TEREPHTHALIC ACID ESTERS FORMATION

CROSS-REFERENCE

[0001] This application claims the benefit of U. S. Provisional Application Serial No. 62/689,597 filed June 25, 2018 which is hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present disclosure relates to the formation of ester derivatives from polyesters and more specifically to the formation of terephthalic acid esters from polyethylene terephthalate (PET). The present disclosure also relates to the formation of dimethyl terephthalate (DMT).

BACKGROUND OF THE INVENTION

[0003] The polyethylene terephthalate (PET) bottle resin market has been growing strongly as PET resins have replaced glass in carbonated soft drink, bottled water and food containers.

[0004] Dimethyl terephthalate (DMT) is primarily used in the manufacture of polyethylene terephthalate (PET) for fiber, film, container plastics, and specialty plastics applications.

[0005] The largest polyester sector is the fibers market where it is used to make clothes, home textiles such as sheets and curtains, carpets and rugs, and industrial products such as tire cord, seat belts, hoses and ropes. PET film is utilized in electrical applications such as dielectric metal foil capacitors and for food packaging.

[0006] The growth in polyester has not been converted into DMT demand. For most grades of polyester used in textiles and food and beverage containers, it is more economical to use purified terephthalic acid rather than DMT.

SUMMARY

[0007] Disclosed herein is a process for the depolymerization of polyethylene terephthalate (PET) to form a terephthalate; the process comprising admixing polyethylene terephthalate (PET) with a mixture comprising a glycoxide.

[0007a] In an aspect of the present disclosure, there is provided a process for the depolymerization of polyethylene terephthalate (PET) to form a terephthalate; the process comprising:

(i) admixing the polyethylene terephthalate (PET) with a first solvent that is methanol to yield a first mixture;

(ii) adding a glycoxide to the first mixture;

(iii) adding a second solvent that is methanol; and

(iv) admixing;

thereby forming the terephthalate.

[0008] In some examples of the process, the mixture further comprises a solvent.

[0009] In some examples of the process, the solvent is selected from methanol, ethanol, n-propanol, isopropanol, t-butanol, ethylene glycol, glycerol, cyclohexane-1,4-dimethanol, phenol, benzyl alcohol, and any combinations thereof. In some examples of the process, the solvent is methanol.

[0010] In some examples of the process, the solvent is added to the polyethylene terephthalate (PET) prior to the addition of the glycoxide.

[0011] In some examples of the process, the polyethylene terephthalate (PET) is mixed with the solvent prior to the addition of the glycoxide for about 15 mins to about 120 mins. In some examples of the process, the polyethylene terephthalate (PET) is mixed with the solvent prior to the addition of the glycoxide for about 60 min.

[0012] In some examples of the process, the polyethylene terephthalate (PET) is mixed with the solvent prior to the addition of the glycoxide at a temperature between about 50 °C to about 100 °C. In some examples of the process, the polyethylene terephthalate (PET) is mixed with the solvent prior to the addition of the glycoxide at a temperature of about 60 °C.

[0013] In some examples of the process, the terephthalate is dimethyl terephthalate (DMT).

[0014] In some examples of the process, the glycoxide is sodium glycoxide. In some examples of the process, the glycoxide is mono sodium glycoxide. In some examples of the process, sodium glycoxide is provided as a suspension.

[0015] In some examples of the process, the mono sodium glycoxide suspension is prepared by a process comprising:

a) heating mono ethylene glycol;

b) adding sodium hydroxide thereby forming mono sodium glycoxide;

c) drying the mono sodium glycoxide;

d) suspending the dried mono sodium glycoxide into a suspending solvent; and

e) aging the suspension.

[0016] In some examples of the process, step (a) is performed at a temperature between about 70 °C to about 100 °C. In some examples of the process, step (a) is performed at a temperature of about 90 °C.

