

PROCESS FOR INSERTING AMIDE LINKAGES INTO POLYOLEFINS

FIELD OF INVENTION

The present invention provides a process for recycling/upcycling polyolefins, more particularly,
5 a process for inserting amide linkages into polyolefins.

BACKGROUND

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10 necessarily be taken as an acknowledgement that the document is part of the state of the art or is common general knowledge.

Polyethylene (PE) forms the bulk of synthetic polymers produced worldwide because of its versatility in a wide range of applications. However, most of them are purposed for single-use
15 applications and are primarily disposed in incinerators and landfills at their end-of-life instead of being recycled. Despite the many alternative materials proposed to replace PE, it is unlikely that the PE market will diminish in the foreseeable future due to the material versatility, established production pipeline and low production cost associated with the polymer. Chemical recycling of polyolefins such as PE is currently impractical due to the very low yields
20 of ethylene monomer (typically < 10%) that can be obtained from PE, under extremely harsh conditions ($T > 400\text{ }^{\circ}\text{C}$) due to the inertness of the polymer structure. Strategies that can confer chemical recyclability to PE under milder conditions are thus highly sought after.

A viable solution to this problem is via post-synthetic modification of PE by installing reversible
25 chemical linkages onto the PE backbone. This method is attractive as it not only confers degradability to the inert polymer structure, but also preserves the current PE production line. Furthermore, such chemically reversible linkages can be broken and reformed under different reaction conditions, enabling the non-degradable PE to demonstrate chemical recyclability.

Previously, the only reversible linkage successfully installed onto the PE backbone are esters. However, they typically come with significant chain cleavages (Arroyave, A. *et al. J Am Chem Soc* **2022**, *144* (51), 23280-23285), or with additional undesirable functional groups (such as hydroxyl, chloro groups, etc.) from side-reactions (Kong, D. *et al. Green Chemistry* **2022**, *24* (5), 2203-2211). Both of which downcycle the original PE due to large alterations in the
30 polymer's physical properties to form polymers with applications that are inferior as compared to their predecessors.

Thus, there is a need for alternative and/or improved process for recycling/upcycling 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 process for inserting amide linkages into a polyolefin, the process comprising the steps of:

- 10 (i) providing a polyoxime derived from the oxidation of a polyolefin into a polyketone and subsequently converting the polyketone into the polyoxime; and
- (ii) subjecting the polyoxime to a Beckmann rearrangement reaction in the presence of a dehydrating reagent to obtain a polyamide.

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2. The process according to clause 1, wherein step (i) comprises:

- (ia) oxidizing the polyolefin into the polyketone in the presence of an oxidizing agent; and
- (ib) converting the polyketone into the polyoxime in the presence of hydroxylamine.

20 3. The process according to clause 2, wherein step (ia) comprises:

- (iaa) oxidizing the polyolefin into the polyketone in the presence of oxygen and benzaldehyde;
- or
- (iab) oxidizing the polyolefin into the polyketone in the presence of oxygen and N-hydroxytetrachlorophthalimide.

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4. The process according to clause 3, wherein one or more of the following applies:

- (a) benzaldehyde is provided in excess of the amount of olefin repeating units in the polyolefin, such as at least 2 molar equivalents relative to the amount of olefin repeating units in the polyolefin, such as at least 3 molar equivalents relative to the amount of olefin repeating units in the polyolefin, optionally wherein benzaldehyde is provided in an amount of about 3
- 30 molar equivalents relative to the amount of olefin repeating units in the polyolefin;

- (b) N-hydroxytetrachlorophthalimide is provided in an amount of from 0.01 to 0.05 molar equivalent relative to the amount of olefin repeating units, such as from 0.015 to 0.035 molar equivalent relative to the amount of olefin repeating units, optionally wherein N-hydroxytetrachlorophthalimide is provided in an amount of about 0.025 molar equivalent
- 35 relative to the amount of olefin repeating units; and/or

(c) 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. .

5. The process according to clause 3 or clause 4, wherein:
- 5 step (iaa) comprises oxidising the polyolefin in the presence of oxygen and benzaldehyde at a temperature of from 110°C to 130°C, such as about 120°C, for a period of from 18 hours to 30 hours, such as about 24 hours; or
- step (iab) comprises oxidising the polyolefin in the presence of oxygen and N-hydroxytetrachlorophthalimide at a temperature of from 110°C to 130°C, such as about 120°C,
- 10 for a period of from 18 hours to 30 hours, such as about 24 hours.
6. The process according to any one of clauses 3 to 5, wherein step (ia) is conducted in a suitable solvent, wherein the solvent is 1,2,4-trichlorobenzene.
- 15 7. The process according to any one of clauses 3 to 6, wherein the degree of ketone functionalisation in step (ia) is from 0.5% to 2.5%, such as about 1.01% or about 2.00%, based on the aliphatic backbone of the polyolefin as measured by ¹H nuclear magnetic resonance spectroscopy.
- 20 8. The process according to any one of clauses 2 to 7, wherein step (ib) comprises converting the polyketone into a polyoxime in the presence of hydroxylamine and a base, optionally wherein the base is selected from a group consisting of sodium methoxide, potassium methoxide.
- 25 9. The process according to clause 8, wherein each of hydroxylamine and the base is provided in an amount of at least 1 molar equivalent relative to the amount of ketone functional groups in the polyketone, such as at least 2 molar equivalents relative to the amount of ketone functional groups in the polyketone, optionally wherein each of hydroxylamine and the base is provided in an amount of about 2.45 molar equivalent relative to the amount of ketone
- 30 functional groups in the polyketone.
10. The process according to clause 8 or clause 9, wherein step (ib) comprises converting the polyketone into a polyoxime in the presence of hydroxylamine and the base at a temperature of from 70°C to 90°C, such as about 80°C or about 90°C, for a period of from 18
- 35 hours to 30 hours, such as about 24 hours.

11. The process according to any one of clauses 8 to 10, wherein step (ib) is conducted in a suitable solvent, wherein the solvent comprises a mixture of
- (i) toluene or 1,2,4-trichlorobenzene or *p*-cymene,
 - (ii) ethanol; and
 - 5 (iii) water.
12. The process according to clause 11, wherein one or more of the following applies:
- (a) the mixture of toluene, ethanol and water is provided in a volume ratio of 30-50: 0.5-2: 0.5-2, optionally wherein the mixture of toluene, ethanol and water is provided in a
 - 10 volume ratio of about 40: 1: 1;
 - (b) the mixture 1,2,4-trichlorobenzene, ethanol and water is provided in a volume ratio of 125-175: 0.5-5: 0.5-5, optionally wherein the mixture of toluene, ethanol and water is provided in a volume ratio of about 150: 4.5: 3; and/or
 - (b) the solvent is provided in a volume of 5 mL to 20 mL per 1g of the polyketone, such
 - 15 as 7.5 mL to 17.5 mL per 1g of the polyketone, optionally wherein the solvent is provided in a volume of about 10.5 mL or about 17.5 mL per 1g of the polyketone.
13. The process according to any one of clauses 8 to 12, wherein the degree of oxime functionalisation in step (ib) is from 0.5% to 2.5%, such as about 0.95% or about 2.00%, based
- 20 on the aliphatic backbone of the polyoxime as measured by ¹H nuclear magnetic resonance spectroscopy.
14. The process according to any one of the preceding clauses, wherein the dehydrating agent is selected from a group consisting of phosphorus pentoxide or phosphorus pentachloride, optionally wherein the dehydrating agent is phosphorus pentoxide.
- 25 15. The process according to any one of the preceding clauses, wherein the dehydrating agent is provided in an amount of at least 2 weight equivalents relative to the amount of oxime functional groups in the polyoxime, such as at least 3 weight equivalents relative to the amount
- 30 of oxime functional groups in the polyoxime, optionally wherein the dehydrating agent is provided in an amount of about 2.5 weight equivalents relative to the amount of oxime functional groups in the polyoxime.
16. The process according to any one of the preceding clauses, wherein step (ii) comprises
- 35 subjecting the polyoxime to a Beckmann rearrangement reaction in the presence of a dehydrating reagent at a temperature of from 55°C to 150°C, such as about 65°C or about 120°C, for a period of from 1.5 hours to 3 hours, such as about 2 hours.

17. The process according to any one of the preceding clauses, wherein step (ii) is conducted in a suitable solvent, wherein the solvent is selected from a group consisting of chloroform, 1,2,4-trichlorobenzene or *p*-cymene.
- 5 18. The process according to clause 17, wherein:
- (a) chloroform is provided in a volume of 200 mL to 300 mL with respect to 10g of polyoxime, optionally wherein chloroform is provided in a volume of about 250 mL with respect to 10g of polyoxime; or
- 10 (b) 1,2,4-trichlorobenzene is provided in a volume of 200 mL to 300 mL with respect to 10 g of polyoxime, optionally wherein chloroform is provided in a volume of about 250 mL with respect to 10g of polyoxime.
19. The process according to any one of the preceding clauses, wherein the process
- 15 further comprises (iia) adding excess iced water to the dehydration reaction mixture of step (ii) to quench the reaction.
20. The process according to any one of the preceding clauses, wherein the degree of amide functionalisation in step (ii) is from 0.5% to 2.5%, such as about 0.86% or about 2.00%,
- 20 based on the aliphatic backbone of the polyamide as measured by ¹H nuclear magnetic resonance spectroscopy.
21. A process to provide a reformed polyamide, the process comprising the steps of:
- (iii) subjecting a polyamide comprising a plurality of amide groups obtained from any one
- 25 of clauses 1 to 20 to hydrolysis conditions to cleave at least a portion of the amide groups to provide an intermediate mixture comprising a plurality of different compounds comprising carboxylic acid groups, amine groups or both; and
- (iv) generating a reformed polyamide from the intermediate mixture in the presence of a suitable catalyst.
- 30 22. The process according to clause 21, wherein the hydrolysis conditions refer to an acidic or basic environment.
23. The process according to clause 21 or clause 22, wherein step (iii) comprises
- 35 hydrolysing the polyamide in the presence of an acid, optionally wherein the acid is selected from aqueous hydrochloric acid, sulfuric acid and nitric acid, optionally wherein the acid is aqueous hydrochloric acid.

