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APPLICATION NO. 23449/92

NOTICE OF ENTITLEMENT

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being authorised by the Applicant(s)/Nominated Person(s) in respect of an application entitled:

ESTER COMPOSITION

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DATED this 12th day of January 19 94

(Signature)

Albertus Wilhelmus Joannes ZEESTRATEN
(Name & Title)

(special proxy)

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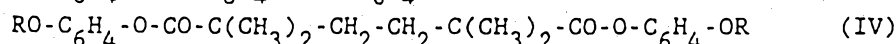
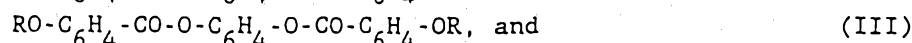
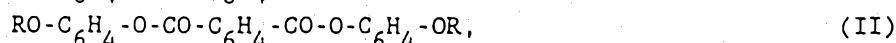
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(57) Claim

1. A method for preparing an ester composition in which at least one phenolic ether group of a molecule, in which the phenolic ether group is derived from a phenol and a secondary-, tertiary alkyl or cycloalkyl group, an allyl- or a benzyl group, is reacted with at least one haloformyl group of another molecule.

2. A method according to claim 1, in which the phenolic ether group is derived from a phenol and a hydrocarbyl radical of the class comprising isopropyl, 2-butyl, tert.-butyl, 2-pentyl, tert.-pentyl, allyl, benzyl and cycloalkyl containing 5 - 8 carbon atoms.

11. A compound of any of the formulae



in which each R independently is a group selected from isopropyl; 2-butyl; tert.-butyl; 2-pentyl; tert.-pentyl; allyl for a compound represented by formulae (I), (II) and (III); or benzyl or cycloalkyl with 5 to 8 carbon atoms for a compound represented by formulae (I) and (IV).

12. A compound of the formula $\text{ClCO-C}_6\text{H}_3\text{(-OCH(CH}_3)_2)_2$ in which the isopropoxy substituents $\text{-OCH(CH}_3)_2$ are in meta positions to each

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other and in which $-C_6H_4-$ is a 1,4-phenylene group or a 1,3-phenylene group.

13. An oligomeric poly(hydroxybenzoate) ester having in the molecules at least one alkoxy end group of the class comprising isopropoxy, 2-butoxy, tert.-butoxy, 2-pentoxy, tert.-pentoxy, allyloxy, benzyloxy and cycloalkoxy with 5 to 8 carbon atoms.

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(54) Title: ESTER COMPOSITION			
(57) Abstract The invention relates to a method for preparing an ester composition in which at least one phenolic ether group of a molecule is reacted with at least one haloformyl group of another molecule. Preferably the molecules contain on average substantially two phenolic ether- and/or haloformyl groups, e.g. they contain one phenolic ether group and one chloroformyl group. The phenolic ether group may be derived from a carboxylated, alkylated or arylated phenol of the class comprising hydroquinone, p,p'-bisphenol, 4- and 3-hydroxybenzoic acid, 3-propyl-4-hydroxy-benzoic acid, a dihydroxynaphthalene and 7-hydroxynaphthalene-carboxylic acid. The phenolic ether group is derived from a phenol and a hydrocarbyl radical of the class comprising isopropyl, 2-butyl, tert.-butyl, 2-pentyl, tert.-pentyl, allyl, benzyl and cycloalkyl containing 5-8 carbon atoms. A preferred compound to use is 4-isopropoxybenzoic acid. The molecule containing at least one haloformyl group may be a benzoylchloride, terephthaloylchloride, naphthaloylchloride, 2,6- and 2,7-naphthalene dicarbonylchloride and the diacylchlorides of aliphatic C4-C9 dicarboxylic acids. A number of diethers are claimed and also a novel poly(-hydroxycarbonate) ester with special endgroups.			

ESTER COMPOSITION

The invention relates to a method for preparing an ester composition, more in particular for preparing a polyester or alternatively an oligomeric ester composition.

5 Polyesters are often prepared by polycondensation of hydroxy-acids or dicarboxylic acids and diols, which reaction proceeds at relatively high temperatures. Suppression of side reactions as decarboxylation, dehydration of the alcohol or ether formation can be achieved by transesterification, which reaction is mainly used for the manufacturing of the important polyesters polyethylene-
10 terephthalate (PET) and polybutyleneterephthalate (PBT). Reaction conditions usually involve prolonged heating to temperatures between 240 and 300°C. Less severe reaction conditions can be used when the carboxylic acid group is activated by using the corresponding acylchloride or mixed anhydride. Dehydrating agents as
15 thionylchloride and phosphorous derivatives have been used to polymerize 4-hydroxybenzoic acid (cf. Polyesters 1965, Elsevier, N.Y. 1, 13 and Makromol. Chem. 1981, 182, 681).

