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(71) Applicant: SUMITOMO CHEMICAL COMPANY, LIMITED [JP/JP]; 2-7-1, Nihonbashi, Chuo-ku, Tokyo 103-6020 (JP).

(72) Inventors: POWELL, Chad; 4500 McGinnis Ferry Road, Alpharetta, GA 30005-3914 (US). BENSON, Bryan; 4500 McGinnis Ferry Road, Alpharetta, GA 30005-3914 (US).

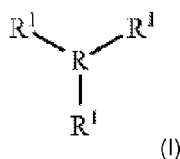
(74) Agent: TANIDA, Tomoki; Rimon P.C., 8300 Greensboro Drive, Suite 500, Mc Lean, VA 22102 (US).

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(54) Title: LIQUID CRYSTALLINE POLYESTER COMPRISING A BRANCH MONOMER

Formula (I)



(57) Abstract: The present disclosure relates to a polyester comprising the recurring units (RU1)-(RU4) and having in reacted form at least one monomer of formula (I); where R¹ is COOH and R is an aryl group, a heteroaryl group or a cycloalkyl group, the proportion of this monomer in the polyester being between 0.10 and 1.0 mol% (this latter value being excluded).



Liquid crystalline polyester comprising a branch monomer

This application claims priority of US provisional application N°63/613,425 filed on 21 December 2023 and European patent application N°24160049.3 filed on 27 February 2024, the content of which being entirely incorporated herein by reference for all purposes. In case of any incoherency between this application and one of the priority applications that would affect the clarity of a term or expression, it should be made reference to this application only.

[Technical Field]

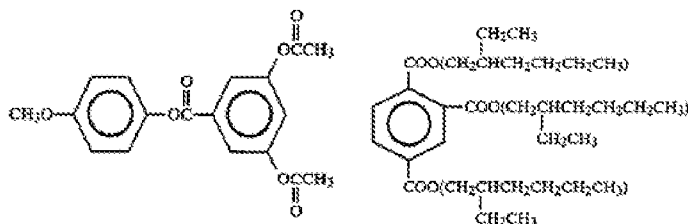
[0001] The present disclosure relates to a composition comprising a polyester (PE) exhibiting a combination of physico-chemical properties, making them well-suited for the preparation of a copper clad laminate (CCL). It also relates to the polyester (PE) itself.

[Background art]

[0002] Several documents disclose liquid crystalline polymers (LCPs).

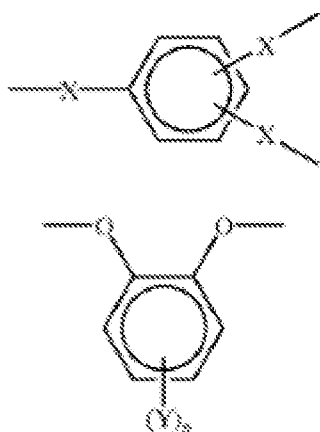
[0003] US 10,654,969 discloses a thin film comprising a polymer formed by reacting p-hydroxybenzoic acid, 6-hydroxy 2-naphthoic acid and a branched monomer such as trimesic acid, the molar ratio branched monomer / other monomers being between 0.25/100 and 0.5/100 and wherein the inherent viscosity of the polymer is between 4 and 6 dL/g. There is no disclosure of the crystallization temperature T_c.

[0004] US 4,710,547 discloses a process for producing a three-dimensionally crosslinked polyester prepared from a polyfunctional monomer. The two following monomers are used in the examples:



[0005] US 2009/118417 and CN101415748 disclose a hyperbranched-polyester comprising at least one kind of a structural unit selected from an aromatic oxycarbonyl unit (P), aromatic and/or aliphatic dioxy units (Q), an aromatic dicarboxy unit (R) and a trifunctional or higher polyfunctional organic residue (B) wherein the content of (B) is within a range of 7.5 to 50 mol% based on the entire monomers constituting the polyester.

[0006] US 6,210,872 discloses an optical film formed from a LCP comprising the following recurring units:



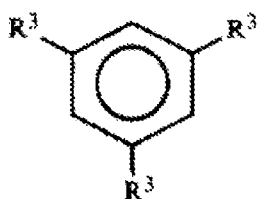
where X represents O or CO independently and Y is independently selected in the group consisting of F, Cl, Br and alkyl groups and n is 0 or 1.

[0007] CN 101649044 discloses an all-aromatic liquid crystal polymer, which is characterized by polycondensation reaction of four monomers, p-hydroxybenzoic acid, triptycene hydroquinone, terephthalic acid and isophthalic acid.

[0008] CN 103665354 discloses LCPs with $\Delta = T_m - T_c \geq 40^\circ\text{C}$ and having a composition different from the polyester of the invention.

[0009] CN 103570927 LCPs based on trimesic acid and 4-hydroxybenzoic acid. CN 103570927 does not disclose the polyester of the invention.

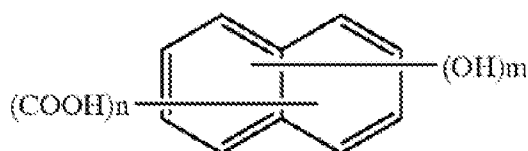
[0010] US 5,306,800 discloses an LCP with recurring units according to formula below:



where R^3 is selected from NH, CO, O and S. There is no disclosure of a polyester as defined in claim 1.

[0011] WO 2021/100759 discloses a composition with a LCP based on terephthalic acid, isophthalic acid, para-hydroxybenzoic acid and 4,4'-biphenol exhibiting a (T_m-T_c) of 41.4°C.

[0012] US 2004/256599 discloses a thermotropic liquid crystalline polymer (LCP), which is obtainable by copolymerizing a trifunctional hydroxynaphthalene carboxylic acid represented by the general formula (I) where one of m and n is 1 and the other is 2, the proportion of which is between 0.01 and 10 mol%:



[0013] **D1** (CN 116178686 A; published 30-May-2023) is directed to branched liquid crystalline polyesters with 0.01-0.5 mol% of the total chain segment, derived from trimesic acid or phloroglucinol. All examples of D1 comprise phloroglucinol and 4-hydroxybenzoic acid.