24. The process according to clause 23, wherein the acid is provided in excess of the amount of amide functional groups in the polyamide, such as at least 2 molar equivalents relative to the amount of amide functional groups in the polyamide, such as at least 4 molar equivalents relative to the amount of amide functional groups in the polyamide, optionally wherein the acid is provided in an amount of about 5 molar equivalents relative to the amount of amide functional groups in the polyamide.
25. The process according to clause 23 or clause 24, wherein step (iii) comprises hydrolysing the polyamide in the presence of an acid at a temperature of from 90°C to 110°C, such as about 100°C, for a period of from 18 hours to 30 hours, such as about 24 hours.
26. The process according to any one of clauses 21 to 25, wherein the catalyst is a Lewis acid selected from a group consisting of a boronic acid and titanium isopropoxide, optionally wherein the catalyst is titanium isopropoxide.
27. The process according to clause 26, wherein the catalyst is provided in an amount of 5 mol% to 15 mol% of the amount of amide functional groups in the polyamide before step (iii), optionally wherein the catalyst is provided in an amount of about 10 mol% of the amount of amide functional groups in the polyamide before step (iii).
28. The process according to clause 26 or clause 27, wherein step (iv) comprises generating a reformed polyamide from the intermediate mixture in the presence of the catalyst at a temperature of from 150°C to 170°C, such as about 160°C, for a period of from 3 hours to 12 hours, such as about 6 hours.
29. The process according to any one of clauses 21 to 28, wherein the reformed polyamide is subjected to compression molding.
30. The process according to any one of the preceding clauses, wherein the polyolefin is polyethylene, optionally wherein the polyethylene is high-density polyethylene or low-density polyethylene.
31. The process according to clause 30, wherein:
when the polyethylene is low-density polyethylene, one or more of the following apply:
(a) the polyamide formed at step (ii) displays an increased elongation at break of more than 200% compared to the low-density polyethylene;

(b) the polyamide formed at step (ii) displays an increased tensile strength compared to the low-density polyethylene;

(c) the reformed polyamide subjected to compression molding displays an increased elongation at break of more than 100% compared to the polyamide formed at step (ii);

5 (d) the reformed polyamide subjected to compression molding displays an increased elongation at break of more than 600% compared to the low-density polyethylene;

(e) the reformed polyamide subjected to compression molding displays an increased tensile strength compared to the low-density polyethylene;

10 (f) the polyamide formed at step (ii) displays an increased water contact angle compared to the low-density polyethylene; and/or

(g) the polyamide formed at step (ii) displays an aggregated induced emission (AIE) effect-like fluorescence behavior when irradiated at 390 nm.

32. The process according to clause 30, wherein:

15 when the polyethylene is high-density polyethylene,

(a) the polyamide formed at step (ii) displays an increased elongation at break of compared to the high-density polyethylene;

(b) the polyamide formed at step (ii) displays an increased tensile strength compared to the high-density polyethylene;

20 (c) the polyamide formed at step (ii) displays an increased water contact angle compared to the high-density polyethylene; and/or

(d) the polyamide formed at step (ii) displays an aggregated induced emission (AIE) effect-like fluorescence behavior when irradiated at 390 nm.

25 BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic representation of the post-synthetic modification of LDPE to prepare a polyamide (LDPA) according to an embodiment of the present invention, illustrating the enhanced physical properties conferred by hydrogen bonding between amide functionalities and the formation of a high-strength thermoset (LDrPA) from a hydrolysed PA (LDhPA).

FIG. 2 is a reaction scheme illustrating each stage of the process according to an embodiment of the present invention.

35 **FIG. 3** is a ^1H NMR of LDPE powder in TCE- d_2 at 80°C according to Example 1 of the present disclosure.

FIG. 4 is a ^1H NMR of LDPEK in TCE-d2 at 80°C according to Example 1 of the present disclosure.

FIG. 5 is a ^{13}C NMR of LDPEK in TCE-d2 at 80°C according to Example 1 of the present disclosure.

FIG. 6 is a ^1H NMR of LDPEOxi in TCE-d2 at 80°C according to Example 2 of the present disclosure.

FIG. 7 is a ^{13}C NMR of LDPEOxi in TCE-d2 at 80°C according to Example 2 of the present disclosure.

FIG. 8 is a ^1H NMR of LDPA in TCE-d2 at 80°C according to Example 3 of the present disclosure.

FIG. 9 is a ^{13}C NMR of LDPA in TCE-d2 at 80°C according to Example 3 of the present disclosure.

FIG. 10 is a stacked ^1H NMR spectra of LDPE, LDPEK, LDPEOxi, LDPA and a model amide in TCE-d2 at 80°C (range of 1.90 – 3.30 ppm was chosen for clarity) according to Examples 1 to 3 of the present disclosure.

FIG. 11 is a ^1H NMR of LDhPA in TCE-d2 at 80°C according to Example 4 of the present disclosure.

FIG. 12 is a ^1H NMR of LDrPA in TCE-d2 at 80°C according to Example 5 of the present disclosure.

FIG. 13 includes stacked IR spectra of LDPEK, LDPEOxi, LDPA, LDhPA and LDrPA according to Example 6 of the present disclosure.

FIG. 14 includes DSC curves of (a) LDPE, (b) LDPEK, (c) LDPA, (d) LDhPA and (e) LDrPA according to Example 7 of the present disclosure.

FIG. 15 includes TGA curves of LDPE, LDPEK, LDPA, LDhPA and LDrPA according to Example 7 of the present disclosure.

FIG. 16 includes the high temperature DSC results for LDrPA according to Example 7 of the present disclosure.

FIG. 17 is a photograph of a fabricated LDPE sample for tensile testing according to Example 8 of the present disclosure.

FIG. 18 is a photograph of a fabricated LDrPA sample for tensile testing according to Example 8 of the present disclosure.

FIG. 19 includes the stress-strain curves of LDPE, LDPA and LDrPA according to Example 8 of the present disclosure.

FIG. 20 includes photographs of room temperature and high temperature acid hydrolysis products of LDrPA in TCE-d₂. Heated mixture leads to swelling of polymer but not dissolution.

FIG. 21 depicts the water contact angle measurement on surface of LDPE dog bone specimen. Average water contact angle for LDPE over three measurements is $100.8 \pm 2.0^\circ$.

FIG. 22 depicts the water contact angle measurement on surface of LDPA dog bone specimen. Average water contact angle for LDPA over three measurements is $106.5 \pm 2.3^\circ$.

FIG. 23 depicts the water contact angle measurement on surface of HDPE dog bone specimen. Average water contact angle for HDPE over three measurements is $88.3 \pm 0.4^\circ$.

FIG. 24 depicts the water contact angle measurement on surface of HDPA dog bone specimen. Average water contact angle for HDPA over three measurements is $103.7 \pm 2.2^\circ$.

FIG. 25 depicts the granularity of HDPE and HDPA surface quantified using particle analysis of the phase images of HDPA and HDPE surfaces by a threshold (45%) detection method. Shaded area denotes detected grains. The formation of micro-protrusions on the HDPA surface due to hydrogen bonding of randomly-spaced in-chain amides is depicted.

FIG. 26 depicts the non-chromophore luminescence of HDPA and LDPA. a. Irradiation of the original PE powders and their in-chain amide-inserted counterparts under ambient lighting (left) and 390 nm (right); b. Stacked emission spectra of LDPA (left) and HDPA (right) when suspended in toluene at RT and dissolved at 50 °C ($\lambda_{\text{ex}} = 390 \text{ nm}$); c. Stacked normalised

emission spectra of LDPA (left) and HDPA (right) in TCB (red) and toluene (blue). All emission spectra were recorded at [polymer] = 1 mg/mL.

FIG. 27 depicts the chemical recyclability of HD/LDPA. **a.** Stacked partial ^1H NMR spectra of HDPA, the acid-hydrolysed and repolymerised products through 3 successive iterations of closed-loop recycling (spectra referenced to 2.38 ppm [CH_2COOH] for clarity due to differing product solubility in TCE-d_2 , necessitating different temperatures); **b.** Representative stress-strain curves of HDPE, HDPA and the reformed polyamides after successive iterations of chemical recycling; **c.** Representative stress-strain curves of LDPE, LDPA and the crosslinked polyamide; **d.** Schematic depiction showing the effects of polymer branches on polyamide recyclability.

DESCRIPTION

The present inventors have developed a process for modifying polyolefins, including polyethylene, by inserting amide linkages into the polyolefin. The modification confers chemical recyclability onto the inert plastic while enabling its successors to have physical properties comparable/greater than that of the original polymer. Recyclability was demonstrated by simple hydrolysis and condensation reactions without the need for additional crosslinking agents to preserve the physical properties of the polymer. The resulting polyamide thermoset showed excellent physical properties, such as increased elongation at break and tensile strength, and chemical resistance. FIG. 2 summarises the chemical transformations that take place when transforming a polyolefin (e.g., low-density polyethylene) into a polyamide and the thermoset according to an embodiment of the present disclosure.

Thus, in a first aspect of the invention, there is provided a process of inserting amide linkages in a polyolefin, the process comprising the steps of:

- (i) providing a polyoxime derived from the oxidation of a polyolefin into a polyketone and subsequently converting the polyketone into the polyoxime; and
- (ii) subjecting the polyoxime to a Beckmann rearrangement reaction in the presence of a dehydrating reagent to obtain the polyamide.

This first aspect may also be seen as a process of preparing a polyamide from a polyolefin, the process comprising the steps of:

- (i) providing a polyoxime derived from the oxidation of a polyolefin into a polyketone and subsequently converting the polyketone into the polyoxime; and
- (ii) subjecting the polyoxime to a Beckmann rearrangement reaction in the presence of a dehydrating reagent to obtain the polyamide.

It will be appreciated that the embodiments below relate to both of these views of the first aspect of the invention, as they both relate to the same process.

