

University of Groningen

Process for preparing zinc dicarboxylate and use thereof as a catalyst in the synthesis of polyalkylene carbonate from co2 by heterogeneous catalysis

Tang, Zhenchen; Pescarmona, Paolo; Sartore, Luciana; Pandini, Stefano; Gnali, Luca; Sala, Giovanni

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version

Publisher's PDF, also known as Version of record

Publication date:

2022

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Tang, Z., Pescarmona, P., Sartore, L., Pandini, S., Gnali, L., & Sala, G. (2022). Process for preparing zinc dicarboxylate and use thereof as a catalyst in the synthesis of polyalkylene carbonate from co2 by heterogeneous catalysis. (Patent No. WO2022118170).

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.



(51) International Patent Classification:

B01J 31/22 (2006.01)

(21) International Application Number:

PCT/IB2021/061063

(22) International Filing Date:

29 November 2021 (29.11.2021)

(25) Filing Language:

Italian

(26) Publication Language:

English

(30) Priority Data:

102020000029237 01 December 2020 (01.12.2020) IT

(71) Applicants: **EPOX-CO2 S.R.L.** [IT/IT]; Via Fratelli Antegnati 12, 25065 Lumezzane (Brescia) (IT). **RIJKSUNIVERSITEIT GRONINGEN** [NL/NL]; Broerstraat 5, Groningen (NL). **UNIVERSITÀ DEGLI STUDI DI BRESCIA** [IT/IT]; Piazza Mercato 15, 25121 Brescia (IT).

(72) Inventors: **TANG, Zhenchen**; c/o RIJKSUNIVERSITEIT GRONINGEN, Broerstraat 5, 9712 CP Groningen (NL). **PESCARMONA, Paolo P.**; c/o RIJKSUNIVERSITEIT GRONINGEN, Broerstraat 5, 9712 CP Groningen (NL). **SARTORE, Luciana**; c/o Università degli Studi di Bres-

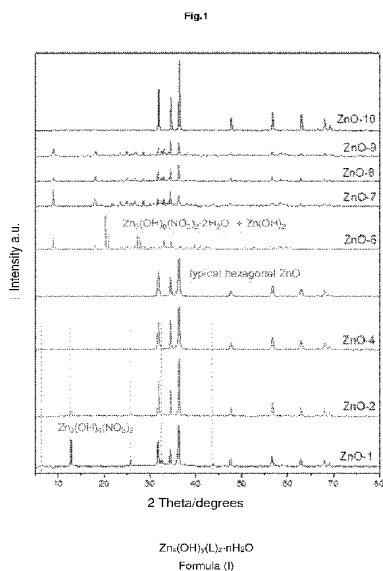
cia, Piazza Mercato 15, 25121 Brescia (IT). **PANDINI, Stefano**; c/o Università degli Studi di Brescia, Piazza Mercato 15, 25121 Brescia (IT). **GNALI, Luca**; c/o EPOX-CO2 S.r.l., Via Fratelli Antegnati 12, 25065 Lumezzane (BRESCIA) (IT). **SALA, Giovanni**; c/o EPOX-CO2 S.r.l., Via Fratelli Antegnati 12, 25065 Lumezzane (BRESCIA) (IT).

(74) Agent: **BIGGI, Cristina** et al.; C/o Bugnion S.P.A., Viale Lancetti 17, 20158 Milano (IT).

(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ,

(54) Title: PROCESS FOR PREPARING ZINC DICARBOXYLATE AND USE THEREOF AS A CATALYST IN THE SYNTHESIS OF POLYALKYLENE CARBONATE FROM CO₂ BY HETEROGENEOUS CATALYSIS



(57) Abstract: The present invention relates to a process for the synthesis of a zinc-based compound having general formula (I): wherein L is selected in the group consisting of: NO₃, CH₃CO₂, (SO₄)_{0.5}, halide, and acetyl acetonate (AcAc), 2x = y + z; wherein x is comprised between 1 and 5, y is comprised between 1 and 8, z is comprised between 1 and 2, and n is comprised between 0 and 20. Said zinc-based compound is then used for the synthesis of a zinc dicarboxylate catalyst to be used for the heterogeneous catalytic copolymerization of a polyalkylene carbonate starting from CO₂ and an alkyl epoxide, preferably containing at least 3 atoms of carbon, said polyalkylene carbonate being characterised by chemical-physical and mechanical properties which make it advantageous for a variety of different applications.



UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

- *with international search report (Art. 21(3))*
- *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

“Process for preparing zinc dicarboxylate and use thereof as a catalyst in the synthesis of polyalkylene carbonate from CO₂ by heterogeneous catalysis”

DESCRIPTION

FIELD OF THE INVENTION

The present invention relates to a process for the synthesis of a zinc-based compound and the subsequent use thereof for the synthesis of a zinc dicarboxylate catalyst to be used for the heterogeneous catalytic copolymerization of a polyalkylene carbonate starting from CO₂ and an alkyl epoxide preferably containing at least 3 atoms of carbon.

PRIOR ART

In the field of materials science, one of the most felt technological needs in the current state of the art is to try to replace the plastic materials obtained from oil with plastic materials (preferably biodegradable) produced from renewable raw materials, while maintaining the existing industrial production chains and the physical-mechanical properties of the final products as much as possible. In fact, the production of plastic is continuously growing and does not show signs of decreasing: from 15 million tons in 1964 to about 400 million in 2016. Today plastic is the third material produced by mankind, with the greatest spread on Earth after steel and cement. The possibility of producing plastics with a minor use of (or ideally without) oil derivatives is therefore a particularly topical area of research and represents, at the same time, a global environmental requirement which cannot be ignored. However, the possibility of reducing dependence on oil resources is still subject to the availability of effective and efficient technologies which should allow a rapid and cost-effective transition towards renewable raw materials, ideally also leading to even more efficient products. The greatest technological frontier to be addressed is not only the replacement of monomers/polymers obtained from oil with monomers/polymers obtained from renewable sources, but also and above all the possibility of finding production processes which allow the performance of the finished products to be maintained (or improved) in terms of mechanical features, economic efficiency and mass production capacity. Every year, the world produces more than 10 billion tons of carbon dioxide due to the combustion of fossil compounds, the refining of oil, fermentation and other production processes. The impact of carbon dioxide emissions is further increased by deforestation and/or fires affecting large portions of forests. This has caused the increase in the concentration of carbon dioxide in the atmosphere, causing an increasingly more serious greenhouse effect. In fact, carbon dioxide (CO₂) is one of the so-called greenhouse-effect gases and the scientific community now commonly accepts the role which the increase of greenhouse gases has in the climate and environmental changes underway. At the same time, carbon dioxide is an important source of carbon in nature, together with the reserves found in the deep ocean, marine sediments,

the terrestrial biosphere and the surface oceans. With the increase in the amount of CO₂ due to human activities, the exploration of new technologies which can use carbon dioxide, currently considered a waste product harmful to the environment, instead as a new resource for new uses, has attracted more and more interest in the scientific community. Among

5 these, the use of carbon dioxide for the production of plastics, in particular polyalkylene carbonates (belonging to the class of polycarbonates), by copolymerization with epoxides has attracted a lot of attention due to the high application value thereof in terms of environmental impact and the prospects for technological development. However, the

10 catalysts used for such a reaction generally have a low catalytic efficiency and/or a high production cost, thereby limiting the use thereof at an industrial level. The catalysts currently most commonly used in industry for this reaction are zinc dicarboxylic acids, especially zinc glutarate. For example, CN101468320A describes the synthesis of a composite material based on zinc oxide which is subsequently used, together with a dicarboxylic acid (such as glutaric acid) to obtain a catalyst used in the copolymerization of an epoxide with carbon

15 dioxide. The synthesis of a zinc oxide-based composite material described herein involves the use of a sulphuric acid solution and a heat treatment cycle to activate an inorganic matrix (such as: montmorillonite, mica or vermiculite) to which a solution of zinc nitrate, anhydrous ethanol and urea is added. The product thus obtained is then calcined until a ZnO/inorganic matrix complex is obtained. However, such a reaction involves the use of a solid phase

20 (represented by the inorganic matrix) and a liquid phase which can potentially have numerous disadvantages such as high costs (related to the raw materials, the numerous synthesis steps and/or a potentially low yield) and, consequently, obtaining a catalyst which does not meet the desired requirements. Therefore, the need remains in the sector to provide an effective catalytic process for the production of plastic materials which are

25 obtained as much as possible, if not totally, from CO₂ instead of from raw materials deriving from oil and which, at the same time, are provided with technical characteristics such as to fully meet industrial needs, both regarding application and process, and therefore able to replace plastics deriving from fossil sources. The present invention solves the problems of the known art by providing a new process for the synthesis of a zinc dicarboxylate catalyst.

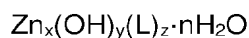
30 The catalyst obtained by the process according to the invention allows to prepare, directly from CO₂, and with a high catalytic activity, high selectivity and high purity, a polyalkylene carbonate having a combination of physical-mechanical characteristics not reported in the known polycarbonates, namely a polyalkylene carbonate which is a thermoplastic polymer, biodegradable, with a high flexibility and ductility, good resistance and/or sufficient rigidity, a

35 high and immediate percentage of strain recovery following a deformation, which presents

self-healing properties and with the desired values of T_g and percentage of ether bonds without the use of plasticizers.

SUMMARY OF THE INVENTION

The present invention relates to a process for the synthesis of a zinc-based compound comprising a mixture of ZnO and a compound having the general formula (I):



Formula (I)

10 wherein L is selected in the group consisting of: NO_3 , CH_3CO_2 , $(\text{SO}_4)_{0.5}$, halide, and acetyl acetate (AcAc),

$2x = y + z$; wherein

x is comprised between 1 and 5,

y is comprised between 1 and 8,

15 z is comprised between 1 and 2, and

n is comprised between 0 and 20,

said process comprising the steps of:

(a) providing a solution of a zinc precursor having the general formula $\text{Zn}(\text{L})_2 \cdot n\text{H}_2\text{O}$, wherein n and L are as defined above;

20 (b) adding a solution of a base to said solution of a zinc precursor, thereby obtaining a precipitate;

(c) separating the precipitate from the supernatant solution and subjecting the solid thus separated to a heat treatment at a temperature comprised between 30 and 400 °C and for a period of time comprised between 20 minutes and 60 hours. The present invention relates to

25 a process for the synthesis of a zinc dicarboxylate catalyst, further comprising the step:

(d) reacting said zinc-based compound obtained in step (c) of the process described above with a dicarboxylic acid, preferably a saturated aliphatic dicarboxylic acid.

The present invention also relates to said zinc-based compound and said zinc dicarboxylate catalyst respectively obtainable by the processes described above. Furthermore, the present

30 invention relates to a process for the synthesis of polyalkylene carbonate by means of a heterogeneous catalytic copolymerization reaction comprising the steps of:

(e) reacting carbon dioxide with an alkyl epoxide, preferably containing at least 3 atoms of carbon, preferably in the absence of an organic solvent, in the presence of said zinc dicarboxylate catalyst as described above. A further object of the present invention is a

35 polyalkylene carbonate obtainable by said process. Preferably, said polyalkylene carbonate has a weight-average molecular weight (M_w) comprised between 10 and 300 kg/mol and is

characterized by having:

- i) a percentage of ether bonds comprised between 0 and 30% (relative to the total carbonate bonds and ether bonds);
 - ii) self-healing properties in a time between 1 minute and 4 days, preferably between 15
5 minutes and 4 days, preferably between 30 minutes and 4 days, preferably between 1 hour and 4 days, preferably between 1 hour and 8 hours, even more preferably between 1 minute and 3 hours, even more preferably between 15 minutes and 3 hours, even more preferably between 1 hour and 3 hours, even more preferably between 2 hours and 4 hours, even more preferably between 2 hours and 3 hours;
 - 10 iii) a strain recovery comprised between 70 and 100% following a percentage elongation greater than 600%;
 - iv) a percentage elongation at break (ϵ_b) greater than 600%;
 - v) an elastic modulus (E) comprised between 50 and 1000 MPa.
- Preferably, said polyalkylene carbonate is characterized in that it further possesses one or
15 more of the following characteristics:
- vi) a yield strength (δ_y) greater than 0.5 MPa; and/or
 - vii) an ultimate tensile strength (δ_b) greater than 1 MPa; and/or
 - viii) a glass transition temperature (T_g) comprised between 0 and 35 °C.

