



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>6</sup> : C08G 63/181, C07D 321/00</p>	<p>A1</p>	<p>(11) International Publication Number: <b>WO 99/14257</b> (43) International Publication Date: 25 March 1999 (25.03.99)</p>
<p>(21) International Application Number: PCT/US98/17141 (22) International Filing Date: 19 August 1998 (19.08.98) (30) Priority Data: 60/058,878 15 September 1997 (15.09.97) US (71) Applicant: EASTMAN CHEMICAL COMPANY [US/US]; 100 North Eastman Road, Kingsport, TN 37660 (US). (72) Inventor: VAN SICKLE, Dale, E.; 2113 Sheffield Street, Kingsport, TN 37660 (US). (74) Agents: LINDEMAN, Jeffrey, A. et al.; Morgan, Lewis &amp; Bockius LLP, 1800 M Street, N.W., Washington, DC 20036 (US).</p>		<p>(81) Designated States: BR, CN, JP, MX, SG, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i></p>
<p>(54) Title: MONOESTERS AND MACROCYCLIC DIESTER OF PHTHALIC ACID AND SYNTHESIS THEREOF (57) Abstract  Monoesters and macrocyclic diesters of 2,2,4-trimethyl-1,3-pentanediol and phthalic acid or a derivative thereof are described. Methods by which such monoesters and diesters may be prepared are also described. The mono- and diesters according to the invention are useful in the preparation of clear, hard thermoplastic polymers. The thermoplastic polymers are useful in coatings, inks, reinforced plastics and packaging materials.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakistan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

-1-

**Monoesters and Macrocylic Diester of Phthalic Acid and Synthesis Thereof**Field of the Invention

5 The invention relates to monoesters and a macrocylic diester of phthalic acid and derivatives thereof. Such esters of phthalic acid and derivatives thereof are useful in the preparation of thermoplastic polymers. The thermoplastic polymers may be used to prepare coatings, inks, reinforced plastics and packaging.

Description of the Related Art

10 The synthesis of lactones, or cyclic esters, derived from either hydroxyacids or from diacids and dihydroxy compounds is well known to the art. (Carothers, W.H., *Collected Papers of Wallace Hume Carothers on High Polymeric Substances*, Eds. H. Mark and G.S. Whitby, Interscience Publishers, Inc., 248-259 (1940)). Examples include  $\delta$ -valerolactone, prepared by cyclization of 5-hydroxypentanoic acid, and lactide, prepared by the dimerization of lactic acid. These simple compounds which contain  
15 six-membered lactone rings are readily prepared in good yield, as are similar lactones with five atoms in the ring, such as  $\gamma$ -butyrolactone. Seven-membered ring lactones, such as, for example,  $\epsilon$ -caprolactone, can also be readily prepared. However, the synthesis of lactones with larger rings, particularly those with eight to twelve ring atoms, has proven to be more difficult.

20 Macrocylic di- and tetraester compounds, including cyclic esters derived from equimolar amounts of  $\sigma$ -phthalic acid and a glycol, have been prepared. (Bradshaw et al., *Chem. Revs.* 79:37 (1979)). However, the diesters, in particular those forming eight- to ten-membered rings, prepared from  $\sigma$ -phthalic acid and simple glycols such as 1,2-dihydroxyethane, 1,3-dihydroxypropane, and 2-methyl-1,3-dihydroxypropane, were  
25 recovered in poor yields of less than 5%. (Ehrhart, W. A., *J. Org. Chem.* 33:2930 (1968)). The poor yields are believed to be due to inherent ring strain as a result of the two carbonyl groups. (Drewes et al., *J.C.S. Perkin I*, 2148 (1972)). The synthesis of a cyclic tetraester compound from phthalic anhydride and 1,3-dihydroxy-2,2-

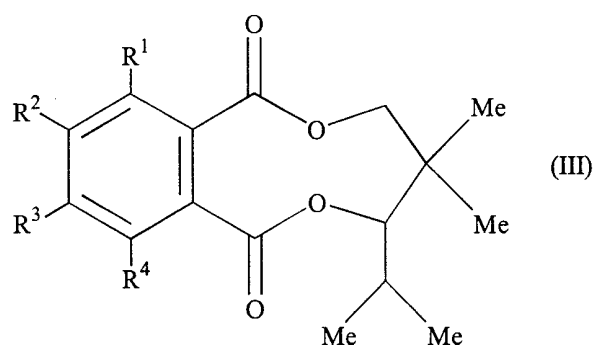
-2-

dimethylpropane was also achieved in very low yields of only 1.7%. (Chen et al., *J. Applied Appl. Polym Sci.* 41:2517 (1990)).