[0014] **D2** (WO 99/52978 A1) discloses a composition comprising: a) a liquid crystalline polymer; b) a functional compound whose functionality is selected from the group consisting of hydroxyl, carboxyl, carboxylate, ester, and primary or secondary amine, said functional compound being from about 5 to about 250 milli equivalents per kg by weight of said liquid crystalline polymer. The preparation of the composition is based on the following specific method: the LCP, in pellet form, was dry blended with the functional compound and then fed to the back of a twin screw extruder.

Technical problem

[0015] To meet the growing demand for device hyperconnectivity, electronic components have become increasingly intricate to accommodate more

complex device design. This increase in device connectivity is facilitated primarily by an increase in data transfer rates and network capacity enabled by 5G cellular networks.

- [0016] To meet the demands of 5G networks, operating at frequencies up to 100 GHz, dielectric insulating materials must demonstrate low dielectric constants (Dk) and dissipation factors (Df, sometimes referred to as the dielectric loss tangent), ideally below 4.0 and 0.0040, respectively. However, there is a push to drive the Dk and Df values even lower as signal attenuation (α) is proportional to both values, see the relationship below (α):

$$\alpha \propto \sqrt{D_k D_f} f, \text{ where } f \text{ is the frequency of the signal}$$

- [0017] Polyimide (PI) films are currently used for dielectric insulator substrates in PCBs and FPCs. These films are traditionally prepared by casting and subsequently heat treating a solution of the polymer solution form as a polymer precursor. The resultant PI films generally have excellent heat resistance and mechanical properties. However, PIs suffer from high moisture uptake. The process of moisture uptake causes a concomitant increase in Df, which is undesirable for performance.
- [0018] In previous telecommunication applications, this increase in Df was tolerable as it did not affect the performance in the frequency ranges utilized for previous generations of cellular networks. However, in the more demanding 5G space, this performance deterioration with moisture uptake causes enhanced signal dampening at the frequencies utilized by 5G.
- [0019] LCPs typically result from the polycondensation of aromatic difunctional monomers. The wholly aromatic structure of many commercial LCPs leads to high melting temperatures due to the high chain rigidity, with the tendency to orient in the flow direction and rapidly crystallize after melt processing. For decades, LCPs have been known for their excellent thermal performance and easy processing via injection molding – a result of their low viscosity and high crystallization rate. More recently, LCPs have gained increasing attention due to their exceptional dielectric performance in the GHz frequency range.
- [0020] Due to the high processing temperatures required for many LCPs, in combination with the chain rigidity and resulting anisotropy under shear-

induced flow, it has proven challenging to produce LCP film via a melt process. The difficulty in melt processing LCPs, outside of injection molding, has considerably limited their application.

[0021] Therefore, polyesters and LCP compositions possessing the desired thermal and dielectric performance (low Dk and Df) for 5G telecommunication applications, but with improved processability are highly sought after. In this sense, improved processability is taken to mean improved rheological properties (higher viscosity at relevant processing shear rates, higher melt elasticity) and a larger processing window (greater $T_m - T_c$).

[0022] The polyester of the invention aims at solving this technical problem.

[Brief description of the invention]

[0023] The invention is set out in the appended set of claims.

[0024] The invention relates to a polyester as defined in any one of claims 1-15.

[0025] The invention relates to a polymer composition as defined in claim 16.

[0026] The invention relates to a use as defined in claim 17.

[0027] The invention relates to a printed circuit board as defined in claim 18.

[0028] More details on these subject-matters are provided below.

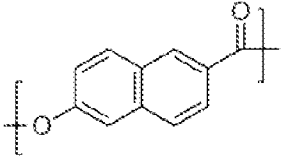
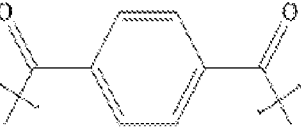
[Definitions]

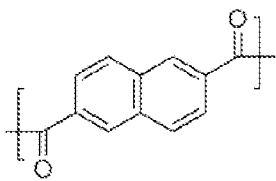
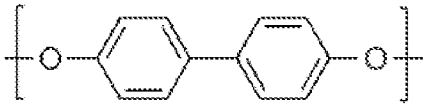
- [0029] These definitions apply to the present disclosure.
- [0030] wt% means % by weight. Mol% means % by mol.
- [0031] When numerical ranges are given herein, unless otherwise indicated, the end-points of the ranges (including the ranges starting with "*between*" and even the open-ended ranges such as those comprising "*at least*", "*at most*", "*lower than*", etc) are included.
- [0032] In the present application, unless otherwise indicated, any specific embodiment or technical feature relating to one of the subject-matters of the invention is applicable to and interchangeable with another embodiment or technical feature relating also to said subject matter and disclosed elsewhere in the application, notably in the claims.
- [0033] A monomer designates a molecule which is capable of combining with like or unlike molecules to form a polymer.
- [0034] A heteroaryl group designates an aromatic ring structure, mono-cyclic or polycyclic, that includes one or more heteroatoms in the ring.
- [0035] As used herein, the terminology '(C_n-C_m)' in reference to an organic group, wherein n and m are integers, respectively, indicates that the group may contain from n carbon atoms to m carbon atoms per group, n and m being included.

[Description of the invention]

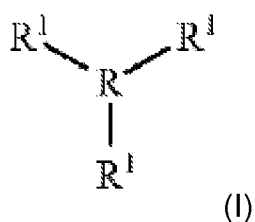
[0036] Polyester (PE)

- [0037] As a first object, the invention relates to a polyester (PE) comprising the following recurring units with the following proportions expressed in mol%:

(RU1)		between 30.0 and 80.0 mol%
(RU2)		between 10.0 and 20.0 mol%

(RU3)		between 1.0 and 10.0 mol%
(RU4)		between 15.0 and 25.0 mol%

and having in reacted form at least one monomer of formula (I):



where R^1 is COOH and R is an aryl group, a heteroaryl group or a cycloalkyl group, the proportion of this monomer in the polyester being between 0.10 and 1.0 mol% (this latter value of 1.0 mol% being excluded),

where all the proportions are given in mol% and based on the total amount of recurring units (RU1), (RU2), (RU3), (RU4) and the units derived from the monomer of formula (I) that are present in the polyester (PE).

