

METHODS FOR PREPARING DICARBOXYLIC ACIDS FROM POLYOLEFINS USING ORGANOCATALYSTS

FIELD OF INVENTION

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The present invention provides methods for preparing dicarboxylic acid mixtures from polyolefins via thermal oxidation degradation.

BACKGROUND

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The listing or discussion of a prior-published document in this specification should not necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

15 Plastics with saturated backbones (including polyolefins, such as polyethylene (PE)) form the bulk of synthetic polymers produced and discarded annually. There are very few options available for end-of-life plastics. Most of them are disposed of in incinerators and landfills after single use, and most are not recycled. This represents a large loss of value embedded in these materials. The inherent chemical unreactivity (due to the inert C-C bonds making up the
20 polymer backbone), hydrophobicity, and high molecular weights also make them non-biodegradable and resistant to biological approaches for degradation.

To recover some value from these end-of-life plastics, the only viable and scalable technology at the moment is pyrolysis, which converts them to shorter hydrocarbons under anaerobic
25 conditions (i.e. chemical cracking). However, pyrolysis is disadvantaged by the high temperatures needed (often >300 °C even in the presence of catalysts), and the hydrocarbon products obtained can only be used for very limited applications such as fuels, waxes, solvents and lubricants. As such, there is a clear unmet need for producing alternative chemicals from plastics that have high existing industrial demand across multiple industries, such as α,ω -
30 dicarboxylic acids. These alternative chemicals represent the next phase of waste plastic upcycling technologies, and can be sufficiently lucrative to sustain a viable post-use plastics economy.

Currently, there are limited techniques to degrade polyethylene (PE). Most of them either
35 require the use of heavy metals such as Fe, Ir and V, or involve harsh conditions such as high temperatures, pressures or microwave-assisted reactions. These techniques have limitations in terms of scalability and are not suitable for real-life practical applications. Other techniques

would either require the attachment of functional groups on the PE backbone before degradation (which results in the use of toxic solvents such as chloroform), or the use of heavy metal-containing catalysts which can contribute to pollution in the environment if irresponsibly disposed.

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Thus, there is a need for alternative and/or improved methods for preparing dicarboxylic acids from polyolefins, including polyethylene.

SUMMARY

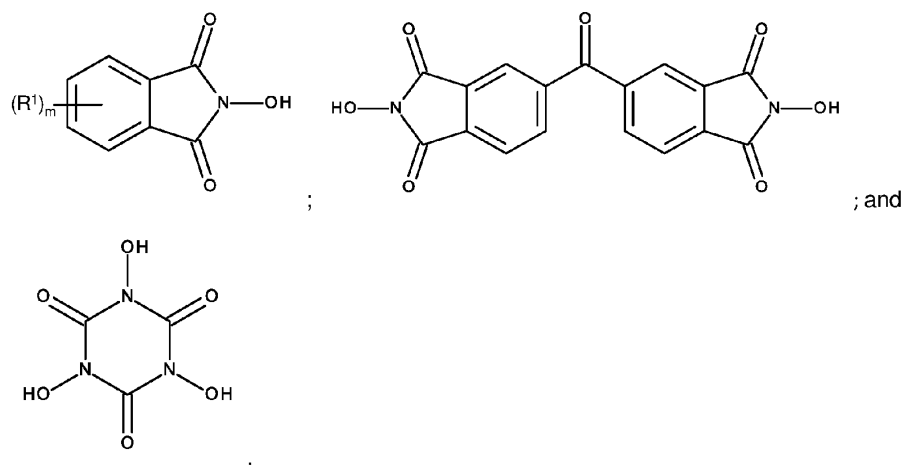
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Aspects and embodiments of the current invention will now be described by reference to the following numbered clauses.

1. A method for preparing a dicarboxylic acid mixture, the method comprising:
 - 15 (a) providing a mixture that comprises a polyolefin, an organocatalyst and a nitrate source; and
 - (b) heating the mixture to a temperature of at least 110°C in the presence of oxygen for a period of time to provide a dicarboxylic acid mixture,
 wherein the organocatalyst comprises at least one hydroxylamine functional group.

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2. The method according to clause 1, wherein the organocatalyst is a compound selected from one or more of a group consisting of:

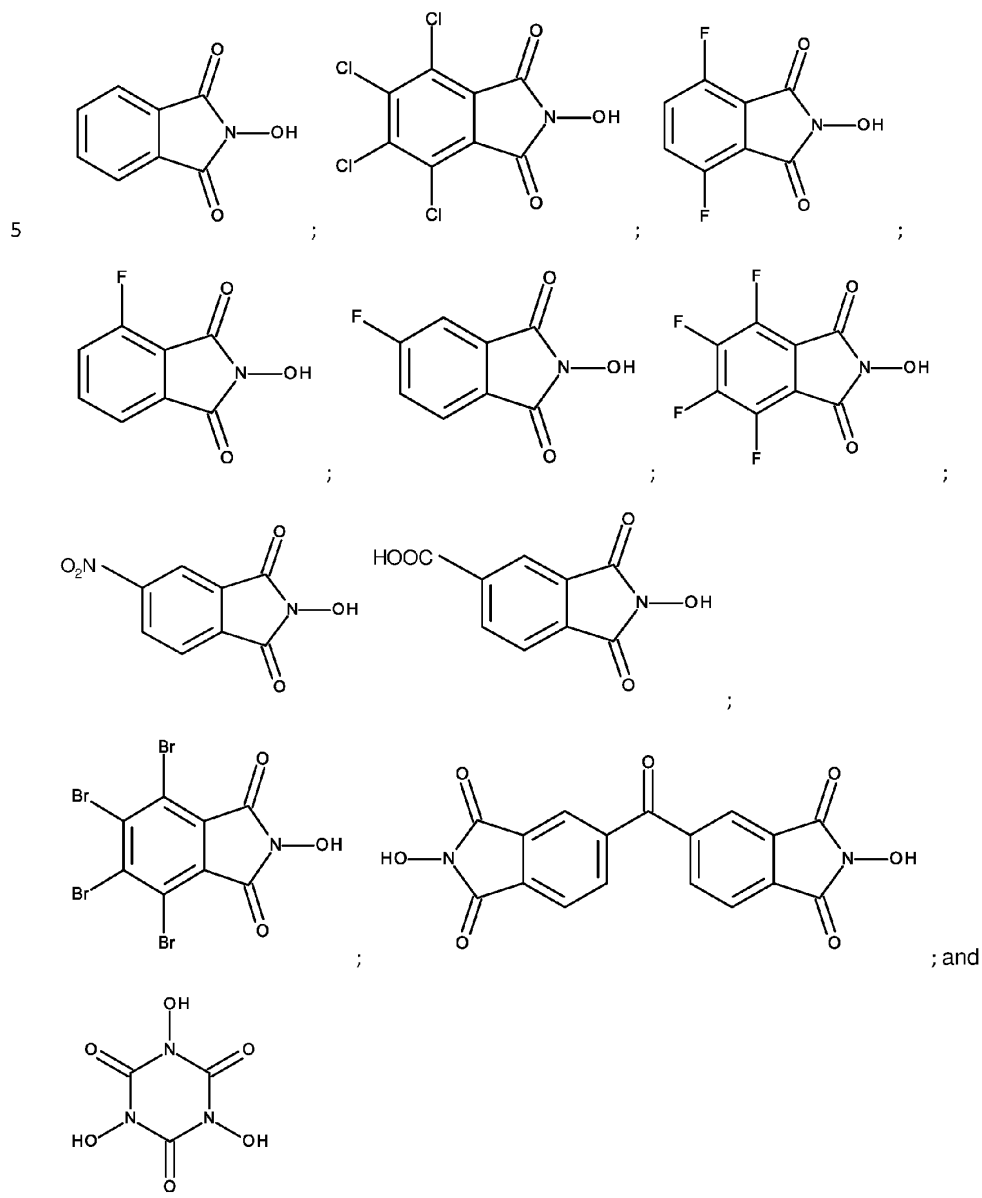


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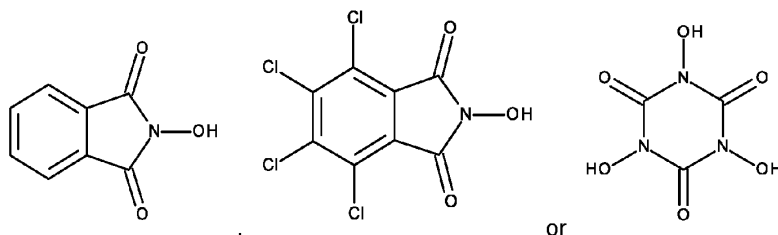
wherein R^1 represents a halo, COOH or NO₂, wherein the halo is F, Cl or Br; and

m is an integer from 0 to 4.

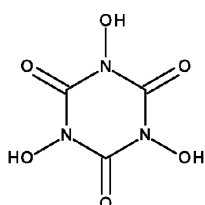
3, The method according to clause 2, wherein the organocatalyst is selected from one or more of a group consisting of:



4. The method according to clause 3, wherein the organocatalyst is one of the following:



5. The method according to clause 4, wherein the organocatalyst is



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6. The method according to any one of the preceding clauses, wherein the organocatalyst is provided in an amount of from 0.01 to 0.3 molar equivalents, such as from 0.025 to 0.25 molar equivalents, such as about 0.1 molar equivalents, relative to the amount of olefin repeating units in the mixture.

7. The method according to any one of the preceding clauses, wherein the nitrate source is selected from one or more of a group consisting of nitric acid and a metal nitrate, optionally wherein the metal nitrate is a Group I metal nitrate (e.g., lithium nitrate, sodium nitrate and potassium nitrate), a Group II metal nitrate (e.g., magnesium nitrate and calcium nitrate), a transition metal nitrate (e.g., $\text{Fe}(\text{NO}_3)_3$) and a lanthanide nitrate (e.g., $\text{La}(\text{NO}_3)_3$), optionally wherein the nitrate source is nitric acid.

8. The method according to any one of the preceding clauses, wherein the nitrate source is provided in at least an equimolar amount relative to the amount of olefin repeating units in the mixture, optionally wherein the nitrate source is provided in an amount of from 1 to 10 molar equivalents, such as from 2 to 5 molar equivalents, such as about 3 molar equivalents, relative to the amount of olefin repeating units in the mixture.

9. The method according to any one of the preceding clauses, wherein the mixture further comprises a solvent, optionally wherein the solvent is selected from one or more of a group consisting of water, formic acid and acetic acid.
- 5 10. The method according to clause 9, wherein the solvent includes acetic acid and wherein the acetic acid is provided in an amount of from about 2 to 15 molar equivalents relative to the amount of nitrate source in the mixture, optionally wherein the acetic acid is provided in an amount of about 2 to 11 molar equivalents relative to the amount of nitrate source, such as about 2 molar equivalents relative to the amount of nitrate source.
- 10 11. The method according to any one of clause 9 to 10, wherein the solvent is substantially free of heavy metal.
12. The method according to any one of the preceding clauses, wherein the oxygen is provided at a concentration of from 21 % vol/vol to 100 % vol/vol, optionally wherein the oxygen is provided at a concentration of about 21% vol/vol.
- 15 13. The method according to any one of the preceding clauses, wherein the method is performed at a temperature of from 110°C to 150°C, such as about 120°C.
- 20 14. The method according to any one of the preceding clauses, wherein the method is performed at a pressure of from 0.5 atm to 5 atm, such as about 1 atm.
- 15 15. The method according to any one of the preceding clauses, wherein the period of time is from about 18 hours to about 72 hours, such as about 24 hours.
- 25 16. The method according to any one of the preceding clauses, wherein the polyolefin is selected from one or more of the group consisting of polyethylene and polypropylene.
- 30 17. The method according to clause 16, wherein when the polyolefin is polyethylene, the dicarboxylic acid mixture comprises a mixture of linear C₄ to C₁₂ dicarboxylic acids.
18. The method according to clause 17, wherein the mixture of linear C₄ to C₁₂ dicarboxylic acids comprises one or more of succinic acid, glutaric acid, adipic acid and undecanedioic acid.
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19. The method according to clause 18, wherein succinic acid makes up at least about 30% of the total mass of dicarboxylic acids, for example, succinic acid makes up at least about 35% of the total mass of the dicarboxylic acid mixture obtained from the method.

5 20. The method according to any one of clauses 16 to 19, wherein the polyethylene is low density polyethylene (LDPE), high density polyethylene (HDPE) or a combination thereof.

21. The method according to any one of the preceding clauses, wherein the polyolefin is
10 a commercial material and further comprises one or more additives selected from the group consisting of a dye, a plasticizer, a pigment, a colouring agent, a printing ink, a filler such as titanium oxide or zinc oxide, a flame retardant, a lubricant, an adhesive, a paper and a cellulose material.

15 BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a ^1H NMR spectrum of the products obtained from the thermal oxidation degradation of polyethylene (PE) according to Example 1A of the present disclosure.

20 FIG. 2 is the ^1H NMR spectrum as shown in FIG. 1, stacked against the spectra of commercially-available pure succinic and adipic acid.

FIG. 3 is a ^1H NMR spectrum of the products obtained from the thermal oxidation degradation of polyethylene (PE) according to Example 2 of the present disclosure.

25 FIG. 4 is the ^1H NMR spectrum as shown in FIG. 3, stacked against the spectra of commercially-available pure succinic and adipic acid.

FIG. 5 is a ^{13}C NMR spectrum of the products obtained from the thermal oxidation degradation of PE according to Example 2 of the present disclosure.

