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(54) Title: SOLID STATE CONVERSION OF BIO-BASED ORGANIC SALTS TO GENERATE POLYMER COATINGS

(57) Abstract: A polyamide is provided that is prepared from the solid-state polymerization of a salt that includes glucaric acid. The polyamide includes units derived from the polymerization of glucarate and units derived from the polymerization of a polyamine. The polyamide may advantageously be a thermoset polymer. Advantageously, the salt that includes glucaric acid may be processed as a waterborne coating.



SOLID STATE CONVERSION OF BIO-BASED ORGANIC SALTS TO GENERATE POLYMER COATINGS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from U.S. provisional patent application Ser. No. 62/322,956 filed on Apr. 15, 2016, which is incorporated herein by reference in its entirety.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] This invention was made with government support under NSF STTR 1521172 awarded by National Science Foundation. The government has certain rights in the invention.

FIELD OF THE INVENTION

[0003] Embodiments are directed to polyamides prepared using glucaric acid and methods of preparing polyamides using glucaric acid. Methods of preparing polyamides include the solid state polymerization of a salt prepared from glucaric acid and a polyamine.

BACKGROUND OF THE INVENTION

[0004] Biobased precursors are desirable for use in chemical reactions due to their wide availability and renewability. Exemplarily biobased precursor include carbohydrates, which may be polymerized into polysaccharides. Certain carbohydrates may also be modified to be suitable in other reactions. For example an aldose may be converted to aldaric acid through an oxidation reactions.

[0005] One area of research where biobased precursors, such as aldaric acids, have been employed is the production of polyamides. U.S. Pat. Nos 9,505,882, 5,473,035, and 5,434,233 disclose typical methods for preparing polyamides from aldaric acids. These polyamides are generally limited by a low molecular weight (<10 kDa) and are soluble in organic solvents such as dimethylsulfoxide. The low molecular weights and high solubility make the polyamides poor choices for uses such as coatings, where a thermoset polymer would be preferred. Further, the methods require multiple steps and reagents to prepare the polyamide. For example, the aldaric acids must first be converted into an ester or an ester-lactone.

[0006] Presently, there is a need in the art for polymers prepared by molecules available as biobased precursor that do not suffer from one or more of the disadvantages of the prior art discussed above.

SUMMARY OF THE INVENTION

[0007] A first embodiment provides a thermoset polyamide comprising: units derived from the polymerization of glucarate and units derived from the polymerization of a polyamine.

[0008] A second embodiment provides thermoset polyamide as in the first embodiment, where the thermoset polyamide is insoluble in water.

[0009] A third embodiment provides thermoset polyamide as in the first or second embodiment, where the thermoset polyamide is insoluble in dimethylsulfoxide.

[0010] A fourth embodiment provides thermoset polyamide as in of the first through third embodiments, where the polyamine has two or more primary amine groups.

[0011] A fifth embodiment provides thermoset polyamide as in of the first through fourth embodiments, where the polyamine has three or more primary amine groups.

[0012] A sixth embodiment provides thermoset polyamide as in of the first through fifth embodiments, where the thermoset polyamide includes units derived from the polymerization of a polyamine with 2 primary amine groups and units derived from the polymerization of a polyamine with 3 primary amine groups.

[0013] A seventh embodiment provides thermoset polyamide as in of the first through sixth embodiments, where the polyamine polymer includes one or more polyamines selected from the group consisting of linear polyamines with two primary amine groups, cyclic polyamines with two primary amine groups, cyclic polyamines with three primary amine groups, and branched polyamines with three primary amine groups.

[0014] An eighth embodiment provides thermoset polyamide as in of the first through seventh embodiments, where the polyamine with two primary amine groups includes one or more polyamines selected from the group consisting of 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,2-diaminobutane, 1,3-diaminobutane, 1,4-diaminobutane, 1,2-diaminopentane, 1,3-diaminopentane, 1,4-diaminopentane, 1,5-diaminopentane, 1,2-diaminohexane, 1,3-diaminohexane, 1,4-diaminohexane, 1,5-diaminohexane, 1,6-diaminohexane, 1,2-diaminoheptane, 1,3-diaminoheptane, 1,4-diaminoheptane, 1,5-diaminoheptane, 1,6-diaminoheptane, 1,7-diaminoheptane, 1,2-

diaminooctane, 1,3-diaminooctane, 1,4-diaminooctane, 1,5-diaminooctane, 1,6-diaminooctane, 1,7-diaminooctane, and 1,7-diaminooctane.

[0015] A ninth embodiment provides thermoset polyamide as in of the first through eighth embodiments, where the cyclic polyamines with two primary amine groups includes one or more polyamines selected from the group consisting of 1,2-cyclopentanediamine, 1,3-Cyclopentanediamine, 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, and 1,4-diaminocyclohexane.

[0016] A tenth embodiment provides thermoset polyamide as in of the first ninth through embodiments, where the cyclic polyamines with three primary amine is 1,3,5-triaminocyclohexane.

[0017] An eleventh embodiment provides thermoset polyamide as in of the first tenth through embodiments, where the branched polyamines with three primary amine groups includes one or more polyamines selected from the group consisting of tris(2-aminomethyl)amine, tris(2-aminoethyl)amine, tris(2-aminopropyl)amine, tris(2-aminobutyl)amine, and tris(2-aminopentyl)amine.

[0018] A twelfth embodiment provides a method of preparing a polyamide comprising: preparing a solid salt from glucaric acid and a polyamine; and inducing the polymerization of the solid salt.