A mild method (reaction temperature 100-150°C) which also enables the manufacture of compounds with both an alcohol functionality and a carboxylic acid halide in a monomer is disclosed in
20 Makromol. Chem. Rapid Commun. 1980, 1, 457 and consists of protecting the alcohol group with trimethylsilylchloride. This method has been used for the preparation of the poly- and oligomeric ester poly(4-hydroxybenzoate) under mild conditions using
25 4-(trimethylsilyloxy)benzoylchloride as starting material. Poly(4-hydroxybenzoate), in particular its copolymers are valuable products in connection with their special physical properties useful as a stable engineering plastic (high crystallinity, extremely low solubility and thermotropic liquid-crystallinity) and many efforts
30 have been made to develop a satisfactory manufacturing process with suitable monomers. This does not only apply for ester compositions

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based on hydroxycarboxylic acid building blocs, but also for ester compositions based on dicarboxylic acid and diol building blocs.

Most of the known ester manufacturing processes outlined above require relatively high reaction temperatures or alternatively they
5 require less accessible, expensive, starting materials like silylated phenols, which materials previously need to be prepared from a phenol and trialkylchlorosilane.

Therefore there is a need for an economically attractive industrial bulk manufacturing process using cheap starting materi-
10 als and operating under attractive economical, environmental and safe conditions, i.e. using rather simple equipment and resulting in a significant reduction of the cost price of the poly- and/or oligomeric ester. Consequently considerable research and development efforts have been made for an improved manufacturing process
15 for these ester compositions.

The present invention provides a method for preparing an ester composition by acylative ether cleavage in which at least one activated phenolic ether group of a molecule is reacted with at least one haloformyl group of another molecule. Under an activated
20 phenolic ether group is here to be understood a phenolic ether derived from a phenol and a secondary-, tertiary alkyl or cycloalkylgroup, an allyl- or a benzyl group. Preferably it is a phenolic ether derived from a phenol and a hydrocarbyl radical of the class comprising isopropyl, 2-butyl, tert.-butyl, 2-pentyl, tert.-pentyl, allyl, benzyl and cycloalkyl containing 5 - 8 carbon
25 atoms.

It is considered surprising that acylative ether cleavage of activated phenolic ethers with a compound having at least one haloformyl group according to the present invention was found to be
30 an attractive synthetic route for preparing an ester composition because normal Friedel Crafts acylation of the aromatic nucleus was to be expected on the basis of the prior art. (cf. Meerwein, H in Houben Weyl, Methoden in der organischen Chemie, fourth edition, 6/3, 155).

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Furthermore the phenolic ether can be derived from a carboxylated, alkylated or arylated phenol, preferably of the class comprising hydroquinone, p,p'-bisphenol, 3- and 4-hydroxybenzoic acid, 3-propyl-4-hydroxybenzoic acid, 6-hydroxynaphthalene carboxylic acid and a dihydroxynaphthalene (more preferably from 4-hydroxybenzoic acid and 2,7- and/or 1,4-dihydroxynaphthalene).

Furthermore the molecule containing at least one haloformyl group is preferably selected among the chloroformyl class of compounds comprising a benzoylchloride (optionally substituted), terephthaloyl(di)chloride, naphthalene(di)carbonylchloride and the diacylchlorides of aliphatic C4-C9 dicarboxylic acids.

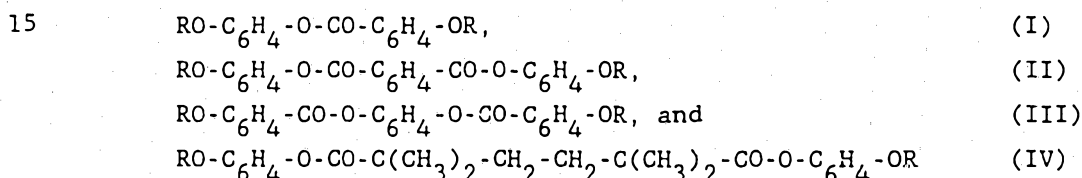
It is further recommended that the reaction conditions when preparing the ester composition are mild, e.g. the reaction can preferably be carried out at a temperature between 20 and 150°C, optionally in the presence of a catalytic amount of a Lewis acid. Under a catalytic amount is here to be understood from 0.1 to 5 % (w.w.) of a Lewis acid. Particularly suitable Lewis acids are stannic tetrachloride, zinc dichloride and ferric chloride. Sometimes the presence of a solvent is also desirable to decrease the catalytic activity to a suitable level. Halogenated hydrocarbons e.g. chlorobenzene and tetrachloroethane are a good choice. The reaction is preferably carried out at atmospheric pressure in an inert atmosphere vis-à-vis the reactants.

In a preferred embodiment of the invention the molecules contain on average substantially two activated phenolic ether- or haloformyl groups, so that the ester composition obtained is essentially unbranched. Particularly suitable molecules which can be reacted with a dihaloformyl compound are 1,4-di-isopropoxybenzene, or bis(4-hydrocarbyloxyphenyl)terephthalate, obtainable by reacting two moles of a monohydrocarbyl ether of hydroquinone with terephthaloylchloride, wherein the hydrocarbyl group is selected from the class comprising isopropyl, 2-butyl, tert.-butyl, 2-pentyl, tert.-pentyl, allyl, benzyl and cycloalkyl containing 5-8 carbon atoms.