FIG. 6 is the ^{13}C NMR spectrum as shown in FIG. 5, stacked against the spectra of commercially-available pure adipic and succinic acid.

35 FIG. 7 includes ^1H NMR spectra of the products obtained from the thermal oxidation degradation of PE according to Example 1B of the present disclosure, stacked against the spectra of commercially-available pure adipic and succinic acid.

FIG. 8 is an ESI-MS spectrum (negative ion mode, $m/z = [M-H]^-$) of the products obtained from the thermal oxidation degradation of PE according to Example 2 of the present disclosure, showing the distribution of the various dicarboxylic acid products.

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FIG. 9 includes ^1H NMR spectra of the products obtained from the thermal oxidation degradation of waste PE according to Examples 3 and 4 of the present disclosure, stacked against the spectra of commercially-available pure adipic and succinic acid.

10 FIG. 10 includes HPLC chromatograms of (a) a mixture of commercially-available pure succinic acid, glutaric acid and adipic acid (top), and (b) a crude reaction mixture obtained from the thermal oxidation degradation of PE according to Example 2 of the present disclosure (bottom).

15 FIG. 11 is a schematic representation of the value-addedness of $\text{C}_3\text{-C}_{13}$ dicarboxylic acid products obtained from the degradation of PE compared with the scrap value of PE. Value-addedness is calculated from prices per tonne of organic acids obtained from various commercial suppliers and compared against the scrap value of PE in 2021 (Toto, D. Plastic scrap prices on the rise. <https://www.recyclingtoday.com/news/plastic-scrap-prices-trend-upward/> (accessed 03 Feb 2022))

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DESCRIPTION

The present inventors have found a cheap, convenient and simple method for breaking down polyolefins, which are amongst the most inert and most challenging plastic substrates, into carboxylic acids. The method avoids the use of toxic heavy metals that may pose a contamination risk to the environment or a toxicity risk if the intended use of the dicarboxylic acids relates to foodstuffs or other consumable goods for humans or animals. The method may be conducted under milder reaction conditions (for example, at 120 °C and 1 atm) when compared to the current state of the art methods for the decomposition of polyolefins. The method may be performed using standard chemistry glassware in a well-ventilated fumehood without any specialised high-pressure equipment (e.g. a microwave reactor). As such, it is believed that the method can be readily scaled-up without the need for significant investment in specialised equipment (e.g. pressure vessels and the like).

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Thus, in a first aspect of the invention, there is provided a method for preparing a dicarboxylic acid mixture, the method comprising:

- (a) providing a mixture that comprises a polyolefin, an organocatalyst and a nitrate source; and
- (b) heating the mixture to a temperature of at least 110°C in the presence of oxygen for a period of time to provide a dicarboxylic acid mixture,
- 5 wherein the organocatalyst comprises at least one hydroxylamine functional group.

In embodiments herein, the word “comprising” may be interpreted as requiring the features mentioned, but not limiting the presence of other features. Alternatively, the word “comprising” may also relate to the situation where only the components/features listed are intended to be present (e.g. the word “comprising” may be replaced by the phrases “consists of” or “consists essentially of”). It is explicitly contemplated that both the broader and narrower interpretations can be applied to all aspects and embodiments of the present invention. In other words, the word “comprising” and synonyms thereof may be replaced by the phrase “consisting of” or the phrase “consists essentially of” or synonyms thereof and *vice versa*.

15 The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to a material where minor impurities may be present. For example, the material may be greater than or equal to 90% pure, such as greater than 95% pure, such as greater than 97% pure, such as greater than 99% pure, such as greater than 99.9% pure, such as greater than 99.99% pure, such as greater than 99.999% pure, such as 100% pure.

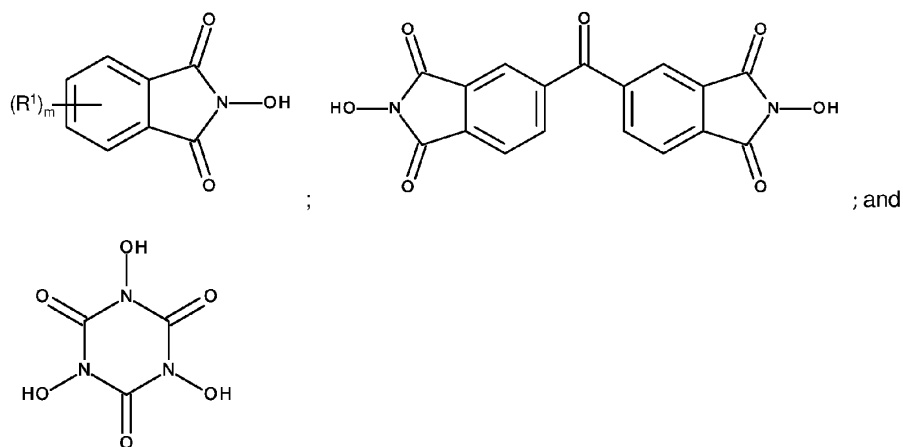
As disclosed herein, the term “polyolefin” refers to a type of polymer with the general formula $(CH_2CHR)_n$ where R is H or an alkyl group.

25 The term “alkyl” as used herein may refer to an unbranched or branched, cyclic or acyclic saturated hydrocarbyl radical, which may be substituted or unsubstituted (with, for example, one or more halo atoms). Where the term “alkyl” refers to an acyclic group, it is preferably C_{1-10} alkyl and, more preferably, C_{1-6} alkyl (such as ethyl, propyl, (e.g. n-propyl or isopropyl), butyl (e.g. branched or unbranched butyl), pentyl or, more preferably, methyl). Where the term “alkyl” is a cyclic group (which may be where the group “cycloalkyl” is specified), it is preferably C_{3-12} cycloalkyl and, more preferably, C_{5-10} (e.g. C_{5-7}) cycloalkyl.

Examples of polyolefins that may be mentioned herein include, but are not limited to polyethylene and polypropylene.