[0019] A thirteenth embodiment provides a method as in the twelfth embodiment, where the step of inducing the polymerization is performed by heating the solid salt.

[0020] A fourteenth embodiment provides a method as in the twelfth or thirteenth embodiments, where the step of inducing the polymerization is performed by exposing the solid salt to microwaves.

[0021] A fifteenth embodiment provides a method as in any of the twelfth through fourteenth embodiments where the solid salt is prepared by combining free glucaric acid in solution with a polyamine to prepare a glucarate-polyamine salt in solution; optionally purifying the glucarate-polyamine salt, and then drying the glucarate-polyamine salt in solution.

[0022] A sixteenth embodiment provides a method of preparing a polyamide comprising providing an aqueous solution containing the salt product of a glucaric acid and a polyamine; removing the water from the aqueous solution to prepare a solid salt; and inducing the polymerization of a solid salt.

[0023] A seventeenth embodiment provides a method as in the sixteenth embodiment, where the aqueous solution containing the salt product of a glucaric acid and a polyamine is from about 15% to about 70% by weight the salt product of a glucaric acid and a polyamine.

[0024] An eighteenth embodiment provides a method as in the sixteenth or seventeenth embodiments, where the aqueous solution containing the salt product of a glucaric acid and a polyamine is from about 20% to about 50% by weight the salt product of a glucaric acid and a polyamine.

[0025] A nineteenth embodiment provides a method as in any of the sixteenth through eighteenth embodiments, further comprising the step of coating a substrate with the aqueous solution containing the salt product of a glucaric acid and a polyamine.

[0026] A twentieth embodiment provides a method as in any of the sixteenth through nineteenth embodiments, where the substrate is a material selected from the group consisting of silica oxide, glass, ceramics, and metal.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

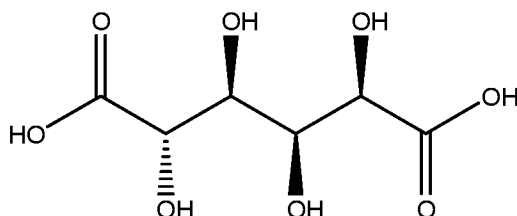
INTRODUCTION

[0027] Embodiments are based, at least in part, on the discovery of a solid-state process for producing a polyamide using glucaric acid. In particular embodiments, a solid salt may be prepared from glucaric acid and a polyamine. The solid salt may then subsequently be polymerized to prepare a polyamide. It has surprisingly been found that polyamides may be prepared from glucaric acid using a solid state process, while other, similar diacids, such as mucic or adipic acid, are not suitable for use in preparing polymers. The polyamides prepared from the solid state polymerization of the salt product of glucaric acid and a polyamine may advantageously be used to prepare a thermoset polymer. The use of a salt product of glucaric acid and a polyamine also allows for a waterborne process for preparing polyamides. Suitable uses for the polyamide prepared using glucaric acid include coatings.

[0028] In one or more embodiments, the polyamide polymer may be prepared from the salt product of glucaric acid and a polyamine. The resulting polymer will include units derived from the polymerization of glucarate and units derived from the polymerization of a polyamine. As used herein, the term "derived from" may be used to describe the portion of a polymer (i.e. mer unit) that results from the polymerization of a monomer. For

example, the resulting polyamide polymer prepared using a polyamine may be described as including a unit derived from polyamine.

[0029] Those skilled in the art will appreciate that glucaric acid, which may also be referred to as saccharic acid, may be defined by the formula



The salt form of glucaric acid may be referred to as a glucarate. For the purposes of this specification, the salt formed from the combination of glucaric acid and a polyamine may be referred to as the glucarate-polyamine salt or the salt product of glucaric acid and a polyamine.

[0030] Polyamines for use in preparing polyamides include amine compounds with two or more primary amine groups. Suitable polyamines may include small molecule polyamines and polymeric polyamines.

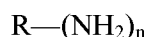
[0031] In one or more embodiments, where the polyamines employed to prepare the polyamide all have 2 primary amine groups, a linear polyamide may be prepared. In other embodiments, where one or more of the polyamines employed include 3 or more primary amine groups, a crosslinked polyamide may be prepared.

[0032] In one or more embodiments, more than one polyamine may be used to the polyamide. In certain embodiments, a polyamine with 2 primary amine groups may be used along with a polyamine with 3 or more primary amine groups. In these or other embodiments, the polyamine with 3 or more primary amine groups may have 3 primary amine groups, in other embodiments 4 primary amine groups, in other embodiments 5 primary amine groups, in other embodiments 6 primary amine groups, in other embodiments 10 primary amine groups. In certain embodiments, the polyamine with 3 or more primary amine groups may be a polymeric polyamine.

[0033] In one or more embodiments, where polyamide is prepared using a mixture of polyamines with 2 primary amine groups and polyamines with 3 or more primary amine groups, the mixture may be characterized by the molar percentage of primary amines of the polyamine with 2 primary amine groups out of the totality of primary amines from all of the polyamines. In one or more embodiments, the molar percentage primary amines

from the polyamines with 2 primary amine groups in the totality of primary amines is from about 1% to about 99%, in other embodiments from about 10% to about 90%, in other embodiments from about 20% to about 80%, in other embodiments from about 30% to about 70%, and in other embodiments from about 40% to about 60%.