BRIEF DESCRIPTION OF THE FIGURES

- 20 Figure 1 shows an XRD diffractogram of the different zinc-based compounds prepared as described in Example 1.
- Figure 2 shows an XRD diffractogram of the different zinc glutarate catalysts prepared as described in Example 2.
- Figure 3 shows an XRD diffractogram of the different zinc dicarboxylate catalysts prepared
25 as described in Example 3.
- Figure 4 shows an $^1\text{H-NMR}$ spectrum of the polypropylene carbonate (sample PPC-12) obtained as described in Example 5.
- Figure 5 shows a $^{13}\text{C-NMR}$ spectrum of the polypropylene carbonate (sample PPC-12-3b) obtained as described in Example 5.
- 30 Figure 6 shows a photo of a film obtained by moulding the sample PPC-6 as described in Example 6, in which the transparency of the film can be appreciated.
- Figure 7 shows a photo depicting the samples of the transversely cut PPC-6 material (left panel). In the right panel, the overlap between the two sections is shown, made on a sheet of graph paper by simply overlapping (without compressing and without heating) the central
35 part by about 4 mm (indicated by the arrows).
- Figure 8 shows the mechanical characteristics of stiffness and extensibility of PPC according

to the present invention compared to the characteristics of softer, more flexible polymers of fossil origin.

DETAILED DESCRIPTION OF THE INVENTION

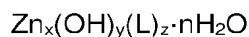
For the purposes of the present invention, the weight-average molecular weight (Mw) and
5 number-average molecular weight (Mn) are determined by gel permeation chromatography (GPC) as, for example, described in Example 5.

For the purposes of the present invention, the extensibility and mechanical return characteristics, i.e., mechanical return (iii), percent elongation at break (iv), modulus of elasticity (v), yield strength (vi) and tensile strength (vii), are determined by uniaxial tensile
10 mechanical testing (testing) using an electromechanical dynamometer as, for example, described in Example 7.

For the purposes of the present invention, said time "between 1 minute and 4 days" means that the self-healing (self-healing) properties of the polyalkylene carbonate according to the present invention are achieved/expected (i.e., in other words, self-healing occurs) in period of
15 time equal to any value between said two extremes, such as, for example, 1 minute, 2 minutes, 3 minutes, 4 minutes, 5 minutes, 6 minutes, 7 minutes, 8 minutes, 9 minutes, 10 minutes, 11 minutes, 12 minutes, 13 minutes, 14 minutes, 15 minutes, 16 minutes, 17 minutes, 18 minutes, 19 minutes, 20 minutes, 21 minutes, 22 minutes, 23 minutes, 24 minutes, 25 minutes, 26 minutes, 27 minutes, 28 minutes, 29 minutes, 30 minutes, 31
20 minutes, 32 minutes, 33 minutes, 34 minutes, 35 minutes, 36 minutes, 37 minutes, 38 minutes, 39 minutes, 40 minutes, 41 minutes, 42 minutes, 43 minutes, 44 minutes, 45 minutes, 46 minutes, 47 minutes, 48 minutes, 49 minutes, 50 minutes, 51 minutes, 52 minutes, 53 minutes, 54 minutes, 55 minutes, 56 minutes, 57 minutes, 58 minutes, 59 minutes, 1 hour, 2 hours, 3 hours, 4 hours, 5 hours, 6 hours, 7 hours, 8 hours, 9 hours, 10
25 hours, 11 hours, 12 hours, 13 hours, 14 hours, 15 hours, 16 hours, 17 hours, 18 hours, 19 hours, 20 hours, 21 hours, 22 hours, 23 hours, 1 day, 2 days, 3 days, 4 days.

The same definition (suitably adapted to individual cases) also applies, for the purposes of the present invention, to similar expressions of numerical intervals as described for the different embodiments of the present invention.

30 The present invention relates to a process for the synthesis of a zinc-based compound comprising a mixture of ZnO and a compound having the general formula (I):



35 Formula (I)

wherein L is selected in the group consisting of: NO₃, CH₃CO₂, (SO₄)_{0,5}, halide, and acetyl

acetate (AcAc),

$2x = y + z$; wherein

x is comprised between 1 and 5,

y is comprised between 1 and 8,

5 z is comprised between 1 and 2, and

n is comprised between 0 and 20,

said process comprising the steps of:

(a) providing a solution of a zinc precursor having the general formula $Zn(L)_2 \cdot nH_2O$, wherein n and L are as defined above;

10 (b) adding a solution of a base to said solution of a zinc precursor, thereby obtaining a precipitate;

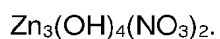
(c) separating the precipitate from the supernatant solution and subjecting the solid thus obtained to a heat treatment at a temperature comprised between 30 and 400 °C and for a period of time comprised between 20 minutes and 60 hours. According to an embodiment of the invention, n is comprised between 0 and 10, or between 0 and 8, or between 0 and 6, or between 2 and 6. According to another embodiment of the invention, n is comprised between 1 and 20, or between 1 and 10, or between 2 and 20, or between 2 and 10. As demonstrated in the Examples section, and in particular as is clear from the data collected in Table 4 related to yield and productivity, the Applicants have found that, thanks to the synthesis conditions of steps (a)-(b) and, in particular, thanks to the heat treatment of step (c), a zinc-based compound can be obtained comprising a mixture of ZnO and a compound of formula (I), i.e., an intermediate compound between the zinc precursor used in the synthesis, $Zn(L)_2 \cdot nH_2O$, and ZnO. Such a mixture allows to obtain a zinc dicarboxylate catalyst having a higher catalytic activity and, consequently, a higher production yield of the polyalkylene carbonate, with respect to the use of a known catalyst obtained from pure ZnO. The temperature and time conditions of step (c) are suitably calibrated and modulated in order to obtain the mixture of ZnO and a compound of formula (I). In particular, if high temperatures (i.e., towards the upper end of the aforementioned range) are applied, the heat treatment times will be shorter (i.e., towards the lower end of the aforementioned range); while if lower temperatures (i.e., towards the lower end of the aforementioned range) are applied, the heat treatment times will be longer (i.e., towards the upper end of the aforementioned range). According to an embodiment of the invention, the heat treatment of step (c) is carried out at a temperature (T): $30^\circ C < T < 90^\circ C$ and for a period of time (t): $20 \text{ hours} < t \leq 60 \text{ hours}$. According to an embodiment of the invention, the heat treatment of step (c) is carried out at a temperature (T): $90^\circ C \leq T \leq 150^\circ C$ and for a period of time (t): $20 \text{ minutes} \leq t < 20 \text{ hours}$. According to an embodiment of the invention, the heat treatment of step (c) is carried out at a

temperature (T): $150\text{ }^{\circ}\text{C} < T \leq 400\text{ }^{\circ}\text{C}$ and for a period of time (t): $20\text{ minutes} \leq t < 20\text{ hours}$, preferably $20\text{ minutes} \leq t \leq 15\text{ hours}$. According to an embodiment of the invention, said zinc-based compound consists of a mixture of ZnO and of said compound having the general formula (I). According to a preferred embodiment of the invention, L is nitrate (NO_3).

5 Preferably, the solution of a zinc precursor of step (a) has general formula $\text{Zn}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$, more preferably $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

According to a preferred embodiment of the invention, said compound having general formula (I) has the following formula: $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

10 According to an embodiment of the invention, said compound having general formula (I) has the following formula:



According to an embodiment of the invention, said zinc-based compound comprises or consists of a mixture of ZnO and of one or more compounds having general formula (I) as described above. According to an embodiment, said solution of a base of step (b) is a

15 solution of a base selected from the group consisting of: ammonia/ammonium hydroxide (NH_4OH), NaOH, KOH. Preferably, said solution of a base is an aqueous solution. More preferably, said solution of a base is an ammonia solution, preferably an aqueous ammonia solution. According to a preferred embodiment, when the heat treatment of step (c) is carried out at a temperature of $90\text{ }^{\circ}\text{C}$ and for a time of 20 hours, a zinc-based compound is obtained

20 comprising a mixture of ZnO and a compound having formula $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$.

According to another embodiment, when the heat treatment of step (c) is carried out at a temperature of $120\text{ }^{\circ}\text{C}$ and for a time of 20 hours, a zinc-based compound is obtained comprising a mixture of ZnO and a compound having formula $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, wherein the relative amount of ZnO in the mixture is higher than the embodiment in which the heat

25 treatment is carried out at $90\text{ }^{\circ}\text{C}$. According to another embodiment, when the heat treatment of step (c) is carried out at a temperature of $150\text{ }^{\circ}\text{C}$ and for a time of 20 hours, a zinc-based compound is obtained comprising a mixture of ZnO and a compound having formula

$\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, wherein the relative amount of ZnO in the mixture is higher than the embodiment in which the heat treatment is carried out at $90\text{ }^{\circ}\text{C}$. Preferably, according to any

30 of the embodiments defined above, said zinc-based compound comprises said ZnO and said compound having general formula (I) in a mass ratio comprised between 0.1 and 10, preferably comprised between 0.2 and 5. The present invention also relates to a zinc-based compound comprising a mixture of ZnO and a compound having general formula (I) as

defined above obtainable by the aforesaid process. The present invention also relates to a

35 process for the synthesis of a zinc dicarboxylate catalyst, comprising steps (a)-(c) as described above and the further step:

(d) reacting said zinc-based compound with a dicarboxylic acid.

Preferably said step (d) of reacting said zinc-based compound with a dicarboxylic acid is carried out in a solvent, preferably in an aprotic solvent. Preferably said solvent is selected from the group consisting of: toluene, benzene, xylene (and the isomers thereof), mesitylene, chloroform, dichloromethane, and a combination thereof. For example, said step (d) is carried out at a reaction temperature comprised between 50 and 130 °C, preferably between 70 and 110 °C. For example, said step (d) of reacting said zinc-based compound with a dicarboxylic acid is carried out for a period of time comprised between 12 and 48 hours, preferably between 18 and 36 hours.

According to a preferred embodiment of the invention, said dicarboxylic acid is a saturated aliphatic dicarboxylic acid i.e. containing neither aromatic groups nor double bonds. Preferably said saturated aliphatic dicarboxylic acid contains from 4 to 12 carbon atoms (C₄-C₁₂). According to a particularly preferred embodiment, said dicarboxylic acid is neither fumaric acid nor terephthalic acid.