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In another preferred embodiment of the invention the molecules contain each one activated phenolic ether group and one haloformyl group, so that the polyester composition obtained is homogeneous. One of the advantages of the method according to the present invention is therefore also that polyesters can be prepared from molecules (monomers) that contain both (protected) phenolic hydroxy groups as well as haloformyl groups. Particularly suitable compounds containing one activated phenolic ether group are 4-isopropoxybenzoylchloride and 4-benzyloxybenzoylchloride.

The present invention also comprises a number of novel compounds which compounds are useful to prepare and/or to modify ester compositions in accordance with one or more of the methods according to the present invention. These compounds are represented by the following formulae:



in which each R independently is a group selected from isopropyl; 2-butyl; tert.-butyl; 2-pentyl; tert.-pentyl; allyl for compounds represented by formulae (I), (II) and (III); or benzyl or cycloalkyl with 5 to 8 carbon atoms for compounds represented by formulae (I) and (IV). In the above formulae the substituents R are preferably the same groups.

In order to obtain polyester compositions with special physical properties it may be useful to adjust the average number of activated phenolic ether- and/or haloformyl groups by incorporation of a minor amount of a trifunctional compound e.g. of the formula $\text{ClCO-C}_6\text{H}_3(\text{-OCH(CH}_3)_2)_2$, in which the isopropoxy substituents $\text{-OCH(CH}_3)_2$ are in meta positions to each other.

For the sake of completeness it is observed that in the above formulae $\text{-C}_6\text{H}_4\text{-}$ is meant to indicate a 1,4-phenylene group or a 1,3-phenylene group, with preference for the former.

The method according to the present invention provides inter alia valuable, novel, poly- and/or oligomeric poly(hydroxybenzoate)

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esters, e.g. with a degree of polymerization (dp) between 3 and 500, having in the molecules as least one end group which is an alkoxygroup of the class comprising isopropoxy, 2-butoxy, tert.-butoxy, 2-pentoxy, tert.-pentoxy, allyloxy, benzyloxy and cycloalkoxy with 5 to 8 carbon atoms. The presence of these endgroups can
5 e.g. be established by NMR-endgroup analysis as described in further detail below.

The polyester materials according to the present invention are inter alia useful as engineering plastics.

10 Example 1

4-Isopropoxyphenyl(4-isopropoxybenzoate) (precursor)

To a stirred solution of 4-isopropoxyphenol (40mmol, 6.08g), 4-isopropoxybenzoylchloride (40mmol, 7.94g) in 200 ml of CH_2Cl_2 , pyridine (80mmol, 6.32g) was added in 20 min (RT). The mixture was
15 stirred for 1 hour and then extracted with 10% HCl (300ml). Evaporation of the solvent and recrystallization of the remaining solid from ethanol (200ml) gave 8.7g (70%) of the ester. Mp 120°C. $^1\text{H-NMR}$ (CDCl_3 , ppm^j(Hz): 1.34^{6.0}(6H); 1.38^{6.0}(6H); 4.51^{6.0}(1H); 4.66^{6.0}(1H); 6.91^{9.0}(2H); 6.94^{8.8}(2H); 7.93^{9.0}(2H); 8.12^{8.8}(2H).

20 Example 2

Polymer from adipoylchloride and 4-isopropoxyphenyl(4-isopropoxybenzoate)

To a solution of adipoylchloride (5 mmol, 0.902g) and 4-isopropoxyphenyl(4-isopropoxybenzoate) (5 mmol, 1.570g) in 30 ml of dried toluene, 50mg of SnCl_4 were added. The mixture was then
25 stirred under nitrogen for 16 hours at 60°C. The solution was filtered, the solid dissolved in 50 ml of trifluoroacetic acid and the polymer precipitated with 100 ml of methanol. After filtration the polymer was recrystallized from pyridine. Filtration followed
30 by washing with methanol and drying gave 0.7 g of a pale grey polymer (41%). End group analysis (NMR in $\text{CF}_3\text{COOD}/\text{CDCl}_3$ (1:1 v.v.)) showed cleavage of 95% of the isopropyl groups, which corresponds with a dp of 10. Differential scanning calorimetry (DSC) of the polymer (heating rate 10°C/min) showed endotherms at 170°C, 178°C
35 (exotherm on cooling at 152°C) and decomposition at 290-320°C.

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Optical microscopy with crossed polarizers showed an anisotropic liquid state above 180°C, and a biphasic (coexisting anisotropic and isotropic phases) region between 240°C and 310°C.