[0034] In one or more embodiments, a small molecule polyamine may be defined by the formula:



where n is at least 2 and R is an organic group having a valency equal to n. In one or more embodiments, the organic group, R, may be a linear, branched, or cyclic hydrocarbon groups or substituted hydrocarbon groups. The organic group may contain from 1 carbon atom, or the appropriate minimum number of carbon atoms to form the group. Suitable substituted hydrocarbon groups include groups where one or more carbon atoms is substituted with a nitrogen. In one or more embodiments, a nitrogen-substituted hydrocarbon group may be used to prepare branched groups. In one or more embodiments, n may be from 2 to about 20, in other embodiments from 3 to about 15, and in other embodiments from about 5 to about 10. In other embodiments, the organic group, R, may contain aromatic groups selected from (C₆-C₁₀)aryl, (C₆-C₁₀)aryl(C₁-C₃)alkyl, (C₆-C₁₀)aryloxy(C₁-C₃)alkyl, (C₅-C₁₀)heteroaryloxy(C₁-C₃)alkyl, (C₆-C₁₀)aryloxy, (C₅-C₁₀)heteroaryloxy. In other embodiments, the organic group, R, may contain oxygen functional groups as ethers, esters, acids, and alcohols. In other embodiments, the organic group, R, may contain nitrogen functional groups where only one or zero hydrogen atoms are bonded to the nitrogen.

[0035] In certain embodiments, the polyamine may be a polymeric polyamine. Suitable polymeric amines include linear, branched, or dendrimeric polyalkylenimines. In one or more embodiments, the polymeric polyamine may have from about 2 to about 1000, in other embodiments from about 3 to about 900, in other embodiments from about 10 to about 850, in other embodiments about 25 to about 700, in other embodiments about 50 to about 600, in other embodiments about 100 to about 500, and in other embodiments from about 200 to about 400 amine groups. Suitable polyalkylenimines include linear or branched polyethyleneimine.

[0036] Examples of linear polyamines with two primary amine groups include, but are not limited to 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,2-

diaminobutane, 1,3-diaminobutane, 1,4-diaminobutane, 1,2-diaminopentane, 1,3-diaminopentane, 1,4-diaminopentane, 1,5-diaminopentane, 1,2-diaminohexane, 1,3-diaminohexane, 1,4-diaminohexane, 1,5-diaminohexane, 1,6-diaminohexane, 1,2-diaminoheptane, 1,3-diaminoheptane, 1,4-diaminoheptane, 1,5-diaminoheptane, 1,6-diaminoheptane, 1,7-diaminoheptane, 1,2-diaminooctane, 1,3-diaminooctane, 1,4-diaminooctane, 1,5-diaminooctane, 1,6-diaminooctane, 1,7-diaminooctane, and 1,7-diaminooctane.

[0037] Examples of cyclic polyamines with two primary amine groups include, but are not limited to, 1,2-cyclopentanediamine, 1,3-cyclopentanediamine, 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, and 1,4-diaminocyclohexane.

[0038] Examples of cyclic polyamines with three primary amine groups include, but are not limited to, 1,3,5-triaminocyclohexane.

[0039] Examples of branched polyamines with three primary amine groups include, but are not limited to, tris(2-aminomethyl)amine, tris(2-aminoethyl)amine, tris(2-aminopropyl)amine, tris(2-aminobutyl)amine, and tris(2-aminopentyl)amine.

[0040] In one or more embodiments, the polymeric polyamine may be characterized by a number average molecular weight, which may be determined through gel permeation chromatography (GPC). In one or more embodiments, the polymeric polyamine has a number average molecular weight of at least 400 g/mol, in other embodiments at least 600 g/mol, and in other embodiments at least 1000 g/mol. In one or more embodiments, the polymeric polyamine has a number average molecular weight of at most 20,000 g/mol, in other embodiments at most 15,000 g/mol, and in other embodiments at most 10,000 g/mol. In one or more embodiments, the polymeric polyamine has a number average molecular weight that is from about 400 g/mol to about 20,000 g/mol, in other embodiments that is from about 600 g/mol to about 15,000 g/mol, and in other embodiments that is from about 1000 g/mol to about 10,000 g/mol.

SALT FORMATION

[0041] In one or more embodiments, a glucarate-polyamine salt may be prepared by mixing glucaric acid and a polyamine in an aqueous solution. Methods for preparing glucarate-polyammonium salts are described in U.S. Pat. No. 9,505,882 and U.S. Pat. No. 6,894,135, both of which have been incorporated herein by reference. In certain embodiments, a solution of glucaric acid in water may be prepared, and then the

polyamine may be added to the solution of glucaric acid either in a neat fashion or as a solution of polyamine in water.

[0042] Those skilled in the art will appreciate that glucarate salts are readily available. These salts may be converted to glucaric acid through the use of an ion-exchange resin. In these or other embodiments, the glucarate salts may be loaded onto the ion exchange resin and then removed as glucaric acid in a filtrate and/or wash solution. In one or more embodiments, the polyamine may be added directly to the filtrate and/or wash solution containing glucaric acid. In other embodiments, the filtrate and/or wash solution containing glucaric acid may be concentrated or diluted prior to adding the polyamine.

[0043] In one or more embodiments, the respective amounts of glucaric acid and polyamine combined to prepare a glucarate-polyamine salt may be characterized by the ratio of carboxylic acid groups in the glucaric acid to primary amine groups in the polyamine compound. In one or more embodiments, the ratio of carboxylic acid groups to primary amine groups may be about 1:1. In certain embodiments, the ratio of carboxylic acid groups to primary amine groups may be from about 1:0.8 to about 0.8:1, in other embodiments from about 1:0.9 to about 0.9:1, and in other embodiments from about 1:0.95 to about 0.95:1.