Preferably, said zinc dicarboxylate catalyst is selected from zinc dicarboxylate compounds having an alkyl chain between the two carboxyl groups. More preferably, said zinc dicarboxylate catalyst is selected from the group consisting of: zinc glutarate (ZnGA), succinate (ZnSA), zinc adipate (ZnAA),; therefore, the dicarboxylic acid of step (d) is selected from the group consisting of glutaric acid, succinic acid, adipic acid, , respectively. According

to a particularly preferred embodiment, said process for the synthesis of said zinc dicarboxylate catalyst optionally comprises, after step (d) also a step (d') of carrying out a solid-liquid separation and subjecting the solid thus separated to a heat treatment at a temperature comprised between 90 and 150 °C. A zinc dicarboxylate catalyst obtainable by the process described above is a further object of the present invention. As mentioned

above, without wishing to be bound by a specific theory, the Applicants have found that, thanks to the synthesis conditions of steps (a)-(b) and, in particular, thanks to the heat treatment of step (c), which allow to obtain a zinc-based compound comprising a mixture of ZnO and a compound having general formula (I) (i.e., of an intermediate compound between the zinc precursor used in the synthesis Zn(L)₂·nH₂O and ZnO), it is possible to obtain a zinc

dicarboxylate catalyst having a particularly high catalytic activity for the copolymerization reaction of a polyalkylene carbonate starting from CO₂. As also demonstrated in the Examples section, the use of a different zinc-based compound with respect to the mixture according to the present invention (such as commercial ZnO or ZnO as reported in literature) in the synthesis of the zinc dicarboxylate catalyst, results in a catalyst having a lower catalytic activity. Similarly, the use of different temperatures and times in the heat treatment of step (c) also results in a different zinc-based compound than that of the present invention

and which does not produce a zinc dicarboxylate catalyst having an equally high catalytic activity. Advantageously, as also demonstrated in the Examples below, the zinc dicarboxylate catalyst according to the present invention is characterized by having a catalytic activity towards the heterogeneous catalytic copolymerization reaction for the synthesis of polyalkylene carbonate starting from carbon dioxide and an alkyl epoxide, preferably containing at least 3 atoms of carbon, which reaches a productivity of 2.8 $\text{g}_{\text{polyalkylene carbonate}}/(\text{g}_{\text{catalyst}} \cdot \text{hour})$ for example in the case where the epoxide is propylene oxide, using 0.5 g catalyst for every 50 mL of propylene oxide, at a CO_2 pressure of 40 bar with a reaction time of 20 hours at 80°C . Furthermore, as demonstrated in the Examples, the zinc dicarboxylate catalyst according to the present invention is also characterized by having a high selectivity towards the heterogeneous catalytic copolymerization reaction for the synthesis of polyalkylene carbonate starting from carbon dioxide and an alkyl epoxide, preferably containing at least 3 atoms of carbon. In addition, without wishing to be bound by a specific theory, the Applicants have nevertheless found that, thanks to the process according to the present invention, in particular thanks to steps (a)-(d), it is possible to obtain a zinc dicarboxylate catalyst having a high degree of purity from XRD. In other words, said catalyst has as main crystalline phase observed in XRD dicarboxylate zinc and negligible impurities of zinc oxide.

The present invention further relates to a process for the synthesis of polyalkylene carbonate by means of a heterogeneous catalytic copolymerization reaction comprising the steps of:

(e) reacting carbon dioxide with an alkyl epoxide, preferably containing at least 3 atoms of carbon, preferably in the absence of an organic solvent, in the presence of at least one zinc carboxylate catalyst as described above. According to a particularly preferred embodiment, said step (e) is carried out by heating at a temperature comprised between 30 and 150°C , more preferably between 40 and 100°C . Preferably, said step (e) is carried out at a pressure (P_{CO_2}) comprised between 1 and 80 bar, preferably between 20 and 60 bar. More preferably, said step (e) is carried out for a period of time comprised between 1 and 40 hours, preferably between 2 and 20 hours. Preferably said polyalkylene carbonate is polypropylene carbonate (PPC) and, therefore, said alkyl epoxide of step (e) is propylene oxide (PO). Preferably, the aforesaid process for the synthesis of a polyalkylene carbonate by means of a heterogeneous catalytic copolymerization reaction according to the present invention, and in particular the use of the zinc dicarboxylate catalyst according to the present invention allows to obtain said polyalkylene carbonate with a reaction yield which reaches $28.7 \text{ g/g}_{\text{cat}}$ in the case where, for example, the alkyl epoxide is propylene oxide and 0.5 g of catalyst are used for every 50 mL of propylene oxide, at a CO_2 pressure of 40 bar with a reaction time of 20 hours at 80°C . According to a particularly preferred embodiment, said step (e) is carried out

by subjecting said alkyl epoxide to a dehydration pretreatment, preferably by anhydrifying said alkyl epoxide with a molecular sieve, more preferably for a period of time of at least 12 hours. Without wishing to be bound by a specific theory, the Applicants have found that said dehydration pretreatment of alkyl epoxide is particularly advantageous, as it allows to obtain

5 a doubled yield of polyalkylene carbonate with respect to a process in which said alkyl epoxide is used in the reaction without said pretreatment. According to such an embodiment, said reaction yield reaches 56.2 g/g_{cat} using for example as alkyl epoxide, propylene oxide and using 0.5 g of catalyst for every 50 mL of propylene oxide, at a CO₂ pressure of 40 bar with a reaction time of 20 hours at 80°C. According to a preferred embodiment, the process

10 according to the present invention (steps (a)-(e)) does not involve the addition of plasticizers. The present invention also relates to a polyalkylene carbonate obtainable by the process described above.

In an embodiment, the present invention relates to a carbonate polyalkylene obtainable by the above-described process, wherein said carbonate polyalkylene has a weight average

15 molecular weight (M_w) between 10 and 300 kg/mol, preferably between 30 and 300 kg/mol and is characterized by having:

- a percentage of ether bonds, relative to the total of carbonate bonds and ether bonds, between 0 and 30%, preferably between 3 and 30%, preferably between 3 and 25%;
- a mechanical return in the range of 70 to 100% following a percent elongation greater than

20 600%;

- a percentage elongation at break (ε_b) greater than 600%;
- an elastic modulus (E) between 50 and 1000 MPa.

According to a preferred embodiment, said polyalkylene carbonate has a weight-average molecular weight (M_w) comprised between 10 and 300 kg/mol, preferably between 30 and

25 300 kg/mol, and is characterized by having:

- i) a percentage of ether bonds (relative to the total of carbonate bonds and ether bonds), comprised between 0 and 30%, preferably comprised between 3 and 30%, preferably between 3 and 25%;
- ii) self-healing properties in a time between 1 minute and 4 days, preferably between 15

30 minutes and 4 days, preferably between 30 minutes and 4 days, preferably between 1 hour and 4 days, preferably between 1 hour and 8 hours, even more preferably between 1 minute and 3 hours, even more preferably between 15 minutes and 3 hours, even more preferably between 1 hour and 3 hours, even more preferably between 2 hours and 4 hours, even more preferably between 2 hours and 3 hours;

- 35 iii) a strain recovery comprised between 70 and 100% following a percentage elongation greater than 600%;

iv) a percentage elongation at break (ϵ_b) greater than 600%;

v) an elastic modulus (E) comprised between 50 and 1000 MPa.

According to an embodiment, said percentage of ether bonds i) is comprised between 4 and 30%, preferably between 4 and 25%, preferably between 5 and 20%, preferably between 5
5 and 15%.

According to an embodiment, said strain recovery iii) is comprised between 70 and 100%, preferably comprised between 75 and 100%, following a percentage elongation greater than 600%, preferably greater than 700%, more preferably greater than 800%, more preferably greater than 900%, even more preferably greater than 950%, more preferably comprised
10 between 600 and 950%. According to an embodiment, said percentage elongation at break iv) is greater than 700%, more preferably greater than 800%, more preferably greater than 900%, even more preferably greater than 950%, more preferably comprised between 600 and 950%. According to an embodiment, said elastic modulus v) is preferably comprised
15 between 100 and 1000 Mpa, more preferably between 100 and 600 Mpa, even more preferably between 100 and 500 MPa.

For the purposes of the present invention, "self-healing properties" means that the polyalkylene carbonate according to the present invention is capable of being completely and autonomously healed or has the ability to recover physical and structural integrity, lost following a cut and/or a break, with total or partial, preferably total, restoration of the
20 mechanical properties without applying any pressure and/or change in temperature conditions.

In other words, the term "self-healing" refers to the ability of the material to repair itself completely and autonomously. More specifically, in the event of defects such as through holes or tears, the material can be repaired by overlapping the flaps surrounding the area
25 affected by the defect. The surfaces thus overlapped, thanks to the self-healing properties of the material, will adhere at first and at a later time interpenetrate each other.

For the purposes of the present invention, the complete (and self-healing) property as defined above is measured by tensile testing (method of evaluating adhesion on overlapping flaps "lap shear joints") and by delamination testing (method of evaluating adhesion by
30 delamination) both performed by means of an electromechanical dynamometer (as described, for example, in Example 8).

Preferably, the polyalkylene carbonate according to the present invention is characterized by having self-healing properties which lead to a complete and autonomously self-healing in a period of time comprised between 1 minute and 4 days, preferably between 15 minutes and
35 4 days, preferably between 30 minutes and 4 days, preferably between 1 hour and 4 days, preferably between 1 hour and 8 hours, even more preferably between 1 minute and 3 hours,

even more preferably between 15 minutes and 3 hours, even more preferably between 1 hour and 3 hours, even more preferably between 2 hours and 4 hours, even more preferably between 2 hours and 3 hours. Advantageously, the aforesaid ether bond percentage values (which make the polyalkylene carbonate a ductile and workable material), in combination with the characteristics of self-healing and high strain recovery, elastic modulus and elongation, (these being new and desirable characteristics for a variety of different applications), make the polyalkylene carbonate of the present invention an extremely versatile material with desired mechanical performance in different fields of application. Preferably, said polyalkylene carbonate is characterized in that it further possesses one or more of the following characteristics:

- vi) a yield strength (δ_y) greater than 0.5 Mpa, preferably greater than 1 Mpa; and/or
- vii) an ultimate tensile strength (δ_o) greater than 1 MPa, preferably greater than 2 MPa, even more preferably comprised between 2 and 20 MPa; and/or
- viii) a glass transition temperature (T_g) comprised between 0 and 35 °C, preferably between 0 and 30 °C, preferably between 0 and 25 °C, preferably between 5 and 25 °C, preferably between 6 and 25 °C, preferably between 5 and 15 °C.

According to an embodiment, said glass transition temperature is comprised between 4 and 35 °C, preferably between 4 and 20 °C, preferably between 4 and 25 °C, preferably between 4 and 15 °C, preferably between 5 and 15 °C. According to a preferred embodiment, said polyalkylene carbonate is characterized in that it further possesses at least two of the characteristics vi)-viii), preferably at least the characteristic vi) and the characteristic vii). According to a particularly preferred embodiment, said polyalkylene carbonate is characterized in that it further and simultaneously possesses all three characteristics vi)-viii).

Without wishing to be bound to a specific theory, it is possible to claim that the presence of the aforementioned ether bonds allows for the desired glass transition temperature (T_g) values as described above and, consequently, the desired characteristics attached thereto.

According to any of the embodiments described above, said polyalkylene carbonate is preferably an amorphous polymer, i.e., a polymer which does not have crystalline phases.

