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(54) Title: FUMARIC ACID/POLYOL POLYESTERS AND THEIR MANUFACTURE AND USE

(57) Abstract: We disclose a composition containing a polyester comprising about 1 mole part polyol units derived from a polyol having m -OH groups, wherein m is an integer from 3 to 8,, and from about 0.98 mole parts fumaric acid units to about 3.03 mole parts fumaric acid units. In one embodiment, the polyol units are sorbitol units. In another embodiment, the composition is in a form selected from the group consisting of a plate, a tray, a bowl, a cup, a bowl lid, a cup lid, a fork, a spoon, a knife, a jewel case, and a packaging article. We also disclose a method of manufacturing the composition. The method includes combining about 1 mole part polyol, from about 0.98 mole parts fumaric acid to about 3.03 mole parts fumaric acid, and from about 0.0002 mole parts to about 0.0020 mole parts of a polyesterfication catalyst, to yield a combination of polyol and fumaric acid; maintaining the combination of polyol and fumaric acid under an inert atmosphere at a temperature from about 130°C to about 190°C for at least about 2 hr, to yield a molten polyester; and cooling the molten polyester, to yield the polyester.

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FUMARIC ACID/POLYOL POLYESTERS AND THEIR MANUFACTURE AND USE

BACKGROUND OF THE INVENTION

The present invention relates generally to the field of polymer chemistry. More particularly, it concerns polyesters, especially biomaterial polyesters, their manufacture, and use.

SUMMARY OF THE INVENTION

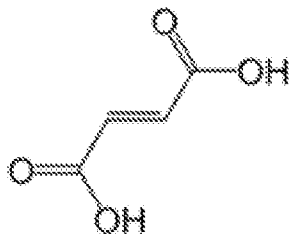
In one embodiment, the present invention relates to a composition containing a polyester comprising about 1 mole part polyol units derived from a polyol having m –OH groups, wherein m is an integer from 3 to 8, and from about 0.98 mole parts fumaric acid units to about 3.03 mole parts fumaric acid units. In one embodiment, the polyol units are sorbitol units. In another embodiment, the composition is in a form selected from the group consisting of a plate, a tray, a bowl, a cup, a bowl lid, a cup lid, a fork, a spoon, a knife, a jewel case, and a packaging article.

In one embodiment, the present invention relates to a method of manufacturing a composition containing a polyester comprising about 1 mole part polyol units derived from a polyol having m –OH groups, wherein m is an integer from 3 to 8, and from about 0.98 mole parts fumaric acid units to about 3.03 mole parts fumaric acid units. The method includes combining about 1 mole part polyol, from about 0.98 mole parts fumaric acid to about 3.03 mole parts fumaric acid, and from about 0.0002 mole parts to about 0.0020 mole parts of a polyesterfication catalyst, to yield a combination of polyol and fumaric acid; maintaining the combination of polyol and fumaric acid under an inert atmosphere at a temperature from about 130°C to about 190°C for at least about 2 hr, to yield a molten polyester; and cooling the molten polyester, to yield the polyester.

DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

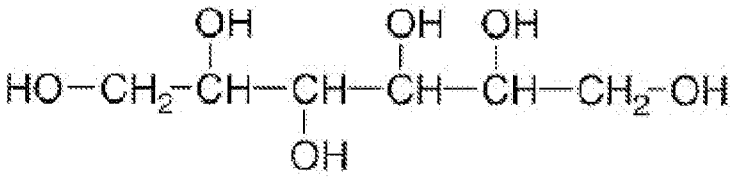
In one embodiment, the present invention relates to a composition containing a polyester comprising about 1 mole part polyol units derived from a polyol having m –OH groups, wherein m is an integer from 3 to 8, and from about 0.98 mole parts fumaric acid units to about 3.03 mole parts fumaric acid units.

Fumaric acid is an organic diacid having the structure:



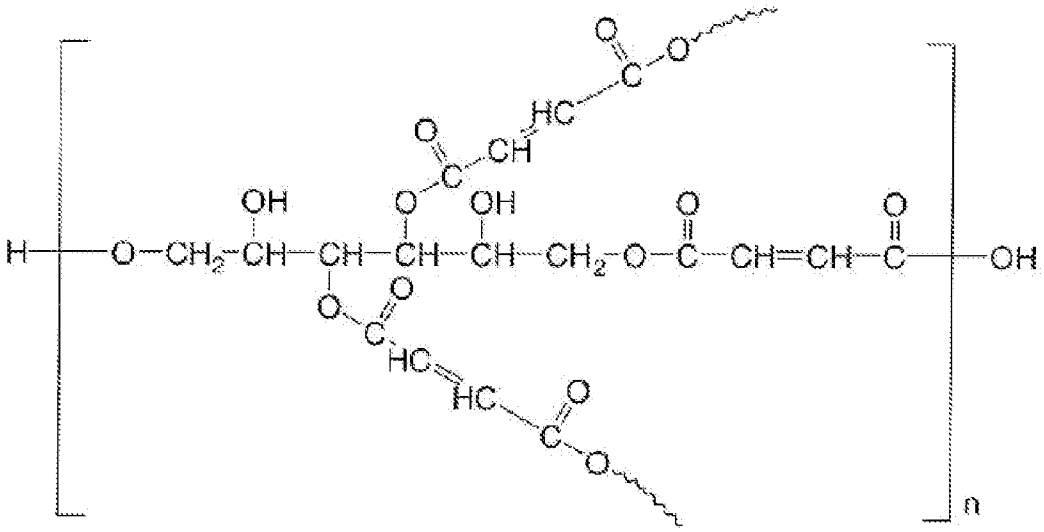
A "fumaric acid unit" is a portion of a polyester which is derived from condensation of one molecule of fumaric acid with one or more alcohols.

"Polyol" is used herein to refer to any organic molecule containing more than two –OH groups, such as three, four, five, six, seven, or eight –OH groups. A "polyol unit" is a portion of a polyester which is derived from condensation of one molecule of a polyol with one or more organic acids. In one embodiment, the polyol is selected from the group consisting of sorbitol, mannitol, glycerol, and xylitol. In a further embodiment, the polyol is sorbitol:



and the polyol units are sorbitol units.

In one embodiment, the polyester has essentially the structure:



The polyester can be prepared by techniques known in the art. Reaction conditions that have been found to produce polyesters having properties desirable for certain uses, as well as those uses, will be discussed below. The conditions of the polyesterification reaction can be selected to yield a polyester having any of a number of values for any of a number of physical properties. One such physical property is the molecular weight of the polyester. As is known in the polymer arts, a polyester's molecular weight can be defined as the weight-average molecular weight (MWw) or the number-average molecular weight (MWn). Another such physical property is the melt flow index (MFI) of the polyester. Still another physical property is the glass transition temperature (Tg).

In addition to the polyester, the composition can contain other components. In one embodiment, the composition contains at least one component selected from the group consisting of a plasticizer, a pigment, and an oxidation inhibitor. The composition can comprise two or more of these components.

The plasticizer can be any material that renders the composition less brittle than it would be in the absence of the material. In one embodiment, the plasticizer is a polyethylene glycol.

The polyester, in dry, solid form, typically has a white color. If the composition is intended for uses where a different color is desired, a pigment can be included. Any pigment known in the art for use in a polyester composition can be used.

The fumaric acid units contain a carbon-carbon double bond. This double bond is susceptible to oxidation, which can lead to degradation of the polyester molecule or cross-

linking of polyester molecules. The oxidation inhibitor can be any material that renders the fumaric acid units less susceptible to oxidation. In one embodiment, the oxidation inhibitor is selected from the group consisting of 2,5-di-*tert*-butyl hydroquinone and vitamin E.

The proportions of the polyester and the at least one component selected from the group consisting of a plasticizer, a pigment, and an oxidation inhibitor are not critical. In one embodiment, the composition contains from about 5 weight parts to about 90 weight parts polyester; if included, from about 0.1 weight parts to about 20 weight parts plasticizer; if included, from about 0.1 weight parts to about 1 weight part pigment, and, if included, from about 0.1 weight parts to about 1 weight part oxidation inhibitor. In a further embodiment, the plasticizer is a polyethylene glycol and the oxidation inhibitor is 2,5-di-*tert*-butyl hydroquinone.

The composition can also comprise other polymers in addition to the polyester in the form of a non-coreacted blend. A non-coreacted blend can be identified by contacting the putative blend with a solvent in which one of the polymers is soluble and the other is not; if greater than or equal to 5 wt% of the soluble polymer is removed from the putative blend, a non-coreacted blend is indicated. In some situations, a non-coreacted blend can be identified as having two glass transition temperatures (Tgs) as measured by differential scanning calorimetry (DSC), although this technique may not be effective in situations in which the Tgs of the two polymers are close enough to have overlapping DSC peaks.

Although the previous paragraph referred to a non-coreacted blend of two polymers, non-coreacted blends of three or more polymers are also contemplated. The person of ordinary skill in the art, having the benefit of the present disclosure, can readily identify non-coreacted blends of three or more polymers as a matter of routine experimentation.