[0038] R is an aryl group, a heteroaryl group or a cycloalkyl group. More particularly, R is a (C₁-C₁₈)-aryl group, a (C₁-C₁₈)-heteroaryl group or a (C₁-C₁₈)-cycloalkyl group.

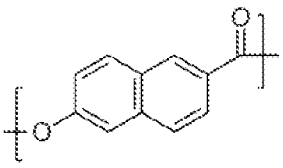
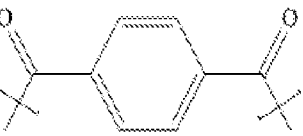
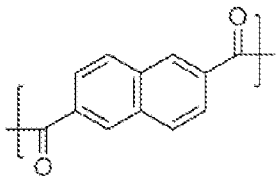
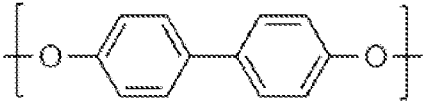
[0039] The recurring units (RU1)-(RU4) and the monomer of formula (I) are linked by ester bonds.

[0040] Because of this composition, the polyester (PE) of the invention is typically designated as a Liquid Crystalline Polyester or LCP. Liquid crystalline polyesters (LCPs) are polyesters that demonstrate order in at least one dimension in the liquid state, *i.e.* anisotropy under conditions suitable for flow. The ordered liquid state of LCPs is often referred to as the nematic phase, and the transition from an ordered solid to an ordered liquid referred to as the crystalline to nematic transition. For simplicity's sake, this transition will be

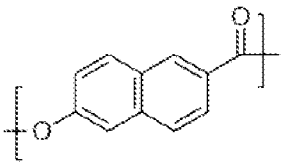
referred to as the “*melting temperature*” or “*melting point*” henceforth. To achieve an anisotropic flow state, LCPs typically must comprise a certain quantity of rigid, linear monomeric units, such as *para*-hydroxybenzoic acid and/or 6-hydroxy-2-naphthoic acid.

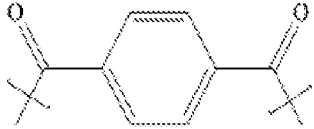
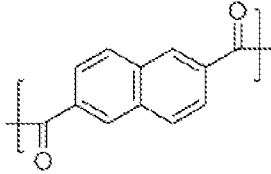
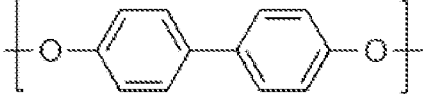
[0041] The proportion of monomer(s) of formula (I) in reacted form is between 0.10 and 1.0 mol% (this latter value of 1.0 mol% being excluded). This proportion may more particularly be between 0.15 and 0.75 mol% or between 0.15 and 0.60 mol% or between 0.15 and 0.55 mol%.

[0042] The relative proportions of recurring units (RU1)-(RU4) in polyester (PE) may more particularly be the following:

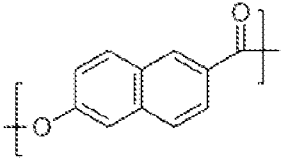
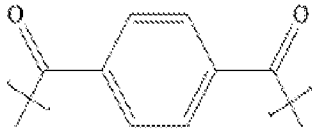
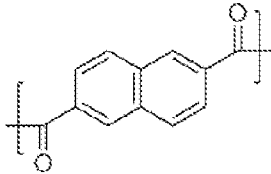
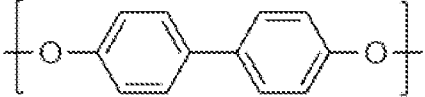
(RU1)		between 53.0 and 65.0 mol%
(RU2)		between 11.0 and 17.0 mol%
(RU3)		between 1.5 and 9.0 mol%
(RU4)		between 15.0 and 24.0 mol%

[0043] The relative proportions of recurring units (RU1)-(RU4) in polyester (PE) may more particularly be the following:

(RU1)		between 55.0 and 65.0 mol%
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(RU2)		between 13.0 and 17.0 mol%
(RU3)		between 2.0 and 7.0 mol%
(RU4)		between 18.0 and 22.0 mol%

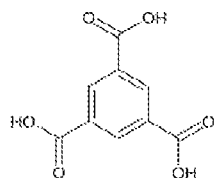
[0044] The relative proportions of recurring units (RU1)-(RU4) in polyester (PE) may more particularly be the following:

(RU1)		between 55.0 and 65.0 mol%
(RU2)		between 11.0 and 15.0 mol%
(RU3)		between 2.0 and 8.0 mol%
(RU4)		between 18.0 and 22.0 mol%

[0045] According to an embodiment, polyester (PE) comprises only one monomer of formula (I) as defined herein.

[0046] The monomer of formula (I) can be 1,2,4-benzenetricarboxylic acid or 1,3,5-benzenetricarboxylic acid or a combination of these two triacids.

[0047] The monomer of formula (I) is preferably trimesic acid of formula:



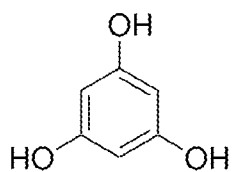
[0048] The units forming the polyester (PE) of the invention consist essentially of or consist of the recurring units (RU1), (RU2), (RU3), (RU4) and the units derived from the monomer of formula (I) that are present in the polyester (PE).

[0049] The expression “*consist essentially*” means in relation to the units of the polyester (PE) that the units consist of the recurring units (RU1), (RU2), (RU3), (RU4) and the units derived from the monomer of formula (I) that are present in the polyester (PE) and up to 2.0 mol%, preferably up to 1.5 mol%, preferably up to 1.0 mol%, preferably up to 0.5 mol% of units different from the (RU1), (RU2), (RU3), (RU4) and units derived from monomer of formula (I).

[0050] According to a preferred embodiment of the present invention, polyester (PE) is free of recurring units derived from 4-hydroxybenzoic acid (HBA). The expression “*free of*” means that the proportion of these recurring units is lower than or equal to 1.50 mol% (≤ 1.50 mol%), preferably lower than or equal to 1.00 mol%, preferably lower than or equal to 0.50 mol%, preferably lower than or equal to 0.25 mol%. According to an embodiment of the present invention, polyester (PE) does not comprise recurring units derived from 4-hydroxybenzoic acid. This ensures that the dielectric constants are low.