[0017] In some examples of the process, the ratio of mono sodium glycoxide to the suspending solvent is between about 0.05:1 to about 0.5: 1 (mol/mol).

[0018] In some examples of the process, the ratio of mono sodium glycoxide to the suspending solvent is about 0.2:1 (mol/mol).

[0019] In some examples of the process, the suspending solvent is methanol.

[0020] In some examples of the process, the suspension is aged for about 1-14 days. In some examples of the process, the suspension is aged for about 1-7 days. In some examples of the process, the suspension is aged for about 7 days.

[0021] In some examples of the process, the ratio of glycoxide to polyethylene terephthalate (PET) is between about 1:2 and about 1:20 (mol/mol).

[0022] In some examples of the process, the ratio of glycoxide to polyethylene terephthalate (PET) is between about 1:5 and about 1:20 (mol/mol).

[0023] In some examples of the process, the ratio of glycoxide to polyethylene terephthalate (PET) is between about 1:10 and about 1:20 (mol/mol).

[0024] In some examples of the process, the ratio of glycoxide to polyethylene terephthalate (PET) is between about 1:10 and about 1:15 (mol/mol).

[0025] In some examples of the process, the terephthalate is obtained in at least about 90 mol% yield. In some examples of the process, the terephthalate is obtained in at least about 95 mol% yield. In some examples of the process, the terephthalate is obtained in at least about 99 mol% yield.

[0026] In some examples of the process, the process further yields mono ethylene glycol. In some examples of the process, the mono ethylene glycol is obtained in at least about 80 mol% yield. In some examples of the process, the mono ethylene glycol is obtained in at least about 85 mol% yield.

[0027] Disclosed herein is a process for the depolymerization of polyethylene terephthalate (PET) to form a terephthalate; the process comprising:

(i) admixing the polyethylene terephthalate (PET) with a first solvent to yield a first mixture;

(ii) adding a glycoxide to the first mixture;

(iii) adding a second solvent; and

(iv) admixing;

thereby forming the terephthalate.

[0028] In some examples of the process, the terephthalate is dimethyl terephthalate (DMT).

[0029] In some examples of the process, the first solvent is selected from methanol, ethanol, n-propanol, isopropanol, t-butanol, ethylene glycol, glycerol, cyclohexane-1,4-dimethanol, phenol, benzyl alcohol, and any combinations thereof. In some examples of the process, the first solvent is methanol.

[0030] In some examples of the process, step (i) is performed for about 15 mins to about 120 mins. In some examples of the process, step (i) is performed for about 60 min.

[0031] In some examples of the process, step (i) is performed at a temperature between about 50 °C to about 100 °C. In some examples of the process, step (i) is performed at a temperature of about 60 °C.

[0032] In some examples of the process, a portion of the first solvent is removed prior to step (ii) to yield a second mixture.

[0033] In some examples of the process, the second mixture is heated at a temperature between about 70 °C to about 100 °C.

[0034] In some examples of the process, the second mixture is heated at a temperature of about 85 °C.

[0035] In some examples of the process, the glycoxide is sodium glycoxide. In some examples of the process, the glycoxide is mono sodium glycoxide. In some examples of the process, the mono sodium glycoxide is provided as a suspension in a suspending solvent.

[0036] In some examples of the process, the mono sodium glycoxide suspension is prepared by a process comprising:

a) heating mono ethylene glycol;

b) adding sodium hydroxide thereby forming mono sodium glycoxide;

c) drying the mono sodium glycoxide;

d) suspending the dried mono sodium glycoxide in a suspending solvent; and

e) aging the suspension.

[0037] In some examples of the process, step (a) is performed at a temperature between about 70 °C to about 100 °C. In some examples of the process, step (a) is performed at a temperature of about 90 °C.

[0038] In some examples of the process, the ratio of mono sodium glycoxide to the suspending solvent is between about 0.05:1 to about 0.5: 1 (mol/mol).