[0044] The concentration at which the glucaric acid and polyamine combined to prepare aqueous solution that includes glucaric acid and polyamine is not particularly limited. In certain embodiments, for convenience, where the glucaric acid is converted from a glucarate salt through the use of an ion-exchange resin, the polyamine may be added directly to the filtrate and/or wash solution containing glucaric acid without concentrating or diluting the glucaric acid solution.

[0045] After the glucaric acid and polyamine are combined the aqueous solution that includes glucaric acid and polyamine should be mixed or agitated for a sufficient amount of time to allow the glucarate-polyamine salt to form. In one or more embodiments, the aqueous solution that includes glucaric acid and polyamine may be mixed for at least 2 hours, in other embodiments at least 2.5 hours, and in other embodiments at least 3 hours. In one or more embodiments, the aqueous solution that includes glucaric acid and polyamine may be mixed for at most 24 hours, in other embodiments at most 18 hours, and in other embodiments at most 12 hours. In one or more embodiments, the aqueous solution that includes glucaric acid and polyamine may be mixed for about 2 hours to about 24 hours, in other embodiments for about 2.5 hours to about 18 hours, and in other embodiments for about 3 hours to about 12 hours.

[0046] After the glucaric acid and polyamine have been mixed to prepare the glucarate-polyamine salt, the glucarate-polyamine salt may optionally be purified. In certain embodiments, the glucarate-polyamine salt may be purified by dissolving the solid salt in hot water and then subsequently precipitating in an organic solvent such as methanol.

[0047] Prior to use the glucarate-polyamine salt solution may be dried to a solid salt or concentrated. A drying or concentrating step may be performed by any conventional means. Exemplary methods of drying or concentrating the glucarate-polyamine salt solution include, rotary evaporator, room temperature evaporation, and vacuum drying.

[0048] In one or more embodiments, where the glucarate-polyamine salt solution is concentrated prior to use, the concentrated glucarate-polyamine salt solution may be characterized by the weight percent of the glucarate-polyamine salt in solution. In one or more embodiments, the glucarate-polyamine salt is from about 15% to about 70% by weight, in other embodiments from about 20% to about 50% by weight, and in other embodiments from about 25% to about 40% by weight of the solution.

POLYMERIZATION

[0049] The polymerization of the glucarate-polyamine salt into a polyamide may be performed as a solid-state polymerization. In these embodiments, the polymerization of the glucarate-polyamine salt may be induced with the glucarate-polyamine salt in the solid state. In one or more embodiments, the polymerization may be induced by heating the solid glucarate-polyamine salt. Polymerization may also be included through the use of microwaves, which may be used separately or in addition to heating heat solid glucarate-polyamine salt.

[0050] Heat treatment of the solid glucarate-polyamine salt may be performed through convection heating such as using an oven, heat gun, hot air blower, or immersion in a heated liquid bath where the liquid does not dissolve the salt or the polymer. In one or more embodiments, the solid glucarate-polyamine salt may be heated at a temperature of about 80 °C to about 250 °C, in other embodiments from about 150 °C to about 220 °C, and in other embodiments from about 120 °C to about 190 °C.

[0051] In one or more embodiments, the solid glucarate-polyamine salt may be heated from about 5 minutes to about 180 minutes, in other embodiments from about 5 minutes to about 120 minutes, and in other embodiments from about 10 minutes to about 60 minutes.

In one or more embodiments, where microwaves are employed to induce the

polymerization of the solid glucarate-polyamine salt, the solid glucarate-polyamine salt may be exposed to radiation with frequencies from 1 GHz to 20 GHz. In one or more embodiments, the solid glucarate-polyamine salt may be exposed to microwaves from about 0.2 minutes to about 10 minutes, in other embodiments from about 0.5 minutes to about 5 minutes, and in other embodiments from about 0.75 minutes to about 2 minutes. In certain embodiments, where the solid glucarate-polyamine salt is both heated and exposed to microwaves to induce polymerization, the shorter times indicated for polymerization using microwaves may be appropriate.

INDUSTRIAL APPLICABILITY

[0052] As noted above, the polyamides are particularly useful as coatings. The polyamides may be used to provide chemical resistance and/or protection from corrosion on a wide array of substrates. Suitable substrates that may be coated with the polyamides are those that may be subjected to the heat required or microwaves required to induce polymerization of the solid glucarate-polyamine salt. Exemplary substrates include silica oxide, glass, ceramics, or metals such as aluminum or stainless steel.

[0053] In one or more embodiments, the glucarate-polyamine salt may be applied as a waterborne coating to the substrate. The coating may be applied to the substrate by various means including flow-coating, draw-down bar, doctor blade, dip coating, spraying, and spin-coating. After the waterborne glucarate-polyamine salt is coated to the substrate it may be dried by any conventional means and then polymerized. In one or more embodiments, the waterbourne coating is organic solvent free (such as volatile organic solvents) or essentially organic solvent free.

[0054] In one or more embodiments, the concentrated glucarate-polyamine salt solution may be coated onto the substrate. In one or more embodiments, the concentrated glucarate-polyamine salt solution may be characterized by the weight percent of the glucarate-polyamine salt in solution. In one or more embodiments, the glucarate-polyamine salt is from about 15% to about 70% by weight, in other embodiments from about 20% to about 50% by weight, and in other embodiments from about 25% to about 40% by weight of the solution.