Example 3

5 Diester from hydroquinone di-isopropylether and acetylchloride

To a stirred mixture of hydroquinone (1mol, 110g), KOH (1.1mol, 61g) in 500ml of methanol, isopropylbromide (1mol, 123g) was added in 2 hours (RT, under N₂). The reaction mixture was then stirred at 50°C for 72 hours. The reaction mixture was cooled to RT and 33% HCl was added (to pH=6). Then CH₂Cl₂ (500ml) was added and the mixture extracted with water (7x 500ml) to remove hydroquinone. Then the organic layer was extracted with KOH (60g in 100ml water). The aqueous layer was extracted twice with CH₂Cl₂ (200ml). The solvent of the combined organic layers was evaporated and the residue distilled to give 31g of hydroquinone di-isopropylether (bp 78°C/0.026kPa), in 16%. The aqueous layer was acidified to pH=5 with 33% HCl and extracted with CH₂Cl₂ (2x 200ml). The combined organic layers were dried over MgSO₄ and the solvent evaporated. Distillation of the residue gave 60-85g (40-55%) of hydroquinone mono-isopropylether (bp 90-100°C/0.026kPa). ¹H-NMR (CDCl₃, ppm^j(Hz)): mono-ether: 1.30^{6.0}(6H); 4.39^{6.0}(1H); 5.4(OH); 6.70-6.83^{AA'BB'}(4H); and the di-ether: 1.30^{6.0}(12H); 4.41^{6.0}(2H); 6.81(4H). Hydroquinone di-isopropylether (5 mmol) was stirred with acetylchloride (10mmol) and 0.1 mmols of SnCl₄ for 3 hours (RT) to give hydroquinone diacetate in a yield of more than 95% together with isopropylchloride.

Example 4

Diester from hydroquinone di-isopropylether and benzoylchloride

Following the procedure described above hydroquinone di-isopropylether (5 mmol) was stirred with benzoylchloride (10mmol) for 3 hours (RT) to give hydroquinone dibenzoate in a yield of above 80% together with isopropylchloride and 4-isopropoxyphenyl acetate in about 10%.

The dibenzoate crystallized from the reaction mixture and prevented efficient stirring.

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$^1\text{H-NMR}$ (CDCl_3 , $\text{ppm}^j(\text{Hz})$): dibenzoate: 7.79 ppm (hydroquinone part) monobenzoate 6.92^{9.2} and 7.12^{9.2} ppm (hydroquinone part) (AA'BB').

Example 5

5 4-Isopropoxybenzoylchloride

To 4-isopropoxybenzoic acid (ex. Janssen, recrystallized from ethanol/water 50/50, mp.166°C) (0.15 mol, 27g), thionylchloride (40ml) was added in 1 hour. After standing overnight, the mixture was distilled and the fraction boiling from 114-118°C/0.26kPa collected, giving 28.8g of isopropoxybenzoylchloride (96%). $^1\text{H-NMR}$ (CDCl_3 , $\text{ppm}^j(\text{Hz})$) 1.37^{6.0} (6H); 4.67^{6.0} (1H); 6.92^{9.0} (2H); 8.04^{9.0} (2H).

Polymerization of 4-isopropoxybenzoylchloride

A sample vial was filled with 2g of isopropoxybenzoylchloride and SnCl_4 was injected. The mixture was homogenized and then kept at the reaction temperature chosen. After the reaction 50mg of the solidified red-brown reaction mixture was hydrolyzed in 1ml of a mixture of $\text{CD}_3\text{OD}/\text{D}_2\text{O}/\text{NaOD}$ (12:3:1, w.w.) (2 hours, 60°C) and the degree of polymerization (dp) was determined by NMR end-group analysis.

20	+ 10mg SnCl_4/RT	dp = 1.5 (24h)	dp = 2.7 (120h)
	+ 30mg SnCl_4/RT	dp = 4.0 (24h)	dp = 4.0 (120h)
	+ 100mg SnCl_4/RT	dp = 4.9 (24h)	dp = 6.0 (120h)
	+ 30mg $\text{SnCl}_4/60^\circ\text{C}$	dp = 4.9 (24h)	
	+ 30mg $\text{SnCl}_4/130^\circ\text{C}$	dp = 21 (24h)	

25 DSC of oligomers with a dp of ca. 4 showed an endotherm at 125°C. Microscopy with crossed polarizers showed above this temperature a highly mobile birefringent phase, which became partly isotropic above 160°C. Temperature of 100% isotropization varied from 170°C for a freshly prepared sample to above 350°C (decomposition) for samples heated for a second time, or samples with a stocktime of several weeks.

30

Example 64-Allyloxybenzoic acid

To a stirred mixture of the sodium salt of methyl-4-hydroxybenzoate (0.1 mol, 17.4g) in dimethylformamide (100 ml),
5 allylchloride (0.12 mol, 9.1g) was added in 20 min (RT). Then the mixture was stirred at 60°C for 4 hours. After cooling, 200ml of ether were added and the mixture extracted with water (3x 100ml). After evaporation of the solvent, the residue was stirred in 100ml of methanol with KOH (0.2 mol, 13g) at 60°C for 4 hours. Then 300ml
10 of water were added, the methanol evaporated and the aqueous layer extracted with 200ml of ether. Precipitation of the acid with HCl, followed by recrystallization from ethanol/water gave 11.5g of allyloxy benzoic acid (65%), mp 165°C.

¹H-NMR (CDCl₃/10% C₅D₅N, ppm^j(Hz)) 4.51^m(2H); 5.28^m(2H);
15 5.98^m(1H); 6.87^{8.7}(2H); 8.03^{8.7}(2H); 6-7(1xOH).

4-Allyloxybenzoylchloride

As described above for isopropoxybenzoylchloride (bp.108-112°C/0.026kPa 13.6g, 66% yield) ¹H-NMR (CDCl₃, ppm^j(Hz))
4.62^m(2H); 5.36^m(2H); 6.04^m(1H); 6.97^{9.0}(2H); 8.06⁹(2H).