35 The organocatalyst used herein may be any suitable molecules that can catalyse the degradation of a polyolefin to a dicarboxylic acid mixture. For example, the organocatalyst

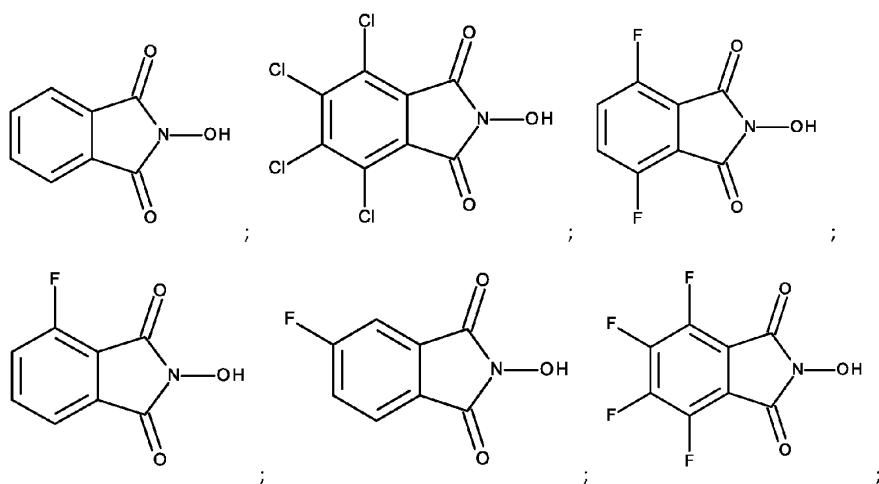
may be a compound that contains at least a hydroxylamino group. More particularly the hydroxylamino group may be present in a ring system. Yet more particularly, the hydroxylamino group may be sandwiched between two ketone groups in a ring system. Thus, in certain embodiments, the organocatalyst may be a compound selected from one or more of a group consisting of:



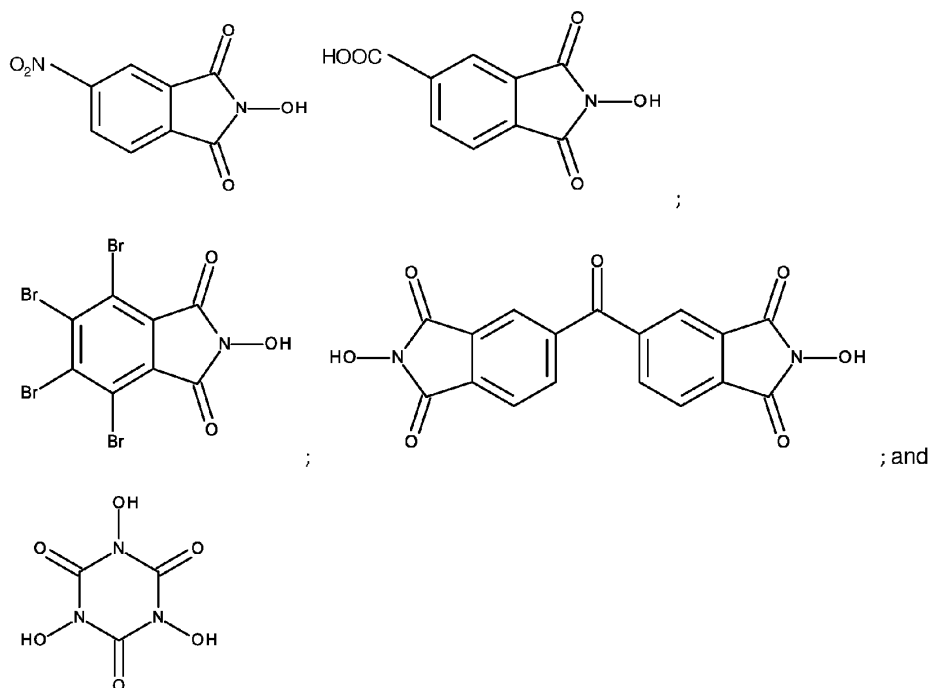
wherein R^1 represents a halo, COOH or NO_2 , wherein the halo is F , Cl or Br ; and m is an integer from 0 to 4.

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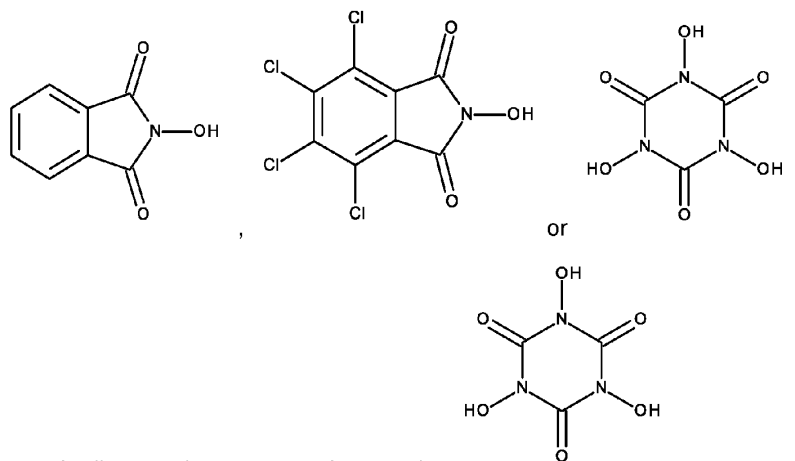
In further embodiments, the organocatalyst may be selected from one or more of a group consisting of:



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- 5 In certain embodiments, the organocatalyst may be one of the following:



In further embodiments, the organocatalyst may be

- The organocatalyst may be provided in any suitable amount relative to the amount of olefin
 10 repeating units present in the mixture (i.e. a theoretical calculated molar amount of olefin

repeating units). As will be appreciated, a suitable amount of the organocatalyst may be an amount sufficient to convert all, or substantially all (e.g. at least 90%, such as 95%, such as 99%, such as 99.95%) of the polyolefin into a different material (e.g. a dicarboxylic acid, side products or shorter polyolefin). For example, the organocatalyst may be provided in an amount of from 0.01 to 0.3 molar equivalents, such as from 0.025 to 0.25 molar equivalents, such as about 0.1 molar equivalents, relative to the amount of olefin repeating units in the mixture. In certain exemplary embodiments, the organocatalyst may be provided in an amount of about 0.1 molar equivalents, relative to the amount of olefin repeating units in the mixture. As the skilled person will appreciate, the amount of organocatalyst can be controlled to give different distributions of the dicarboxylic acid products.

When used herein, the term "the amount of olefin repeating unit" is derived from the following formula:

$$\text{Amount of olefin repeating unit} = \frac{\text{mass of polyolefin}}{\text{molar mass of olefin repeating unit}}$$

As will be appreciated, the term "the amount of olefin repeating unit" refers to a calculated theoretical amount. For example, ethylene has a molecular weight of 28g/mol, so molar amount of polyethylene can be calculated by [(mass of PE)/28] to provide a molar amount with respect to olefin units. It will be appreciated that when using a copolymer or a blended polyolefin material that similar calculations can be conducted based on the relative proportions of the co-monomers or polymers in the blend.

When used herein, the term "about", in the context of concentrations of components in a mixture, molar amounts, temperatures, pressures and periods of time, may mean a variation of $\pm 5\%$ of the stated value, more typically $\pm 4\%$ of the stated value, more typically $\pm 3\%$ of the stated value, more typically, $\pm 2\%$ of the stated value, even more typically $\pm 1\%$ of the stated value, and even more typically $\pm 0.5\%$ of the stated value.