[0055] In certain embodiments, the polyamide may be used in a layered coating. In these or other embodiments, one or more layers of polyamide coating may be added (with optional non-polyamide intermediate layers) over a polyamide coating. In these or other embodiments, a substrate is coated with a glucarate-polyamine salt which is then

polymerized to prepare a first polyamide coating. An additional layer of glucarate-polyamine salt may then be coated on the first polyamide coating, which is then polymerized to prepare a second polyamide coating. In one or more embodiments, a layered polyamide coating may have from about 1 to about 20 coating layers, in other embodiments from about 1 to about 10 coatings, and in other embodiments from about 2 to about 3 coatings.

PROPERTIES

[0056] In one or more embodiments, the polyamide may be characterized by an advantageous resistance to solvent, which may be measured by solvent rub such as ASTM D5402-15. In one or more embodiments, the polyamide was unchanged in appearance after at least 25, rubs in other embodiments at least 50 rubs, and in other embodiments at least 100 rubs using toluene. In one or more embodiments, the polyamide was unchanged in appearance after at least 25, rubs in other embodiments at least 50 rubs, and in other embodiments at least 100 rubs using methyl ethyl ketone. In one or more embodiments, the polyamide was unchanged in appearance after at least 25, rubs in other embodiments at least 50 rubs, and in other embodiments at least 100 rubs using dimethylsulfoxide. In one or more embodiments, the polyamide was unchanged in appearance after at least 25, rubs in other embodiments at least 50 rubs, and in other embodiments at least 100 rubs using N,N-dimethylformamide. In one or more embodiments, the polyamide was unchanged in appearance after at least 25, rubs in other embodiments at least 50 rubs, and in other embodiments at least 100 rubs using water.

[0057] In one or more embodiments, the polyamide may be characterized by an advantageous insolubility in organic solvents or water, which may be determined by dipping a sample of the polyamide in a solvent and viewing the sample for visual damage after an hour. In one or more embodiments, the polyamide may be insoluble in one or more of the following solvents 1,4-dioxane, ethanol, acetone, hexane, acetonitrile, methyl ethyl ketone, chloroform, tetrahydrofuran, N,N-dimethylformamide, toluene, dimethylsulfoxide, and water.

[0058] In one or more embodiments, the polyamide may be characterized by advantageously protecting substrates from corrosion, which may be measured by electrochemical impedance spectroscopy of the coating on the substrate of interest in 1M aqueous sodium chloride solution. In one or more embodiments, the polyamide is characterized by a corrosion resistance (absolute value of the impedance at 0.01 Hz) that is

at least 10^7 ohm/cm², in other embodiments at least 10^8 ohm/cm², and in other embodiments at least 10^9 ohm/cm². In these or other embodiments, the polyamide is characterized by a corrosion resistance that is at most 2×10^9 ohm/cm², in other embodiments at most 3×10^9 ohm/cm², and in other embodiments at most 9×10^9 ohm/cm². In certain embodiments, the polyamide is characterized by a corrosion resistance that is from about 5.7×10^9 ohm/cm² to about 8.2×10^9 ohm/cm², in other embodiments from about 2×10^8 ohm/cm² to about 2.5×10^9 ohm/cm², and in other embodiments from about 3×10^6 ohm/cm² to about 2×10^9 ohm/cm².

[0059] In one or more embodiments, the polyamide may be characterized by advantageous hardness, which may be measured by a pencil hardness test (ASTM 3363). In one or more embodiments, the polyamide is characterized by a hardness that achieves an F or better on the relative scale for ASTM method 3363.

[0060] The cross-hatch of the thermoset polyamide products described in Examples 1-4 was tested using was measured by ASTM D3359 method B. Each sample was tested three times. For each thermoset polyamide product the result of the test was 5B, which indicates good adhesion to the substrate, where the edges of the cuts are completely smooth, and none of the squares of the lattice is detached.

[0061] In one or more embodiments, the polyamide may be characterized by advantageous adhesion to a substrate, which may be measured by a cross-hatch test such as ASTM D3359-09 '2. In one or more embodiments, the polyamide exhibits good adhesion where all of the cuts after performing the cross-hatch test are completely smooth. In these or other embodiments, cross-hatch test of the polyamide exhibits good adhesion where all of the squares of the lattice are not detached after performing the cross-hatch test.

[0062] While particular embodiments of the invention have been disclosed in detail herein, it should be appreciated that the invention is not limited thereto or thereby inasmuch as variations on the invention herein will be readily appreciated by those of ordinary skill in the art. The scope of the invention shall be appreciated from the claims that follow.

EXAMPLES

Example 1 Poly(1,6-hexamethylene D-glucaramide) Themoset Polyamide Product

[0063] Step 1. 1,6-Hexamethylenediammonium D-glucarate. Cation exchange resin (DOWEX 50WX8-100, 43 mL was washed with deionized water 3 times.

Monopotassium D-glucaric acid (20.00 g, 80.57 mmol) was added to the resin in 100 mL of water and mixed for 10 minutes. The resin was removed by filtration and washed with water. The wash water was combined with the filtrate. 1,6-Hexamethylene (9.77g 84.1 mmol) was added to the filtrate and stirred for three hours. The solution was concentrated on a rotary evaporator. The 1,6-hexamethylenediammonium D-glucarate was precipitated by adding 200 mL of methanol to the concentration aqueous solution after stirring for 24 hours. The solid precipitate was recovered by filtration. The obtained salt was dissolved in hot water (17 mL), diluted with methanol (30 mL), and recrystallized for 24h. The recrystallized solid was recovered by filtration and dried in a vacuum oven for 24h.