Polymerization of 4-allyloxybenzoylchloride

As described for isopropoxybenzoylchloride. (2g of the acid chloride was reacted at ambient temperature with 100mg of SnCl₄ for 2 hours and gave a red-brown solid with a dp of 4.4).

Example 74-Benzyloxybenzoic acid

As described for 4-allyloxybenzoic acid. Yield 14.3g (63%), mp 192°C ¹H-NMR (CDCl₃, ppm^j(Hz)): 4.96(2H); 6.88^{8.8} 8.00^{8.8}(2H).

Polymerization of 4-benzyloxybenzoylchloride

The acid (2g) was stirred in CHCl₃-CHCl₂ (10ml) and thionylchloride (2ml) for 18 hours at ambient temperature. Then at 60°C
30 and reduced pressure, excess of thionylchloride was distilled, together with ca. 5ml of the tetrachloroethane. After cooling to ambient temperature, SnCl₄ (0.1g) was added. The reaction mixture remained colourless and solidified in ca. 2 hours. After 24 hours

solvent and benzylchloride formed were evaporated (RT, 13.3 Pa) and the remaining pale grey solid analyzed as described above, which showed a dp of 7.5.

Example 8

5 Di(4-isopropoxyphenyl)terephthalate

To a solution of 4.56g (30mmol) 4-isopropoxyphenol in 40ml dry pyridine, was added a solution of 3.05g (15mmol) tetramethyl-adipoylchloride in 20ml tetrachloroethane. After stirring at room temperature overnight, and another 3 hours at 60°C, methanol
10 (250ml) was added. The precipitate was washed with methanol, dried at 60°C under vacuum, to give 6.4g (quantitative yield) of crude product. mp: 192-194°C. ¹H-NMR (CDCl₃): δ 8.30 (s, 4H), 7.12 (d, 4H), 6.91 (d, 4H), 4.51 (q, 2H), 1.35 (d, 12H). In trifluoroacetic acid (TFA): 10.80 (d, 4H), 9.57 (d, 4H), 9.57 (s, 4H), 7.10 (q, 2H), 3.85 (d, 12H). ¹³C-NMR (CDCl₃): 166.7, 155.3, 144.5, 130.6,
15 130.5, 122.1, 117.8, 73.4, 21.0. IR (nujol): 1725 (C=O) cm⁻¹.

Example 9

Ester from hydroquinone isopropyl-n-propylether and acetylchloride.

Hydroquinone isopropyl-n-propylether was reacted with acetylchloride for 3 hours (RT) to give 4-n-propoxyphenyl acetate (yield
20 > 98%) together with isopropylchloride.

¹H-NMR (CDCl₃, ppm^j(Hz)) of the acetate : 1.00^{7.5}(3H);
1.76^{7.5}(2H); 2.24(3H); 3.87^{7.5}(2H); 6.84^{9.2}(2H); 6.95^{9.2}(2H)
(AA'BB').

25 Example 10

Ester from hydroquinone isopropyl-n-propylether and benzoylchloride.

Hydroquinone isopropyl-n-propyl ether was reacted with benzoylchloride for 3 hours (RT) to give 4-n-propoxyphenyl benzoate
30 (yield more than 80%) together with isopropylchloride.

¹H-NMR (CDCl₃, ppm^j(Hz)) of the benzoate: 1.04^{7.5}(3H);
1.82^{7.5}(2H); 3.92^{7.5}(2H); 6.93^{9.1}(2H); 7.12^{9.1}(2H) (AA'BB'); Benzoate protons were hidden under excess of benzoylchloride.

Example 114-Benzyloxy-3-propyl-benzoic acid and polymerization

To a stirred solution of the sodium salt of methyl 4-hydroxy-benzoate (0.5mol, 87g) in dimethylformamide (400ml) allylchloride (0.55mol, 42g) was added in 2 hours (inert atmosphere, RT). After stirring in addition for 20 hours, diethylether (400ml) was added and the mixture extracted with 400ml of water, 400ml of 5% HCl and 400ml of water. Then the ethereal solution was dried over $MgSO_4$, the solvent evaporated and the residue analyzed, showing almost pure 4-allyloxymethyl benzoate. 1H -NMR ($CDCl_3$, ppm^j(Hz)): 3.86(3H); 4.56^m(2H); 5.25-5.45^m(2H); 6.03^m(1H); 6.91^{8.8}(2H); 7.97^{8.8}(2H).

The ether-ester obtained was heated to 220°C for 4 hours giving 3-allyl-4-hydroxybenzoate (contaminated with ca. 20% of the corresponding coumaran and ca. 25% of the corresponding styrene). 1H -NMR ($CDCl_3$, ppm^j(Hz)): 3.42^m(2H); 3.88(3H); 5.10^m(2H); 6.00^m(1H); 6.88^{8.4}(1H); 7.81^{8.4}(1H); 7.84(1H); 5.0(-OH).

The Claisen product so obtained was stirred in ethanol (400ml) under a hydrogen atmosphere for 18 hours using 10% Pd/C (8g) as a catalyst. After filtration and evaporation of the solvent, the residue (88g) consisted of 3-propyl-4-hydroxymethyl benzoate (contaminated with the coumaran, ca. 20%).