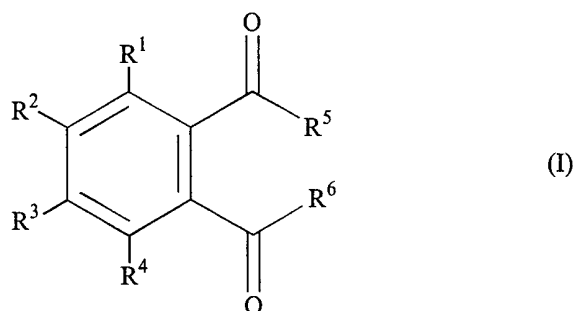
There still exists a need in the art for a synthetic route to prepare cyclic esters or lactones from a phthalic acid derivative and a simple glycol in high yield and purity. The cyclic esters provide unique intermediates in the production of thermoplastic polymers such as polyesters. These polyesters can be used in coatings, inks, reinforced plastics and packaging.

### Summary of the Invention

The invention relates a macrocyclic diester of formula (III):



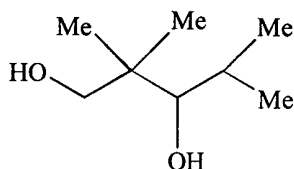
The invention also relates methods of preparing a diester of formula (III) by contacting, optionally in the presence of a catalyst, a phthalic acid derivative of formula (I):



-3-

with the glycol 2,2,4-trimethyl-1,3-pentane diol (TMPD):

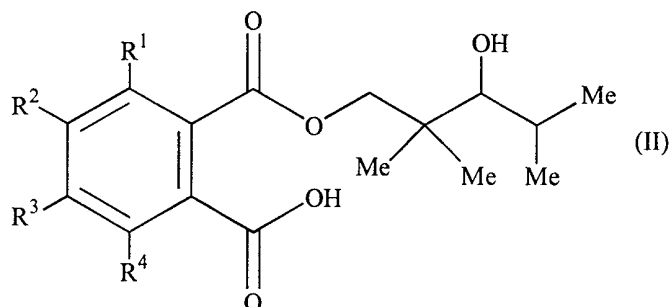
5



10 The invention also relates a thermoplastic polymer resulting from the ring opening polymerization of a diester of formula (III).

The invention still further relates a monoester of formula (II):

15



20

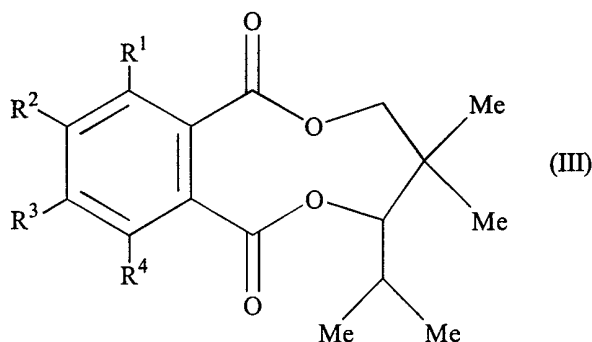
A monoester of formula (II) is an intermediate which can be isolated in the reaction of a phthalic acid derivative of formula (I) with TMPD to form a macrocyclic diester of formula (III).

#### Detailed Description of the Invention

25

One embodiment of the invention is a macrocyclic diester of formula (III):

-4-

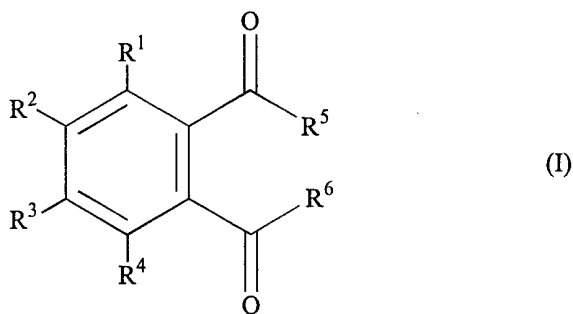


10 In formula (III), R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are, independently, hydrogen, a substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkyl, aryl, or heteroaryl group, a nitro group, a halo group (F, Cl, Br, and I), a thio group, or an amino group. A combination of any two adjacent substituents, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup>, together with the phenyl ring may also form a fused aromatic ring structure such as anthracene or naphthalene. Preferably, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are each a hydrogen. Alternatively, at least one of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> is a C<sub>1</sub>-C<sub>4</sub> alkyl group.

15

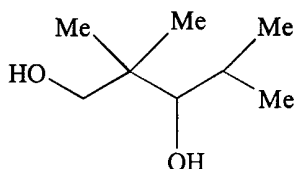
The invention also includes a method of preparing a macrocyclic diester of formula (III) via an esterification reaction. In a method of the invention, a macrocyclic diester of formula (III) may be prepared by contacting under suitable reaction conditions, for example in a suitable solvent and, optionally, in the presence of a catalyst, a phthalic acid derivative of formula (I):

20



-5-

with 2,2,4-trimethyl-1,3-pentane diol (TMPD):



10 In formula (I), R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are as defined above while R<sup>5</sup> and R<sup>6</sup> are independently a hydroxyl group, a chloride group or, when taken together, an oxygen to form a phthalic acid anhydride or its derivative. The reaction may be carried out using typical esterification reaction conditions known in the art. Preferably, such a method is conducted under azeotropic distillation conditions known in the art. Azeotropic distillation conditions remove water from the reaction and moves the reaction toward completion, *i.e.* the formation of a macrocyclic diester of formula (III).