According to any of the embodiments described above, said polyalkylene carbonate is preferably a thermoplastic polymer. According to any of the embodiments described above, said polyalkylene carbonate may comprise at least one additive selected in the group consisting of: a colourant, a pigment, a filler, preferably an inorganic filler, a natural fibre, wood flour, a crosslinker, a plasticizer, an antistatic, an antioxidant, an active pharmaceutical ingredient or a pharmaceutical formulation comprising it, an active cosmetic ingredient or a cosmetic formulation comprising it, a fertilizer, or a combination thereof. Preferably, said polyalkylene carbonate is thermally stable up to a temperature ≥ 190 °C, more preferably \geq

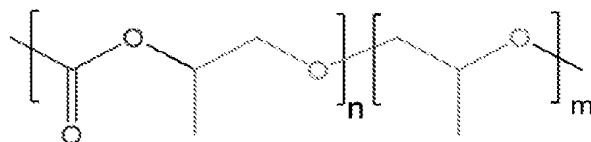
200 °C, even more preferably at a temperature comprised between 190 and 250 °C.

According to a preferred form of embodiment, the polyalkylene carbonate obtainable by the process of the present invention as described above is characterized by comprising an amount of cyclic alkylene carbonate > 0%, preferably between >0% and 5%, more preferably
 5 between 0.5 and 5%, even more preferably between 1% and 5% by weight. In other words, according to such a preferred embodiment, the polyalkylene carbonate obtainable by the process according to the present invention may contain a certain amount of cyclic alkylene carbonate as described above.

Without wishing to be bound by a specific theory, it can be argued that, as in the case of the
 10 ether bonds described above, the presence of said cyclic alkylene carbonate within the polyalkylene carbonate also contributes to obtaining the desired glass transition temperature (T_g) values described above and, consequently, also the other characteristics related to said glass transition temperature which make the polyalkylene carbonate of the present invention an extremely versatile material with desired performance in different fields of application.

15 According to a particularly preferred embodiment of the present invention, said polyalkylene carbonate is polypropylene carbonate (PPC).

Preferably, according to such an embodiment, the polypropylene carbonate has the general formula (II):



(II)

20 wherein m is comprised between 0 and $0.43n$, preferably between $0.031n$ and $0.43n$, preferably between $0.031n$ and $0.33n$. Without wishing to be bound by a specific theory, the Applicants have found that the polyalkylene carbonate obtainable by the process according to the present invention, preferably polypropylene carbonate (PPC), possesses the chemical-
 25 physical and mechanical characteristics listed above which make it advantageous for a variety of different applications.

Preferably, according to such a preferred embodiment, the polypropylene carbonate (PPC) obtainable by the process of the present invention as described above is characterized by comprising an amount of cyclic propylene carbonate (CPC) > 0%, preferably between >0%
 30 and 5%, more preferably between 0.5% and 5%, even more preferably between 1% and 5% by weight. In other words, according to such a preferred embodiment, the polypropylene carbonate obtainable by the process according to the present invention may contain a certain amount of cyclic propylene carbonate (CPC) as described above.

Without wishing to be bound by a specific theory, it can be argued that, as in the case of the ether bonds described above, the presence of said cyclic propylene carbonate within the carbonated polypropylene also contributes to obtaining the desired glass transition temperature (T_g) values described above and, consequently, also the other characteristics related to said glass transition temperature which make the carbonated polypropylene of the present invention an extremely versatile material with desired performance in different fields of application.

EXAMPLES

Example 1 – preparation of the zinc-based compound (comprising a mixture of ZnO and the compound of general formula (I)) as a precursor for the synthesis of zinc carboxylate catalysts

The zinc-based compound according to the present invention was synthesized according to the following.

Zn(NO₃)₂·6H₂O (29.8 g) was dissolved in Milli-Q water (1000 mL) to form a 0.1 mol/L zinc nitrate solution. An aqueous ammonia solution (13.6 g, 25% ammonia by weight) was added in drops to said zinc nitrate solution under vigorous mechanical stirring (at a rate of 400 rpm) until a suspension comprising a white precipitate was obtained. Said suspension was then subjected to an aging treatment at room temperature (RT) for 2 hours (2h) under stirring. Subsequently, it was filtered and washed with 1 L of water. The white powder thus obtained was subjected to a heat treatment at different temperatures (shown in Table 1) for 20 hours (20h). Each sample of zinc-based compound obtained following each heat treatment was classified as a "ZnO-X" sample (with X indicating the number of the experimental test performed and identifying the different samples), as follows.

Table 1

ZnO-X	Source of zinc	Synthesis conditions	Heat-treatment temperature	Notes
ZnO	Commercial			Aldrich
ZnO-01	Zn(NO ₃) ₂ + 2 NH ₃ ·H ₂ O	RT, 2h, 400 rpm	180 °C	
ZnO-02	Zn(NO ₃) ₂ + 2 NH ₃ ·H ₂ O	RT, 2h, 400 rpm	180 °C, 20h	Same conditions as ZnO-01, but not reactive in the synthesis.
ZnO-03	Zn(NO ₃) ₂ + 2 NH ₃ ·H ₂ O	RT, 2h, 400 rpm	250 °C, 20h	

ZnO-04	$\text{Zn}(\text{NO}_3)_2 + 2 \text{NH}_3 \cdot \text{H}_2\text{O}$	RT, 2h, 400 rpm	180 °C, 20h	
ZnO-06	$\text{Zn}(\text{NO}_3)_2 + 2 \text{NH}_3 \cdot \text{H}_2\text{O}$	RT, 2h, 400 rpm	RT	
ZnO-07	$\text{Zn}(\text{NO}_3)_2 + 2 \text{NH}_3 \cdot \text{H}_2\text{O}$	RT, 2h, 400 rpm	90 °C, 20h	mixture
ZnO-08	$\text{Zn}(\text{NO}_3)_2 + 2 \text{NH}_3 \cdot \text{H}_2\text{O}$	RT, 2h, 400 rpm	120 °C, 20h	mixture
ZnO-09	$\text{Zn}(\text{NO}_3)_2 + 2 \text{NH}_3 \cdot \text{H}_2\text{O}$	RT, 2h, 400 rpm	150 °C, 20h	mixture
ZnO-10	$\text{Zn}(\text{NO}_3)_2 + 2 \text{NH}_3 \cdot \text{H}_2\text{O}$	RT, 2h, 400 rpm	180 °C, 20h	Same conditions as ZnO-01 but shows a XRD diffractogram wherein the $\text{Zn}_3(\text{OH})_4(\text{NO}_3)_2$ signal is absent.

From the XRD diffractograms shown in Figure 1, it can be seen how, among the different zinc-based compounds synthesized, the compounds subjected to a heat treatment at a temperature of 180 °C for 20 hours (20h) (such as in the case of ZnO-02, ZnO-04 or ZnO-10) have the characteristic peaks of ZnO indicating that a transformation has occurred in zinc oxide. Conversely, in the absence of such a heat treatment (see sample ZnO-6), the compound does not comprise peaks which can be connected to the presence of ZnO but instead has characteristic peaks of zinc dihydroxide ($\text{Zn}(\text{OH})_2$) and an intermediate species of zinc hydroxylate nitrate (zinc hydroxy-nitrate) having formula $\text{Zn}_5(\text{OH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_2$. In the case of heat treatment at intermediate temperatures, it is possible to observe how these compounds show peaks related to the presence of zinc hydroxy-nitrate and peaks related to ZnO, the latter having a lower intensity than a typical ZnO peak. This indicates a less defined structure. Without wishing to be bound by a specific theory, it is however possible to argue that the presence of a phase of zinc hydroxy-nitrate together with zinc oxide, with respect to a pure ZnO, is a favourable characteristic in the subsequent reaction with a dicarboxylic acid to obtain a zinc dicarboxylate catalyst with high activity in the copolymerization between CO_2 and an epoxide. In light of this, it can therefore be concluded that, in the case of heat treatment at temperatures comprised between 90 and 150 °C, there is actually the formation of a mixture of ZnO (see characteristic peaks) and intermediate compounds having general formula (I), in particular:

in the case of ZnO-7, a mixture of ZnO and $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$;

in the case of ZnO-8, a mixture of ZnO and $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, wherein the relative amount of ZnO in the mixture is higher than in the sample ZnO-7;

and in the case of ZnO-9, a mixture of ZnO and $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$, wherein the relative amount of ZnO in the mixture is higher than in the sample ZnO-7:

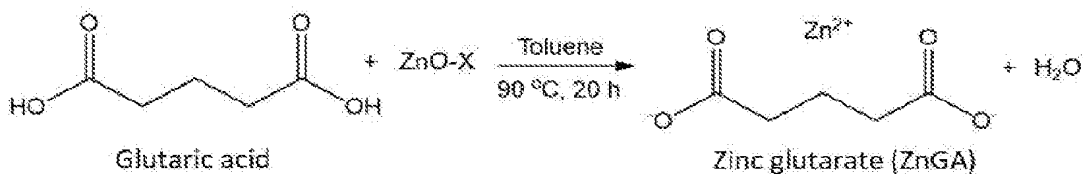
5 said compounds presenting different percentages of ZnO and said intermediate compounds having general formula (I). From such results it is possible to observe how, by increasing the temperature of the heat treatment, zinc hydroxy-nitrate (RT) is gradually transformed into zinc oxide (> 180 °C for 20 hours of treatment), passing through intermediate mixtures in the case of samples ZnO-07, Zn-08, Zn-09, or samples in which the heat treatment was carried out at a temperature of 90 °C, 120 °C and 150 °C for 20 hours, respectively. However, in the case of the diffractogram of compound ZnO-01 it is possible to note, in addition to the characteristic peak of zinc oxide, also a further peak, characteristic of an intermediate zinc hydroxylate compound (zinc hydroxy-nitrate) having the formula: $Zn_3(OH)_4(NO_3)_2$ (see Figure

10 1). Such a result indicates that the heat treatment of such a compound resulted in a zinc-based compound according to the present invention, i.e., comprising ZnO and an intermediate compound of general formula (I). In this case it may be hypothesized that the initially set heat-treatment conditions (180 °C for 20 hours) were actually carried out at a lower temperature or for a shorter period of time so as to avoid the complete transformation into ZnO (as instead occurred in the case of the other samples, see for example ZnO-10). The Applicants have found that the use of a zinc-based compound comprising ZnO and a compound having general formula (I) such as that of the present invention and synthesized in accordance with the process described above instead of a commercial ZnO (or obtained according to a different process) allows to obtain a zinc dicarboxylate catalyst with a higher heterogeneous catalytic copolymerization reaction activity of a polyalkylene carbonate starting from CO_2 and an epoxide. Without wishing to be bound by a specific theory, it is in fact possible to argue that the commercial ZnO (or obtained according to a different procedure) is resistant to the complete formation of the zinc dicarboxylate catalyst, thus resulting in a partially incomplete or in any case more difficult reaction with respect to that of the present invention.

Example 2 – preparation of the zinc glutarate catalyst according to the present invention

Several zinc glutarate catalyst samples were prepared using the different zinc-based compounds synthesized as in Example 1, according to the following steps and reaction diagram:

35 Diagram 1



The zinc-based compound (ZnO-X, 2.0 g) and glutaric acid (3.26 g) were added in a glass flask. Subsequently toluene (150 mL) was added as the reaction solvent. The flask was then connected to a condenser and heated at 90 °C under stirring (600 rpm) for 24 hours until a suspension comprising a white precipitate was obtained. Said suspension was then allowed to cool to room temperature and the white precipitate was filtered, washed with ethanol (500 mL) and dried at 120 °C overnight. In some cases, the reaction was performed under supercritical CO₂ conditions (in a stainless steel autoclave). Each zinc glutarate catalyst sample obtained was classified as follows (Table 2).