1H -NMR ($CDCl_3$, ppm^j(Hz)): 2.096^{7.8}(3H); 1.65^{7.8}(2H); 2.61^{7.8}(2H); 3.94(3H); 6.81^{8.4}(1H), 7.7-8.6(2H); 6.4(-OH) (Characteristic signals of the coumaran 1.48^{6.4}(3H); 2.82^{7.5-15.4}(1H); 3.33^{8.0/15.4}(1H); 5.00^{6.4/7.5/8.0}.

The ester was dissolved in dimethylformamide (400ml) and potassium-t-butyrate 0.5mol, (61g) was added in 1 hour, followed by the addition of benzylchloride (0.5mol, 63.3g) in 1 hour (RT). After stirring for 48 hours the mixture was worked up as described for the allyl ether, giving 122g of 4-benzyloxy-3-propylmethyl benzoate (together with the coumaran).

1H -NMR ($CDCl_3$, ppm^j(Hz)): 1.00^{7.3}(3H); 1.71^{7.3}(2H); 2.72^{7.3}(2H); 3.91(3H); 5.16(2H); 6.93^{10.3}(1H); 7.3-7.5(5H); 7.91^m(2H).

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The benzyl ether was dissolved in a mixture of ethanol (400ml), water (100ml) and KOH (0.5mol, 33g) and stirred for 6 hours at 60°C. Then the ethanol was evaporated, water (300ml) was added and the solution acidified with HCl (33%) to pH-4. The solid
5 was collected and recrystallized from ethanol/water (50/50), methanol/toluene (30/70) and finally ethanol (100%) giving 66g of pure 4-benzyloxy-3-propylbenzoic acid (overall yield 49%, mp 163°C).

¹H-NMR (CDCl₃/10% pyridine-D₅, ppm^j(Hz)): 0.77^{7.3}(3H);
10 1.501^{7.3}(2H); 2.51^{7.3}(2H); 4.93(2H); 6.75^{9.0}(1H); 7.1-7.3(5H), 7.83^m(2H); 4.6(-OH).

Polymerization

The ether acid (20mmol, 5.4g) was stirred in tetrachloroethane (100ml) and SOCl₂ (5ml) for 16 hours at 50°C. Then at this tempera-
15 ture excess of SOCl₂ and 50ml of tetrachloroethane (TCE) were distilled off at diminished pressure. After the addition of SnCl₄ (0.4g) the solution was stirred at 50°C for 40 hours. Then methanol (150ml) was added and the polymer precipitated by centrifugation. Decantation of the solvent followed by dissolving the polymer in
20 tetrachloroethane (50ml) and repeating the precipitation, gave, after drying, 3.3g of polymer (ca. 94%). ¹H-NMR showed that benzyl-ation of had occurred to an extent of ca. 13%.

¹H-NMR (CDCl₃/TCE ppm): 1.09(3H); 1.74(2H); 2.70(2H); 3.95(0.3H); 6.8-7.4(2.9H); 8.21(2H).

25 Differential scanning calorimetry (DSC) at a heating rate of 10°C/min showed an endotherm at 243°C on heating (exotherm at 181°C on cooling) and decomposition starting above 360°C.

Microscopy (crossed polarizers) showed meltflow above 234°C (nematic Schlieren texture) and isotropization at 390°C (decomposi-
30 tion and isotropic behaviour afterwards).

Gel permeation chromatography (tetrahydrofuran, polystyrene standard) showed a weight average of 150,000 and a polydispersity of 2.3.

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Example 12Hydroquinone di(4-isopropoxybenzoate)

To a stirred mixture of 4-isopropoxybenzoylchloride (15mmol, 2.97g) and hydroquinone (7.5mmol, 0.825g) in CH_2Cl_2 (50ml), pyridine (2ml) was added in 15 minutes. After stirring for 1 hour, the mixture was extracted with water, 10% HCl and water (100ml each). Then the solvent was evaporated and the remaining solid recrystallized from ethanol/ CH_2Cl_2 (70/30), giving 2.56g of the product (yield 79%, mp 195°C).

$^1\text{H-NMR}$ (CDCl_3 , ppm^j(Hz)): 1.39^{6.0}(12H); 4.68^{6.0}(2H); 6.96^{8.8}(4H); 7.25(4H); 8.14^{8.8}(4H)

Example 13Bis(4-isopropoxyphenyl)tetramethyladipate

To a solution of 4.56g (30mmol) 4-isopropoxyphenol in 20ml dry pyridine, was added a solution of 3.59g (15mmol) tetramethyladipoylchloride in 10 ml tetrachloroethane. After stirring at room temperature overnight, water (100ml) and tetrachloroethane (50ml) were added. The tetrachloroethane layer was washed with water, dried (MgSO_4), and the solvent evaporated. The crude product was recrystallized from ether to yield 71% of theory of the above named compound, mp 100°C, $^1\text{H-NMR}$ (acetone): δ 6.98 (d, 4H), 6.87 (d, 4H), 4.54 (q, 2H), 1.75 (s, 4H), 1.32 (s, 12H), 1.26 (d, 12H).