15 To prepare a macrocyclic diester of formula (III), the molar ratio of a phthalic acid derivative of formula (I) to TMPD is preferably about 1:1. A slight molar excess of TMPD may be used without effecting the yield of a diester of formula (III). A large molar excess of generally greater than about 50% of either reactant should be avoided since such conditions renders purification of the desired macrocyclic diester of formula  
20 (III) difficult by increasing the production of potential by-products. Such by-products may include a monoester resulting from the reaction between the phthalic acid derivative and the secondary alcohol position of 2,2,4-trimethyl-1,3-pentane diol (TMPD) and diester isomers. By using a large molar excess of either reactant, the overall yield of the desired macrocyclic diester may be significantly reduced.

25 The phthalic acid derivative may be any phthalic acid derivative of formula (I) as described above capable of forming ester linkage(s) upon reaction with TMPD. Preferably the phthalic acid derivative is phthalic anhydride, phthalic acid or phthaloyl chloride.

-6-

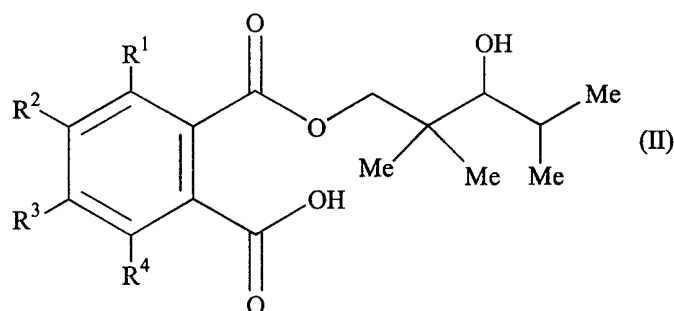
The esterification reaction is preferably accomplished using a catalyst. The catalyst may be any esterification catalyst known in the art. The catalyst preferably increases the rate of the reaction and the yield of desired product. Examples of suitable catalysts, include, but are not limited to, sulfonic acids, stannic acid, titanium salts, manganese salts, and the like. Preferably the catalyst is butyl stannic acid  
5 [(BuSn(O)OH)]. Butyl stannic acid is sold as FASCAT® 4100 available from Elf Atochem of Philadelphia, PA. Preferably, about 0.001 to 0.01 moles catalyst per mole of phthalic acid derivative of formula (I) is used.

Suitable solvents for the esterification reaction are those which dissolve the reactants or facilitate esterification. Preferably, the solvent facilitates the removal of  
10 water as an azeotrope, *i.e.* azeotropic distillation as discussed above. Examples of suitable solvents include, but are not limited to, benzene, toluene and xylene. Preferably, the solvent is toluene or xylene. The amount of solvent used allows for combined reactant concentrations of between 10%-40% by weight of the reaction system. Excess  
15 solvent increases costs of production due to the added cost of the excess solvent, cost of recovery and/or disposal of the excess solvent, and cost of extra equipment required to run the reaction. Too little solvent produces high reactant concentrations which may promote oligomer formation at the expense of diester formation.

The esterification reaction may be conducted at temperatures ranging from about  
20 50°-150°C. More preferably, the reaction temperature ranges from about 100°-135°C. Oligomer formation may also be promoted by excessively high reaction temperatures, especially in combination with high reactant concentrations.

In a method of the invention, the esterification reaction of a phthalic acid derivative of formula (I) with 2,2,4-trimethyl-1,3-pentane diol (TMPD) may be conducted  
25 to first form a monoester of formula (II):

-7-



5

In formula (II), R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are as defined above. If desired, the monoester of  
10 formula (II) may be isolated and purified by techniques known in the art such as, for  
example, recrystallization from toluene. A macrocyclic diester of formula (III) may be  
prepared by heating an isolated monoester of formula (II) under suitable reaction  
conditions, for example in a suitable solvent and, optionally, in the presence of a catalyst.  
15 Preferably, the conversion of an isolated monoester of formula (II) to a macrocyclic  
diester of formula (III) is conducted under azeotropic distillation conditions as described  
above.

To promote the production of a monoester of formula (II) without conversion of  
the monoester to a macrocyclic diester of formula (III), the reaction may be conducted at  
20 temperatures ranging between 50-90°C. Preferably, monoester production is conducted  
at temperatures ranging between 75-85°C. Conducting this reaction within the above  
temperature range favors production of the monoester without conversion to the diester.

Completion of the esterification reactions discussed above may be determined by  
monitoring reactant consumption and macrocyclic diester or monoester formation.  
Consumption of the reactants and production of the macrocyclic diester may be monitored  
25 by techniques known in the art. These techniques include, for example, chromatography  
with vapor phase chromatography (vpc) being a preferred technique. When using vpc, to  
obtain a better analysis, the sample may first be derivatized, for example, with  
trimethylsilyl groups using bis(trimethylsilyl)trifluoroacetamide (BSTFA, commercially  
available from Aldrich Chemical Company of Milwaukee, WI).