[0064] Step 2. Poly(1,6-hexamethylene D-glucaramide) Themoset Polyamide Product. 1,6 hexamethylenediammonium D-glucarate was dissolved in deionized water to prepare a 30 wt% solution. The solution was flow coated onto aluminum panels at 5 mm/s at 85°C. After coating the films were annealed at 185°C for 1h in air.

Example 2 Poly(1,6-hexamethylene:tris(2-ethyl)amino (1:9) D-glucaramide)

Themoset Polyamide Product.

[0065] Step 1. 1,6-hexamethylenediammonium:tris(2-ethylammonium)amino (1:9) D-glucarate. Cation exchange resin (DOWEX 50WX8-100, 43 mL) was washed with deionized water 3 times. Monopotassium D-glucaric acid (10.00 g, 40.29 mmol) was added to the resin in 100 mL of water and mixed for 15 minutes. The resin was removed by filtration and washed with water. The wash water was combined with the filtrate. 1,6 hexamethylenediamine (4.4 g, 38 mmol) and tris(2-aminoethyl) amine (0.41g, 2.8 mmol) were added to the filtrate and stirred for three hours. The 1,6-hexamethylenediammonium:tris(2-ethylammonium)amino (1:9) D-glucarate was precipitated by adding methanol (100 mL) to the aqueous solution and stirring for 24 hours. The white, solid precipitate was filtered and dried for 24 hours under vacuum. The product (8g) was redissolved in water (12mL), diluted with methanol (30 mL), recrystallized for 24 h, filtered and dried under vacuum for 24h.

[0066] Step 2. Poly(1,6-hexamethylene:tris(2-ethyl)amino (1:9) D-glucaramide) Themoset Polyamide Product. 1,6-Hexamethylenediammonium:tris(2-ethylammonium)amino (1:9) D-glucarate was dissolved in deionized water to prepare a 30 wt% solution. The solution was flow coated onto aluminum panels at 5 mm/s at 85°C. After coating the films were annealed at 185°C for 1h in air.

Example 3 Poly(1,6-hexamethylene:tris(2-ethyl)amino (2:8) D-glucaramide)**Thermoset Polyamide Product.**

[0067] **Step 1. 1,6-hexamethylenediammonium:tris(2-ethylammonium)amino (2:8) D-glucarate.** Cation exchange resin (DOWEX 50WX8-100, 43 mL) was washed with deionized water 3 times. Monopotassium D-glucaric acid (10.00 g, 40.29 mmol) was added to the resin in 100 mL of water and mixed for 15 minutes. The resin was removed by filtration and washed with water. The wash water was combined with the filtrate. 1,6-hexamethylenediamine (3.9 g, 34 mmol) and tris(2-aminoethyl) amine (0.82 g, 5.6 mmol) were added to the filtrate and stirred for three hours. The 1,6-hexamethylenediammonium:tris(2-ethylammonium)amino (2:8) D-glucarate was precipitated by adding methanol (100 mL) to the aqueous solution and stirring for 24 hours. The white, solid precipitate was filtered and dried for 24 hours under vacuum. The product (10 g) was redissolved in water (12 mL), diluted with methanol (30 mL), recrystallized for 24 h, filtered and dried under vacuum for 24h.

[0068] **Step 2. Poly(1,6-hexamethylene:tris(2-ethyl)amino (2:8) D-glucaramide) Thermoset Polyamide Product.** 1,6-hexamethylenediammonium:tris(2-ethylammonium)amino (2:8) D-glucarate was dissolved in deionized water to prepare a 30 wt% solution. The solution was flow coated onto aluminum panels at 5 mm/s at 85°C. After coating the films were annealed at 185°C for 1h in air.

Example 4 Poly(1,6-hexamethylene:tris(2-ethyl)amino (5:5) D-glucaramide)**Thermoset Polyamide Product.**

[0069] **Step 1. 1,6-hexamethylenediammonium:tris(2-ethylammonium)amino (5:5) D-glucarate.** Cation exchange resin (DOWEX 50WX8-100, 43 mL) was washed with deionized water 3 times. Monopotassium D-glucaric acid (10.00 g, 40.29 mmol) was added to the resin in 100 mL of water and mixed for 15 minutes. The resin was removed by filtration and washed with water. The wash water was combined with the filtrate. 1,6-hexamethylenediamine (2.40 g, 20.69 mmol) and tris(2-aminoethyl) amine (2.04 g, 13.97 mmol) were added to the filtrate and stirred for three hours. The 1,6-hexamethylenediammonium:tris(2-ethylammonium)amino (5:5) D-glucarate was precipitated by adding methanol (100 mL) to the aqueous solution and stirring for 24 hours. The white, solid precipitate was filtered and dried for 24 hours under vacuum. The product (10 g) was redissolved in water (12 mL), diluted with methanol (30 mL), recrystallized for 24 h, filtered and dried under vacuum for 24h.

[0070] **Step 2. Poly(1,6-hexamethylene:tris(2-ethyl)amino (2:8) D-glucaramide) Themoset Polyamide Product.** 1,6-hexamethylenediammonium:tris(2-ethylammonium)amino (2:8) D-glucarate was dissolved in deionized water to prepare a 30 wt% solution. The solution was flow coated onto aluminum panels at 5 mm/s at 85°C. After coating the films were annealed at 185°C for 1h in air.