Example 14Polymerization of 2,6-naphthalenedicarbonylchloride and 2,7-di-benzyloxynaphthalene

To a solution of the benzyloether (5mmol, 1.70g) and the acid chloride (5mmol, 1.67g) in dry tetrachloroethane (10ml) SnCl_4 (0.1g) was added and the mixture stirred for 40 hours at 50°C under a nitrogen atmosphere. Precipitation with methanol and subsequent drying gave 1.82g of an amorphous light brown polymer showing $^1\text{H-NMR}$ signals at 4.0, 7.2, and 7.6-8.6 ppm.

Example 15Polymerization and synthesis of 3-benzyloxybenzoic acid

The reactions were carried out as described for 4-benzyloxybenzoic acid. 3-Benzyloxybenzoic acid was obtained in 66% yield (mp 135°C).

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$^1\text{H-NMR}$ ($\text{CDCl}_3/10\% \text{C}_5\text{D}_5\text{N}$, ppm): 4.86(2H); 6.88-7.26(8H); 7.56^m(1H); 4.6(OH).

The acid ether was converted into its chloride as described for 4-benzyloxybenzoic acid and the polymerization was carried out at 50°C for 40 hours. The polymer partly separated from the tetrachlorethane solution as an amorphous darkbrown tar. Additional polymer precipitated upon the addition of methanol. After drying a brittle amorphous polymer (1.0g) was obtained. A chloroform soluble fraction (ca. 50%) showed an $^1\text{H-NMR}$ spectrum identical to the one published by Kricheldorf et al (POLYMER, 1982, 23, p.1821). Additional signals at 3.9ppm indicated benzylation of the polymer to an extent of ca. 7%. End groups were not detected by NMR. The only solvent found that completely dissolved the polymer consisted of a mixture of quinoline and phenol (50/50 w.w.).

Example 16

Preparation and polymerization of 3,5-diisopropoxybenzoic acid

To a homogenized mixture of 3,5-dihydroxy methylbenzoate (50mmol, 8.4g), potassium tert-butyrate (110mmol, 8.4g) in dimethylformamide, isopropylbromide (110mmol, 13.5g) was added at RT in 2 hours under an inert atmosphere. Then the mixture was stirred for 16 hours at 60°C, cooled to ambient temperature and diethyl-ether (200ml) and 5% HCl (100ml) were added. The organic layer was separated and twice extracted with water (200ml). After drying over MgSO_4 , the solvent was evaporated and the residue stirred in a mixture of ethanol (100ml), KOH (0.11m) and water (20ml) at 70°C for 6 hours. Then the ethanol was evaporated, water (150ml) was added and the solution acidified with 33% HCl to pH4. The solid was filtrated and recrystallized twice from ethanol/ H_2O (70/30) to give 11.9g of the ether-acid (64%, mp 114°C).

$^1\text{H-NMR}$ ($\text{CDCl}_3/10\% \text{C}_5\text{D}_5\text{N}$), ppm^j(Hz): 1.31^{6.0}(12H); 4.56^{6.0}(2H); 6.60^{2.3}(1H); 7.24^{2.3}(2H); 10.1(OH).

The acid (14mmol, 4g) was stirred with SOCl_2 (6ml) overnight. Then the reaction mixture was distilled at reduced pressure giving 3,5-diisopropoxybenzoylchloride (1.7g, 40%). Bp 120-122°C/0.17kPa.

$^1\text{H-NMR}$ (CDCl_3 , ppm^j(Hz)): 1.33^{6.0}(12H); 4.56^{6.0}(2H); 6.69^{2.3}(1H); 7.17^{2.3}(2H).

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The polymerization was carried in tetrachloroethane (10ml) using 1g of the ether halide and 0.1g of SnCl_4 (4 hours at 70°C). ^1H -NMR of the reaction mixture showed a $\text{dp} > 20$ based on ratio of isopropoxy groups and isopropylchloride formed. Extraction of the reaction mixture with K_2CO_3 (5%) followed by evaporation of the tetrachlorethane gave 0.75g of an amorphous polymer (The CDCl_3 soluble fraction of the polymer of ca 30% showed broad NMR-signals at 1.3, 4.6 and 6.4-7.6 ppm).

Example 1710 2,7-Dibenzyloxynaphthalene

To a stirred solution of 2,7-dihydroxynaphthalene (50mmol, 8.0g) and benzylchloride (0.11 mol, 13.9g) in dimethylformamide (200ml), potassium tert-butyrate (0.11mol, 13.4g) was added in 3 hours (under nitrogen, 30°C). After stirring for 5 hours, CH_2Cl_2 (300ml) was added and the mixture extracted with water (3x 300ml), dried over MgSO_4 and the solvent evaporated. Recrystallization of the residue from ethanol gave 5.5g of the ether (32% yield, mp 161°C).

15 ^1H -NMR (CDCl_3 , ppm^j(Hz)): 5.18(4H); 7.12^m(4H); 7.32-7.54^m(10H); 7.70^{8.5}(2H).