When the esterification reaction is complete, the reaction solvent may be removed to yield a solid containing the desired product, *e.g.*, the macrocyclic diester of formula (III) or the monoester of formula (II). The reaction solvent may be removed using techniques known in the art, such as distillation, particularly distillation under reduced pressure, for example using a rotary evaporator.

The product macrocyclic diester of formula (III) or diester of formula (II) may then be purified using known techniques such as recrystallization from an appropriate solvent. A macrocyclic diester of formula (III) may be recrystallized from solvents such as ethanol, methanol and the like. A monoester of formula (II) may be recrystallized from solvents such as toluene, xylene and the like. Preferably, a macrocyclic diester of formula (III) may be recrystallized from methanol, and a monoester of formula (II) may be recrystallized from toluene. As is known on the art, the purified product may then be washed, for example with a small amount of the recrystallization solvent, to remove residual impurities.

Using reaction conditions discussed above, a macrocyclic diester of formula (III) may be obtained in yields of about 40% or greater. After purification, using techniques known in the art as described above, the macrocyclic diester of formula (III) of >99% purity may be isolated by techniques known in the art such as vacuum filtration.

Another embodiment of the invention is a thermoplastic polymer formed from a diester of formula (III). A thermoplastic polymer of a diester of formula (III) may be prepared by a ring opening polymerization of a diester of formula (III) in the presence of a catalyst and heat. Ring opening polymerizations of cyclic diesters to form polyesters are known in the art and may be used to form the thermoplastic polymer of the invention. (Löfgren et al., *J.M.S. Rev. Mocaromo. Chem. Phys.*, C35(3), 379-418 (1995)). The catalyst may be any ring opening polymerization catalyst known in the art, with dibutyl tin oxide being a preferred catalyst. The ring opening polymerization reaction may be conducted at temperature ranging between 150°-250°C, preferably, between 160°-180°C. Excessively high temperatures of >250°C should be avoided since polymer darkening and degradation may result. The ring opening polymerization process is also preferably

-9-

conducted in an inert atmosphere and at pressures ranging from reduced pressure to slightly superatmospheric pressure. Preferably, the combination of temperature and pressure is such that little to none of diester of formula (III) volatilizes and escapes from the system.

5           The thermoplastic polymer according to the invention exhibits exceptional resistance to weathering and hydrolysis due to the highly substituted nature of TMPD. In addition, the thermoplastic polymer according to the invention exhibits high molecular weight and low polydispersity. A polyester of the invention may be used as the resin base in coatings, inks, reinforced plastics and packaging materials.

10           The following examples are given to illustrate the present invention. It should be understood, however, that the invention is not to be limited to the specific conditions or details described in these examples.

**Example 1:**

15           **Synthesis of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione in the Presence of a Catalyst**

          A solution of 14.8 g (0.10 mol) of phthalic anhydride, 16.1 g (0.11 mol) of 2,2,4-trimethyl-1,3-pentanediol (TMPD), and 0.036 g of butyl stannic acid, [(BuSn(O)OH)], (FASCAT® 4100 catalyst) in 125 mL of toluene was refluxed under a short packed column fitted with a Dean-Stark trap for removal of water as it formed, until analysis by vapor phase chromatography (vpc) indicated that reaction was complete. Distillation of the residue (30.0 g) at ~0.9 torr, with gentle heating of the still pot by means of a 1200 watt heat gun, gave 11.3 g (40% yield) of product which distilled at a vapor temperature between 140° and 155° C. The distillate formed a hard cake on standing which was recrystallized from methanol (recoveries, 62-67%) to give pure 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione, m.p. (differential scanning calorimetry) 101.24°C.

20

25

-10-

Analysis: Mol. wt. calcd. for C<sub>16</sub>H<sub>20</sub>O<sub>4</sub>: 276. Found: (FDMS; M<sup>+</sup>), 277. <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ 7.86 (1H); 7.74-7.58 (m, 3H); 4.09 (d, 1H); 3.96 (d, 1H); 3.49 (d, 1H); 1.93 (m, 1H); 1.30 (s, 3H); 1.00 (d, 3H); 0.92 (s, 3H); 0.90 (d, 3H).

5 **Example 2:**

**Synthesis of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione in the Presence of a Catalyst**

A mixture of 74.0 g (0.50 mol) of phthalic anhydride, 80.5 g (0.55 mol) of 2,2,4-trimethyl-1,3-pentanediol (TMPD), and 600 mL of toluene was stirred and warmed. When the solid had dissolved, 0.2 g of butyl stannic acid (FASCAT® 4100 catalyst) was added and the resulting mixture was heated to reflux. After approx. 90 hr, analysis of the mixture by vapor phase chromatography (vpc) indicated that, on a toluene-free basis, it contained 74.23% of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione, 4.05% of TMPD, 1.84% of phthalic anhydride, 0.63% and 1.78%, respectively of each of the two isomeric monoesters of phthalic acid and TMPD, and 1.12%, 6.76%, and 9.22%, respectively, of each of the three diesters of phthalic acid and TMPD. No phthalic acid was present.