- 5 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
10 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*.

- The phrase, “consists essentially of” and its pseudonyms may be interpreted herein to refer to
15 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.

- 20 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.

- 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,
25 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.

- 30 Examples of polyolefins that may be mentioned herein include, but are not limited to polyethylene, including low-density polyethylene and high-density polyethylene.

In certain embodiments, step (i) may comprise:

- 35 (ia) oxidizing the polyolefin into the polyketone in the presence of an oxidizing agent; and
(ib) converting the polyketone into the polyoxime in the presence of hydroxylamine.

The oxidizing agent used herein may be any suitable oxidizing agent that is capable of oxidizing a polyolefin into a polyketone. In certain embodiments, step (ia) may comprise:

(iaa) oxidizing the polyolefin into the polyketone in the presence of oxygen and benzaldehyde;

or

- 5 (iab) oxidizing the polyolefin into the polyketone in the presence of oxygen and N-hydroxytetrachlorophthalimide.

Benzaldehyde may be provided in any suitable amount relative to the amount of olefin repeating units (i.e. a theoretical calculated molar amount of olefin repeating units). In certain
10 embodiments, benzaldehyde may be provided in excess of the amount of olefin repeating units in the polyolefin, such as at least 2 molar equivalents relative to the amount of olefin repeating units in the polyolefin, such as at least 3 molar equivalents relative to the amount of olefin repeating units in the polyolefin. In certain exemplary embodiments, benzaldehyde may be provided in an amount of about 3 molar equivalents relative to the amount of olefin
15 repeating units in the polyolefin. It will be appreciated that any suitable substitute for benzaldehyde may be used herein in roughly the same quantities mentioned herein.

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

20
$$\text{Amount of olefin repeating unit} = \frac{\text{mass of polyolefin}}{\text{molar mass of olefin repeating unit}}$$

The term "about" as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, within 1%, within 0.5%, within 0.1%, within 0.05%, within 0.01%, within 0.005%, or within 0.001% of a stated value or of a stated limit of a range, and
25 includes the exact stated value or range.

N-hydroxytetrachlorophthalimide may be provided in any suitable amount relative to the amount of olefin repeating units. In certain embodiments, N-hydroxytetrachlorophthalimide may be provided in an amount of from 0.01 to 0.05 molar equivalent relative to the amount of
30 olefin repeating units, such as from 0.015 to 0.035 molar equivalent relative to the amount of olefin repeating units. In certain exemplary embodiments, N-hydroxytetrachlorophthalimide may be provided in an amount of about 0.025 molar equivalent relative to the amount of olefin repeating units. Again, any suitable substitute for N-hydroxytetrachlorophthalimide may be used herein in roughly the same amounts mentioned above.

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Oxygen, when used as part of the oxidising agent, may be provided in any suitable concentration to enable step (iaa) or (iab) to proceed to completion. In certain embodiments, oxygen may be provided at a concentration of from 21 % vol/vol (atmospheric air) to 100 % vol/vol (pure oxygen). In certain exemplary embodiments, oxygen may be provided at a
5 concentration of about 21 % vol/vol (atmospheric air).

Step (iaa) or (iab) disclosed herein may be performed at any suitable temperature. Furthermore, the period of time for step (iaa) or (iab) to be conducted may be determined by the skilled person based on their knowledge of the field and whether the reaction has been
10 deemed to be completed or not. For example, step (iaa) may comprise oxidising the polyolefin in the presence of oxygen and benzaldehyde at a temperature of from 110°C to 130°C, such as about 120°C, for a period of from 18 hours to 30 hours, such as about 24 hours. For example, step (iab) may comprise oxidising the polyolefin in the presence of oxygen and N-hydroxytetrachlorophthalimide at a temperature of from 110°C to 130°C, such as about 120°C,
15 for a period of from 18 hours to 30 hours, such as about 24 hours.

Step (ia) may be conducted in a suitable solvent, when necessary to solubilise the polyolefin. In certain embodiments, the solvent may be 1,2,4-trichlorobenzene.

20 As demonstrated in the Example section of the present disclosure, the degree of ketone functionalisation may be measured by ¹H nuclear magnetic resonance spectroscopy by comparing the integral of CH₂-C=O proton peak with respect to the aliphatic backbone CH₂ proton peak. In certain embodiments, the degree of ketone functionalisation in step (ia) may be from 0.5% to 2.5%, such as about 1.01% or about 2.00%.

25 In certain embodiments, step (ib) may comprise converting the polyketone into a polyoxime in the presence of hydroxylamine and a base. Any suitable base may be used herein. In certain embodiments, the base may be selected from a group consisting of sodium methoxide, potassium methoxide.

30 Each of hydroxylamine and the base may be provided in any suitable amount relative to the amount of ketone functional groups in the polyketone. In certain embodiments, each of hydroxylamine and the base may be provided in an amount of at least 1 molar equivalent relative to the amount of ketone functional groups in the polyketone, such as at least 2 molar
35 equivalents relative to the amount of ketone functional groups in the polyketone. In certain exemplary embodiments, each of hydroxylamine and the base may be provided in an amount

of about 2.45 molar equivalents relative to the amount of ketone functional groups in the polyketone.

Step (ib) disclosed herein may be performed at any suitable temperature. Furthermore, the period of time for step (ib) 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. In certain embodiments, step (ib) may comprise converting the polyketone into a polyoxime in the presence of hydroxylamine and the base at a temperature of from 70°C to 90°C, such as about 80°C or 90°C, for a period of from 18 hours to 30 hours, such as about 24 hours.

Step (ib) may be conducted in any suitable solvent to solubilise the polyketone. In certain embodiments, the solvent may comprise a mixture of

- (i) toluene or 1,2,4-trichlorobenzene or *p*-cymene,
- (ii) ethanol; and
- (iii) water.

As will be appreciated, the composition and/or volume of the solvent used to solubilise the polyketone may vary depending on various factors, such as the molecular weight of the polyolefin and temperature and will be readily apparent to the skilled person in the art based on their knowledge of the field. As such, in certain embodiments, one or more of the following may apply:

- (a) the mixture of toluene, ethanol and water may be provided in a volume ratio of 30-50: 0.5-2: 0.5-2, optionally wherein the mixture of toluene, ethanol and water is provided in a volume ratio of about 40: 1: 1;
- (b) the mixture 1,2,4-trichlorobenzene, ethanol and water may be provided in a volume ratio of 125-175: 0.5-5: 0.5-5, optionally wherein the mixture of toluene, ethanol and water is provided in a volume ratio of about 150: 4.5: 3; and/or
- (c) the solvent may be provided in a volume of 5 mL to 20 mL per 1g of the polyketone, such as 7.5 mL to 17.5 mL per 1g of the polyketone, optionally wherein the solvent is provided in a volume of about 10.5 mL or about 17.5 mL per 1g of the polyketone.

As demonstrated in the Example section of the present disclosure, the degree of oxime functionalisation may be measured by ¹H nuclear magnetic resonance spectroscopy by comparing the integral of CH₂-C=N-OH proton peak with respect to the aliphatic backbone CH₂ proton peak. In certain embodiments, the degree of oxime functionalisation in step (ib) may be from 0.5% to 2.5%, such as about 0.95% or about 2.00%,

The dehydrating agent used herein may be any suitable dehydrating agent that is capable of subjecting the polyoxime to a Beckmann rearrangement reaction to obtain a polyamide. In certain embodiments, the dehydrating agent may be selected from a group consisting of phosphorus pentoxide or phosphorus pentachloride. In certain exemplary embodiments, the dehydrating agent may be phosphorus pentoxide.

The dehydrating agent may be provided in any suitable amount relative to the amount of oxime functional groups in the polyoxime. In certain embodiments, the dehydrating agent may be provided in an amount of at least 2 weight equivalents relative to the amount of oxime functional groups in the polyoxime, such as at least 3 weight equivalents relative to the amount of oxime functional groups in the polyoxime. In certain embodiments, the dehydrating agent may be provided in an amount of about 2.5 weight equivalents relative to the amount of oxime functional groups in the polyoxime.

Step (ii) disclosed herein may be performed at any suitable temperature. Furthermore, the period of time for step (ii) 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. In certain embodiments, step (ii) may comprise subjecting the polyoxime to a Beckmann rearrangement reaction in the presence of a dehydrating reagent at a temperature of from 55°C to 150°C, such as about 65°C or about 120°C, for a period of from 1.5 hours to 3 hours, such as about 2 hours.

Step (ii) may be conducted in a suitable solvent to solubilise the polyoxime. In certain embodiments, the solvent may be selected from a group consisting of chloroform, 1,2,4-trichlorobenzene or *p*-cymene.

As will be appreciated, the composition and/or volume of the solvent used to solubilise the polyoxime may vary depending on various factors, such as the molecular weight of the polyolefin and temperature and will be readily apparent to the skilled person in the art based on their knowledge of the field. As such, in certain embodiments, one or more of the following may apply:

(a) chloroform may be provided in a volume of 200 mL to 300 mL with respect to 10g of polyoxime, optionally wherein chloroform is provided in a volume of about 250 mL with respect to 10g of polyoxime; or

(b) 1,2,4-trichlorobenzene may be provided in a volume of 200 mL to 300 mL with respect to 10 g of polyoxime, optionally wherein chloroform is provided in a volume of about 250 mL with respect to 10 g of polyoxime.

- 5 In certain embodiments, the process may further comprise (iia) adding excess iced water to the dehydration reaction mixture of step (ii) to quench the reaction.

As demonstrated in the Example section of the present disclosure, the degree of amide functionalisation may be measured by ^1H nuclear magnetic resonance spectroscopy by
10 comparing the integral of $\text{CH}_2\text{-C(O)-NH-CH}_2$ proton peak with respect to the aliphatic backbone CH_2 proton peak. In certain embodiments, the degree of amide functionalisation in step (ii) may be from 0.5% to 2.5%, such as about 0.86% or about 2.00%.