As disclosed herein, the term "nitrate source" refers to any suitable chemical reagent that is capable of providing nitrate ions to the reaction medium. In certain embodiments, the nitrate source may be selected from one or more of a group consisting of nitric acid and a metal nitrate. Any suitable metal nitrate may be used herein. Examples of metal nitrates that may be used include, but are not limited to, a Group I metal nitrate (e.g., lithium nitrate, sodium nitrate and potassium nitrate), a Group II metal nitrate (e.g., magnesium nitrate and calcium nitrate), a transition metal nitrate (e.g., $\text{Fe}(\text{NO}_3)_3$) and a lanthanide nitrate (e.g., $\text{La}(\text{NO}_3)_3$). In certain exemplary embodiments, the nitrate source may be nitric acid.

The nitrate source may be provided in any suitable amount relative to the amount of olefin repeating units in the mixture. For example, the nitrate source may be provided an equimolar amount or in a molar excess relative to the amount of olefin repeating units in the mixture.

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In certain embodiments, the nitrate source may be provided in at least an equimolar amount relative to the amount of olefin repeating units in the mixture. In certain embodiments, the nitrate source may be provided in an amount of from 1 to 10 molar equivalents, such as from 2 to 5 molar equivalents, such as about 3 molar equivalents, relative to the amount of olefin repeating units in the mixture. In certain exemplary embodiments, the nitrate source may be provided in an amount of about 3 molar equivalents, relative to the amount of olefin repeating units in the mixture. As the skilled person will appreciate, the amount of nitrate source can be controlled to give different distributions of the dicarboxylic acid products.

15 In certain embodiments, the method may not require a separate solvent to be present. This may be because the nitrate source is in the form of a suitable liquid. In other embodiments, the mixture may further comprise a solvent. In certain embodiments, the solvent may be selected from one or more of acetic acid, formic acid and water. In certain embodiments that may be mentioned herein, the solvent may be acetic acid. It is noted that acetic acid, formic acid and water are green solvents. As the skilled person will appreciate, this means that the method disclosed herein does not need any toxic aromatic or chlorinated solvents.

Any suitable amount of solvent may be present in the mixture. For example, in certain embodiments, when the mixture further comprises acetic acid, the acetic acid may be provided in an amount of from about 2 to 15 molar equivalents relative to the amount of nitrate source in the mixture. In further embodiments, the acetic acid may be provided in an amount of about 2 to 11 molar equivalents relative to the amount of nitrate source. In certain exemplary embodiments, the acetic acid may be provided in an amount of about 2 molar equivalents relative to the amount of nitrate source. Similar amounts of water or formic acid may be used though it will be understood that higher amounts of the solvents may be used if a more dilute reaction mixture is desired.

In certain embodiments, when the mixture further comprises a solvent, the solvent may be substantially free of heavy metal. As the skilled person will appreciate, the use of toxic heavy metals that may pose a contamination risk to the environment or a toxicity risk if the intended use of the dicarboxylic acids relates to foodstuffs or other consumable goods for humans or animals. The term "heavy metal" when used herein may refer to any metallic chemical element

that has a relatively high density (e.g., a density of greater than or equal to 5 g/cm³ for the pure elemental metal) and is toxic or poisonous at low concentrations. Examples of heavy metals include, but are not limited to mercury, cadmium, arsenic, chromium, thallium, and lead.

- 5 Oxygen may be provided in any suitable concentration to enable the reaction to proceed to completion. For example, oxygen may be provided at a concentration of from 21 % vol/vol (atmospheric air) to 100 % vol/vol. In certain embodiments, the oxygen may be provided at a concentration of about 21% vol/vol (atmospheric air), which is advantageously more accessible and hence, creates more convenience. As will be appreciated, reference to the
10 concentration of oxygen refers to its concentration in the gas supplied to the reaction mixture. By "supplied", this may simply mean that the reaction vessel is left open to the ambient environment, or the reaction vessel is evacuated and then filled with a particular gas in order to achieve a desired oxygen concentration in order for the reaction to proceed.
- 15 The method disclosed herein may be performed at any suitable temperature. As noted this temperature may be 110°C or greater. It will be appreciated that the upper bound of the temperature will be governed by the components of the reaction and how the temperature affects the speed of reaction and ratio of desired product to undesired side-products. Thus, in certain embodiments of the invention that may be mentioned herein, the method may be
20 performed at a temperature of from 110°C to 150°C. For example, the method may be performed at a temperature of about 120°C. In certain embodiments, the method may be performed at any suitable pressure. For example, the method may be performed at a pressure of from 0.5 atm to 5 atm. In certain embodiments, the method may be performed at about 1 atm. Advantageously, these conditions are significantly milder than those used in current state
25 of the art methods for the decomposition of polyolefins.

As will be appreciated, the period of time for the method to be conducted may be determined by the skilled person based on their knowledge of the field and whether the reaction has been deemed to be completed or not. For example, the period of time may be from about 18 hours
30 to about 72 hours. In certain embodiments, the period of time may be about 24 hours. Without wishing to be bound by theory, it is believed that a longer period of time may result in a higher yield and higher distribution of dicarboxylic acids with shorter chain lengths produced from the method. As will be appreciated, the length of time may be preferred to be controlled to maximize the yield of the desired dicarboxylic acids and avoid the production of undesired
35 side products (e.g. carbon dioxide and the like).

- As demonstrated herein, the disclosed method can break down polyolefins into useful dicarboxylic acids. In certain embodiments, when the polyolefin is polyethylene, the dicarboxylic acid mixture may comprise a mixture of linear C₄ to C₁₂ dicarboxylic acids. In further embodiments, the mixture of linear C₄ to C₁₂ dicarboxylic acids may comprise one or more of succinic acid, glutaric acid, adipic acid and undecanedioic acid. In certain embodiments, the succinic acid may make up at least about 30% of the total mass of dicarboxylic acids. In certain exemplary embodiments, the succinic acid may make up at least about 35% of the total mass of the dicarboxylic acid mixture obtained from the method.
- As demonstrated herein, the disclosed method can make use of commercial waste (e.g. low-density polyethylene (LDPE) clingwrap or high-density polyethylene (HDPE) plastic bags) in at least the gram-scale. This shows that the method can tolerate additives (e.g. plasticisers) which are commonly added to commercial materials. It is also believed that the method disclosed herein is capable of being scaled up for use on an industrial scale.
- In certain embodiments, the polyolefin may be polyethylene, polypropylene or a combination thereof. In further embodiments, the polyethylene may be low density polyethylene (LDPE), high density polyethylene (HDPE) or a combination thereof. In even further embodiments, the polyolefin may be a commercial material and further comprises one or more additives selected from the group consisting of a dye, a plasticizer, a pigment, a colouring agent, a printing ink, a filler such as titanium oxide or zinc oxide, a flame retardant, a lubricant, an adhesive, a paper and a cellulose material. As the skilled person will appreciate, these additives are commonly found in commercial materials.
- The invention has been described broadly and generically herein. Those of ordinary skill in the art will readily appreciate that all parameters, dimensions, materials, and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, kit, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, kits, and/or methods, if such features, systems, articles, materials, kits, and/or methods are not mutually inconsistent,

is included within the scope of the present invention. Further, each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the invention. This includes the generic description of the invention with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

The following Examples illustrate the invention.