Toluene was removed from the mixture on a rotary evaporator (20 torr., 70° C). The residue (151.9 g) was a thick syrup which crystallized slowly on standing. This residue was stirred with 150 mL of methanol, the mixture chilled to 0° C overnight, then filtered at -10° C. The solid was washed with a small amount of chilled methanol and dried to give 73.7 g (75% pure by vpc; 40% yield) of crude 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione. Recrystallization of 50.0 g of crude 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione from 100 mL of methanol with cooling to approx. 0° C gave 42.5 g (85% recovery) of pure 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione as a white crystalline solid.

Analysis: (vapor phase chromatography; diphenyl internal standard): 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione, 99.97%.

**Example 3:****Synthesis of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione in a More Concentrated Solution**

Following the procedure of Examples 1 or 2, 7-Isopropyl-8,8-dimethyl-8,9-  
5 dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione was prepared from a solution of  
14.81 g (0.1 mole) of phthalic anhydride and 16.30 g (0.11 mole) of  
2,2,4-trimethyl-1,3-pentanediol (TMPD) in 75 mL of xylene. The catalyst was 49.4 mg of  
FASCAT® 4100 catalyst. Xylene was removed on a rotary evaporator and the residue  
distilled to give 11.09 g of distillate,  $b_{0.5}$  130-160°C which was found by vapor phase  
10 chromatography (vpc) to consist of 84% of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-  
6,10-dioxabenzocyclononene-5,11-dione (40% yield). The residue from this distillation  
weighed 17.65 g.

**Example 4:****15 Synthesis of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione in a More Dilute Solution, Without the Addition of a Catalyst.**

A solution of 114.82 g (0.10 mole) of phthalic anhydride and 16.31 g (0.11 mole)  
of 2,2,4-trimethyl-1,3-pentanediol (TMPD) in 250 mL of xylene was heated for 96 hr as  
described in Examples 1-3. Xylene was removed on a rotary evaporator at 20 torr, at a  
20 base temperature of 68° C. The residue (30.0 g) was diluted with 30 mL of methanol and  
the resulting slurry cooled to 1° C, filtered, and washed with methanol which had been  
chilled to -20° C to give 15.9 g (58% yield) of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-  
6,10-dioxabenzocyclononene-5,11-dione, which was 99.9% pure by vapor phase  
chromatography (vpc). The methanol washing from recovery of 7-Isopropyl-8,8-  
25 dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione contained, on a  
methanol-free basis, 16.4% of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-  
dioxabenzocyclononene-5,11-dione, while the residue from stripping xylene from the  
original reaction mixture contained 41.2% of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-  
6,10-dioxabenzocyclononene-5,11-dione.

**Example 5:****Synthesis of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione in the Presence of a 100% Molar Excess of 2,2,4-trimethyl-1,3-pentanediol (TMPD)**

5           The procedure of the preceding examples was followed, with a solution of 14.81 g (0.1 mole) of phthalic anhydride and 29.27 g (0.20 mole) of 2,2,4-trimethyl-1,3-pentanediol (TMPD) in 250 mL of xylene. Analysis of the residue, after removal of the xylene solvent indicated that it contained 41.3% of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione, 30.9% of diesters of phthalic acid and TMPD, and 24.0% of TMPD. The residue (28.17 g) was distilled at 2-3  
10           torr and a pot temperature of 200-220°C to give a distillate (12.60 g) which contained by vapor phase chromatography (vpc) 78.9% of TMPD and 15.5% of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione. The residue was diluted with cold methanol, filtered, and the crystals washed with cold methanol to give  
15           13.21 g (99.0% pure by vpc; 48% yield) of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione. The residue and washings from this separation of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione contained, on a methanol-free basis, 13.1% of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione and 52.6% of diesters of phthalic acid and  
20           TMPD.

**Example 6:****Preparation of a Linear Polymer by Ring Opening of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione**

25           A mixture of 1.994 g of recrystallized 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione and 8.0 mg of dibutyltin oxide was placed in a tube, degassed with the cyclic diester just above the melting point (101° C) and sealed under vacuum. The tube was heated in an oil bath at 170° C for approx. 96 hr. The resulting viscous, yellow product solidified to a hard glass at room temperature. Gel

phase chromatography indicated that the product contained phthalic anhydride and some residual monomer but that the polymeric portion had number average molecular weight ( $M_n$ ) = 6700; weight average molecular weight ( $M_w$ )=9600. The glass transition temperature (differential scanning calorimetry; second heat) was 39.0 °C.

5

**Example 7:****Preparation of 1-(2,2,4-Trimethyl-1,3-pentanediol) monophthalate**

A solution of 4.98 g (0.033 mole) of phthalic anhydride and 5.42 g (0.037 mole) of TMPD in 40 mL of toluene was stirred and heated at 80° C for approximately 30 hr.