In one embodiment, the composition further comprises a starch. In one embodiment, the composition further comprises polylactic acid. The proportions of the polyester and the starch or polylactic acid are not critical. In one embodiment, the composition contains from about 5 weight parts to about 90 weight parts polyester and from about 10 weight parts to about 95 weight parts of a second polymer selected from the group consisting of starch or polylactic acid. In a further embodiment, the composition contains from about 5 weight parts to about 50 weight parts polyester and from about 50 weight parts to about 95 weight parts polylactic acid. In still a further embodiment, the composition contains from about 10 weight

parts to about 30 weight parts polyester and from about 70 weight parts to about 90 weight parts polylactic acid.

In one embodiment, the polyol and fumaric acid, and their corresponding units in the polyester, are derived from biomass. "Derived from biomass" means that substantially all the carbon atoms in the polyol and the fumaric acid were fixed from atmospheric carbon dioxide within about one hundred years before production of the polyester, such as within about ten years, about two years, or about one year. For example, fumaric acid can be extracted from fumitory (*Fumaria officinalis*), bolete mushrooms (*e.g.*, *Boletus fomentarius* var. *pseudo-igniarius*), lichen, and Iceland moss, or it can be produced by the oxidation of furfural, which reactant can be derived from bran, corn cob, or wood. An exemplary polyol, sorbitol, can be extracted from drupes (stone fruit) or berries of the genus *Sorbus*.

In one embodiment, the present invention relates to a method of manufacturing a composition containing a polyester comprising about 1 mole part polyol units derived from a polyol having m –OH groups, wherein m is an integer from 3 to 8, and from about 0.98 mole parts fumaric acid units to about 3.03 mole parts fumaric acid units. The method includes combining about 1 mole part polyol, from about 0.98 mole parts fumaric acid to about 3.03 mole parts fumaric acid, and from about 0.0002 mole parts to about 0.0020 mole parts of a polyesterfication catalyst, to yield a combination of polyol and fumaric acid; maintaining the combination of polyol and fumaric acid under an inert atmosphere at a temperature from about 130°C to about 190°C for at least about 2 hr, to yield a molten polyester; and cooling the molten polyester, to yield the polyester.

The polyol and the fumaric acid have been described above. The polyesterification catalyst can be any material known in the art for catalysis of esterification. In one embodiment, the polyesterification catalyst is selected from the group consisting of tin(II) chloride, tin(II) octonate, sulfuric acid, n-butyl stannoic acid, p-toluene sulfonic acid, and mixtures thereof.

The combining step can be performed in any appropriate reaction vessel known in the art. The materials can be combined in any order. The result of the combining step is a combination of polyol and fumaric acid.

After the materials are combined, the combination of polyol and fumaric acid is maintained under an inert atmosphere at a temperature from about 130°C to about 190°C for

at least about 2 hr. In one embodiment, the temperature is from about 130°C to about 165°C. It should be borne in mind that electrical heaters can produce hot spots having local temperatures greater than about 190°C even if the electrical heater is set to a nominal temperature below about 190°C, such as about 165°C. Therefore, it is desirable to heat the reaction vessel non-electrically.

The inert atmosphere can be nitrogen, argon, or a mixture thereof. The duration and temperature are typically enough to yield a molten polyester.

The molten polyester is then cooled, such as to ambient temperature, to yield the polyester. The cooling step can be performed in the reaction vessel or in another vessel. In one embodiment, the cooling step involves extrusion of the molten polyester to yield a sheet of cooled polyester.

The sheet can be produced by any technique known in the art of monolayer or coextrusion. Such techniques include sheet extrusion either as a single extruded layer or a plurality of coextruded layers. In a typical sheet extrusion process, molten material from an extruder flows through a flat die to form a sheet which is passed through a chill roll stack. Chill roll stacks typically consist of at least three cooled rolls. Typically the sheet produced has a thickness of between about 5 mils and about 20 mils.

In another embodiment, the molten polyester is coextruded with a second polymer selected from the group consisting of starch or polylactic acid, as described above. In another embodiment, the molten polyester is coextruded with at least one component selected from the group consisting of a plasticizer, a pigment, and an oxidation inhibitor, as described above.

In embodiments wherein the polyester is formed into a sheet, the sheet can be stored until later use. In one embodiment, the sheet of the composition is molded to form a plate, a tray, a bowl, a cup, a bowl lid, a cup lid, a fork, a spoon, a knife, a jewel case, and a packaging article. Molding techniques are known in the art.