In a second aspect of the invention, there is provided a process to provide a reformed
15 polyamide, the process comprising the steps of:

- (iii) subjecting a polyamide comprising a plurality of amide groups obtained from the process disclosed hereinbefore to hydrolysis conditions to cleave at least a portion of the amide groups to provide an intermediate mixture comprising a plurality of different compounds comprising carboxylic acid groups, amine groups or both; and
20 (iv) generating a reformed polyamide from the intermediate mixture in the presence of a suitable catalyst.

In certain embodiments, the hydrolysis conditions may refer to an acidic or basic environment. Any suitable acid may be used herein to cleave the amide groups in the polyamide. In certain
25 embodiments, step (iii) may comprise hydrolysing the polyamide in the presence of an acid, optionally wherein the acid is selected from aqueous hydrochloric acid, sulfuric acid and nitric acid. In certain exemplary embodiments, the acid may be aqueous hydrochloric acid.

The acid may be provided in any suitable amount relative to the amount of amide functional
30 groups in the polyamide. In certain embodiments, the acid may be provided in excess of the amount of amide functional groups in the polyamide, such as at least 2 molar equivalents relative to the amount of amide functional groups in the polyamide, such as at least 4 molar equivalents relative to the amount of amide functional groups in the polyamide. In certain exemplary embodiments, the acid may be provided in an amount of about 5 molar equivalents
35 relative to the amount of amide functional groups in the polyamide.

Step (iii) disclosed herein may be performed at any suitable temperature. Furthermore, the period of time for step (iii) 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. In certain embodiments, step (iii) may comprise hydrolysing the polyamide in the presence
5 of an acid at a temperature of from 90°C to 110°C, such as about 100°C, for a period of from 18 hours to 30 hours, such as about 24 hours.

The catalyst used herein may be any suitable catalyst that is capable of generating a reformed polyamide from the intermediate mixture. In certain embodiments, the catalyst may be a Lewis
10 acid. As used herein, the term "Lewis acid" refers to any chemical species which is able to accept electron pairs from a Lewis base. In certain embodiments, the catalyst may be selected from a group consisting of a boronic acid and titanium isopropoxide. In certain exemplary embodiments, the catalyst may be titanium isopropoxide.

The catalyst may be provided in any suitable amount relative to the amount of amide functional groups in the polyamide. In certain embodiments, the catalyst may be provided in an amount of 5 mol% to 15 mol% of the amount of amide functional groups in the polyamide before
15 hydrolysis in step (iii). In certain exemplary embodiments, the catalyst may be provided in an amount of about 10 mol% of the amount of amide functional groups in the polyamide before
20 hydrolysis in step (iii).

Step (iv) disclosed herein may be performed at any suitable temperature. Furthermore, the period of time for step (iv) 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
25 not. In certain embodiments, step (iv) may comprise generating a reformed polyamide from the intermediate mixture in the presence of the catalyst at a temperature of from 150°C to 170°C, such as about 160°C, for a period of from 3 hours to 12 hours, such as about 6 hours.

As explained in the Examples section of the present disclosure, the reformed polyamide provided by the process disclosed hereinbefore display thermosetting properties with no
30 melting point (T_m). As such, in certain embodiments, the reformed polyamide may be subjected to compression molding.

In certain embodiments, the polyolefin may be polyethylene. In certain exemplary
35 embodiments, the polyethylene may be low-density polyethylene or high-density polyethylene.

As demonstrated in the Examples section of the present disclosure, the polyamide and/or reformed polyamide provided by the processes disclosed hereinbefore may display superior physical properties compared to the original polyethylene and other properties such as aggregated induced emission (AIE) effect-like fluorescence behavior and chemical resistance.

- 5 Furthermore, these superior properties of the polyamide or reformed polyamide may be exhibited to different extents depending whether low-density polyethylene or high-density polyethylene is used.

10 As such, when polyethylene is low-density polyethylene, one or more of the following may apply:

- (a) the polyamide formed at step (ii) may display an increased elongation at break of more than 200% compared to the low-density polyethylene;
- (b) the polyamide formed at step (ii) may display an increased tensile strength compared to the low-density polyethylene;
- 15 (c) the reformed polyamide subjected to compression molding may display an increased elongation at break of more than 100% compared to the polyamide formed at step (ii);
- (d) the reformed polyamide subjected to compression molding may display an increased elongation at break of more than 600% compared to the low-density polyethylene;
- 20 (e) the reformed polyamide subjected to compression molding may display an increased tensile strength compared to the low-density polyethylene;
- (f) the polyamide formed at step (ii) may display an increased water contact angle compared to the low-density polyethylene; and/or
- (g) the polyamide formed at step (ii) may display an aggregated induced emission (AIE)
- 25 effect-like fluorescence behavior when irradiated at 390 nm.

When polyethylene is high-density polyethylene, one or more of the following may apply:

- (a) the polyamide formed at step (ii) may display an increased elongation at break of compared to the high-density polyethylene;
- 30 (b) the polyamide formed at step (ii) may display an increased tensile strength compared to the high-density polyethylene;
- (c) the polyamide formed at step (ii) may display an increased water contact angle compared to the high-density polyethylene; and/or
- (d) the polyamide formed at step (ii) may display an aggregated induced emission (AIE)
- 35 effect-like fluorescence behavior when irradiated at 390 nm.

Further aspects and embodiments of the invention will now be discussed by reference to the following non-limiting examples.

EXAMPLES

5

Materials

Unless otherwise stated, all materials were obtained from commercial sources (e.g. Sigma Aldrich).

10

Abbreviations

LDPE: low density polyethylene

LDPEK: low density ketone functionalised polyethylene

15 LDPEOxi: low density oxime functionalised polyethylene

LDPA: low density amide-functionalised polyethylene

LDhPA: low density hydrolysed amide-functionalised polyethylene

LDrPA: low density reformed amide-functionalised polyethylene

HDPE: high density polyethylene

20 HDPEK: high density ketone-functionalized polyethylene

HDPEOxi: high density oxime functionalised polyethylene

HDPA: high density amide-functionalised polyethylene

HDhPA: high density hydrolysed amide-functionalised polyethylene

HDrPA: high density reformed amide-functionalised polyethylene

25

Example 1: Benzaldehyde oxidation of LDPE to ketone-functionalized LDPE (PEK)

10 g of LDPE (0.35 mol w.r.t ethylene repeating unit) and 110 mL of benzaldehyde (3 equivalents, 1.05 mol) were added into a 250 mL round-bottom flask attached with a
30 condenser. The mixture was heated to 120 °C with stirring. Compressed air was bubbled into the reaction mixture throughout the duration. After 24 h, the reaction mixture was poured into stirring methanol to precipitate the polymer product. The precipitated polymer product was filtered and re-dissolved in hot toluene, then re-precipitated in stirring methanol again. The precipitate was then filtered and the solids were dried under reduced pressure. Ketone
35 functionality was determined via ¹H NMR by comparing the integral of CH₂-C=O proton peak

(δ : 2.39 ppm) with respect to the aliphatic backbone CH₂ proton peak (δ : 1.32 ppm). (See FIG. 4 and FIG. 5 for ¹H and ¹³C NMR characterization respectively).

The full spectrum for the original LDPE powder (Mn: 7.7 kDa, Mw: 35 kDa) is shown in FIG. 3, which shows absence of any chemical functionality. Nuclear magnetic resonance (NMR) was recorded using a JEOL 500 MHz spectrometer (Tokyo, Japan) in Tetrachloroethane-d₂ (TCE-d₂). After benzaldehyde oxidation, the initial LDPE polymer gained ketone functionality as evident from the triplet peak at 2.39 ppm in the ¹H NMR spectrum (FIG. 4) and the singlet peak at 211.22 ppm in ¹³C NMR spectrum of PEK (FIG. 5). The ketone functionality was calculated to be 1.01% with respect to the aliphatic backbone peak (δ : 1.32 ppm) in the ¹H NMR. Similarly, from the IR spectrum (FIG. 13), the sharp peak at 1720 cm⁻¹ could be assigned to the C=O stretching expected of a ketone group.

Calculations for ketone functionalization is as follows (w.r.t FIG. 3):

$$\% \text{ ketone in LDPEK} = \frac{\text{no. of } H_k}{\text{no. of } H_e} \times 100\% = \frac{\int 2.39 \text{ ppm}}{\int 1.32 \text{ ppm}} \times 100\% = \frac{1.01}{100} \times 100\% = 1.01\%$$

Example 2: Conversion of LDPEK to oxime-functionalized LDPE (LDPEOxi)

4 g of LDPEK (~1% ketone functionality, 0.69 mmol w.r.t ketone groups) was added into a 100 mL round-bottom flask attached with a condenser. The air in the flask was exchanged for an inert argon atmosphere. 40 mL of toluene was then added into the flask and the mixture was heated with stirring at 80 °C until the polymer was fully dissolved. In a separate 10 mL glass vial, 118.6 mg of hydroxylamine (1.70 mmol), 91.5 mg of sodium methoxide (1.70 mmol), 1 mL of ethanol and 1 mL of water were added and sonicated until full dissolution of solids. The aqueous-ethanolic mixture was then added into the round-bottom flask. The reaction mixture was kept under reflux conditions with stirring over 24 h. After 24 h, the reaction mixture was poured into stirring methanol to precipitate the polymer product. The solids were filtered and dried under reduced pressure. Oxime functionality was determined via ¹H NMR by comparing the integral of CH₂-C=N-OH proton peak (δ : 2.19 ppm and 2.36 ppm) with respect to the aliphatic backbone CH₂ proton peak (δ : 1.32 ppm). (See FIG. 6 and FIG. 7 for ¹H and ¹³C NMR characterization respectively).

After reaction with hydroxylamine, LDPEK lost its ketone functionality and gained oxime functionality as evident from the disappearance of the triplet peak centered at 2.39 ppm and the appearance of two triplet peaks with the same integral centered at 2.19 ppm and 2.36 ppm in the ¹H NMR spectrum of LDPEOxi (FIG. 6). The oxime functionality was calculated to be

0.95% with respect to the aliphatic backbone peak (δ : 1.32 ppm). The singlet peak in the ^{13}C NMR (FIG. 7) was also found to be more upfield at 162.87 ppm as expected from the conversion of a carbonyl carbon to oxime carbon. Similarly, from the IR spectrum (FIG. 13), the sharp peak at 1726 cm^{-1} and the broad peak at 3296 cm^{-1} could be assigned respectively to the C=N stretching and the O-H stretching expected of an oxime group.