10

The solvent was evaporated and the crystalline residue washed with cold toluene and dried to give 5.95 g of 2,2,4-Trimethyl-1,3-pentanediol monophthalate. Crude 2,2,4-Trimethyl-1,3-pentanediol monophthalate (1.00 g) was recrystallized from 5 mL of toluene and washed to give 0.95 g of pure 1-(2,2,4-Trimethyl-1,3-pentanediol) monophthalate, m. p. (differential scanning calorimetry) 127.0°C.

15

Analysis: Calcd for  $C_{16}H_{22}O_5$ : Mol. wt., 294.1467. Found (mass spectrometry): 294.1461.

**Example 8:****Conversion of 1-(2,2,4-Trimethyl-1,3-pentanediol) monophthalate to 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione**

20

A solution of 29.4 g (0.100 mol) of 2,2,4-Trimethyl-1,3-pentanediol monophthalate in 250 mL of toluene was allowed to stand over a weekend, 32.6 mg of catalyst FASCAT 4100® was added, and the solution was allowed to reflux under a Dean-Stark trap for 102 hr, when 1.40 mL of water had collected in the trap. Toluene was removed on the rotary evaporator. Analysis of this residue by vapor phase chromatography (vpc) indicated that it contained 72% of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione, as well as minor amounts of 2,2,4-trimethyl-1,3-pentanediol (TMPD), phthalic anhydride, 1-(2,2,4-Trimethyl-1,3-pentanediol) monophthalate, 3-(2,2,4-Trimethyl-1,3-pentanediol)

25

-14-

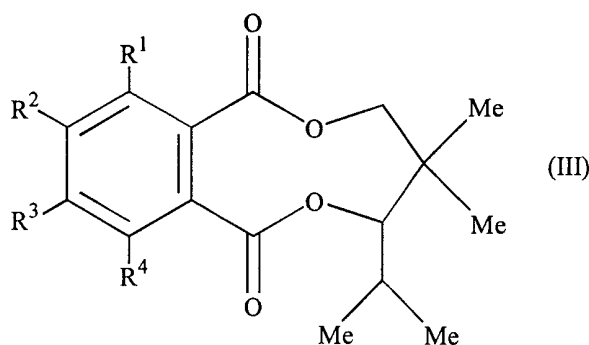
monophthalate, and diesters of phthalic acid and TMPD. This residual oil (28.9 g.) was diluted with 30 mL of methanol, seeded with a small crystal of the pure 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione and cooled to 0°C, and filtered. The crystals were washed with methanol. The purified solid weighed 15.33 g. Analysis by vpc indicated that it was 99% pure 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione (55% yield).

The filtrate from the methanol recrystallization was evaporated to remove the solvent. The residual oil (13.3 g.) was analyzed by vpc. It contained 24.1% of 7-Isopropyl-8,8-dimethyl-8,9-dihydro-7H-6,10-dioxabenzocyclononene-5,11-dione, together with lesser amounts of the components noted in the residual oil from the original toluene evaporation.

-15-

The claimed invention is:

1. A macrocyclic diester of formula (III):



where  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are, independently, hydrogen, a substituted or unsubstituted  $C_1$ - $C_{10}$  alkyl, aryl, or heteroaryl group, a nitro group, a halo group, a thio group, or an amino group; and

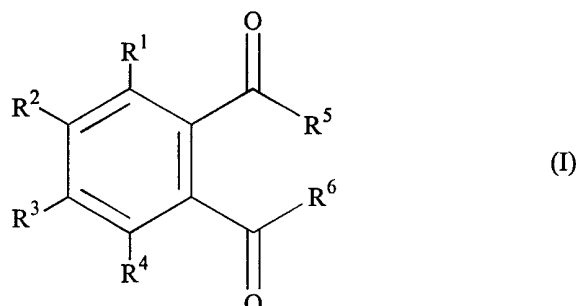
15 any two adjacent substituents of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  when taken together with the phenyl ring forms a fused aromatic ring structure.

2. A macrocyclic diester of claim 1, wherein  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are independently a hydrogen, or a  $C_1$ - $C_4$  alkyl group; or any two adjacent substituents,  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$ ,  
20 together with the phenyl ring form a fused aromatic ring structure selected from anthracene and naphthalene.

3. A macrocyclic diester of claim 1, wherein  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are each a hydrogen.

25 4. A method of preparing a macrocyclic diester comprising the step of:  
contacting, optionally in the presence of a catalyst, 2,2,4-trimethyl-1,3-pentanediol and a phthalic acid derivative of formula (I):

-16-

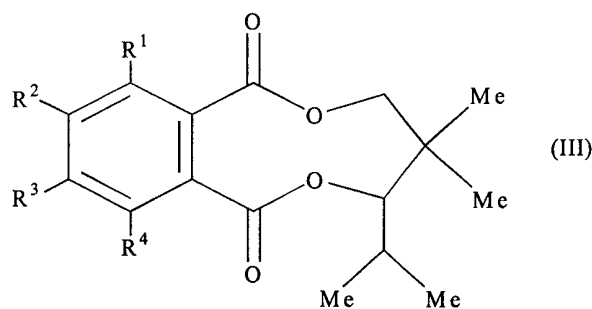


10 where  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are, independently, hydrogen, a substituted or unsubstituted  $C_1$ - $C_{10}$  alkyl, aryl, or heteroaryl group, a nitro group, a halo group, a thio group, or an amino group;

any two adjacent substituents of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  when taken together with the phenyl ring forms a fused aromatic ring structure; and