[0051] The polyester (PE) of the invention preferably does not comprise units derived from any other monomer (i) not complying with formula (I) and (ii) having at least three groups X selected in the group consisting of COOH, OH and combination thereof.

[0052] According to an embodiment, polyester (PE) does not contain units derived from phloroglucinol (*aka* benzene-1,3,5-triol) of formula:



[0053] The composition of the polyester (PE) can be determined by conventional analytical methods such as ^1H NMR. Another method consists in subjecting

the polyester (PE) to hydrolysis under basic conditions and analyzing the resultant mixture by ^1H NMR or by liquid chromatography-mass spectrometry (LC-MS). The method disclosed in the Experimental Section illustrates this other method and can be followed for the analysis of the composition of the polyester (PE) of the invention.

[0054] **Preparation of the polyester (PE)**

[0055] The polyester (PE) is prepared by polycondensation.

[0056] The polyester (PE) is prepared by polycondensing a monomer mixture (MM) comprising, consisting essentially of or consisting of:

- monomer (M1): 6-hydroxy-2-naphthoic acid (HNA);
- monomer (M2): terephthalic acid (TPA);
- monomer (M3): 2,6-naphthalene dicarboxylic acid (NDA);
- monomer (M4): 4,4'-biphenol (BP); and
- at least one monomer of formula (I).

[0057] The expression "*consist essentially*" means in relation to the monomer mixture (MM) that the monomer mixture (MM) consists of (M1), (M2), (M3), (M4), at least one monomer of formula (I) and up to 2.0 mol%, preferably up to 1.5 mol%, preferably up to 1.0 mol%, preferably up to 0.5 mol% of at least one monomer M_x having two functions X_1 and X_2 selected in the group consisting of $-\text{OH}$, $-\text{COOH}$, and $-\text{NH}_2$, or derivatives thereof, said monomer M_x being different from monomers (M1), (M2), (M3), (M4) and monomer (I).

[0058] Monomer mixture (MM) preferably comprises or consists of the following components or derivatives thereof:

- monomer (M1): 6-hydroxy-2-naphthoic acid (HNA);
- monomer (M2): terephthalic acid (TPA);
- monomer (M3): 2,6-naphthalene dicarboxylic acid (NDA);
- monomer (M4): 4,4'-biphenol (BP); and
- at least one monomer of formula (I).

[0059] If desired, the polycondensation may proceed through the acetylation of the monomers as known in the art. The $-\text{OH}$ groups of monomers (M1) and (M4) may be partly or totally replaced respectively by $-\text{O}-\text{C}(=\text{O})-\text{Q}$ groups where Q is a C_1 - C_6 linear or branched alkyl group. The replacement $\text{OH} \Rightarrow -\text{O}-\text{C}(=\text{O})-$

Q prior to the polycondensation is performed with the use of an acylating agent.

[0060] The acylation may conveniently be accomplished by using acetic anhydride as the acylating agent. In such cases where acetic anhydride is used as the acetylating agent, the acylation reaction is referred to as acetylation. Acetylation is generally initiated at temperatures of about 90° C. During the initial stage of the acetylation, reflux may be employed to maintain vapor phase temperature below the point at which acetic acid byproduct and anhydride begin to distill. Temperatures during acetylation typically range from between 90°C to 150°C. If reflux is used, the vapor phase temperature typically exceeds the boiling point of acetic acid, but remains low enough to retain residual acetic anhydride. For example, acetic anhydride vaporizes at temperatures of about 140° C. Thus, providing the reactor with a vapor phase reflux at a temperature of from about 110° C to about 130° C is particularly desirable. To ensure substantially complete acetylation, an excess amount of acetic anhydride may be employed. The amount of excess anhydride will vary depending upon the particular acetylation conditions employed, including the presence or absence of reflux. The use of an excess of from about 1 to about 10 mole percent of acetic anhydride, based on the total moles of reactant hydroxyl groups present is not uncommon.

[0061] The acylation may be performed *in situ* within the polycondensation reactor vessel or in a separate reactor vessel. When separate reactor vessels are employed, one or more of the monomers may be introduced to the acylation reactor and subsequently transferred to the polycondensation reactor. Likewise, one or more of the monomers may also be directly introduced to the reactor vessel without undergoing pre-acetylation.

[0062] The proportion of monomers in the monomer mixture (MM) is such that the molar ratio groups -OY₁ from monomers / groups -COOY₂ from monomers is between 0.80 and 1.20, preferably between 0.90 and 1.10, even more preferably between 0.95 and 1.05, where Y₁ and Y₂ designates H and/or -C(=O)-Q.

[0063] The polycondensation of the monomer mixture (MM) is performed by heating a reaction mixture (RM) comprising the monomer mixture (MM) at a

temperature sufficient to induce the polycondensation of the monomers with the formation of the ester bonds. The temperature at which the monomer mixture (MM) is heated is generally at least 150°C.

[0064] The reaction mixture (RM) preferably includes a catalyst, e.g. potassium acetate and/or magnesium acetate.

[0065] The reaction mixture (RM) is further heated to remove the volatiles. The solid material recovered from the reaction mixture (RM) is generally then further heated under a continuous nitrogen flow to complete the polycondensation. The temperature at which the solid material is further heated is generally at least 250°C.

[0066] The conditions given in the Experimental Section may more particularly be followed to prepare the polyester (PE) of the invention.

[0067] The polyester (PE) of the invention can also be characterized by the following physico-chemical properties.

[0068] **Melting temperature (T_m)**

[0069] The polyester (PE) exhibits a melting temperature T_m of at least 295°C. This ensures that the composite film of the invention exhibits thermal resistance.

[0070] T_m is preferably at least 300.0°C.

[0071] T_m is generally at most 330.0°C.

[0072] T_m is measured by Differential Scanning Calorimetry ("DSC") according to ASTM D3418, notably using a heating of 20 °C/min and cooling rate of 10 °C/min.

[0073] More particularly, T_m is measured by Differential Scanning Calorimetry ("DSC") according to ASTM D3418 according to protocol (p) defined in the Experimental Section.

[0074] **Crystallization temperature (T_c)**

[0075] The polyester (PE) exhibits a crystallization temperature T_c of at most 280.0°C.