Calculations for oxime functionalization is as follows (w.r.t FIG. 6):

$$\begin{aligned}\% \text{ oxime in LDPEOxi} &= \frac{\text{no. of } H_{ox}}{\text{no. of } H_e} \times 100\% = \frac{\int 2.19 \text{ ppm} + \int 2.36 \text{ ppm}}{\int 1.32 \text{ ppm}} \times 100\% \\ &= \frac{0.47 + 0.48}{100} \times 100\% = 0.95\%\end{aligned}$$

10

Example 3: Beckmann rearrangement of LDPEOxi to amide-functionalized LDPE (LDPA)

10 g of LDPEOxi (~1% oxime functionality, 1.36 mmol w.r.t oxime groups) was added into a 500 mL round-bottom flask attached with a condenser. The air in the flask was exchanged for an inert argon atmosphere. 250 mL of chloroform was then added into the flask and the mixture was heated with stirring at 65°C until the polymer was fully soluble. 25 g of phosphorus pentoxide (2.5 wt equivalents) was then added into the flask under argon flow and mixture was left to reflux for 2 h. After 2 h, the reaction mixture was poured into stirring iced water and left to stir overnight for precipitation of the polymer product and quenching of phosphorus pentoxide present. The next day, solids were collected via filtration and dried under reduced pressure. Amide functionality was determined via ^1H NMR by comparing the integral of $\text{CH}_2\text{-C(O)-NH-CH}_2$ proton peak (δ : 2.15 ppm and 3.25 ppm) with respect to the aliphatic backbone CH_2 proton peak (δ : 1.32 ppm). (See FIG. 8 and FIG. 9 for ^1H and ^{13}C NMR characterization respectively).

25

Upon reaction with P_2O_5 , LDPEOxi lost its oxime functionality for amide functionality as evident from the disappearance of the two triplet peaks at 2.19 ppm and 2.36 ppm and the appearance of one triplet peak at 2.15 ppm and one quartet peak at 3.25 ppm in the ^1H NMR spectrum of LDPA (FIG. 8). The amide functionality was calculated to be 0.86% with respect to the aliphatic backbone peak at 1.32 ppm. The singlet peak in the ^{13}C NMR (FIG. 9) was also found to shift slightly downfield to 172.90 ppm as expected from the conversion of an oxime carbon to amide carbon. Similarly, from the IR spectrum (FIG. 13), the sharp peak at 1647 cm^{-1} and the broad peak at 3037 cm^{-1} could be assigned respectively to the C=O stretching and the N-H stretching expected of an amide group.

35

Calculations for amide functionalization is as follows (w.r.t FIG. 8):

$$\begin{aligned}\% \text{ amide in LDPA} &= \frac{\text{no. of } H_a}{\text{no. of } H_e} \times 100\% = \frac{\int 2.15 \text{ ppm} + \int 3.25 \text{ ppm}}{\int 1.32 \text{ ppm}} \times 100\% \\ &= \frac{0.43 + 0.43}{100} \times 100\% = 0.86\%\end{aligned}$$

5 **Example 4: Hydrolysis of LDPA to diacids, diamines and amino acids (LDhPA – hydrolysed PA)**

4 g of LDPA (~1% amide functionality, 0.68 mmol w.r.t amide groups) was added into a 500 mL round-bottom flask attached with a condenser. The air in the flask was exchanged for an inert argon atmosphere. 270 mL of aqueous HCl (~33 %) was then added into the flask and
10 the mixture was heated with stirring at 100 °C for 24 h under argon flow. After 24 h, the reaction mixture was filtered, and solids were washed with water and dried under reduced pressure. Acid functionality was determined via ¹H NMR by comparing the integral of CH₂-C(O)-OH proton peak (δ: 2.38 ppm) with respect to the aliphatic backbone CH₂ proton peak (δ: 1.32 ppm). The broad peak near 3.05 ppm could be assigned to the CH₂-NH₃⁺. Due to the overlap
15 of the CH₂-C(O)-NH-CH₂ amide and CH₂-NH₂ amine proton peaks near 3.25 ppm, the amide functionality was back-calculated with assumption that the acid and amine functionalities were equivalent. (See FIG. 11 for ¹H NMR characterization).

Upon hydrolysis of LDPA, the amide functionality was replaced by amine functionality as
20 evident from the disappearance of the quartet peak at 3.25 ppm and the appearance of a two triplet peaks at 3.25 ppm and 2.38 ppm which corresponds to the amine and carboxylic acid functionalities. A broad peak at 3.07 ppm can also be observed, corresponding to the cationic amine salt form due to acid hydrolysis. From the IR spectrum (FIG. 13), the broad peaks at 3030 cm⁻¹ and 3363 cm⁻¹ could be assigned respectively to the N-H stretching and the O-H
25 stretching.

Calculations of functionality were performed based on the following equations (w.r.t FIG. 11):

$$\begin{aligned}\% \text{ acid in LDhPA} &= \frac{\text{no. of } H_{ac}}{\text{no. of } H_e} \times 100\% = \frac{\int 2.38 \text{ ppm} \times 2}{\int 1.32 \text{ ppm}} \times 100\% = \frac{0.20 \times 2}{100} \times 100\% \\ &= 0.40\%\end{aligned}$$

30 $\% \text{ amine in LDhPA} = \% \text{ acid in LDhPA} = 0.40\%$

$$\begin{aligned}
 \% \text{ amide in LDhPA} &= \frac{\text{no. of } H_a}{\text{no. of } H_e} \times 100\% \\
 &= \frac{(\text{no. of } H_{az+am} + \text{no. of } H_{am} - \text{no. of } H_{ac}) \times 2}{\text{no. of } H_e} \times 100\% \\
 &= \frac{[\int 3.25 \text{ ppm} + \int 3.07 \text{ ppm} - \int 2.38 \text{ ppm}] \times 2}{\int 1.32 \text{ ppm}} \times 100\% \\
 &= \frac{[0.34 + 0.08 - 0.20] \times 2}{100} \times 100\% = 0.44\%
 \end{aligned}$$

5

Example 5: Reaction procedure for reforming of LDPA from LDhPA (LDrPA – reformed PA):

3 g of LDhPA (0.51 mmol w.r.t. amide groups before hydrolysis) was added into a 250 mL flame dried Schlenk flask and heated at 100 °C under reduced pressure with stirring for 1 h to remove any form of trace moisture. 20.64 uL of titanium (IV) isopropoxide (0.0697 mmol) was added into the flask under argon flow then the mixture was heated to 160 °C under argon flow and stirred for another hour. The flask was kept at 160 °C for another 5 h under reduced pressure. After 5 h, the reaction mixture was left to stir overnight in methanol. Solids were collected, washed with methanol and dried under reduced pressure. Acid, amine, and amide functionalities of the reformed LDPA (LDrPA) were calculated from the ¹H NMR peak integrals in the same manner as for the LDhPA. (See FIG. 12 for ¹H NMR characterization).

Upon condensation of LDhPA mixture, the amide functionality was observed again as a quartet at 3.25 ppm. However, it is evident that the reformation was not fully completed as carboxylic acid peaks can still be observed as a triplet at 2.38 ppm.

Calculations of functionality were performed based on the following equations (w.r.t FIG. 12):

$$\begin{aligned}
 \% \text{ acid in LDrPA} &= \frac{\text{no. of } H_{ac}}{\text{no. of } H_e} \times 100\% = \frac{\int 2.38 \text{ ppm} \times 2}{\int 1.32 \text{ ppm}} \times 100\% = \frac{0.27 \times 2}{100} \times 100\% \\
 &= 0.54\%
 \end{aligned}$$

25

$$\% \text{ amine in LDrPA} = \% \text{ acid in LDrPA} = 0.54\%$$

$$\begin{aligned}
 \% \text{ amide in LDrPA} &= \frac{\text{no. of } H_a}{\text{no. of } H_e} \times 100\% \\
 &= \frac{(\text{no. of } H_{az+am} + \text{no. of } H_{am} - \text{no. of } H_{ac}) \times 2}{\text{no. of } H_e} \times 100\% \\
 &= \frac{[\int 3.25 \text{ ppm} + \int 3.07 \text{ ppm} - \int 2.38 \text{ ppm}] \times 2}{\int 1.32 \text{ ppm}} \times 100\% \\
 &= \frac{[0.46 + 0 - 0.27] \times 2}{100} \times 100\% = 0.38\%
 \end{aligned}$$

5

Example 6: FTIR analysis

The presence of functional groups, such as ketone, oxime, amide, carboxylic acid and amine, was further verified via Fourier-transform infrared (FTIR) spectroscopy using a Bruker VERTEX 80v spectrometer (Karlsruhe, Germany) in the attenuated total reflectance (ATR) mode from 4000 to 400 cm^{-1} .

Incorporation of ketone groups into LDPE was supported by the presence of a prominent C=O stretch absorption band at 1720 cm^{-1} . The two-step Beckmann rearrangement of these ketone groups to amides was evidenced by the appearance of the C=N stretch of the oxime intermediate at 1726 cm^{-1} and a broad O-H stretch at 3296 cm^{-1} , followed by the appearance of a new signal at 1647 cm^{-1} corresponding to amide C=O stretch and a broad 3037 cm^{-1} signal corresponding to the N-H stretch (FIG. 13).

After amide hydrolysis, the presence of carboxylic acid and amine groups was characterised by the absorption bands at 3363 cm^{-1} and 3030 cm^{-1} attributed to the O-H stretch and N-H stretch, respectively. Successful reforming of the amide bonds was indicated by the reappearance of peaks at 3051 cm^{-1} along with the disappearance of the two broader bands characteristic of O-H and N-H stretch.