10

Table 2

ZnGA-X	Reagents	Temperature (°C)	Time (hours)	Solvent
ZnGA-03	ZnO-01 + glutaric acid	90	20	Toluene
ZnGA-04	ZnO-01 + glutaric acid	90	20	Toluene & supercritical CO ₂
ZnGA-07	ZnO-02 + glutaric acid	110	72	Toluene
ZnGA-09	ZnO-04 + glutaric acid	90	24	Toluene
ZnGA-11	ZnO-06 + glutaric acid	90	24	Toluene
ZnGA-12	ZnO-07 + glutaric acid	90	24	Toluene
ZnGA-13	ZnO-08 + glutaric acid	90	24	Toluene
ZnGA-14	ZnO-09 + glutaric acid	90	24	Toluene

ZnGA-15	ZnO-10 + glutaric acid	90	24	Toluene
---------	---------------------------	----	----	---------

Example 3 – preparation of zinc succinate (ZnSA), adipate (ZnAA), zinc terephthalate (ZnTPA) and zinc fumarate (ZnFA) catalysts according to the present invention

With the ZnO-X samples prepared according to Example 1, and following the synthesis reported for ZnGA in Example 2 (appropriately adapting the dicarboxylic acid used for each catalyst: adipic acid, terephthalic acid and fumaric acid, respectively), Zinc adipate (ZnAA), zinc terephthalate (ZnTPA) and zinc fumarate (ZnFA) catalysts were also synthesised. For the ZnAA catalyst, a higher reaction temperature and a longer reaction time were necessary in order to promote the complete conversion of ZnO with adipic acid. Each sample obtained was classified as follows (Table 3).

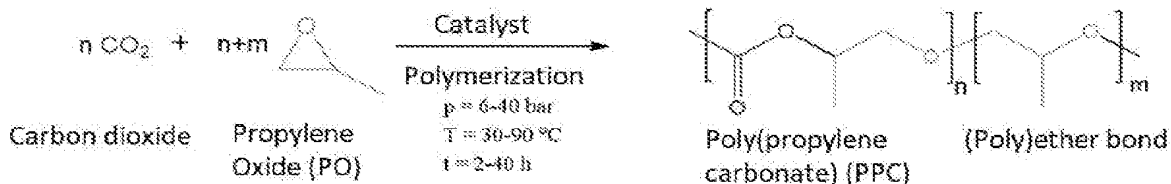
Table 3

Catalyst	Reagents	Temperature (°C)	Time (hours)	Solvent
ZnSA-01	ZnO-01 + succinic acid	90	20	toluene
ZnAA-01	ZnO-01 + adipic acid	90	20	toluene
ZnAA-02	ZnO-01 + adipic acid	110	72	toluene
ZnTPA-01	ZnO-04 + teraphthalic acid	90	24	toluene
ZnTPA-03	ZnO-9 + teraphthalic acid	90	24	toluene
ZnFA-01	ZnO-9 + fumaric acid	90	24	toluene

Example 4 – Catalytic tests: synthesis of polypropylene carbonate PPC

The catalysts obtained as described in Examples 2 and 3 were then tested in the copolymerization reaction, in heterogeneous phase, of polypropylene carbonate according to the following reaction diagram:

Diagram 2



The zinc glutarate and zinc adipate catalysts showed the best catalytic activity in PPC synthesis. The highest productivity was recorded with the catalysts ZnGA-12, ZnGA-13 and ZnGA-14, or the catalysts obtained respectively with zinc-based compounds ZnO-07, ZnO-08 and ZnO-09, or zinc-based compounds subjected to a heat treatment at 90°, 120° and 150 ° C for 20 hours. Among these, the best catalyst was ZnGA-12 whose productivity was further increased by using it together with the propylene oxide subject to a dehydration pretreatment. In order to compare the results obtained with the catalysts of the present invention, other types of glutarates with various different metal ions (MgGA, Al₂GA₃, TiGA₂, Fe₂GA₃, CuGA) were also tested as catalysts. All of these catalysts showed almost no catalytic activity, suggesting that it is the zinc ion which plays the key role of active site for such a type of reaction. The zinc glutarate catalysts ZnGA-07, ZnGA-09 and ZnGA-15 (i.e., respectively obtained with the zinc-based compounds ZnO-02, ZnO-03, ZnO-04 and ZnGA-10 subjected to heat treatment at 180 °C or 250 °C for 20 hours), and zinc glutarate catalyst ZnGA-11 (i.e., obtained with the zinc-based compound ZnO-06, i.e., a zinc-based compound not subjected to heat treatment [RT]) showed no catalytic activity. With regard to the zinc dicarboxylate catalysts with different dicarboxylates (adipate, succinate, fumarate and terephthalate), ZnAA and ZnSA showed some activity. The specific conditions of synthesis and the results obtained for each sample are summarized in Table 4 below.

Table 4

Catalysts	Temperature °C	Time (hours)	CO ₂ pressure	PPC yield (g/gcat.)	Productivity (g/gcat*hour)	PPC
ZnGA-03	80	20	40	30.0	1.50	PPC-5 (15.0 g)
ZnGA-04	80	20	40	31.0	1.55	PPC-6 (15.5 g)
ZnSA-01	80	20	40	7.2	0.36	PPC-

						9 (3.6 g)
ZnAA-02	80	20	40	46.0	2.30	PPC-10 (23.0 g)
CuGA	80	20	40	< 1	< 0.05	-
Fe ₂ GA ₃	80	20	40	< 1	< 0.05	-
TiGA ₂	80	20	40	< 1	< 0.05	-
Al ₂ GA ₃	80	20	40	< 1	< 0.05	-
MgGA	80	20	40	< 1	< 0.05	-
ZnGA-3+ZnAA-2	80	20	40	29.0	1.45	PPC-11 (14.5 g)
ZnGA-07	80	20	40	< 1	< 0.05	-
ZnGA-09	80	20	40	< 1	< 0.05	-
ZnGA-11	80	20	40	< 1	< 0.05	-
ZnGA-12	80	20	40	28.7	1.44	PPC-12
ZnGA-13	80	20	40	12.4	0.62	PPC-13
ZnGA-14	80	20	40	18.7	0.94	PPC-14
ZnGA-15	80	20	40	7.6	0.38	PPC-15
ZnTPA-1	80	20	40	< 1	< 0.05	-
ZnTPA-3	80	20	40	< 1	< 0.05	-
ZnFA-1	80	20	40	< 1	< 0.05	-
ZnAA-02*	80	20	40	8.6	0.43	PPC-10-2b-3b
ZnAA-02*	80	20	40	8.6	0.43	PPC-10-2b-3b
ZnAA-	80	20	40	6.4	0.32	PPC-

02*						10-4b (3.2 g)
ZnGA- 12**	80	20	40	56.2	2.8	PPC- 12-2b (28.1 g)
ZnGA- 12**	80	20	40	43.6	2.2	PPC- 12-3b (21.8 g)

Reaction conditions: catalyst amount, 0.5 g; PO volume, 50 mL; mechanical stirring rate, 300 rpm. *These two PPC samples were mixed to form a single sample PPC-10-2b-3b. **PO was dried by 5Å molecular sieve for > 24 hours.

Example 5 – Chemical-physical analysis

- 5 The PPCs obtained as described in Example 4 were characterized in order to assess the molecular characteristics, selectivity and percentage of ether bonds thereof (Table 5). The weighted average molecular weight (M_w) and the number average molecular weight (M_n) were determined by gel permeation chromatography (GPC) (Erma Inc. chromatograph) and Shodex KF columns. The calibration curve was obtained with 16 narrowly distributed
- 10 polystyrene standards (Polymer Laboratories) with molar masses ranging from 3.18×10^6 to 162 g/mol. The percentage of polypropylene carbonate (PPC) with respect to cyclic propylene carbonate (CPC) and the percentage of ether units with respect to polycarbonate units were determined by $^1\text{H-NMR}$ spectrometry (see for example Figure 4).

Table 5

PPC	Selectivity in solid material obtained (%)		Ether bond (%)	M_w	M_n
	PPC	CPC			
PPC-5	98.3	1.7	7.9	216k	35.6k
PPC-6	98.5	1.5	7.8	124k	18.6k
PPC-10	96.5	3.5	6.9	116k	33.7k
PPC-11	-	-	-	-	-
PPC-12	97.9	2.1	9.2	109k	9.7k
PPC-13	98.7	1.3	9.0	186k	8.6k
PPC-14	98.1	1.9	7.1	104k	16k
PPC-15	98.2	1.8	5.2	58k	6k

PPC-10-4b	98.4	1.6	3.4	14k	11k
PPC-12-3b	98.8	1.2	8.9	76k	2k

Example 6: Thermo-mechanical characterization

The thermal properties of the PPCs prepared according to Example 4 were evaluated by Differential Scanning Calorimeter (DSC) (DSC Q100, TA Instruments, New Castle, DE, USA) by performing three successive heating and cooling scans and further heating. Calorimetric properties were evaluated in the third scan. It was observed that all the polymers obtained by the process according to the present invention are amorphous. No transition indicative of the presence of crystalline phase or recrystallization of the material was found in any sample. For all the samples, a single glass transition temperature (T_g) was highlighted at values comprised between -5 and 30°C. The thermal stability of the PPCs was evaluated in air by thermogravimetry (TGA) (TGA Q500, TA Instruments, New Castle, DE, USA) using high-resolution dynamic method. It was observed that the degradation of the PPCs starts significantly only at temperatures above 200-210 °C, so there is no impediment to the transformation and forming thereof with the methods usually used for polymers and plastics. By way of example, the samples PPC-5, PPC-6 and PPC-10 were subjected to compression moulding (Collin P200E, Maitenbeth Germany) by means of a press with a special time/temperature/pressure programme (3 min/180 °C/30 atm) in order to obtain thin films. All the films have homogeneity, good to excellent transparency and thicknesses varying from about 100 to 250 μm (as shown for example in Figure 6). The films were then cut to obtain specimens for the mechanical tests. The uniaxial tensile test was carried out with an electromechanical dynamometer (Instron model 3366). The Elastic Modulus (E), yield strength (δ_y), elongation at break (ϵ_b) and the load corresponding to 900% elongation ($\delta_{900\%}$) were evaluated on specimens 0.2 mm thick, 10 mm wide and with 80 mm useful length at a speed of 200 mm/min. Furthermore, the specimens were mounted on a paper frame to facilitate gripping at the traction machine.

From such tests it was possible to observe that, if stressed in traction, the samples stretch by more than 900% (beyond the measurement limits of the machine used) but do not break, and for this reason the load corresponding to 900% elongation was calculated for each sample instead of the ultimate tensile strength. The results are shown in the following table (Table 6).

Table 6

Sample	E (Mpa)	δ_y (Mpa)	ϵ_b (%)	$\delta_{900\%}$ (Mpa)
PPC-5	139±34	0.85±0.11	> 910	2.91±0.18

PPC-6	121±31	0.72±0.09	> 910	2.28±0.17
PPC-10	128±35	1.1±0.01	> 910	3.03±0.08

Furthermore, when compared with known polymers, as can be seen in Figure 8, the mechanical properties of the polypropylene carbonates according to the present invention are comparable to those of the softer, more flexible polymers of petrochemical origin, and their extensibility can reach values not achievable by other known polymers in the present state of the art.

Example 7: Extensibility and Mechanical Return of PPC Films

The materials were also subjected to uniaxial tensile testing using an electromechanical dynamometer (Instron Model 3366) to evaluate of extensibility and mechanical return characteristics.