Example 5 Poly(branched polyethyleneimine D-glucaramide) Themoset Polyamide Product.

[0071] **Step 1. Branched Polyethyleneimine D-Glucarate salt.** Cation exchange resin (DOWEX 50WX8-100, 43 mL) was washed with deionized water 3 times. Monopotassium D-glucaric acid (10.00 g, 40.29 mmol) was added to the resin in 100 mL of water and mixed for 15 minutes. The resin was removed by filtration and washed with water. The wash water was combined with the filtrate. Branched polyethyleneimine (600 g/mol, 8g) was added to the filtrate and stirred for 3h. The aqueous solution was concentrated to a viscous syrup on a rotatory evaporator.

[0072] **Step 2. Poly(branched polyethyleneimine D-glucaramide) Themoset Polyamide Product.** The viscous syrup from step 1 was diluted with water and flow coated on an aluminum panel at 70°C. The coated film was annealed for 1h at 190°C under air.

Comparative Example 1. 1,6-Hexamethylenediammonium Mucate salt product.

[0073] Mucic acid (7.2 g, 34 mmol) was mixed with deionized water (70 mL) to form a slurry. 1,6 hexamethylenediamine (4g 34.5 mmol) was added to the slurry and stirred for 6 hours at 80°C to form a solution. Ethanol was added to the solution and stirred for 12h to precipitate the product salt as a white solid. The solid was recovered by filtration and dried under vacuum for 24 hours. The resulting white solid product was insoluble in water at room temperature.

Comparative Example 2. Poly(1,6-hexamethylene adipamide) Thermoset Polyamide Product.

[0074] **Step 1. 1,6- Hexamethylene Ammonium Adipate.** Adipic acid (10.07g, 69 mmol) was dissolved in 50 mL ethanol. 1,6 hexamethylenediamine (8g, 69 mmol) was dissolved in ethanol (6.5 mL) and added to the Adipic acid/ethanol solution. A gel-like solid was formed, which was diluted with water to form a solution. The solid product was

precipitated by addition of ethanol (130 mL) and stirring for 12h. The precipitate was recovered by filtration and dried under vacuum for 12h to obtain 1,6-hexamethylene diammonium adipate.

[0075] **Step 2.** An aqueous solution of the 1,6-hexamethylene diammonium adipate was flow-coated on an aluminum panel and annealed at 220°C for 2h. The crystallization of the 1,6-hexamethylene ammonium adipate during flow-coating produced a rough film.

Example 6. Preparation of Poly(1,6-hexamethylene D-glucaramide) Thermoset Polyamide Product By Microwave Heating.

[0076] **Step 1. 1,6-Hexamethylenediammonium D-glucarate.** See method for Step 1, Example 1.

[0077] **Step 2. 1,6-Hexamethylenediammonium D-glucarate was flow-coated on silicon substrate.** The film was annealed at 4W, final 185 °C for 45-75s to produce the Poly(1,6-hexamethylene D-glucaramide) Thermoset Polyamide product.

Example 7. Solvent Resistance of Thermoset Polyamide Products Tested by Immersion in Solvent

[0078] The solvent resistance of the thermoset polyamide products described in Examples 1-5 was tested by immersing the film in solvent for 1 hour. In step 2 of the preceding examples, silicon substrates were used to prepare films. Hexane, toluene, 1,4-dioxane, tetrahydrofuran, N,N-dimethylformamide, water, acetone, ethanol, chloroform, and methyl ethyl ketone were used as the test solvents. No film dissolution was observed after removal of the film from the test solvent.

Example 10. Solvent Resistance of Thermoset Polyamide Products Tested by Solvent Rubs

[0079] The solvent resistance of the thermoset polyamide products described in Examples 1-5 was tested using ASTM D5402-15 Standard Practice for Assessing the Solvent Resistance of Organic Coatings Using Solvent Rubs. Toluene, methyl ethyl ketone, dimethylsulfoxide, N,N-dimethylformamide, and water were used as test solvents. For the thermoset polyamide product produced in Example 1, N,N-dimethylformamide produced a change in the film appearance after 50 double rubs. The film was unchanged after 100 rubs using toluene, methyl ethyl ketone, dimethylsulfoxide and water. For the thermoset polyamide product produced by Examples 2-4 the film were unchanged after

100 rubs using toluene, methyl ethyl ketone, dimethylsulfoxide, N,N-dimethylformamide, and water.

Example 11. Crosshatch Adhesion Characterization

[0080] The cross-hatch of the thermoset polyamide products described in Examples 1-4 was tested using was measured by ASTM D3359 method B. Each sample was tested three times. For each thermoset polyamide product the result of the test was 5B, which indicates good adhesion to the substrate, where the edges of the cuts are completely smooth, and none of the squares of the lattice is detached.