Example 7: Thermal analyses

Thermogravimetric analysis (TGA) was conducted using TA Instruments Q500 (Delaware, USA) under nitrogen atmosphere with a flow rate of 60 mL/min. Each sample (ca. 5 mg) was heated from 35 to 800°C at a rate of 20°C/min. Differential scanning calorimetry (DSC) was performed using TA Instruments PDSC Q100 (Delaware, USA) under nitrogen at a heating rate of 10 °C/ min over a temperature range of 0 to 150 or 200 °C. The T_c (crystallization temperature) and T_m (melt temperature) were collected from the first cycle of cooling and second cycle of heating, respectively. T_d (decomposition temperature) was collected from TGA via extrapolated onset temperature.

Table 1: Thermal properties of LDPE, LDPEK, LDPA, LDhPA and LDrPA

	LDPE	LDPEK	LDPA	LDhPA	LDrPA
$T_c / ^\circ\text{C}$	78.52	82.88	70.37	69.45	64.38*
$T_m / ^\circ\text{C}$	94.43	95.31	93.93	90.57	88.24*
$T_d / ^\circ\text{C}$	464.1	375.6	449.6	454.7	454.1

* T_m and T_c detected was determined to be from leftover LDhPA mixtures as detected in ^1H NMR. This conclusion was drawn due to the physical observation of LDrPA not melting in the vacuum oven up to temperatures of 170°C . Hence, this led us to raise the scanning limit of DSC runs to 350°C (FIG. 16).

As seen from FIG. 16, LDrPA does not melt even at higher temperatures up to 350°C , displaying only the T_m of the residual LDhPA. Hence, this observation led us to believe that LDrPA is a thermoset with crosslinked amide linkages, which could have been possible due to the branched nature of LDPE used (see FIG. 1).

Example 8: Evaluation of tensile properties

Tensile properties were tested using Force Gauge Test Stand: IMADA MX2 SERIES. Here we have evaluated the mechanical properties of LDPA and LDrPA with respect to the original LDPE. Both LDPA and original LDPE samples were fabricated using a vacuum oven by melting the plastic at 120°C under vacuum for 1 h. A representative example for the fabrication of original LDPE is shown in FIG. 17.

As LDrPA is a thermoset with no T_m , sample was fabricated using compression molding instead. The sample was subjected to a sequence of heating and pressure: 260°C for 5 min with no pressure applied, followed by 260°C for 5 min at 5 bar, and lastly 260°C for 5 min at 20 bar. A representative example was shown in FIG. 18.

Table 2: Tensile properties of LDPE, LDPA and LDrPA

	LDPE	LDPA	LDrPA
Young's Modulus (Pa)	1.09×10^8	9.52×10^7	2.86×10^7
% Elongation at break (%)	31.90	104.60	233.18
Max stress at break (MPa)	5.81	8.83	5.98
Ultimate tensile strength (MPa)	6.04	9.23	6.39

Comparing the physical properties of LDPE to LDPA, we found significant improvements in the tensile strength and ductility of the plastic upon amide functionalization. While LDPA is

only slightly more elastic (slightly lower Young's modulus), it is much more ductile as seen from its improved % elongation at break (more than 3 times w.r.t LDPE). Similarly, both the max stress and ultimate tensile strength of LDPA were superior to that of the original LDPE. The improved physical properties of LDPA could be attributed to hydrogen bonding
5 interactions from the amide linkages which forms a polymer network with reversible crosslinking interactions. Because of its superior physical properties, LDPA could be used in similar or better applications as its original LDPE.

Comparing LDrPA with its predecessors, we noticed that the polymer is more elastic as
10 compared to both LDPA and LDPE, which is another indication of chemical crosslinking to form a thermoset. Similarly, an improvement in % elongation at break (more than 7 times w.r.t LDPE) could be observed. However, we do notice a drop in max stress and ultimate tensile strength as compared to LDPA, probably due to shorter polymer chains as LDrPA is not fully converted during the condensation reaction (as seen in FIG. 12). Despite so, LDrPA still has
15 superior properties as compared to the original LDPE and could still be used for similar applications.

Example 9: Chemical Resistance of the Polyamide Thermoset (LDrPA)

Despite performing hydrolysis of thermoset LDrPA under various harsh conditions, the
20 material did not degrade significantly due to the extensive crosslinking nature of LDPE (see FIG. 1). The following conditions was performed in an attempt to hydrolyse LDrPA:

High temperature acid hydrolysis

155 mg of LDrPA (assume ~1% amide functionality according to original LDPA, 0.01 mmol
25 w.r.t amide groups) and 10 mL conc HCl (~33%) was added to a reaction flask. The reaction was heated to 100 °C over 72 h under argon conditions. The resulting mixture was filtered, washed with water, and dried under reduced pressures. The resulting solid was still an insoluble polymer that is insoluble in organic solvents even at high temperatures (see FIG. 20).

30

High temperature base hydrolysis

155 mg of LDrPA (assume ~1% amide functionality according to original LDPA, 0.01 mmol
w.r.t amide groups), 56 mg of KOH (1 mmol) and 10 mL of ethanol was added to a reaction
35 flask. The reaction was heated to 85 °C over 24 h under argon conditions. The resulting mixture was filtered, washed with water, and dried under reduced pressures. The resulting solid was still an insoluble polymer that is insoluble in organic solvents even at high temperatures similar to that in FIG. 20.

Microwave-assisted acid hydrolysis

60 mg of LDrPA (assume ~1% amide functionality according to original LDPA, 0.01 mmol w.r.t amide groups) and 15 mL of 1M HCl (aq) was added to a microwave reaction vessel. The reaction vessel was heated to 160 °C over 5 min at a stir rate of 600 rpm. The temperature and stir rate were maintained for 30 min and eventually cooled to 55 °C. The resulting mixture was filtered, washed with water, and dried under reduced pressures. The resulting solid was still an insoluble polymer that is insoluble in organic solvents even at high temperatures similar to that in FIG. 20.

Microwave-assisted base hydrolysis (using 1M KOH)

60 mg of LDrPA (assume ~1% amide functionality according to original LDPA, 0.01 mmol w.r.t amide groups), 42.9 μ L of 1M KOH (aq) and 15 mL ethanol was added to a microwave reaction vessel. The reaction vessel was heated to 160 °C over 5 min at a stir rate of 600 rpm. The temperature and stir rate were maintained for 1 h and eventually cooled to 55 °C. The resulting mixture was filtered, washed with water, and dried under reduced pressures. The resulting solid was still an insoluble polymer that is insoluble in organic solvents even at high temperatures similar to that in FIG. 20.

Microwave-assisted base hydrolysis (using MeOH/NaOMe)

60 mg of LDrPA (assume ~1% amide functionality according to original LDPA, 0.01 mmol w.r.t amide groups), 2.3 mg of NaOMe and 15 mL methanol was added to a microwave reaction vessel. The reaction vessel was heated to 150 °C over 5 min at a stir rate of 600 rpm. The temperature and stir rate were maintained for 1 h and eventually cooled to 55 °C. The resulting mixture was filtered, washed with water, and dried under reduced pressures. The resulting solid was still an insoluble polymer that is insoluble in organic solvents even at high temperatures similar to that in FIG. 20.

Example 10: Procedure for Amide insertion onto HDPE*Conversion of HDPE to ketone-functionalized HDPE (HDPEK)*

10 g of HDPE (0.35 mol w.r.t ethylene repeating unit), 2.69 g of N-hydroxytetrachlorophthalimide, Cl₄-NHPI (8.9 mmol) and 150 mL of trichlorobenzene (TCB) were added into a 250 mL round-bottom flask attached with a condenser. The mixture was heated in an oil bath at 120 °C with stirring in open air (~21% O₂). After 24 h, the reaction mixture was poured into stirring MeOH to precipitate the polymer product. The precipitated polymer product was filtered and re-dissolved in hot toluene, then re-precipitated in stirring

MeOH again. The precipitated polymer product was filtered and washed thoroughly with MeOH, then dried in a vacuum oven at 80 °C to obtain 9.66 g of HDPEK as a pale-yellow powder.

% ketone in HDPEK as determined via ^1H NMR = 2.00%

5 *Conversion of HDPEK to oxime-functionalized HDPE (HDPEOxi)*

9 g of HDPEK (~2% ketone functionality, 3.21 mmol w.r.t ketone groups) was added into a 250 mL round-bottom flask attached with a condenser. The atmosphere in the flask was purged and refilled with argon gas. 150 mL of TCB was added into the flask and the mixture was heated in an oil bath at 100 °C with stirring until the polymer was fully dissolved. In a
10 separate glass vial, 560 mg of $\text{NH}_2\text{OH}\cdot\text{HCl}$ (8.05 mmol), 432 mg of NaOMe (8.02 mmol), 2.5 mL of EtOH and 3 mL of water were added and sonicated until full dissolution of solids. The aqueous-ethanolic mixture was then added into the reaction mixture. The reaction mixture was maintained at oil bath temperature of 90 °C with stirring over 24 h under argon flow. 2 mL of EtOH was added at the 12 h interval. After 24 h, the reaction mixture was poured into stirring
15 MeOH to precipitate the polymer product. The precipitated polymer product was filtered and washed thoroughly with MeOH, then dried in a vacuum oven at 60 °C to obtain 8.91 g of HDPEOxi as a pale-yellow powder. It is noted that *p*-cymene can be used to replace TCB as the solvent.

% oxime in HDPEOxi as determined via ^1H NMR = 2.00%

20 *Conversion of HDPEOxi to high density polyamides (HDPA)*

8.57 g HDPEOxi (~2% oxime functionality, 2.41 mmol w.r.t oxime groups) was added into a 500 mL round-bottom flask attached with a condenser. The atmosphere in the flask was purged and refilled with argon gas. 220 mL of TCB was then added into the flask and the mixture was heated in an oil bath at 120 °C with stirring until the polymer was fully dissolved.
25 21.5 g of P_2O_5 (2.5 wt eqv) was then added into the flask under argon flow and mixture was left to react at 120 °C for 2 h. After 2 h, the reaction mixture was left to stir in excess iced water overnight. The next day, solids were filtered, washed thoroughly with water, then with MeOH. The sample was then dried in a vacuum oven at 60 °C to obtain 8.05 g of HDPA as a yellowish-tan powder. It is noted that *p*-cymene can be used to replace TCB as the solvent.