[0039] In some examples of the process, the ratio of mono sodium glycoxide to the suspending solvent is about 0.2:1 (mol/mol).

[0040] In some examples of the process, the suspending solvent is methanol.

[0041] In some examples of the process, the suspension is aged for about 1-14 days. In some examples of the process, the suspension is aged for about 1-7 days. In some examples of the process, the suspension is aged for about 7 days.

[0042] In some examples of the process, the ratio of glycoxide to polyethylene terephthalate (PET) is between about 1:2 and about 1:20 (mol/mol). In some examples of the process, the ratio of glycoxide to polyethylene terephthalate (PET) is between about 1:5 and about 1:20 (mol/mol). In some examples of the process, the ratio of glycoxide to polyethylene terephthalate (PET) is between about 1:10 and about 1:20 (mol/mol). In some examples of the process, the ratio of glycoxide to polyethylene terephthalate (PET) is between about 1:10 and about 1:15 (mol/mol).

[0043] In some examples of the process, the second solvent is selected from methanol, ethanol, n-propanol, isopropanol, t-butanol, ethylene glycol, glycerol, cyclohexane-1,4-dimethanol, phenol, benzyl alcohol, and any combinations thereof. In some examples of the process, the second solvent is methanol.

[0044] In some examples of the process, step (iv) is performed for about 60 mins to about 600 mins. In some examples of the process, step (iv) is performed for about 360 min.

[0045] In some examples of the process, step (iv) is performed at a temperature between about 70 °C to about 100 °C. In some examples of the process, step (iv) is performed at a temperature of about 85 °C.

[0046] In some examples of the process, the process further comprises step (v) filtrating the terephthalate.

[0047] In some examples of the process, the terephthalate is obtained in at least about 90 mol% yield. In some examples of the process, the terephthalate is obtained in at least about 95 mol% yield. In some examples of the process, the terephthalate is obtained in at least about 99 mol% yield.

[0048] In some examples of the process, the process further yields mono ethylene glycol. In some examples of the process, the mono ethylene glycol is obtained in at least about 80 mol% yield. In some examples of the process, the mono ethylene glycol is obtained in at least about 85 mol% yield.

[0049] Also disclosed herein is process for preparing a mono sodium glycoxide suspension; the process comprising:

a) heating mono ethylene glycol;

b) adding sodium hydroxide thereby forming mono sodium glycoxide;

c) drying the mono sodium glycoxide;

d) suspending the dried mono sodium glycoxide into a suspending solvent; and

e) aging the suspension.

[0050] In some examples of the process, step (a) is performed at a temperature between about 70 °C to about 100 °C. In some examples of the process, step (a) is performed at a temperature of about 90 °C.

[0051] In some examples of the process, the ratio of mono sodium glycoxide to the suspending solvent is between about 0.05:1 to about 0.5: 1 (mol/mol). In some examples of the process, the ratio of mono sodium glycoxide to the suspending solvent is about 0.2:1 (mol/mol).

[0052] In some examples of the process, the suspending solvent is methanol.

[0053] In some examples of the process, the suspension is aged for about 1-14 days. In some examples of the process, the suspension is aged for about 1-7 days. In some examples of the process, the suspension is aged for about 7 days.

DETAILED DESCRIPTION OF THE INVENTION

[0054] Dimethyl terephthalate (DMT) is used in the production of polyesters, including polyethylene terephthalate (PET), polytrimethylene terephthalate (PTT), and polybutylene terephthalate (PBT). Because DMT is volatile, it is an intermediate in some schemes for the recycling of PET, e.g. from plastic bottles. Hydrogenation of DMT affords the diol 1, 4-cyclohexanedimethanol, which is a useful monomer in the formation of polyester resins.