CLAIMS

What is claimed is:

1. A thermoset polyamide comprising:
units derived from the polymerization of glucarate and
units derived from the polymerization of a polyamine.
2. The thermoset polyamide of claim 1, where the thermoset polyamide is insoluble in water.
3. The thermoset polyamide of claim 1, where the thermoset polyamide is insoluble in dimethylsulfoxide.
4. The thermoset polyamide of claim 1, where the polyamine has two or more primary amine groups.
5. The thermoset polyamide of claim 1, where the polyamine has three or more primary amine groups.
6. The thermoset polyamide of claim 1, where the thermoset polyamide includes units derived from the polymerization of a polyamine with 2 primary amine groups and units derived from the polymerization of a polyamine with 3 primary amine groups.
7. The thermoset polyamide of claim 1, where the polyamine polymer includes one or more polyamines selected from the group consisting of linear polyamines with two primary amine groups, cyclic polyamines with two primary amine groups, cyclic polyamines with three primary amine groups, and branched polyamines with three primary amine groups.
8. The thermoset polyamide of claim 7, where the polyamine with two primary amine groups includes one or more polyamines selected from the group consisting of 1,2-

diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,2-diaminobutane, 1,3-diaminobutane, 1,4-diaminobutane, 1,2-diaminopentane, 1,3-diaminopentane, 1,4-diaminopentane, 1,5-diaminopentane, 1,2-diaminohexane, 1,3-diaminohexane, 1,4-diaminohexane, 1,5-diaminohexane, 1,6-diaminohexane, 1,2-diaminoheptane, 1,3-diaminoheptane, 1,4-diaminoheptane, 1,5-diaminoheptane, 1,6-diaminoheptane, 1,7-diaminoheptane, 1,2-diaminooctane, 1,3-diaminooctane, 1,4-diaminooctane, 1,5-diaminooctane, 1,6-diaminooctane, 1,7-diaminooctane, and 1,7-diaminooctane.

9. The thermoset polyamide of claim 7, where the cyclic polyamines with two primary amine groups includes one or more polyamines selected from the group consisting of 1,2-cyclopentanediamine, 1,3-Cyclopentanediamine, 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, and 1,4-diaminocyclohexane.
10. The thermoset polyamide of claim 7, where the cyclic polyamines with three primary amine is 1,3,5-triaminocyclohexane.
11. The thermoset polyamide of claim 7, where the branched polyamines with three primary amine groups includes one or more polyamines selected from the group consisting of tris(2-aminomethyl)amine, tris(2-aminoethyl)amine, tris(2-aminopropyl)amine, tris(2-aminobutyl)amine, and tris(2-aminopentyl)amine.
12. A method of preparing a polyamide comprising:
preparing a solid salt from glucaric acid and a polyamine; and
inducing the polymerization of the solid salt.
13. The method of claim 12, where the step of inducing the polymerization is performed by heating the solid salt.
14. The method of claim 12, where the step of inducing the polymerization is performed by exposing the solid salt to microwaves.
15. The method of claim 12, where the solid salt is prepared by combining free glucaric acid in solution with a polyamine to prepare a glucarate-polyamine salt in

solution; optionally purifying the glucarate-polyamine salt, and then drying the glucarate-polyamine salt in solution.

16. A method of preparing a polyamide comprising:
providing an aqueous solution containing the salt product of a glucaric acid and a polyamine;
removing the water from the aqueous solution to prepare a solid salt; and
inducing the polymerization of a solid salt.
17. The method of claim 16, where the aqueous solution containing the salt product of a glucaric acid and a polyamine is from about 15% to about 70% by weight the salt product of a glucaric acid and a polyamine.
18. The method of claim 16, where the aqueous solution containing the salt product of a glucaric acid and a polyamine is from about 20% to about 50% by weight the salt product of a glucaric acid and a polyamine.
19. The method of claim 16, further comprising the step of coating a substrate with the aqueous solution containing the salt product of a glucaric acid and a polyamine.
20. The method of claim 19, where the substrate is a material selected from the group consisting of silica oxide, glass, ceramics, and metal.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 17/27907

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08G 69/26; C08G 69/30; C08G 69/04; C08K 5/17; C08K 5/20 (2017.01)

CPC - C08G 69/26; C08G 69/30; C08G 69/06; C08G 69/04; C08L 77/06; C08L 77/02; C08K 5/17; C08L 2201/54; C08J 2377/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014/0228452 A1 (KIELY et al.) 14 August 2014 (14.08.2014) para [0007], [0014]-[0015], [0026]-[0028], [0034], [0038], [0044]-[0045], [0050], [0062]	1-11
X	US 8,246,857 B2 (GUZMANN et al.) 21 August 2012 (21.08.2012) col 1, ln 4-5; col 2, ln 28-35; col 3, ln 17-27; col 4, ln 13-23, 33-34, 56-67; col 5, ln 12-15, 33-47; col 6, ln 50-53	12-18
—		19-20
Y	US 4590103 A (AHNE et al.) 20 May 1986 (20.05.1986) abstract; col 8, ln 1-2; col 9, ln 64-65; col 10, ln 11, 48-49; claim 1	19-20
Y		
A	WO 2016/001949 A1 (TOYO INK SC HOLDINGS CO., LTD.) 07 January 2016 (07.01.2016) para [0009], [0031], [0042]-[0043]	1-11
A	Kiely et al., "Synthetic polyhydroxypolyamides from galactaric, xylaric, D-glucaric, and D-mannaric acids and alkylenediamine monomers?some comparisons" J. Polym. Sci. A Polym. Chem., Vol. 38, No. 3, pg 594-603 (2000) entire document	2
A	US 2015/0048539 A1 (MITADERA) 19 February 2015 (19.02.2015) entire document	1-20
A	US 3,420,852 A (BLACK et al.) 07 January 1969 (07.01.1969) entire document	1-20
A	US 5,128,442 A (PIPPER et al.) 07 July 1992 (07.07.1992) entire document	1-20

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

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