30 % amide in HDPA as determined via ^1H NMR = 2.00%

Example 11: Analysis of properties for the polyamides (LDPA and HDPA)

Material strength

LDPA displayed a greater improvement in terms of tensile strength. Improvements was also demonstrated in HDPA, albeit to a lower extend of improvement.

Table 3: Overview of HDPA and LDPA as compared to their predecessors

	T_c /°C ^a	T_m /°C ^a	T_d /°C ^b	Young Modulus /10 ⁸ Pa ^c	Elongati on at break /% ^c	Max stress at break /MPa ^c	UTS /MPa ^c	Water contact angle /° ^d
HDPE	113.5	129.2	461.8	2.66 ± 0.31	87.2 ± 16.4	11.98 ± 0.60	14.34 ± 0.24	88.3 ± 0.4
HDPA	85.4	111.5	434.4	2.72 ± 0.58	117.2 ± 17.8	13.78 ± 0.88	16.33 ± 0.57	103.7 ± 2.2
LDPE	78.5	94.4	326.0	1.19 ± 0.42	30.4 ± 3.0	5.94 ± 0.05	5.98 ± 0.09	100.8 ± 2.0
LDPA	70.4	93.9	449.6	0.92 ± 0.14	102.1 ± 5.5	8.17 ± 0.81	8.38 ± 0.81	106.5 ± 2.3

Determined via ^aDSC and ^bTGA. ^cDetermined from tensile analyses, values are the averages of three repeats; ^dValues are the average of three repeats

Hydrophobicity effects

Although the inclusion of polar amide linkages is expected to increase polymer hydrophilicity, we unexpectedly observed an increase in surface hydrophobicity, with HDPA showing a greater increase in water contact angle (WCA) (~15°) compared to LDPA (~6°). Comparing the surface granularity of HDPE and HDPA dog-bone specimens indicated a possible origin of this phenomenon (**FIG. 25**): HDPA possessed ~8.8 times more grains detected with a total detected granularity area ~3.7 times more than HDPE. More extensive granularity suggests that HDPA's enhanced microscale roughness can enhance surface hydrophobicity via a 'pseudo-lotus effect', akin to the villi-structured papillae of lotus leaves eliciting superhydrophobicity. This may be attributed to the random, sporadic locations of the amide linkages in the polymer chain, whose NH...O hydrogen bonding induces irregular chain folding by alignment of hydrophobic polymer segments to form surface protrusions upon annealing. The greater increase in hydrophobicity upon amide insertion to HDPE compared to LDPE is a consequence of the former's originally more regular polymer packing, leading to a greater change in surface roughness upon polymer skeletal editing. Notably, this phenomenon contrasts with polyamides comprising of regularly-spaced amide linkages, which are more hydrophilic than PE.

Aggregated induced emission (AIE) effect

The strong hydrogen bonding between localized clusters of amide linkages, which account for the aforementioned surface roughness enhancement, can also form polar group clusters with fluorescent properties arising from through-space conjugations. As shown in FIG. 26, as little as 1% in-chain amide linkages was sufficient to elicit chromophore-free, aggregation-induced emission (AIE)-like fluorescence behaviour for both LDPE and HDPE when irradiated at 390 nm that was absent in the PE starting materials. When suspended in toluene (25 °C), strong emission (peak λ_{em} = 442 nm) was observed, unlike the PE precursors. Further evidence of the AIE origins of the fluorescence was seen from dissolution of the polymers in toluene at 50°C, resulting in complete fluorescence quenching – a consequence of disruption of the solid-state hydrogen bonding clusters. Solid-state solvatochromism of HDPA and LDPA was observed when suspended in different solvents, with TCB eliciting a distinct emission profile (peak λ_{em} = 495 nm) from toluene. Conferring chromophore-free AIE fluorescence to PE via amide insertion offers new potential uses for sensing, as well as acting as intrinsic fluorescent markers to facilitate polymer sorting from mixtures without the need for luminescent marker additives.

Example 12: Chemical recyclability comparison of LDPA and HDPA

Chemical recycling of the amide-inserted PE was evaluated through repeated cycles of polymer hydrolysis and amide reformation. The process used was the same for both LDPA and HDPA.

Using HDPA, successful amide hydrolysis was evident from the appearance of the distinct ¹H NMR signals of the α -methylenes to -COOH (triplet centred ~2.38 ppm) and -NH₂ (broad peak centred ~3.05 ppm) groups, with a corresponding reduction in the relative intensity of the amide signal (CH₂-CONH, ~2.15 ppm) (FIG. 27a). Subsequent reformation of the polyamide was achieved using the neat hydrolysed polymer fragments in the presence of titanium (IV) isopropoxide (TIP) (FIG. 27a). We were able to demonstrate three successive cycles of hydrolysis and amide reformation on HDPA with no loss of thermal stability of the reformed polyamides. In all iterations, the reformed polyamide retained >90% of the HDPA feed. Notably, the mechanical properties of the polyamides were found to improve after successive cycles of reformation (Table 4), with ultimate tensile strength and elongation at break increasing by ~48% and ~23% respectively compared to the original HDPA (FIG. 27b), likely due to further extensions of the polymer chains upon repeated amide formation. Additionally, it offers the possibility to compensate for any loss in polymer mechanical properties resulting from the initial PE skeletal modification, simply by controlling degree of polymerisation of the hydrolysed HDPA fragments.

Attempts at chemical recycling of LDPA resulted in very different outcomes. Following successful hydrolysis, polyamide reformation using TIP formed a crosslinked polymer (LDrPA) (68% gel fraction) with distinct thermal and mechanical properties from both LDPE and LDPA.

5 Despite crosslink formation, LDrPA was still amenable to compression moulding for analysis of mechanical properties: Firstly, a significant reduction in Young's modulus was observed – a likely consequence of the reduction in crystallinity upon crosslinking, which hindered chain packing. Secondly, the polymer crosslinking resulted in greatly improved polymer ductility, with LDrPA possessing 7.5x and 2.2x increased elongation at break compared to LDPE and LDPA

10 respectively as a result of polymer chain interconnection (FIG. 27c). We further explored the chemical resistance of LDrPA by subjecting it to a series of solubility tests using 1,1,2,2-tetrachloroethane or 1,2,4-trichlorobenzene at 130 °C for up to 72 h, as well as thermal and microwave-assisted hydrolysis and alcoholysis. In all cases, no visible polymer dissolution or degradation was detected, suggesting the potential suitability of LDrPA in moderate chemi-

15 resistive applications.

The dramatic difference in recyclability between HDPA and LDPA could be attributed to the random location of the amide linkages on the polymer chains (FIG. 27d): hydrolysis of amides located on the numerous branches of LDPA results in formation of extensive crosslinkable sites. In contrast, the fewer branches on HDPE resulted in greater statistical likelihood of amide insertion into the main chain.

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Table 4: Overview of the properties for all materials

	T _c /°C ^a	T _m /°C ^a	T _d /°C ^b	Young Modulus /10 ⁸ Pa ^c	Elongati on at break /% ^c	Max stress at break /MPa ^c	UTS /MPa ^c	Water contact angle /° ^d
HDPE	113.5	129.2	461.8	2.66 ± 0.31	87.2 ± 16.4	11.98 ± 0.60	14.34 ± 0.24	88.3 ± 0.4
HDPA	85.4	111.5	434.4	2.72 ± 0.58	117.2 ± 17.8	13.78 ± 0.88	16.33 ± 0.57	103.7 ± 2.2
HDrPA <u>1</u>	99.8	117.5	438.2	3.03 ± 0.07	124.7 ± 1.0	14.54 ± 0.47	16.13 ± 0.69	-
HDrPA <u>2</u>	103.0	115.8	438.5	2.45 ± 0.69	149.6 ± 10.6	14.61 ± 0.85	16.31 ± 0.56	-

HDrPA	100.3	114.8	441.8	2.24	144.4	22.36	24.29	-
<u>3</u>				± 0.12	± 47.9	± 2.01	± 1.22	
LDPE	78.5	94.4	326.0	1.19	30.4	5.94	5.98	100.8
				± 0.42	± 3.0	± 0.05	± 0.09	± 2.0
LDPA	70.4	93.9	449.6	0.92	102.1	8.17	8.38	106.5
				± 0.14	± 5.5	± 0.81	± 0.81	± 2.3
LDrPA	64.4 ^e	88.2 ^e	454.1	0.27	233.2	5.97	6.39	-
				NA	NA	NA	NA	

Determined via ^aDSC and ^bTGA. ^cDetermined from tensile analyses, values are the averages of three repeats; ^d Values are the average of three repeats; ^e Due to crosslinked nature of LDrPA, exothermic and endothermic peaks in its DSC curve corresponds to the crystallization and melting of residual hydrolysed fragments or loosely crosslinked segments.