[0055] DMT has been produced in a number of ways. Conventionally and still of commercial value is the direct esterification of terephthalic acid. Alternatively, it is prepared by alternating oxidation and methyl-esterification steps from para-xylene via methyl para-toluate. The method for the production of DMT from para-xylene and methanol consists of four major steps: oxidation, esterification, distillation, and crystallization. A mixture of para-xylene and pare-toluic ester is oxidized with air in the presence of a transition metal catalyst (Co/Mn). The acid mixture resulting from the oxidation is esterified with methanol to produce a mixture of esters. The crude ester mixture is distilled to remove all the heavy boilers and residue produced; the lighter esters are recycled to the oxidation section. The raw DMT is then crystallized to remove DMT isomers, residual acids, and aromatic aldehydes.

[0056] An Improvement in DMT production from PET recycling: due to the growing use of PET and PETG in the packaging and fiber (carpet and other textile) industries there is a need for an efficient, low energy, high yielding, and cost effective way to form DMT from PET or PETG.

POLYESTERS

[0057] Described herein is a process for the transformation of a polyester into an ester derivative; the process comprising admixing the polyester with a mixture comprising a glycoxide.

[0058] In some embodiments, the polyester is selected from polyethylene terephthalate (PET), poly(ethylene glycol-*co*-1,4-cyclohexanedimethanol terephthalate) (PETG), polyglycolide or polyglycolic acid (PGA), polylactic acid (PLA), polycaprolactone (PCL), polyhydroxybutyrate (PHB), polyethylene adipate (PEA), polybutylene succinate (PBS), poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), polybutylene terephthalate (PBT), polytrimethylene terephthalate (PTT), polyethylene naphthalate (PEN), Vectran®, cutin, and any combinations thereof.

CLAIMS

What is claimed is:

1. A process for the depolymerization of polyethylene terephthalate (PET) to form a terephthalate; the process comprising:
   (i) admixing the polyethylene terephthalate (PET) with a first solvent that is methanol to yield a first mixture;
   (ii) adding a glycoxide to the first mixture;
   (iii) adding a second solvent that is methanol; and
   (iv) admixing;
   thereby forming the terephthalate.
2. The process of claim 1, wherein the terephthalate is dimethyl terephthalate (DMT).
3. The process of claim 1, wherein step (i) is performed for about 15 mins to about 120 mins.
4. The process of claim 1, wherein step (i) is performed at a temperature between about 50 °C to about 100 °C.
5. The process of claim 1, wherein a portion of the first solvent is removed prior to step (ii) to yield a second mixture.
6. The process of claim 5, wherein the second mixture is heated at a temperature between about 70 °C to about 100 °C.
7. The process of claim 1, wherein the glycoxide is mono sodium glycoxide.
8. The process of claim 7, wherein the mono sodium glycoxide is provided as a suspension in a suspending solvent.
9. The process of claim 8, wherein the mono sodium glycoxide suspension is prepared by a process comprising:
   a) heating mono ethylene glycol;
   b) adding sodium hydroxide thereby forming mono sodium glycoxide;
   c) drying the mono sodium glycoxide;
   d) suspending the dried mono sodium glycoxide in a suspending solvent; and
   e) aging the suspension.
10. The process of claim 9, wherein step (a) is performed at a temperature between about 70 °C to about 100 °C.
11. The process of claim 9, wherein the ratio of mono sodium glycoxide to the suspending solvent is between about 0.05:1 to about 0.5: 1 (mol/mol).
12. The process of claim 9, wherein the suspending solvent is methanol.
13. The process of claim 9, wherein the suspension is aged for about 1-14 days.
14. The process of claim 1, wherein the ratio of glycoxide to polyethylene terephthalate (PET) is between about 1:2 and about 1:20 (mol/mol).

15. The process of claim 1, wherein step (iv) is performed for about 60 mins to about 600 mins.
16. The process of claim 1, wherein step (iv) is performed at a temperature between about 70 °C to about 100 °C.
17. The process of claim 1, wherein the terephthalate is obtained in at least about 90 mol% yield.
18. The process of claim 1, wherein the process further yields mono ethylene glycol.