[0076] T_c is generally at least 250.0°C.

[0077] T_c is measured by Differential Scanning Calorimetry ("DSC") according to ASTM D3418, notably using a heating of 20 °C/min and cooling rate of 10 °C/min.

[0078] More particularly, T_c is measured by Differential Scanning Calorimetry ("DSC") according to ASTM D3418 according to protocol (p) defined in the Experimental Section.

[0079] The polyester (PE) has interestingly such a low T_c , so that the difference $\Delta = (T_m - T_c)$ is at least 40.0°C, preferably at least 41.0°C, preferably at least 42.0°C, preferably at least 43.0°C, preferably at least 44.0°C, preferably at least 45.0°C.

[0080] Δ is preferably at most 60.0°C.

[0081] **Rheological properties**

[0082] The polyester (PE) preferably exhibits the following rheological properties:

- a viscosity V of at least 100 Pa s measured at $T_m + 25^\circ\text{C}$, as defined above, and at a shear rate of 100 s⁻¹;
and/or
- a storage modulus G' of at least 20.0 kPa measured at $T_m + 25^\circ\text{C}$, as defined above, and at a shear rate of 100 s⁻¹.

[0083] Viscosity V is typically at most 2500 Pa s at 100 s⁻¹ (measured in the same conditions as mentioned above).

[0084] These rheological properties (V and G') are measured using a parallel plate rheometer under oscillatory shear.

[0085] The conditions given in the Experimental Section are conveniently followed.

[0086] **Polymer composition (PC)**

[0087] The polymer composition (PC) of the invention comprises, consists essentially of or consists of:

- at least one polyester (PE) as disclosed herein;
- optionally at least one filler (F), notably selected in the group consisting of glass fibers (GF), carbon fibers (CF), silica, alumina, aluminium borate, silicon carbide, mica, talc, clay, titanium oxide, zirconia, kaolin, calcium carbonate, magnesium carbonate, calcium sulfate, barium sulfate, magnesium hydroxide, quartz, graphite, bentonite, calcium phosphate;
- optionally at least one additive (A) different from filler (F) and selected in the group consisting of plasticizers, light and weathering stabilizers, antistatic

agents, ultraviolet absorbing agents, dyes, pigments, viscosity agents, impact modifiers and lubricants;

the filler(s) (F) and additive(s) (A) (if any) being blended with the polyester.

[0088] The function of the filler (F) is generally to improve the thermal and mechanical properties of the polymer composition (PC).

[0089] According to an embodiment, the polymer composition (PC) of the invention comprises, consists essentially of or consists of:

- at least one polyester (PE) as disclosed herein;
- at least one filler (F), notably selected in the group consisting of glass fibers (GF), hollow glass spheres, carbon fibers (CF), dielectric constant modifiers, electrically conductive fillers, silica, alumina, aluminium borate, silicon carbide, mica, talc, clay, titanium oxide, zirconia, kaolin, calcium carbonate, magnesium carbonate, calcium sulfate, barium sulfate, magnesium hydroxide, quartz, graphite, bentonite, calcium phosphate; the filler(s) (F) and additive(s) (A) (if any) being blended with the LCP.

[0090] The polymer composition (PC) of the invention may also further comprise at one polymer different from the polyester (PE) of the invention, such as a fluoropolymer.

[0091] The proportion of the polyester(s) (PE) of the invention in the polymer composition (PC) is generally between 30.0 and 85.0 wt%. This proportion may be between 45.0 and 75.0 wt% or between 50.0 and 70.0 wt%.

[0092] The proportion of additive(s) (A) is generally at most 10.0 wt%. This proportion may more particularly be between 0.1 and 10.0 wt%.

[0093] The proportions of components of the polymer composition (PC) are given in wt% relative to the total weight of the polymer composition (PC).

[0094] According to an embodiment, the polyester (PE) of the invention or the polymer composition (PC) of the invention is in the form of a film. The thickness of the film may be between 0.010 mm and 10.0 mm, preferably between 0.01 and 1.0 mm, and even more preferably between 0.020 and 0.50 mm.

[0095] The polymer composition (PC) is obtained by conventional techniques of blending polymers with additives and fillers. A preferred technique consists in blending the additive(s) and/or filler(s) while the polyester is in the molten

state. This is generally performed with the help of an extruder, a kneader or a Banbury mixer. The polymer composition (PC) is preferably prepared by melt processing the polyester and the components of the polymer composition in an extruder.

[0096] **End-use applications of the polyester (PE) or the polymer composition (PC) of the invention**

[0097] The polyester (PE) or the polymer composition (PC) in the form of a film can be used as the dielectric material in printed circuit boards (PCBs). The invention thus also relates to the use of the LCP or the polymer composition (PC) of the invention, notably in the form of a film, for the preparation of a printed circuit board (PCB).

[0098] More specifically, for PCBs used in high-frequency transmission modules/components such as 5G-compatible antennas or mobile devices. More specifically, films of these compositions may be prepared via melt extrusion to produce dielectric insulating substrates for flexible printed circuit boards (FPCs). FPCs with the appropriate dielectric properties have application in mobile electronic devices, 5G antenna arrays, 5G base stations, flexible electronic devices, wearable electronic devices, automobiles, and medical devices that require high-speed data transmission.

[0099] Other applications may include parts, made by injection molding or other common melt processing techniques, for high performance, 5G-compatible connectors or housing for telecommunication or electronic components such as an antennas or components thereof.

[EXPERIMENTAL SECTION]

[00100] The disclosure will be now described in more detail with reference to the following examples disclosed in **Table III**.

[00101] **Starting Materials**

[00102] **Table I**

Name	Alias	RN CAS
6-hydroxy-2-naphthoic acid	HNA	16712-64-4
Terephthalic acid	PTA	100-21-0
2,6-Naphthalenedicarboxylic acid	NDA	1141-38-4
4,4'-Biphenol	BP	92-88-6
Acetic anhydride	Ac ₂ O	108-24-7
Trimesic acid		554-95-0
Potassium acetate	KOAc	127-08-2
Magnesium acetate tetrahydrate	Mg(OAc) ₂	16674-78-5

[00103] The polyesters disclosed in Table III were prepared by polycondensation according to the recipe given below.