CLAIMS

1. A process for inserting amide linkages into a polyolefin, the process comprising the steps of:
 - (i) providing a polyoxime derived from the oxidation of a polyolefin into a polyketone and subsequently converting the polyketone into the polyoxime; and
 - (ii) subjecting the polyoxime to a Beckmann rearrangement reaction in the presence of a dehydrating reagent to obtain a polyamide.
2. The process according to claim 1, wherein step (i) comprises:
 - (ia) oxidizing the polyolefin into the polyketone in the presence of an oxidizing agent; and
 - (ib) converting the polyketone into the polyoxime in the presence of hydroxylamine.
3. The process according to claim 2, wherein step (ia) comprises:
 - (iaa) oxidizing the polyolefin into the polyketone in the presence of oxygen and benzaldehyde; or
 - (iab) oxidizing the polyolefin into the polyketone in the presence of oxygen and N-hydroxytetrachlorophthalimide.
4. The process according to claim 3, wherein one or more of the following applies:
 - (a) benzaldehyde is provided in excess of the amount of olefin repeating units in the polyolefin, such as at least 2 molar equivalents relative to the amount of olefin repeating units in the polyolefin, such as at least 3 molar equivalents relative to the amount of olefin repeating units in the polyolefin, optionally wherein benzaldehyde is provided in an amount of about 3 molar equivalents relative to the amount of olefin repeating units in the polyolefin;
 - (b) N-hydroxytetrachlorophthalimide is provided in an amount of from 0.01 to 0.05 molar equivalent relative to the amount of olefin repeating units, such as from 0.015 to 0.035 molar equivalent relative to the amount of olefin repeating units, optionally wherein N-hydroxytetrachlorophthalimide is provided in an amount of about 0.025 molar equivalent relative to the amount of olefin repeating units; and/or
 - (c) 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. .
5. The process according to claim 3 or claim 4, wherein:
 - step (iaa) comprises oxidising the polyolefin in the presence of oxygen and benzaldehyde at a temperature of from 110°C to 130°C, such as about 120°C, for a period of from 18 hours to 30 hours, such as about 24 hours; or

step (iab) comprises oxidising the polyolefin in the presence of oxygen and N-hydroxytetrachlorophthalimide at a temperature of from 110°C to 130°C, such as about 120°C, for a period of from 18 hours to 30 hours, such as about 24 hours.

6. The process according to any one of claims 3 to 5, wherein step (ia) is conducted in a suitable solvent, wherein the solvent is 1,2,4-trichlorobenzene.

7. The process according to any one of claims 3 to 6, wherein the degree of ketone functionalisation in step (ia) is from 0.5% to 2.5%, such as about 1.01% or about 2.00%, based on the aliphatic backbone of the polyolefin as measured by ¹H nuclear magnetic resonance spectroscopy.

8. The process according to any one of claims 2 to 7, wherein step (ib) comprises converting the polyketone into a polyoxime in the presence of hydroxylamine and a base, optionally wherein the base is selected from a group consisting of sodium methoxide, potassium methoxide.

9. The process according to claim 8, wherein each of hydroxylamine and the base is provided in an amount of at least 1 molar equivalent relative to the amount of ketone functional groups in the polyketone, such as at least 2 molar equivalents relative to the amount of ketone functional groups in the polyketone, optionally wherein each of hydroxylamine and the base is provided in an amount of about 2.45 molar equivalent relative to the amount of ketone functional groups in the polyketone.

10. The process according to claim 8 or claim 9, wherein step (ib) comprises converting the polyketone into a polyoxime in the presence of hydroxylamine and the base at a temperature of from 70°C to 90°C, such as about 80°C or about 90°C, for a period of from 18 hours to 30 hours, such as about 24 hours.

11. The process according to any one of claims 8 to 10, wherein step (ib) is conducted in a suitable solvent, wherein the solvent comprises a mixture of

- (i) toluene or 1,2,4-trichlorobenzene or *p*-cymene,
- (ii) ethanol; and
- (iii) water.

12. The process according to claim 11, wherein one or more of the following applies:

(a) the mixture of toluene, ethanol and water is provided in a volume ratio of 30-50: 0.5-2: 0.5-2, optionally wherein the mixture of toluene, ethanol and water is provided in a volume ratio of about 40: 1: 1;

(b) the mixture 1,2,4-trichlorobenzene, ethanol and water is provided in a volume ratio of 125-175: 0.5-5: 0.5-5, optionally wherein the mixture of toluene, ethanol and water is provided in a volume ratio of about 150: 4.5: 3; and/or

(b) the solvent is provided in a volume of 5 mL to 20 mL per 1g of the polyketone, such as 7.5 mL to 17.5 mL per 1g of the polyketone, optionally wherein the solvent is provided in a volume of about 10.5 mL or about 17.5 mL per 1g of the polyketone.

13. The process according to any one of claims 8 to 12, wherein the degree of oxime functionalisation in step (ib) is from 0.5% to 2.5%, such as about 0.95% or about 2.00%, based on the aliphatic backbone of the polyoxime as measured by ¹H nuclear magnetic resonance spectroscopy.

14. The process according to any of the preceding claims, wherein the dehydrating agent is selected from a group consisting of phosphorus pentoxide or phosphorus pentachloride, optionally wherein the dehydrating agent is phosphorus pentoxide.

15. The process according to any of the preceding claims, wherein the dehydrating agent is provided in an amount of at least 2 weight equivalents relative to the amount of oxime functional groups in the polyoxime, such as at least 3 weight equivalents relative to the amount of oxime functional groups in the polyoxime, optionally wherein the dehydrating agent is provided in an amount of about 2.5 weight equivalents relative to the amount of oxime functional groups in the polyoxime.

16. The process according to any of the preceding claims, wherein step (ii) comprises subjecting the polyoxime to a Beckmann rearrangement reaction in the presence of a dehydrating reagent at a temperature of from 55°C to 150°C, such as about 65°C or about 120°C, for a period of from 1.5 hours to 3 hours, such as about 2 hours.

17. The process according to any of the preceding claims, wherein step (ii) is conducted in a suitable solvent, wherein the solvent is selected from a group consisting of chloroform, 1,2,4-trichlorobenzene or *p*-cymene.

18. The process according to claim 17, wherein:

(a) chloroform is provided in a volume of 200 mL to 300 mL with respect to 10g of polyoxime, optionally wherein chloroform is provided in a volume of about 250 mL with respect to 10g of polyoxime; or

(b) 1,2,4-trichlorobenzene is provided in a volume of 200 mL to 300 mL with respect to 10 g of polyoxime, optionally wherein chloroform is provided in a volume of about 250 mL with respect to 10g of polyoxime.

19. The process according to any of the preceding claims, wherein the process further comprises (iia) adding excess iced water to the dehydration reaction mixture of step (ii) to quench the reaction.

20. The process according to any one of the preceding claims, wherein the degree of amide functionalisation in step (ii) is from 0.5% to 2.5%, such as about 0.86% or about 2.00%, based on the aliphatic backbone of the polyamide as measured by ^1H nuclear magnetic resonance spectroscopy.

21. A process to provide a reformed polyamide, the process comprising the steps of:

(iii) subjecting a polyamide comprising a plurality of amide groups obtained from any one of Claims 1 to 20 to hydrolysis conditions to cleave at least a portion of the amide groups to provide an intermediate mixture comprising a plurality of different compounds comprising carboxylic acid groups, amine groups or both; and

(iv) generating a reformed polyamide from the intermediate mixture in the presence of a suitable catalyst.

22. The process according to claim 21, wherein the hydrolysis conditions refer to an acidic or basic environment.

23. The process according to claim 21 or claim 22, wherein step (iii) comprises hydrolysing the polyamide in the presence of an acid, optionally wherein the acid is selected from aqueous hydrochloric acid, sulfuric acid and nitric acid, optionally wherein the acid is aqueous hydrochloric acid.

24. The process according to claim 23, wherein the acid is provided in excess of the amount of amide functional groups in the polyamide, such as at least 2 molar equivalents relative to the amount of amide functional groups in the polyamide, such as at least 4 molar equivalents relative to the amount of amide functional groups in the polyamide, optionally

wherein the acid is provided in an amount of about 5 molar equivalents relative to the amount of amide functional groups in the polyamide.

25. The process according to claim 23 or claim 24, wherein step (iii) comprises hydrolysing the polyamide in the presence of an acid at a temperature of from 90°C to 110°C, such as about 100°C, for a period of from 18 hours to 30 hours, such as about 24 hours.

26. The process according to any one of claims 21 to 25, wherein the catalyst is a Lewis acid selected from a group consisting of a boronic acid and titanium isopropoxide, optionally wherein the catalyst is titanium isopropoxide.

27. The process according to claim 26, wherein the catalyst is provided in an amount of 5 mol% to 15 mol% of the amount of amide functional groups in the polyamide before step (iii), optionally wherein the catalyst is provided in an amount of about 10 mol% of the amount of amide functional groups in the polyamide before step (iii).

28. The process according to claim 26 or claim 27, wherein step (iv) comprises generating a reformed polyamide from the intermediate mixture in the presence of titanium isopropoxide at a temperature of from 150°C to 170°C, such as about 160°C, for a period of from 3 hours to 12 hours, such as about 6 hours.

29. The process according to any one of claims 21 to 28, wherein the reformed polyamide is subjected to compression molding.

30. The process according to any one of the preceding claims, wherein the polyolefin is polyethylene, optionally wherein the polyethylene is high-density polyethylene or low-density polyethylene.

31. The process according to claim 30, wherein:

when the polyethylene is low-density polyethylene, one or more of the following apply:

(a) the polyamide formed at step (ii) displays an increased elongation at break of more than 200% compared to the low-density polyethylene;

(b) the polyamide formed at step (ii) displays an increased tensile strength compared to the low-density polyethylene;

(c) the reformed polyamide subjected to compression molding displays an increased elongation at break of more than 100% compared to the polyamide formed at step (ii);

(d) the reformed polyamide subjected to compression molding displays an increased elongation at break of more than 600% compared to the low-density polyethylene;

(e) the reformed polyamide subjected to compression molding displays an increased tensile strength compared to the low-density polyethylene;

(f) the polyamide formed at step (ii) displays an increased water contact angle compared to the low-density polyethylene; and/or

(g) the polyamide formed at step (ii) displays an aggregated induced emission (AIE) effect-like fluorescence behavior when irradiated at 390 nm.

32. The process according to claim 30, wherein:
when the polyethylene is high-density polyethylene,

(a) the polyamide formed at step (ii) displays an increased elongation at break of compared to the high-density polyethylene;

(b) the polyamide formed at step (ii) displays an increased tensile strength compared to the high-density polyethylene;

(c) the polyamide formed at step (ii) displays an increased water contact angle compared to the high-density polyethylene; and/or

(d) the polyamide formed at step (ii) displays an aggregated induced emission (AIE) effect-like fluorescence behavior when irradiated at 390 nm.