Example 18Hydroquinone di(4-isopropoxybenzoate)

To a stirred mixture of 4-isopropoxybenzoylchloride (15mmol, 2.97g) and hydroquinone (7.5mmol, 0.825g) in CH_2Cl_2 (50ml), pyridine (2ml) was added in 15 min. After stirring for 1 hour, the mixture was extracted with water, 10% HCl and water (100ml each). Then the solvent was evaporated and the remaining solid recrystallized from ethanol/ CH_2Cl_2 (70/30), giving 2.56g of the product (yield 79%, mp 195°C).

30 ^1H -NMR (CDCl_3 , ppm^j(Hz)): 1.39^{6.0}(12H); 4.68^{6.0}(2H); 6.96^{8.8}(4H); 7.25(4H); 8.14^{8.8}(4H).

C L A I M S

1. A method for preparing an ester composition in which at least one phenolic ether group of a molecule, in which the phenolic ether group is derived from a phenol and a secondary-, tertiary alkyl or cycloalkyl group, an allyl- or a benzyl group, is reacted with at least one haloformyl group of another molecule.
5
2. A method according to claim 1, in which the phenolic ether group is derived from a phenol and a hydrocarbyl radical of the class comprising isopropyl, 2-butyl, tert.-butyl, 2-pentyl, tert.-pentyl, allyl, benzyl and cycloalkyl containing 5 - 8 carbon atoms.
- 10 3. A method according to any of claims 1 or 2, in which the phenolic ether group is derived from a carboxylated, alkylated or arylated phenol of the class comprising hydroquinone, p,p'-bisphenol, 4- and 3-hydroxybenzoic acid, 3-propyl-4-hydroxybenzoic acid, a dihydroxynaphthalene and 6-hydroxynaphthalenecarboxylic acid.
15
4. A method according to any of claims 1 to 3, in which the molecule containing at least one haloformyl group is selected from the class comprising a benzoylchloride, terephthaloylchloride, naphthaloylchloride, 2,6- and 2,7-naphthalenedicarbonylchloride and the diacylchlorides of aliphatic C4-C9 dicarboxylic acids.
20
5. A method according to any of claims 1 to 3, in which the molecules contain on average substantially two phenolic ether- or haloformyl groups.
- 25 6. A method according to claim 5, in which the molecule containing substantially two phenolic ether groups is selected from the class comprising 1,4-di-isopropoxybenzene, and bis(4-hydrocarbyloxyphenyl)terephthalate, wherein the hydrocarbyl group is selected from the class comprising isopropyl, 2-butyl, tert.-butyl, 2-pentyl, tert.-pentyl, allyl, benzyl and cycloalkyl containing 5-8 carbon atoms.
30

7. A method according to any of claims 1 to 3, in which the molecules contain one phenolic ether group and one chloroformyl group.
8. A method according to any of claims 1 to 3, in which the molecules containing one phenolic ether group and one haloformyl group are selected from the class comprising 4-isopropoxybenzoylchloride, and 4-benzyloxybenzoylchloride.
9. A method according to any of the preceding claims in which the reaction is carried out at a temperature between 20 and 150°C, optionally in the presence of a catalytic amount of a Lewis acid.
10. A method according to claim 9, in which the reaction is carried out in the presence of a catalytic amount of stannic tetrachloride.
11. A compound of any of the formulae
- 15 $\text{RO-C}_6\text{H}_4\text{-O-CO-C}_6\text{H}_4\text{-OR,}$ (I)
 $\text{RO-C}_6\text{H}_4\text{-O-CO-C}_6\text{H}_4\text{-CO-O-C}_6\text{H}_4\text{-OR,}$ (II)
 $\text{RO-C}_6\text{H}_4\text{-CO-O-C}_6\text{H}_4\text{-O-CO-C}_6\text{H}_4\text{-OR, and}$ (III)
 $\text{RO-C}_6\text{H}_4\text{-O-CO-C(CH}_3)_2\text{-CH}_2\text{-CH}_2\text{-C(CH}_3)_2\text{-CO-O-C}_6\text{H}_4\text{-OR}$ (IV)
- in which each R independently is a group selected from isopropyl; 2-butyl; tert.-butyl; 2-pentyl; tert.-pentyl; allyl for a compound represented by formulae (I), (II) and (III); or benzyl or cycloalkyl with 5 to 8 carbon atoms for a compound represented by formulae (I) and (IV).
12. A compound of the formula $\text{ClCO-C}_6\text{H}_3\text{(-OCH(CH}_3)_2)_2$ in which the isopropoxy substituents $\text{-OCH(CH}_3)_2$ are in meta positions to each other and in which $\text{-C}_6\text{H}_4\text{-}$ is a 1,4-phenylene group or a 1,3-phenylene group.
13. An oligomeric poly(hydroxybenzoate) ester having in the molecules at least one alkoxy end group of the class comprising isopropoxy, 2-butoxy, tert.-butoxy, 2-pentoxy, tert.-pentoxy, allyloxy, benzyloxy and cycloalkoxy with 5 to 8 carbon atoms.

INTERNATIONAL SEARCH REPORT

PCT/EP 92/01638

International Application No

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁵		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 C07C67/24; C07C69/017; C07C65/03		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	C07C	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
	No relevant documents disclosed -----	
¹⁰ Special categories of cited documents : ¹⁰ "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "A" document member of the same patent family		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
08 OCTOBER 1992	03. 11. 92	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	KINZINGER J.M.	