The films obtained by compression as previously described were cut to obtain specimens of thickness 0.2 mm, width 10 mm and useful length equal to 80 mm which were then mounted on a paper frame to facilitate gripping at the tensile machine. The tensile test was performed at a speed of 200 mm/min.

The specimens were subjected to an elongation of 920% (about 73 cm) without reaching breakage and were then released from the traction machine and it was possible to verify an immediate and almost complete recovery of the original size. From the initial and final length, the strain recovery was thus estimated according to the following formula:

$$[L_i - (L_f - L_i)] \cdot 100 / L_i$$

Wherein L_i is the initial length of the specimen (before the elongation test) and L_f is the length following elongation and release. As shown in the following table (Table 7), the samples have a strain recovery between 80% and over 90%.

Table 7

Sample	Specimen length before test (L_i)	Specimen length after test (L_f)	Strain recovery (%)
PPC5	8	8.65	92
PPC6	8	9.2	85
PPC10	8	9.0	87.5

Example 8: Self-healing of PPC films and evaluation of the time required for complete self-healing

The samples were also subjected to mechanical tests of uniaxial traction after physical-mechanical damage had been done on them in order to evaluate the self-healing capacity of

the materials. In a first set of tests, the specimens of sample PPC-6 were cut transversely and the two pieces thus obtained were placed, on a sheet of graph paper, by simply overlapping (without compressing and/or without heating) the central part of about 4 mm (Figure 7) and get a single specimen. The uniaxial tensile test was then carried out on these samples after 4 days and after having exactly evaluated the length of the overlap with an optical microscope. The elastic modulus (E , Mpa), yield strength ($\bar{\delta}_y$, MPa), ultimate tensile strength ($\bar{\delta}_b$, MPa) and elongation at break (ε_b , %) were then calculated for each specimen obtained from sample PPC-6. The cut previously made was no longer visible, the specimens were completely repaired, and, after the uniaxial tensile test, no failure was observed in the area corresponding to the self-healing. The mechanical properties measured after self-healing are comparable to those of the original specimens.

The results are shown in the following table (Table 8).

Table 8

Specimen	E (MPa)	$\bar{\delta}_y$ (MPa)	ε_b (%)	$\bar{\delta}_b$ (MPa)
specimen 0	251.8	2.86	617.3	4.37
specimen 1	415.7	2.38	684.0	3.52
specimen 2	455.2	2.53	830.2	4.10
specimen 3	335.6	2.26	795.0	4.05
specimen 4	316.8	2.02	838.2	3.88
specimen 5	312.0	1.77	732.6	2.93
specimen 6	360.2	1.99	577.8	2.59
specimen 7	236.1	1.33	847.2	3.30

Despite slight fluctuations due to the different degree of overlap, the results confirm that films printed with the polypropylene carbonate according to the present invention have excellent self-healing capabilities.

A second set of experiments was developed to evaluate the effectiveness of the self-healing mechanism and the minimum time required to achieve complete self-healing. These experiments were conducted according to two mechanical characterization methods:

- method of adhesion evaluation on overlapping flaps ("lap shear joints"): two strips of material with a width of 10 mm and a length of about 40 mm were overlapped one on the other for a length equal to 5 mm to constitute a single strip with a length of about 75 mm and the same width and thickness of the starting strips; the strip thus obtained was then subjected to a tensile test with an electromechanical dynamometer to evaluate the effectiveness of the welding;

- method of assessing adhesion by delamination: two strips of material 10 mm wide and about 80 mm long were overlapped one on top of the other for a length of 40 mm to make up a specimen, half of which was made up of the overlapping portions, and half of which was made up of the non-overlapping flaps, to be subjected to delamination tests with an electromechanical dynamometer and assess the effectiveness of welding.

The overlapping of the two areas was performed at room temperature and without exerting significant pressure on the two flaps, other than gentle manual pressure to promote good contact between the overlapping surfaces. Both test methods were performed using an electromechanical dynamometer (Instron, Mod. 3366), operating at room temperature and at a speed of 50 mm/min.

In order to verify the minimum time needed to have an effective weld, the tests were conducted at various times, varying between 10 minutes and a week, after the overlap of the two flaps ("welding time"). The results obtained are briefly reported in Table 9 and showed two failure modes:

- for "short" times, varying from a few minutes to 2 to 3 hours, the material shows an adhesive-type failure that occurs in the welded area by disconnection of the two flaps from each other;

- for longer times, more than 2/3 hours, the material shows a cohesive type of breakage, which occurs in the areas outside the welded area and confirms the effective self-welding of the two flaps.

In fact, the self-repair mechanism occurs according to a two-stage process: in a first stage, taking advantage of a moderate "tackyness" of the material, the two flaps simply keep adhering to each other; in a second stage, which both tests have shown to occur for times longer than 2/3 hours, the two flaps interpenetrate and self-weld.

Table 9

Welding time	"lap shear joints" method	Delamination method
10 minutes	Adhesive failure, inside the welded zone	Adhesive failure, inside the welded zone
30 minutes	Adhesive failure, inside the welded zone	Adhesive failure, inside the welded zone
1 hour	Adhesive failure, inside the welded zone	Adhesive failure, inside the welded zone
2 hours	Cohesive failure, external to the welded zone	Cohesive failure, external to the welded zone

1 day	Cohesive failure, external to the welded zone	Cohesive failure, external to the welded zone
4 days	Cohesive failure, external to the welded zone	Cohesive failure, external to the welded zone
1 week	Cohesive failure, external to the welded zone	Cohesive failure, external to the welded zone

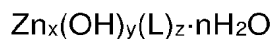
CLAIMS

1. A process for the synthesis of a zinc dicarboxylate catalyst, comprising the steps of:

(a) providing a solution of a zinc precursor having the general formula $Zn(L)_2 \cdot nH_2O$,
 5 wherein n is comprised between 0 and 20, L is selected in the group consisting of:
 NO_3 , CH_3CO_2 , $(SO_4)_{0.5}$, halide, and acetyl acetonate (AcAc);

(b) adding a solution of a base to said solution of a zinc precursor, thereby obtaining a precipitate;

(c) separating the precipitate from the supernatant solution and subjecting the solid
 10 thus obtained to a heat treatment thereby obtaining a zinc-based compound comprising a mixture of ZnO and a compound having the general formula (I):



Formula (I)

wherein L is as defined in step (a),

15 $2x = y + z$; wherein

x is comprised between 1 and 5,

y is comprised between 1 and 8,

z is comprised between 1 and 2, and

n is comprised between 0 and 20;

20 wherein said heat treatment is carried out

- at a temperature (T): $30\text{ }^\circ\text{C} < T < 90\text{ }^\circ\text{C}$ and for a period of time (t): $20\text{ hours} < t \leq 60\text{ hours}$; or

- at a temperature (T): $90\text{ }^\circ\text{C} \leq T \leq 150\text{ }^\circ\text{C}$ and for a period of time (t): $20\text{ minutes} \leq t \leq 20\text{ hours}$; or

25 - at a temperature (T): $150\text{ }^\circ\text{C} < T \leq 400\text{ }^\circ\text{C}$ and for a period of time (t): $20\text{ minutes} \leq t < 20\text{ hours}$;

(d) reacting said zinc-based compound with a saturated aliphatic dicarboxylic acid.

2. A process for the synthesis of a zinc-based compound comprising a mixture of ZnO and a compound having the general formula (I):

30 $Zn_x(OH)_y(L)_z \cdot nH_2O$

Formula (I)

wherein L is selected in the group consisting of: NO_3 , CH_3CO_2 , $(SO_4)_{0.5}$, halide, and acetyl acetonate (AcAc),

$2x = y + z$; wherein

x is comprised between 1 and 5,

y is comprised between 1 and 8,

z is comprised between 1 and 2, and

5 n is comprised between 0 and 20,

said process comprising the steps of:

(a) providing a solution of a zinc precursor having the general formula $Zn(L)_2 \cdot nH_2O$, wherein n and L are as defined above;

10 (b) adding a solution of a base to said solution of a zinc precursor, thereby obtaining a precipitate;

(c) separating the precipitate from the supernatant solution and subjecting the solid thus separated to a heat treatment:

- at a temperature (T): $30\text{ }^\circ\text{C} < T < 90\text{ }^\circ\text{C}$ and for a period of time (t): $20\text{ hours} < t \leq 60\text{ hours}$; or

15 - at a temperature (T): $90\text{ }^\circ\text{C} \leq T \leq 150\text{ }^\circ\text{C}$ and for a period of time (t): $20\text{ minutes} \leq t \leq 20\text{ hours}$; or

- at a temperature (T): $150\text{ }^\circ\text{C} < T \leq 400\text{ }^\circ\text{C}$ and for a period of time (t): $20\text{ minutes} \leq t < 20\text{ hours}$

20 3. The process according to claim 1 or according to claim 2, wherein said mixture comprises said ZnO and said compound having the general formula (I) in a mass ratio comprised between 0.1 and 10, preferably comprised between 0.2 and 5.

25 4. The process according to claims 1 or 3 for the synthesis of a zinc dicarboxylate catalyst selected in the group consisting of: zinc glutarate, zinc adipate, zinc succinate, wherein the dicarboxylic acid of step (d) is selected from among glutaric acid, adipic acid, succinic acid.

5. A zinc-based compound comprising ZnO and a compound having the general formula (I), obtainable by the process according to any one of claims 2-4.

6. A zinc dicarboxylate catalyst obtainable by the process according to any one of claims 1 and 3-4.

30 7. A process for the synthesis of polyalkylene carbonate by means of a heterogeneous catalytic copolymerization reaction comprising the steps of:

(e) reacting carbon dioxide with an alkyl epoxide containing at least 3 atoms of carbon, preferably in the absence of an organic solvent, in the presence of the zinc

dicarboxylate catalyst according to claim 6.

8. The process according to claim 7, wherein said step (e) is carried out by heating at a temperature comprised between 30 and 150 °C, preferably at a pressure (P_{CO_2}) comprised between 1 and 80 bar and, more preferably, for a period of time
5 comprised between 1 and 40 hours.

9. The process for the synthesis of polyalkylene carbonate according to claim 7 or 8, wherein said polyalkylene carbonate is polypropylene carbonate (PPC) and wherein the alkyl epoxide of step (e) is propylene oxide (PO).