EXAMPLES

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Materials

N-hydroxytetrachlorophthalimide (Cl₄-NHPI), Acetic acid (glacial, ≥99%), Nitric acid (70%), Succinic acid (≥99.0%), Adipic acid (99%) were all purchased from Sigma-Aldrich. N,N',N''-trihydroxyisocyanuric acid (THICA, 95%) and N-hydroxyphthalimide (NHPI, > 99%) were sourced from Angene International Ltd and Tokyo Chemical Industry (TCI) respectively.

Polyethylene used were sourced as follows: polyethylene resin (powder, low density, 500 micron) was obtained from Alfa Aesar and was used for small-scale reactions (114 mg reactions). Actual polyethylene wastes were obtained from products with SPI code 2 (HDPE) and SPI code 4 (LDPE) and were used without further treatment other than cutting them to smaller pieces to fit a round bottom flask.

Methods

¹H nuclear magnetic resonance (NMR): NMR was recorded using a JEOL 500 MHz spectrometer (Tokyo, Japan) in DMSO-d₆ and the chemical shift was recorded in ppm. ~6 mg of the crude reaction mixture was added to a 4 mL vial and ~0.6 mL of DMSO-d₆ was added. The vial was sonicated to ensure dissolution of the mixture. The solution was then added to an NMR glass tube and was used directly for analysis.

ESI mass spectroscopy: ESI mass spectroscopy was performed with Agilent 6200 series TOF/6500 series Q-TOF B.09.00 (B9044.1 SP1). The crude reaction mixture was dissolved in 2mL of MeOH (~1 ppm concentration). The solution was filtered through a syringe filter (0.2 μm) into a 2 mL glass vial and was used directly for analysis.

High-performance Liquid Chromatography (HPLC) Analysis: A reverse-phase HPLC method was used for the identification and quantification of dicarboxylic acids obtained from the

degradation of PE. Chromatographic separation was achieved on an Acclaim™ Organic Acid (OA) column (4 mm i.d. x 150 mm length, particle size of 5 µm) by isocratic elution with 0.1 M Na₂SO₄, adjusted to pH 2.65 with methanesulfonic acid. The flow rate of the mobile phase and the temperature of the column oven was maintained at 0.6 ml/min and 50°C, respectively. The injection volume was 10 µL, and UV detection of all samples was carried out at 210 nm. Peak identification was done by matching the retention time of the chromatographic peaks as well as the UV-Vis spectrum of the test sample with those of pure standards. Quantification was estimated using external calibration method. The test sample was prepared by dissolving 16.3 mg of material in 7 ml of mobile phase with sonication. All standard solutions and samples were filtered through a 0.2-µm membrane filter before analysis.

General Preparation Method 1: PE degradation with acetic acid

114 mg of PE (4 mmol based on the amount of ethylene repeating unit) and 0.4 mmol of N-hydroxyl catalyst (10 mol% relative to PE) were added to a Schlenk tube. 8 mL of acetic acid (~140 mmol) and 0.8 mL of HNO₃ (~70% w/w; ~12.5 mmol) were added. The mixture was heated to temperatures of 120 °C with stirring in the open air for 24 h. After cooling down to room temperature, the reaction mixture was dried under reduced pressure. The solid residue was collected, and was dissolved and extracted with ethyl acetate, washed with water and brine and dried under reduced pressure. The presence of short-chain dicarboxylic acids was determined via ¹H and ¹³C NMR using DMSO-d₆ as the solvent.

General Preparation Method 2: PE degradation without acetic acid

114 mg of PE (4 mmol based on the amount of ethylene repeating unit) and 0.4 mmol of N-hydroxyl catalyst (10 mol% relative to PE) were added to a Schlenk tube. 0.8 mL of HNO₃ (~70% w/w; ~12.5 mmol) was added. The mixture was heated to temperatures of 120 °C with stirring in the open air for 24 h. After cooling down to room temperature, the reaction mixture was dried under reduced pressure. The solid residue was collected, and was dissolved and extracted with ethyl acetate, washed with water and brine and dried under reduced pressure. The presence of short-chain dicarboxylic acids was determined via ¹H and ¹³C NMR using DMSO-d₆ as the solvent.

Example 1A: PE degradation (with acetic acid) using THICA as catalyst

Results and Discussion: When General Preparation Method 1 was performed with N,N',N''-trihydroxyisocyanuric acid (THICA) as the catalyst, succinic acid was the major compound as detected in the ¹H NMR spectrum, along with a multitude of unknown, presumably dicarboxylic acids longer than succinic acid (e.g., adipic acid). As seen from FIG. 1 and 2, succinic acid made up ~22% of the overall integration of the ¹H NMR spectrum.

Example 1B: PE degradation (with acetic acid) using NHPI and Cl₄-NHPI as catalysts

Results and Discussion: When General Preparation Method 1 was repeated with the catalyst changed to N-hydroxyphthalimide (NHPI) or Cl₄-NHPI, thermal oxidative degradation still occurs but at a lowered efficacy. As seen from **FIG. 7**, the distribution of succinic acid as compared to other longer-chain dicarboxylic acids is much lower when compared to that observed in **FIG. 1 and 2**.

Example 2: PE degradation (without acetic acid) using THICA as catalyst

Results and Discussion: When General Preparation Method 2 was performed with THICA as the catalyst, a stronger oxidative degradation process was observed with a dicarboxylic acid mixture containing a higher distribution of succinic acid as compared to other longer-chain dicarboxylic acids. As seen from **FIG. 3 and 4**, succinic acid made up ~54% of the overall integration of the ¹H NMR spectrum.

To further confirm the presence of succinic acid in the product mixture, ¹³C NMR and electrospray ionization-mass spectroscopy (ESI-MS) were performed. As seen from the ¹³C NMR spectrum (**FIG. 5 and 6**), succinic acid was the major product, along with a multitude of longer-chain dicarboxylic acids (e.g., adipic acid). From the ESI-MS spectrum (**FIG. 8**), a range of dicarboxylic acids were detected after PE degradation, ranging from succinic acid to undecanedioic acid.

HPLC was performed to identify and quantify the dicarboxylic acids obtained from the PE degradation process as well. Cross-validation by chromatographic retention time and UV-Vis profile (see **FIG. 10**) reveals that succinic acid, glutaric acid and adipic acid were formed. As shown in **Table 1**, the percentage composition (by mass) of succinic acid, glutaric acid and adipic acid in the final dicarboxylic mixture was estimated to be 35.5%, 18.8% and 1.6%, respectively, by external calibration.