15  $R^5$  and  $R^6$  are independently a hydroxyl group, a chloride group or when taken together an oxygen;

under conditions sufficient to produce a diester of formula (III):

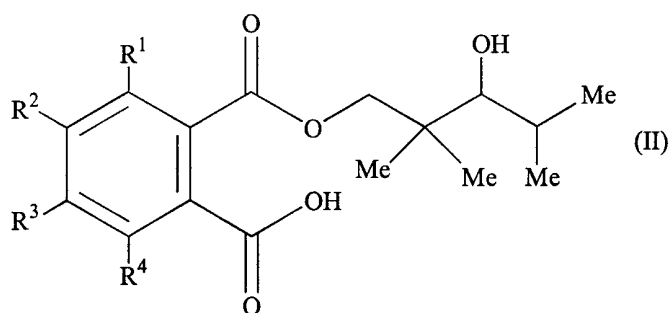


25 where  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are, independently, hydrogen, a substituted or unsubstituted  $C_1$ - $C_{10}$  alkyl, aryl, or heteroaryl group, a nitro group, a halo group, a thio group, or an amino group; and

-17-

any two adjacent substituents of R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> when taken together with the phenyl ring form a fused aromatic ring structure.

5. A method of claim 4, wherein said phthalic acid derivative is selected from the group consisting of phthalic anhydride, phthalic acid and phthaloyl chloride.
6. A method of claim 4, wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are each a hydrogen.
7. A method of claim 4, wherein said catalyst is butyl stannic acid.
8. A method of claim 4, wherein said contacting step is performed under azeotropic distillation conditions.
9. A method of claim 4, wherein said contacting step of 2,2,4-trimethyl-1,3-pentanediol and a phthalic acid derivative of formula (I) first forms a monoester of formula (II) prior to said diester:

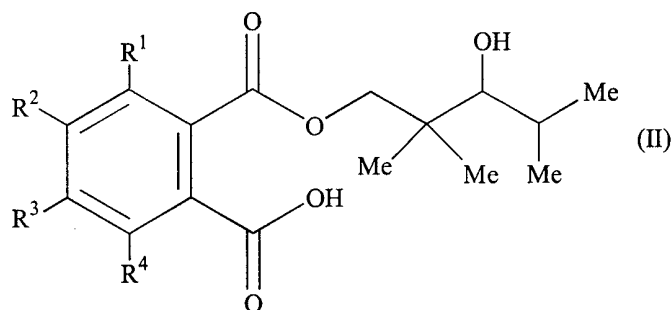


where R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are, independently, hydrogen, a substituted or unsubstituted C<sub>1</sub>-C<sub>10</sub> alkyl, aryl, or heteroaryl group, a nitro group, a halo group, a thio group, or an amino group; and

-18-

any two adjacent substituents of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  when taken together with the phenyl ring forms a fused aromatic ring structure.

10. A method of preparing a macrocyclic diester comprising the step of:  
 5 heating, optionally in the presence of a catalyst, a monoester of formula (II):



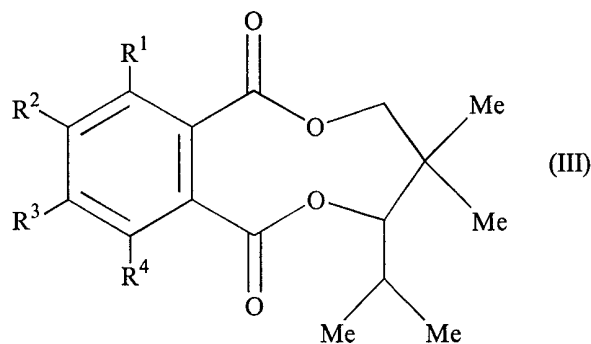
15

where  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are, independently, hydrogen, a substituted or unsubstituted  $C_1$ - $C_{10}$  alkyl, aryl, or heteroaryl group, a nitro group, a halo group, a thio group, or an amino group; and

20

any two adjacent substituents of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  when taken together with the phenyl ring forms a fused aromatic ring structure;  
 under conditions sufficient to produce a macrocyclic diester of formula (III):

25



-19-

where  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are, independently, hydrogen, a substituted or unsubstituted  $C_1$ - $C_{10}$  alkyl, aryl, or heteroaryl group, a nitro group, a halo group, a thio group, or an amino group; and

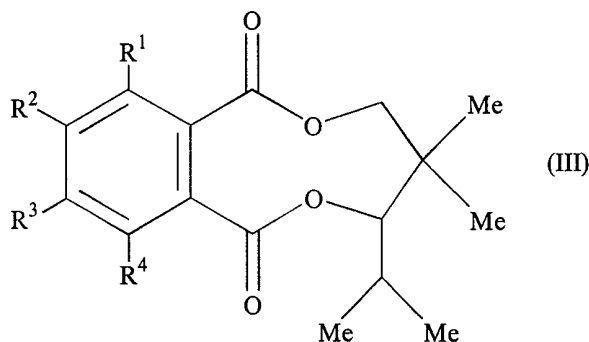
any two adjacent substituents of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  when taken together with the phenyl ring forms a fused aromatic ring structure.