Fig.1

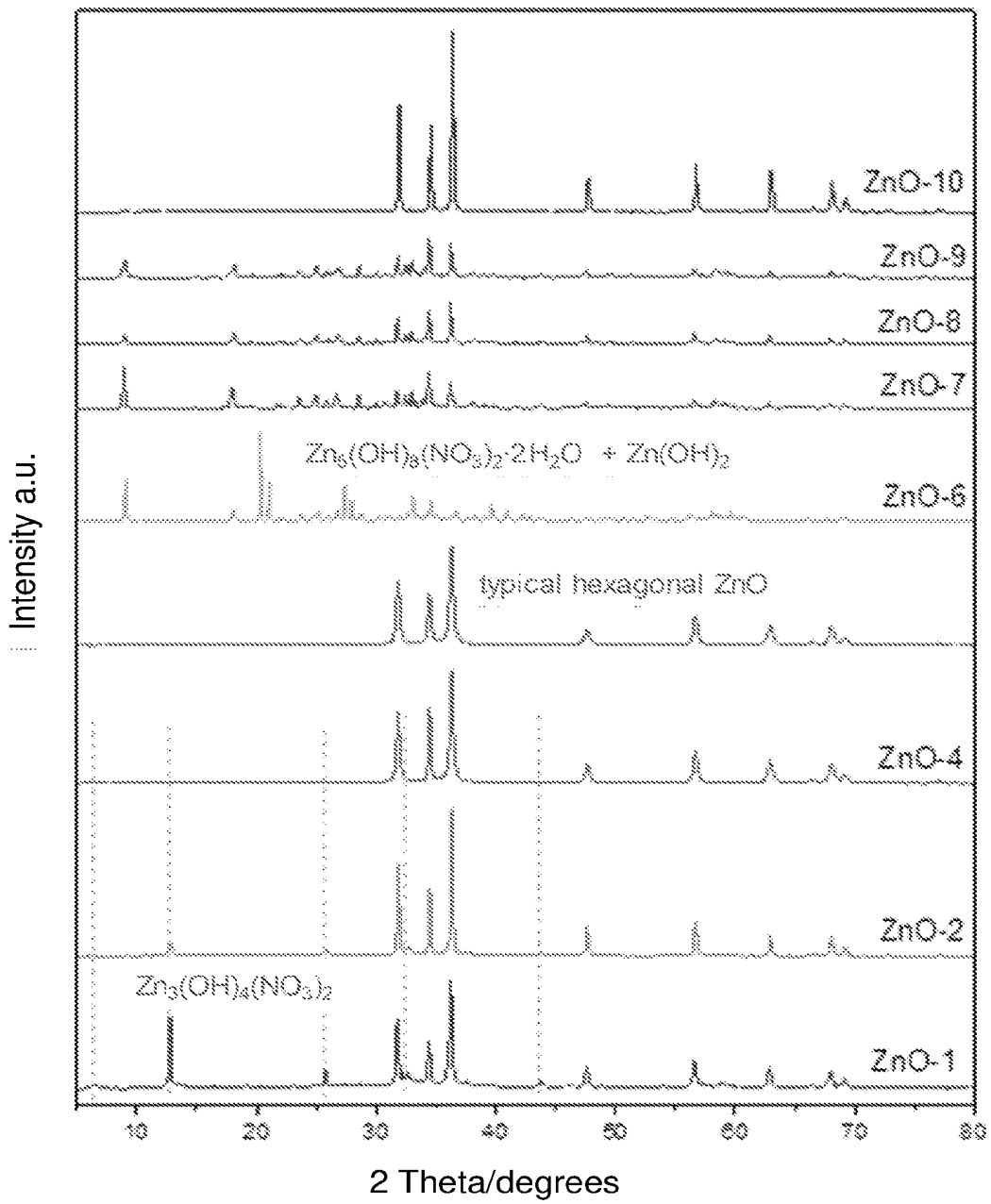


Fig.2

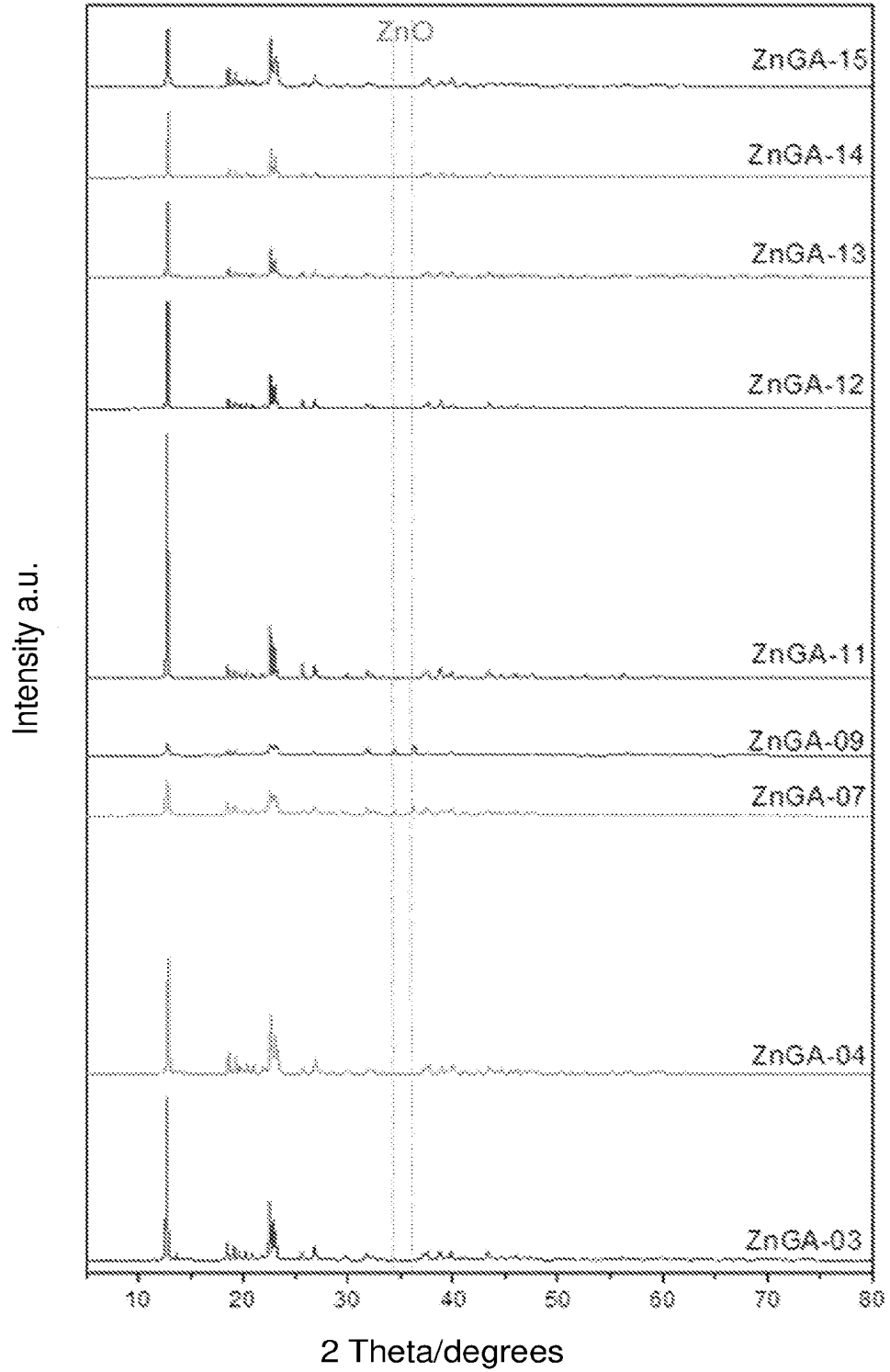


Fig.3

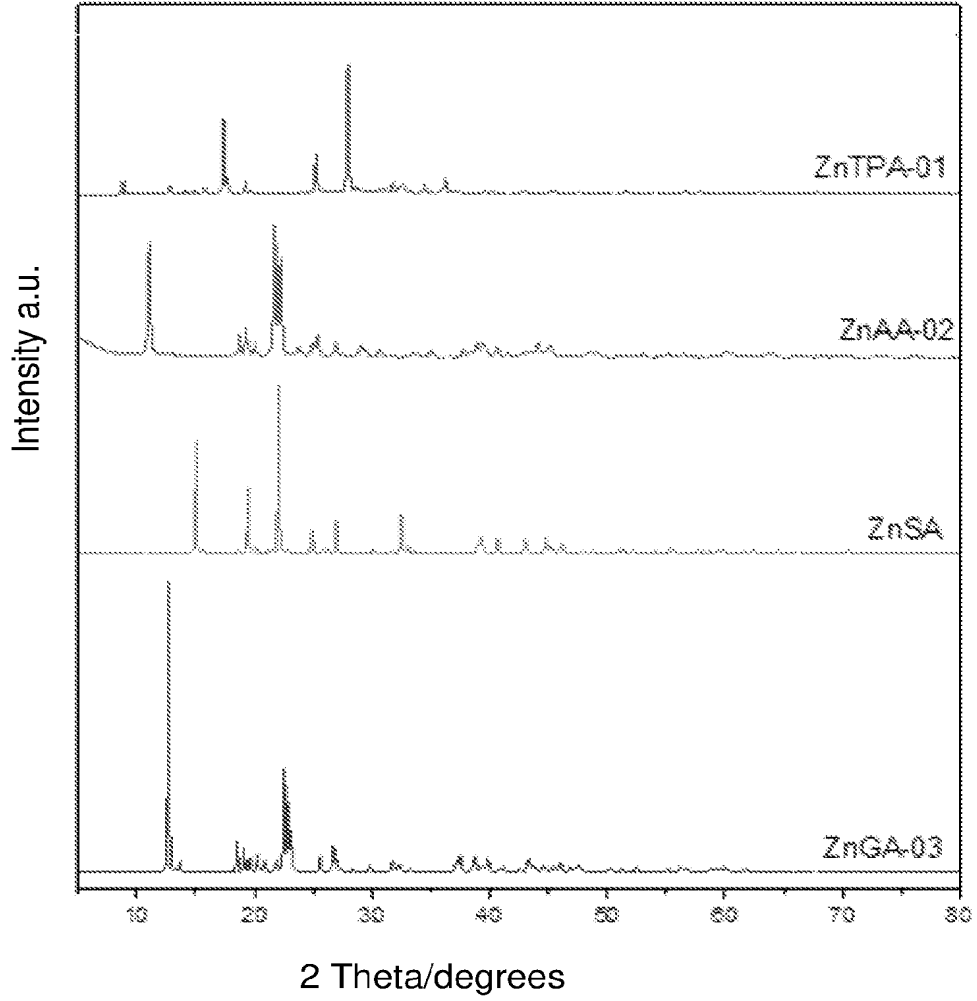


Fig.4

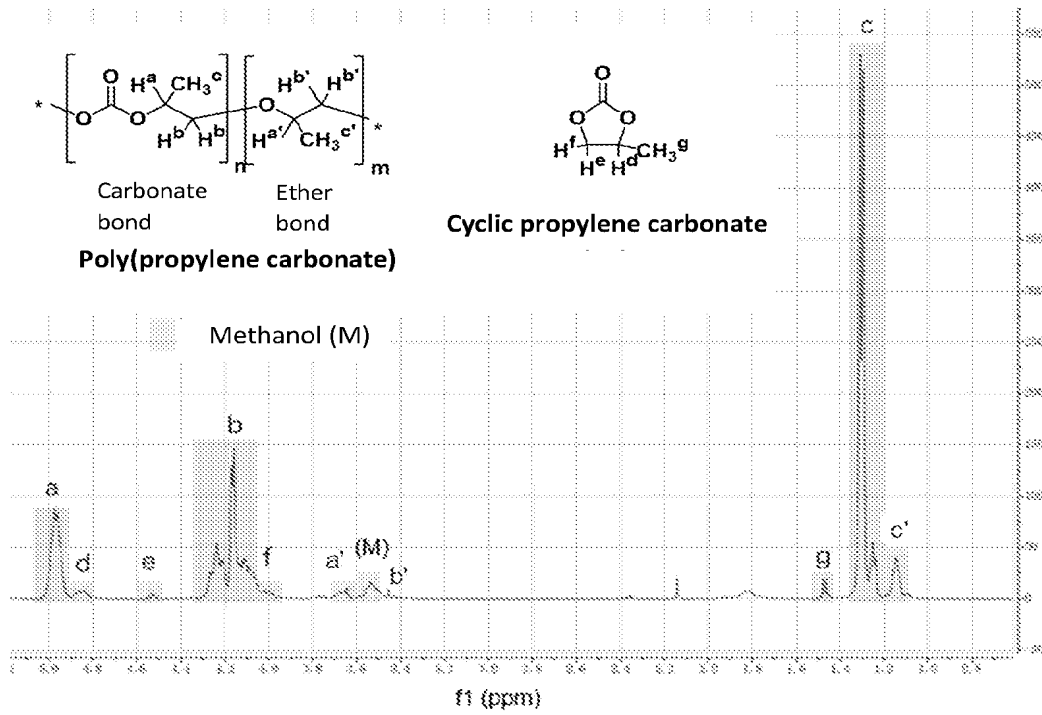


Fig.5

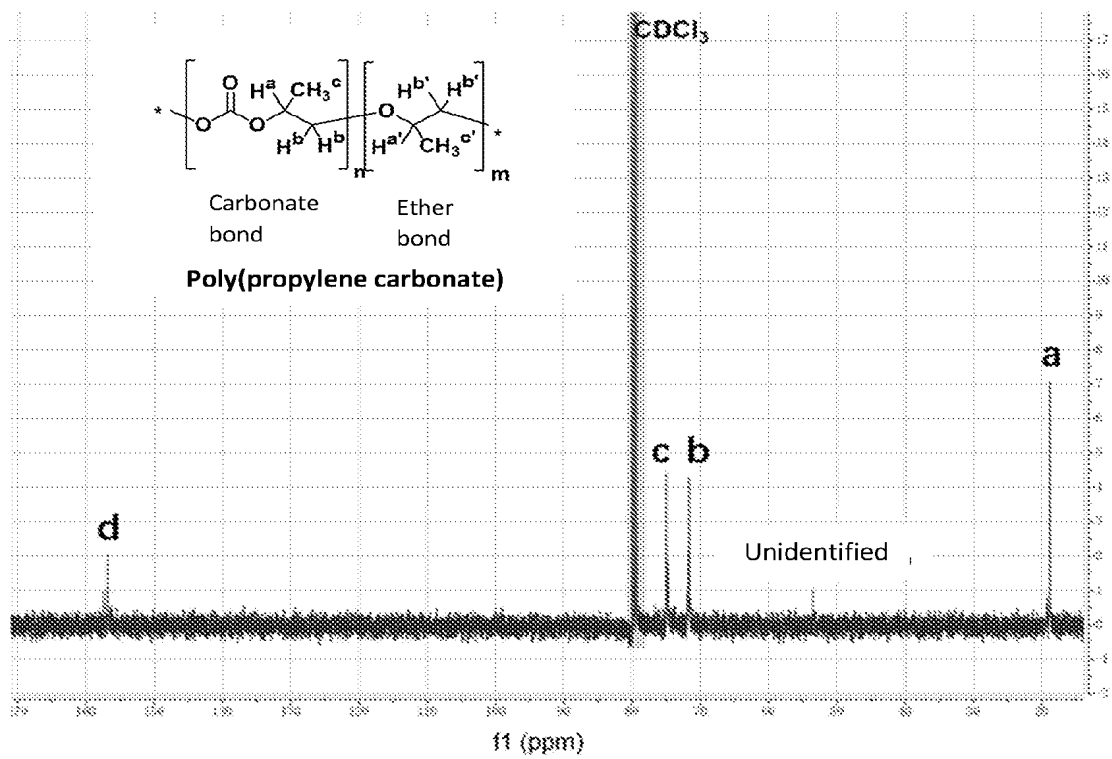


Fig.6

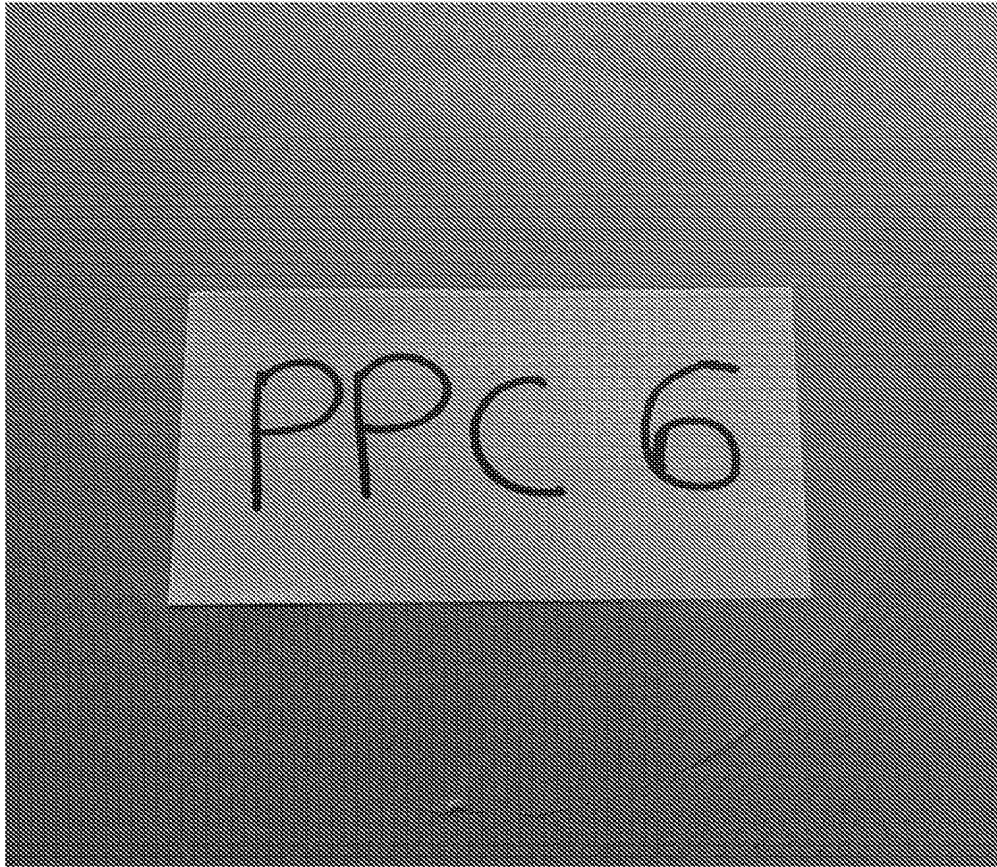


Fig.7

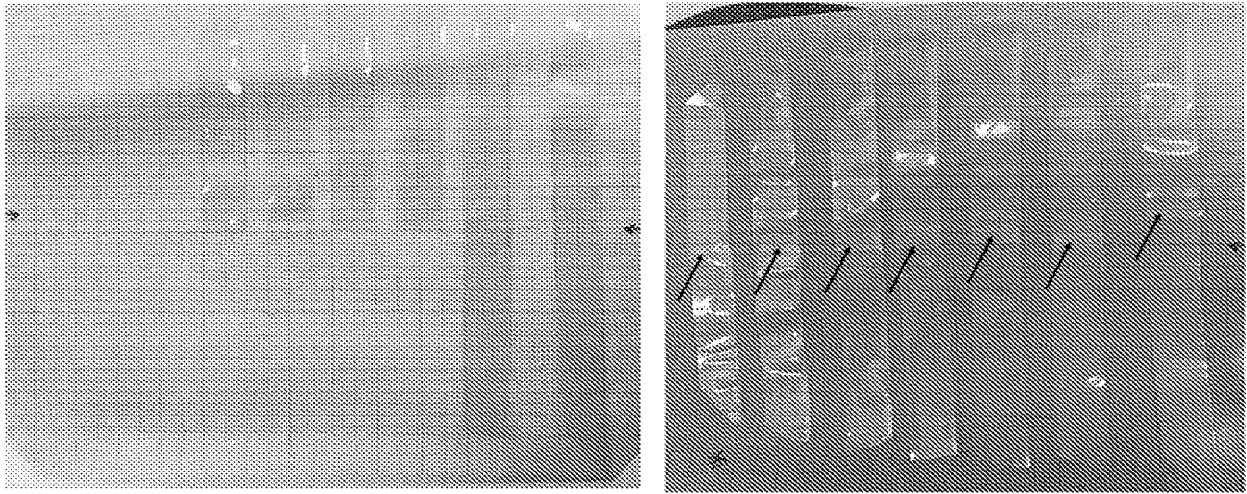
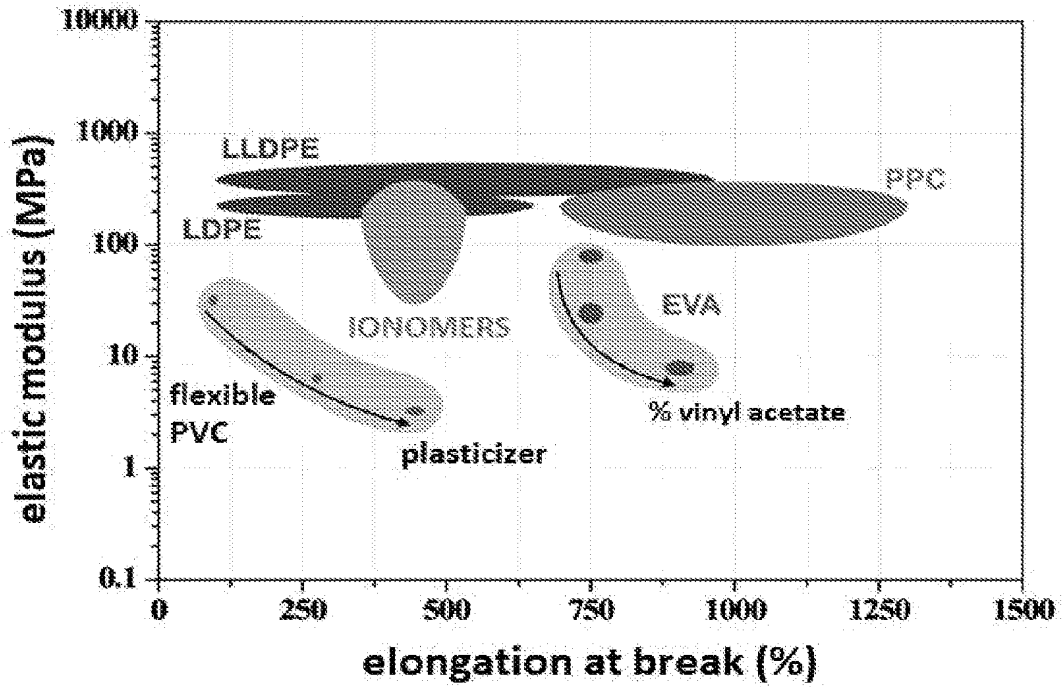


Fig. 8



INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2021/061063

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J31/22
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)
B01J

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, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/034489 A1 (BASF SE [DE]; BRYM ANNA KATHARINA [DE] ET AL.) 14 March 2013 (2013-03-14) claim 11; tables 5, 6 -----	1-9
X	US 2011/218320 A1 (STEINKE TOBIAS HEINZ [DE] ET AL) 8 September 2011 (2011-09-08) paragraphs [0006], [0008], [0098]; claim 1 -----	1-9

Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p>
---	---

Date of the actual completion of the international search 3 March 2022	Date of mailing of the international search report 15/03/2022
--	---

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 Klaes, Daphne
--	--

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2021/061063

Patent document cited in search report	Publication date	Patent family member(s)	Publication date	
WO 2013034489	A1	14-03-2013	CN 103781817 A	07-05-2014
			EP 2753653 A1	16-07-2014
			KR 20140062130 A	22-05-2014
			US 2014200328 A1	17-07-2014
			WO 2013034489 A1	14-03-2013

US 2011218320	A1	08-09-2011	NONE	