Table 1: Determination of percentage composition of succinic acid and adipic acid in the final dicarboxylic mixture obtained after PE degradation.

	Succinic acid	Glutaric acid	Adipic acid
Calibration curve equation	y = 577.047x	y = 662.959x	y = 640.897x
Average peak area of 2 runs	476772 mAU	289590 mAU	19745 mAU
Concentration in test sample	0.8262 mg/ml	0.4368 mg/ml	0.0308 mg/ml
Composition by mass	35.5%	18.8%	1.3%

Example 3: Scaled-up degradation of LDPE cling wrap

In this Example, General Preparation Method 1 was used to degrade low-density polyethylene (LDPE) cling wrap. 5 g of LDPE cling wrap (178.6 mmol based on the amount of ethylene repeating unit) and 775 mg of N,N',N''- trihydroxyisocyanuric acid (THICA) (4.38 mmol; 2.5 mol% relative to PE) was added to a 500 ml round bottom flask with a condenser attached. 357 ml of acetic acid (~6248 mmol) and 35.7 ml of HNO₃ (~70% w/w; ~558 mmol) were added to the flask and the reaction mixture was heated to 120°C for 24 hours with stirring. After cooling down to room temperature, the reaction mixture was dried under reduced pressure. The solid residue was collected, and was dissolved and extracted with ethyl acetate, washed with water and brine and dried under reduced pressure. The presence of short-chain dicarboxylic acids was determined via ¹H NMR using DMSO-d₆ as the solvent.

Example 4: Scaled-up degradation of HDPE plastic bags

In this Example, General Preparation Method 2 was used to degrade high-density polyethylene (HDPE) plastic bags. 5 g of HDPE plastic bags (178.6 mmol based on the amount of ethylene repeating unit) and 775 mg of N,N',N''- trihydroxyisocyanuric acid (THICA) (4.38 mmol; 2.5 mol% relative to PE) was added to a 100 ml round bottom flask with a condenser attached. 35.7 ml of HNO₃ (~70% w/w; ~558 mmol) was added to the flask and the reaction mixture was heated to 120°C for 24 hours with stirring. The reaction mixture was monitored for the first hour and was physically mixed with a glass rod to ensure the mixture was mixed properly. After 24 hours, the reaction mixture was cooled down to room temperature and dried under reduced pressure. The solid residue was collected, and was dissolved and extracted with ethyl acetate, washed with water and brine and dried under reduced pressure. The presence of short-chain dicarboxylic acids was determined via ¹H NMR using DMSO-d₆ as the solvent.

Results and Discussion: **FIG. 9** includes ¹H NMR spectra of the products obtained from the thermal oxidation of waste PE according to Examples 3 and 4 of the present disclosure, stacked against the spectra of commercially-available pure adipic and succinic acid. As seen from the Figure, the method according to the present disclosure has been demonstrated to break down commercial waste in at least the gram scale. The method has also been demonstrated to tolerate additives (e.g. plasticisers) which are commonly added to commercial products.

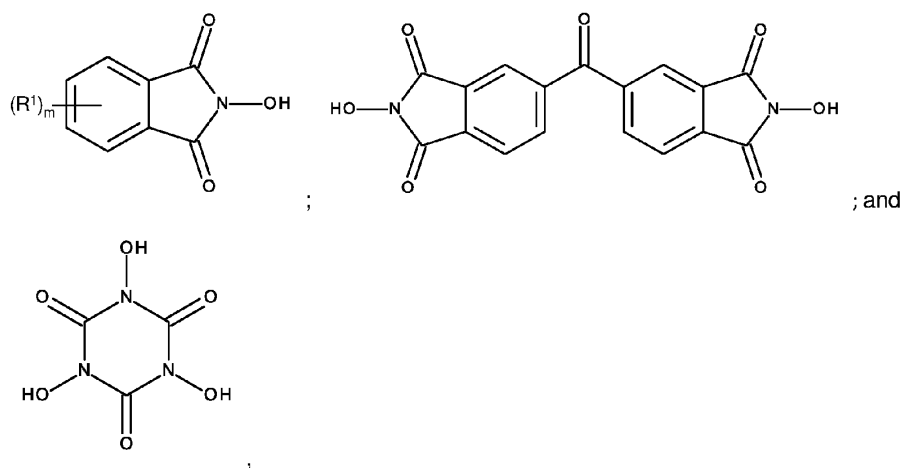
CONCLUSION

In conclusion, a thermal oxidative degradation method is disclosed herein for breaking down polymers containing saturated C-C backbones (such as PE) into useful dicarboxylic acids. The disclosed method may be conducted under milder reaction conditions when compared to the current state of the art methods for the decomposition of polyolefins, and only requires
5 readily-available reagents. The disclosed method avoids the use of heavy metal that may pose a contamination risk to the environment or a toxicity risk if the intended use of the dicarboxylic acids relates to foodstuffs or other consumable goods for humans or animals. The disclosed method is also useful in waste plastics upcycling to convert waste plastics into high-value chemicals (see **FIG. 11**).

