moles d'acide isophtalique et, d'une façon correspondante, de 5 à 20 pourcent en moles d'acide téréphtalique.