11. A method of claim 10, wherein  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are each a hydrogen.

12. A method of claim 10, wherein said catalyst is butyl stannic acid.

13. A method of claim 10, wherein said heating step is performed under azeotropic distillation conditions.

14. A polymer comprising the ring opening polymerization product of a diester of formula (III):



where  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are, independently, hydrogen, a substituted or unsubstituted  $C_1$ - $C_{10}$  alkyl, aryl, or heteroaryl group, a nitro group, a halo group, a thio group, or an amino group; and

any two adjacent substituents of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  when taken together with the phenyl ring form a fused aromatic ring structure.

-20-

15. A polymer of claim 14, wherein  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are independently a hydrogen, or a  $C_1$ - $C_4$  alkyl group; or any two adjacent substituents,  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$ , together with the phenyl ring form a fused aromatic ring structure selected from anthracene and naphthalene.

5

16. A polymer of claim 14, wherein  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are each a hydrogen.

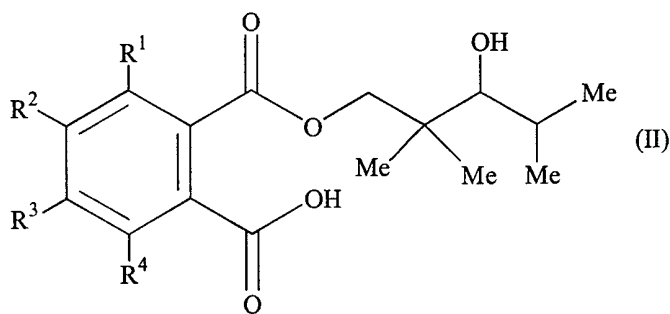
17. A polymer of claim 14, wherein said ring opening polymerization product is a catalyzed ring opening polymerization product.

10

18. A polymer of claim 14, wherein said catalyzed ring opening polymerization product is prepared in the presence of a catalyst of dibutyl tin oxide.

19. A monoester of formula (II):

15



20

where  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  are, independently, hydrogen, a substituted or unsubstituted  $C_1$ - $C_{10}$  alkyl, aryl, or heteroaryl group, a nitro group, a halo group, a thio group, or an amino group; and

25

any two adjacent substituents of  $R^1$ ,  $R^2$ ,  $R^3$ , and  $R^4$  when taken together with the phenyl ring form a fused aromatic ring structure.

-21-

20. A monoester of claim 19, wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are independently a hydrogen, or a C<sub>1</sub>-C<sub>4</sub> alkyl group; or any two adjacent substituents, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup>, together with the phenyl ring form a fused aromatic ring structure selected from anthracene and naphthalene.

5

21. A monoester of claim 19, wherein R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, and R<sup>4</sup> are each a hydrogen.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/17141

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 6 C08G63/181 C07D321/00

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

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C07D

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

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

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category <sup>o</sup>	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	CHEMICAL ABSTRACTS, vol. 127, no. 21, 24 November 1997 Columbus, Ohio, US; abstract no. 293666, XP002085220 see abstract & JIANG HONGYAN ET AL.: SCI. CHINA., SER. B: CHEM., vol. 40, no. 5, 1997, pages 495-502, ---	1-21
A	DATABASE WPI Week 9711 Derwent Publications Ltd., London, GB; AN 97115341 XP002085221 & JP 09 003175 A (AGENCY OF IND. SCI. & TECHNOLOGY), 7 January 1997 see abstract ---	1-21

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

<sup>o</sup> Special categories of cited documents:

- "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 when the document is taken alone
- "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.
- "&" document member of the same patent family

Date of the actual completion of the international search

20 November 1998

Date of mailing of the international search report

04/12/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Frelon, D

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/17141

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 234 902 A (TAKEMOTA YUSHI KABUSHIKI KAISHA) 2 September 1987 -----	1-21

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 98/17141

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 234902 A	02-09-1987	JP 1014255 B	10-03-1989
		JP 1527572 C	30-10-1989
		JP 62195041 A	27-08-1987
		JP 1876773 C	07-10-1994
		JP 6002872 B	12-01-1994
		JP 63003056 A	08-01-1988
		JP 1845823 C	25-05-1994
		JP 63006048 A	12-01-1988
		AU 628192 B	10-09-1992
		AU 5901290 A	01-11-1990
		AU 6908987 A	27-08-1987
		CA 1313433 A	02-02-1993
		DE 3778730 A	11-06-1992
		US 5122553 A	16-06-1992

---