CLAIMS

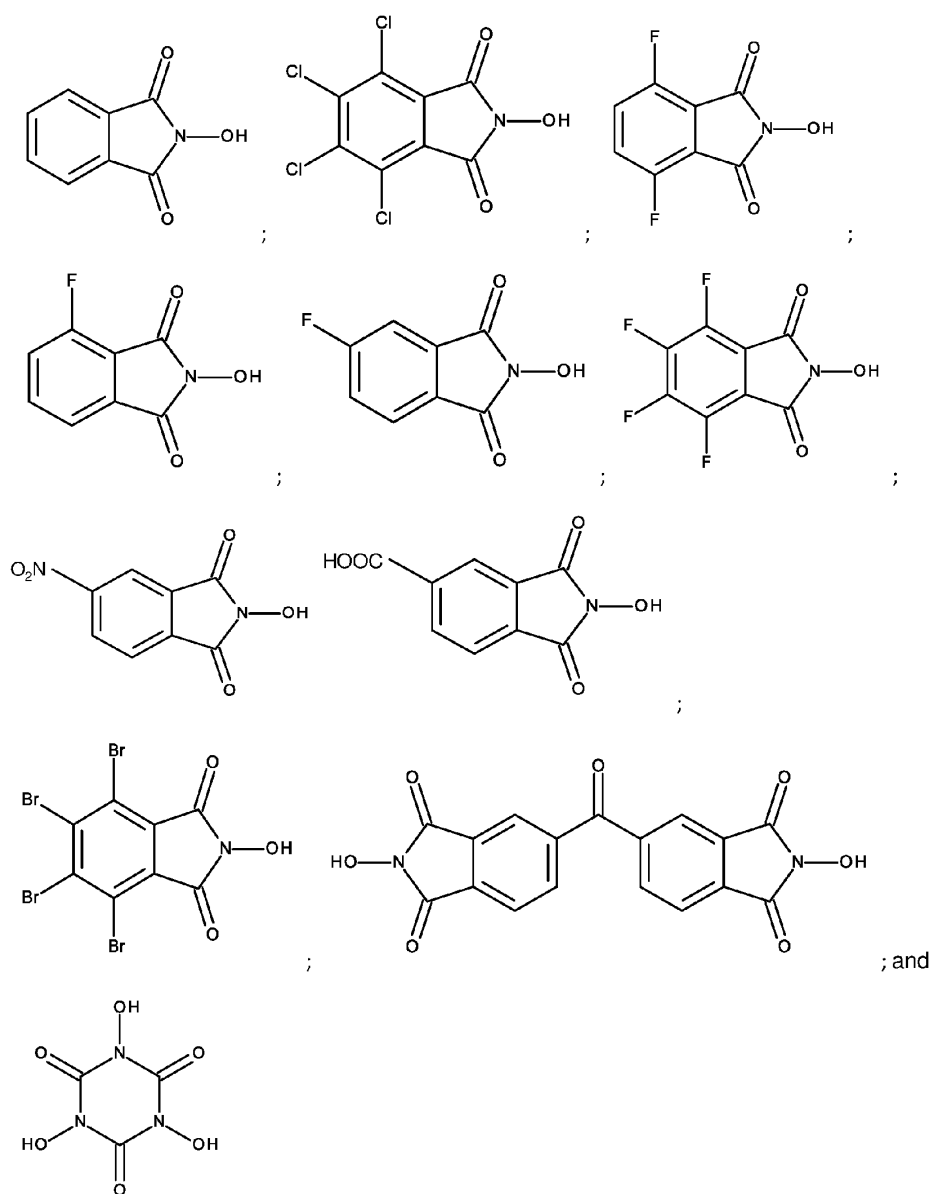
1. A method for preparing a dicarboxylic acid mixture, the method comprising:
- (a) providing a mixture that comprises a polyolefin, an organocatalyst and a nitrate source; and
 - (b) heating the mixture to a temperature of at least 110°C in the presence of oxygen for a period of time to provide a dicarboxylic acid mixture,
- wherein the organocatalyst comprises at least one hydroxylamine functional group.

2. The method according to Claim 1, wherein the organocatalyst is a compound selected from one or more of a group consisting of:

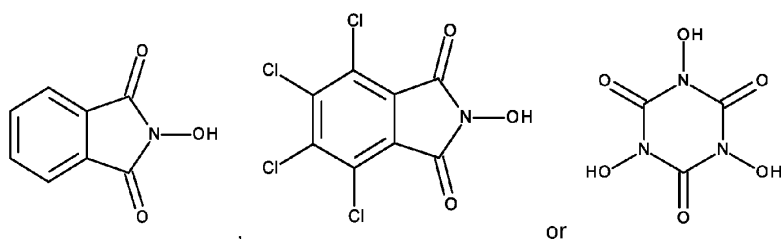


wherein R^1 represents a halo, COOH or NO₂, wherein the halo is F, Cl or Br; and m is an integer from 0 to 4.

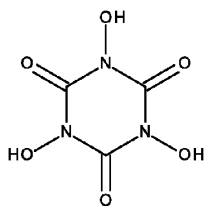
3. The method according to Claim 2, wherein the organocatalyst is selected from one or more of a group consisting of:



4. The method according to Claim 3, wherein the organocatalyst is one of the following:



5. The method according to Claim 4, wherein the organocatalyst is



6. The method according to any one of the preceding claims, wherein the organocatalyst is provided in an amount of from 0.01 to 0.3 molar equivalents, such as from 0.025 to 0.25 molar equivalents, such as about 0.1 molar equivalents, relative to the amount of olefin repeating units in the mixture.
7. The method according to any one of the preceding claims, wherein the nitrate source is selected from one or more of a group consisting of nitric acid and a metal nitrate, optionally wherein the nitrate source is nitric acid.
8. The method according to any one of the preceding claims, wherein the nitrate source is provided in at least an equimolar amount relative to the amount of olefin repeating units in the mixture, optionally wherein the nitrate source is provided in an amount of from 1 to 10 molar equivalents, such as from 2 to 5 molar equivalents, such as about 3 molar equivalents, relative to the amount of olefin repeating units in the mixture.
9. The method according to any one of the preceding claims, wherein the mixture further comprises a solvent, optionally wherein the solvent is selected from one or more of a group consisting of water, formic acid and acetic acid.
10. The method according to claim 9, wherein the solvent includes acetic acid and wherein the acetic acid is provided in an amount of from about 2 to 15 molar equivalents relative to the

amount of nitrate source in the mixture, optionally wherein the acetic acid is provided in an amount of about 2 to 11 molar equivalents relative to the amount of nitrate source, such as about 2 molar equivalents relative to the amount of nitrate source.

11. The method according to any one of claims 9 to 10, wherein the solvent is substantially free of heavy metal.
12. The method according to any one of the preceding claims, wherein the oxygen is provided at a concentration of from 21 % vol/vol to 100 % vol/vol, optionally wherein the oxygen is provided at a concentration of about 21% vol/vol.
13. The method according to any one of the preceding claims, wherein the method is performed at a temperature of from 110°C to 150°C, such as about 120°C.
14. The method according to any one of the preceding claims, wherein the method is performed at a pressure of from 0.5 atm to 5 atm, such as about 1 atm.
15. The method according to any one of the preceding claims, wherein the period of time is from about 18 hours to about 72 hours, such as about 24 hours.
16. The method according to any one of the preceding claims, wherein the polyolefin is selected from one or more of the group consisting of polyethylene and polypropylene.
17. The method according to claim 16, wherein when the polyolefin is polyethylene, the dicarboxylic acid mixture comprises a mixture of linear C₄ to C₁₂ dicarboxylic acids.
18. The method according to claim 17, wherein the mixture of linear C₄ to C₁₂ dicarboxylic acids comprises one or more of succinic acid, glutaric acid, adipic acid and undecanedioic acid.
19. The method according to claim 18, wherein succinic acid makes up at least about 30% of the total mass of dicarboxylic acids, for example, succinic acid makes up at least about 35% of the total mass of the dicarboxylic acid mixture obtained from the method.
20. The method according to any one of claims 16 to 19, wherein the polyethylene is low density polyethylene (LDPE), high density polyethylene (HDPE) or a combination thereof.

21. The method according to any one of the preceding claims, wherein the polyolefin is a commercial material and further comprises one or more additives selected from the group consisting of a dye, a plasticizer, a pigment, a colouring agent, a printing ink, a filler such as titanium oxide or zinc oxide, a flame retardant, a lubricant, an adhesive, a paper and a cellulose material.