[00104] **Preparation of polyester**

[00105] A 2 L glass kettle was charged with PTA (102.9 g, 0.7277 mol), NDA (78.6 g, 0.363 mol), HNA (631.2 g, 3.354 mol), BP (218.6 g, 1.174 mol), trimesic acid (5.7157 g, 0.028518 mol). A glass head equipped with a mechanical stirrer, nitrogen inlet, and distillate adapter equipped with a stopcock was placed on the kettle and the kettle was put under positive nitrogen pressure, visualized by mineral oil bubbler. Subsequently, Ac₂O (628.9 g, 6.160 mol) was charged and the reaction was set to stir. KOAc (0.01738 g) and Mg(OAc)₂ (0.2563 g) were charged as catalysts. The mixture was then heated to an internal temperature of 135 °C to begin reflux to facilitate monomer acetylation. The reflux was held for 2 h, after which the stopcock on the distillate adapter was opened to begin collection of the distilled vapor. The internal temperature was then increased at a rate of 0.5 °C/min to 320 °C while continuously distilling the acetic acid byproduct. The polymerization was stopped once 96 % of the theoretical distillate yield was obtained. The resulting prepolymer was cooled to room temperature, discharged, and ground to a powder for subsequent solid-state advancement.

[00106] The prepolymer was solid-state advanced in a rotary oven (Grieve Corp.) by heating to a set point of 300 °C over the course of 8 h and holding at the 300

°C set point for 4 h with continuous nitrogen flow throughout the process. The resulting powder was discharged and analyzed “as-is”.

[00107] **Test methods**

[00108] **Rheological properties**

[00109] Viscosity and modulus were determined with a rotational rheometer equipped with 25 mm diameter stainless steel parallel plates. Data were acquired at $T_m + 25$ °C, unless otherwise stated. Data reported were acquired using an oscillatory frequency sweep under constant strain with constant N₂ flow in accordance with ASTM D4440. The linear viscoelastic region was determined by first performing a strain amplitude sweep at the testing temperature. The resin powder was dried at 150 °C for 16-24 h under vacuum with an N₂ sweep prior to rheology testing. Rheology samples were prepared by sandwiching the sample powder in between two, 25 mm diameter aluminum cups and subsequently heating while applying pressure on the sandwich within the rheometer for 2-5 min at the testing temperature to sufficiently mold the sample into a disc shape. The aluminum cups were then removed from the molded disc and the disc was loaded between the rheometer plates for testing. The final sample dimensions for testing were 25x1 mm (diameter x gap thickness).

[00110] The rheometer is typically a ARES G2 rheometer.

[00111] **Thermal properties**

Protocol (p)

Thermal properties were measured by DSC under nitrogen flow per ASTM D3418. The LCP powder samples were subject to a heat, cool, heat, cool cycle 200-360 °C. The heating rate for the heat portion of the cycles was 20 °C/min and the cooling rate was 10 °C/min for the cool portion of the cycles. The melting temperature (T_m) is reported as the peak of the endothermic transition from the second heat portion of the cycle and the crystallization temperature (T_c) is reported as the peak of the exothermic transition on the first cool portion of the cycle.

[00112] The DSC used is a TA Instruments QA20-2 or TA Instruments DSC250.

[00113] **Dielectric performances (Dk, Df)**

[00114] The microwave dielectric properties were measured using a Split Cylinder Resonator operating at 20 GHz frequency on compression molded samples

according to IPC-TM-650-2-5-5-13. Samples were compression molded with a 90x90 mm square stainless steel shim with a thickness of 0.18 mm using a Carver hydraulic press pre-heated to 330 °C. The molding procedure followed a press/release/press cycle wherein the material was molded with 2 MT applied force applied for 45 s, followed by a brief release of the force, and a subsequent second application of 2 MT of force for 45 s. The compression molded samples were dried at 100 °C for 1 h prior to testing. Data is reported as the average of three compression molded samples.

[00115] **Digestion and analysis of the polyester (PE) by Liquid Chromatography (LC)**

[00116] Digestion (or hydrolysis): the sample of polyester was weighed to approximately 40 mg and transferred to a glass culture tube equipped with a stir bar. The sample mass was accurately recorded. The culture tube was charged with diethylsulfoxide DMSO (4 mL) and 5 N aqueous KOH solution (1 mL). The exact masses of each reagent were recorded after addition. The solution was then heated to 120 °C while stirring for 30 min. The sample was cooled to room temperature, neutralized with 85 wt. % phosphoric acid (6 mL), and further diluted with DMSO (30 mL). The exact mass of each reagent was recorded after addition. The sample was homogenized using a vortex mixer and an aliquot (15 mL) was transferred to a conical centrifuge tube and centrifuged for 10 min. The supernatant was transferred to an LC vial and diluted by a factor of 10 for analysis.

[00117] Analysis of the mixture: the LC data were acquired using an Agilent 1290 UPLC equipped with an ACQUITY HSS PFP column (1.8 µm, 2.1 x 150 mm) and photodiode array detector monitoring the 190-500 nm region. The column compartment was maintained at 40 °C and a flow rate of 0.350 mL/min was employed using the gradient shown in **Table II**. Mobile phase A is comprised of 0.1 % formic acid in water and mobile phase B, acetonitrile. A sample volume of 2 µL was used for the sample injection.

Table II

Time (min.)	% A	% B
0.00	95	5
1.00	95	5
13.00	0	100
15.00	0	100
15.50	95	5
20.00	95	5

Table III

Ex.	Proportions of monomers in mol%						Thermal propertie s (°C)	Rheolog y V (Pa s) and G' (kPa) @ Tm+25°C °C & 100 1/s (see also comment below for v*)	Dk Df
	hydroxyaci d		diacid		dio l	monomer of formula (I)			
	HNA	HBA	PT A	ND A	BP	Trimesi c acid	Tm Tc Δ=Tm-Tc		
E1	59.7	0	15.0	4.4	20. 4	0.50	315 269 46	V=1445 G'=138	3.35 0.001 3
E2	59.4	0	12.9	6.4	20. 8	0.50	300 255 45	V=506 G'=43.8	
E3	59.6	0	12.9	7.0	20. 4	0.20	304.5 258.1 46.4	v*=392.8 (340°C ; 100 s-1)	3.38 0.001 2
E4	54.7	0	13.9	8.5	22. 4	0.50	300.3 256.2 44.1	v*=546.7 (340°C ; 100 s-1)	3.40 0.001 3
E5	63.7	0	15.9	2.0	17. 9	0.50	331.7 289.7 42.0	v*=335.2 (340°C ; 100 s-1)	3.39 0.001 1
CE 1	60.0	0	13.0	7.0	20. 0	0	310.3 281.2 29.1	v*=311.1 (340°C ; 100 s-1)	3.47 0.001 1

HBA: 4-hydroxybenzoic acid

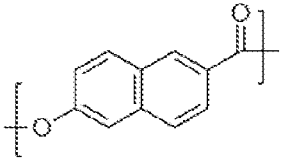
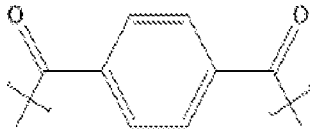
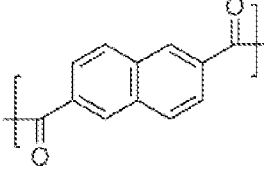
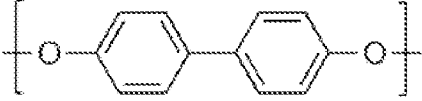
v*: viscosity in Pa s measured at 340°C and at a shear rate of 100 s-1 with a capillary rheometer

[00118] As can be seen with the results in **Table III**, the polyester of the invention makes it possible to have a combination of the following properties:

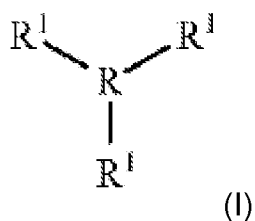
- an improved processing window ($\Delta \geq 40^{\circ}\text{C}$) while maintaining a sufficiently high T_m for Surface Mount Technology (SMT) compatibility;
- a greater storage modulus for a given viscosity at shear rates relevant to film extrusion (100 1/s);
- dielectric properties that are suitable for 5G applications: D_k (@20 GHz) ~ 3.2 -3.5 and D_f (@20 GHz) < 0.002 .

Claims

Claim 1. Polyester (PE) comprising the following recurring units (RU1)-(RU4) with the following proportions expressed in mol%:

(RU1)		between 30.0 and 80.0 mol%
(RU2)		between 10.0 and 20.0 mol%
(RU3)		between 1.0 and 10.0 mol%
(RU4)		between 15.0 and 25.0 mol%

and having in reacted form at least one monomer of formula (I):



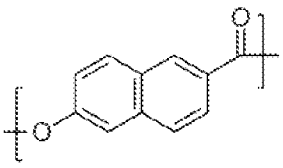
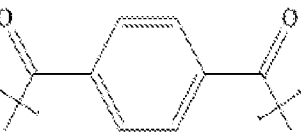
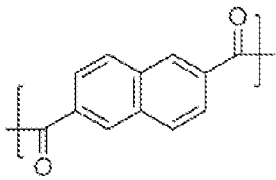
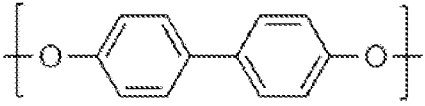
where R^1 is COOH and R is an aryl group, a heteroaryl group or a cycloalkyl group, the proportion of this monomer in the LCP being between 0.10 and 1.0 mol% (this latter value of 1 mol% being excluded),

where all the proportions are given in mol% and based on the total amount of recurring units (RU1), (RU2), (RU3), (RU4) and the units derived from the monomer of formula (I) that are present in the polyester (PE).

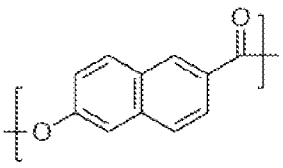
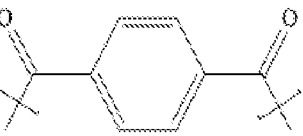
Claim 2. Polyester (PE) according to claim 1, wherein the proportion of monomer of formula (I) in reacted form is:

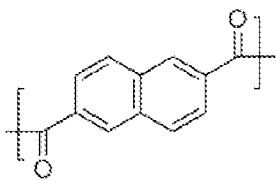
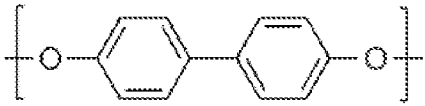
- between 0.15 and 0.75 mol%; or
- between 0.15 and 0.60 mol%; or
- between 0.15 and 0.55 mol%; or
- between 0.45 and 0.55 mol%; or
- between 0.15 and 0.25 mol%.

Claim 3. Polyester (PE) according to claim 1 or 2, wherein the proportions of the recurring units (RU1)-(RU4) are the following ones:

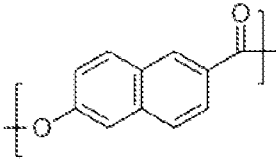
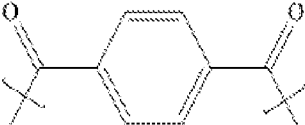
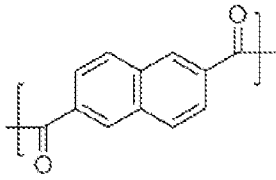
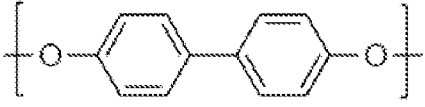
(RU1)		between 53.0 and 65.0 mol%
(RU2)		between 11.0 and 17.0 mol%
(RU3)		between 1.5 and 9.0 mol%
(RU4)		between 15.0 and 24.0 mol%

or the following ones:

(RU1)		between 55.0 and 65.0 mol%
(RU2)		between 13.0 and 17.0 mol%

(RU3)		between 2.0 and 7.0 mol%
(RU4)		between 18.0 and 22.0 mol%

or the following ones:

(RU1)		between 55.0 and 65.0 mol%
(RU2)		between 11.0 and 15.0 mol%
(RU3)		between 2.0 and 8.0 mol%
(RU4)		between 18.0 and 22.0 mol%

Claim 4. Polyester (PE) according to any one of the preceding claims, wherein the monomer of formula (I) is 1,2,4-benzenetricarboxylic acid or 1,3,5-benzenetricarboxylic acid or a combination of these two triacids.

Claim 5. Polyester (PE) according to any one of the preceding claims, wherein polyester (PE) is free of recurring units derived from 4-hydroxybenzoic acid, the expression "*free of*" meaning that the proportion of these recurring units in polyester (PE) is lower than or equal to 1.50 mol%, preferably lower than or equal to 1.00 mol%, preferably lower than or equal to 0.50 mol%, preferably lower than or equal to 0.25 mol%.

Claim 6. Polyester (PE) according to any one of the preceding claims, wherein polyester (PE) does not comprise recurring units derived from 4-hydroxybenzoic acid.

Claim 7. Polyester (PE) according to any one of the preceding claims, exhibiting a melting temperature T_m which is:

- at least 295.0°C; and/or

- at most 330.0°C;

T_m being measured by Differential Scanning Calorimetry ("DSC") according to ASTM D3418 according to protocol (p) defined in the Experimental Section.

Claim 8. Polyester (PE) according to any one of the preceding claims, exhibiting a crystallization temperature T_c which is:

- at least 250.0°C; and/or

- at most 280.0°C;

T_c being measured by Differential Scanning Calorimetry ("DSC") according to ASTM D3418 according to protocol (p) defined in the Experimental Section.

Claim 9. Polyester (PE) according to any one of the preceding claims, exhibiting a melting temperature T_m and a crystallization temperature T_c such that the difference $\Delta=(T_m - T_c)$ is at least 40.0°C, preferably at least 41.0°C, preferably at least 42.0°C, preferably at least 43.0°C, preferably at least 44.0°C, preferably at least 45.0°C; and preferably at most 60.0°C, T_m and T_c being measured by Differential Scanning Calorimetry ("DSC") according to ASTM D3418 according to protocol (p) defined in the Experimental Section.

Claim 10. Polyester (PE) according to any one of the preceding claims, exhibiting the following rheological properties:

- a viscosity V of at least 100 Pa s measured at $T_m+25^\circ\text{C}$ and at a shear rate of 100 s⁻¹; and/or

- a storage modulus G' of at least 20.0 kPa measured at $T_m+25^\circ\text{C}$ and at a shear rate of 100 s⁻¹;

these rheological properties (V and G') being measured using a parallel plate rheometer under oscillatory shear, notably according to the method of the Experimental Section.

Claim 11. Polyester (PE) according to any one of the preceding claims, prepared by polycondensing a monomer mixture (MM) comprising, consisting essentially of or consisting of:

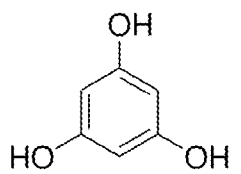
- monomer (M1): 6-hydroxy-2-naphthoic acid (HNA);
- monomer (M2): terephthalic acid (TPA);
- monomer (M3): 2,6-naphthalene dicarboxylic acid (NDA);
- monomer (M4): 4,4'-biphenol (BP); and
- at least one monomer of formula (I);

where the $-OH$ groups of monomers (M1) and (M4) are optionally partly or totally replaced by $-O-C(=O)-Q$ groups where Q is a C_1-C_6 linear or branched alkyl group, preferably Q is Me.

Claim 12. Polyester (PE) according to any one of the preceding claims, wherein the units forming the polyester consist essentially of or consist of the recurring units (RU1), (RU2), (RU3), (RU4) and the units derived from the monomer of formula (I) that are present in the polyester (PE).

Claim 13. Polyester (PE) according to any one of the preceding claims, wherein the polyester (PE) does not comprise units derived from a monomer (i) not complying with formula (I) and (ii) having at least three groups X selected in the group consisting of $COOH$, OH and combination thereof.

Claim 14. Polyester (PE) according to any one of the preceding claims, wherein the polyester (PE) does not contain units derived from phloroglucinol of formula:



Claim 15. Polyester (PE) according to any one of claims 1-15 in the form of a film.

Claim 16. Polymer composition (PC) of the invention comprises, consists essentially of or consists of:

- at least one polyester (PE) as disclosed in any one of claims 1-15;
 - optionally at least one filler (F), notably selected in the group consisting of glass fibers (GF), carbon fibers (CF), silica, alumina, aluminium borate, silicon carbide, mica, talc, clay, titanium oxide, zirconia, kaolin, calcium carbonate, magnesium carbonate, calcium sulfate, barium sulfate, magnesium hydroxide, quartz, graphite, bentonite, calcium phosphate;
 - optionally at least one additive (A) different from filler (F) and selected in the group consisting of plasticizers, light and weathering stabilizers, antistatic agents, ultraviolet absorbing agents, dyes, pigments, viscosity agents, impact modifiers and lubricants;
- the filler(s) (F) and additive(s) (A) (if any) being blended with the polyester (PE).

Claim 17. Use of the polyester (PE) as defined in any one of claims 1-15 or the polymer composition (PC) as defined in claim 16, notably in the form of a film, for the preparation of a printed circuit board (PCB).

Claim 18. Printed circuit board (PCB) comprising the polyester (PE) as defined in any one of claims 1-15 or the polymer composition (PC) as defined in claim 16, notably in the form of a film.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/059447

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08G63/60 C08K3/013

ADD.

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)

C08G C08K

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 practicable, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 116 178 686 A (KINGFA SCIENCE & TECHNOLOGY CO ET AL.) 30 May 2023 (2023-05-30) paragraph [0005]; example 2; table 1 -----	1 - 18
X	WO 99/52978 A1 (DU PONT [US]) 21 October 1999 (1999-10-21) example 8; table II -----	1 - 18



Further documents are listed in the continuation of Box C.



See patent family annex.

* 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 application or patent 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

14 March 2025

Date of mailing of the international search report

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Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2

NL - 2280 HV Rijswijk

Tel. (+31-70) 340-2040,

Fax: (+31-70) 340-3016

Authorized officer

Hoffmann, Michael

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2024/059447

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 116178686	A	30-05-2023	NONE
WO 9952978	A1	21-10-1999	CA 2327674 A1 21-10-1999
		CN 1296508 A	23-05-2001
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