In one embodiment, the composition is heat resistant. "Heat resistant" herein means the composition will have a heat deflection temperature (HDT), as can be measured according to ASTM Method D 648-06, of at least about 60°C. In one embodiment, the composition is heat resistant and has a melting temperature (Tm), such as can be measured by differential scanning calorimetry (DSC), such that a plate, a tray, a bowl, a cup, a bowl lid, a cup lid, a fork, a spoon, a knife, a jewel case, and a packaging article formed from the

composition to be used in the packaging of hot foods and beverages or to be readily stored and transported at high temperatures (such as from about 40°C to about 50°C), such as those that may prevail during summer in the southern or western United States and comparable or warmer climates.

In one embodiment, the polyester has a Tg of at least about 50°C, such as from about 50°C to about 90°C.

In one embodiment, a polyester derived from the stated compositions can be reacted with a chain extending agent to link one chain to another and/or to alter the physical properties of the polyester. The physical properties that can be altered by the use of a chain extending agent include, but are not limited to, molecular weight and MFI.

The chain extending agent can be any one known to be useful in the art for polyester chain extension. In one embodiment, the chain extending agent is selected from the group consisting of isocyanates, epoxides, acyl chlorides, anhydrides, acrylics, aziridines, phosphate esters, multivalent metals, polyacids, polyols, oxazolines, polymers or copolymers containing any of the foregoing functional groups, and mixtures thereof..

Examples of isocyanate compounds include 4,4'-methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI or HDMI), isophorone diisocyanate (IPDI), lysine diisocyanate (LDI), trimethylxylene diisocyanate (TMDI or TMXDI), polyisocyanate compounds (such as Desmodur® polyisocyanates manufactured by Bayer A.G), and mixtures thereof.

In one embodiment, the chain extending agent is introduced into a molten polyester. This can be done either in a continuous process such as extrusion or in a batch process such as a batch reactor. The molten polyester can be still molten from its polymerization or can be a remelt of already-formed and cooled polyester.

The chain-extended polymer may exhibit an increase in molecular weight and a concomitant increase in viscosity of the molten material. The resulting polymer may also exhibit a significant improvement in mechanical properties over the non-chain-extended polymer, including improved impact strength, tensile strength, and elongation until break. A significant increase in flexibility may also be observed.

The following example is included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the example which follows represent techniques discovered by the inventor to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

Example 1

Sorbitol (313.90 g, 1.732 mol), 600.00 g (5.169 mol) of fumaric acid, and 0.51 g (2.25 x 10^{-3} mol) of Tin (II) Chloride (0.07 wt %) were charged into a 1-L resin kettle equipped with a mechanical stirrer, heating mantle with thermocouple temperature control, nitrogen inlet, and condenser with a moisture trap. When charging the monomers, liquid monomers or the lowest-melting-point monomers were loaded first into the reactor to help solublize the other monomers and prevent charring. The f_{avg} was calculated to be 3 and the critical extent of reaction (p_c) was 0.667. The theoretical water of polymerization was 186-mL, therefore the polymerization needed to be stopped at 124 mL water (186*0.667) to prevent cross-linking. The polymerization was then heated to 160°C under a low nitrogen flow. After approximately 1.0 h, the mixture was at 160°C and 40 mL of water had been collected. The polymerization was held for 15 min at 160°C and an additional 5 mL of water (total water 45 mL) were collected. The temperature was then increased to 170°C and a total of 60 mL of water were collected. The temperature was then increased to 180°C, and. after 15 min a total of 84 mL of water had been collected. The polymerization was then stopped due to the high viscosity of polymer. The heat was turned off, the reactor taken apart, and the polymer resin poured in to a silicon baking pan and cooled. The polymer was weighed (722.52 g, 98% yield) broken up, and stored. Samples were removed for testing by differential scanning calorimetry (DSC), TGA, and GPC.

The cooled product then underwent DSC, which determined the glass transition temperature (Tg) is dependent on the amount of water removed. For example, one polymer which had a total of 74 mL of water removed had a Tg of 53°C and a second polymer which had a total of 84 mL of water removed had a Tg of 84°C. However, both polymers were

thermally stable to 218°C.

Example 2

The procedures of Example 1 were followed to produce polymers having the following proportions:

Polymer 2A: 1 mole part glycerol units/1 mole part fumaric acid units

Polymer 2B: 2 mole parts glycerol units/3 mole parts fumaric acid units

Polymer 2C: 1 mole part sorbitol units/2 mole parts fumaric acid units

Polymer 2D: 1 mole part sorbitol units/3 mole parts fumaric acid units

The polymers were observed and some underwent DSC to determine their Tg values.

Polymer 2A formed a stiff rubbery solid. Polymer 2B formed a hard crystalline solid. Polymer 2C formed a hard crystalline solid with a Tg of about 60°C. Polymer 2D formed a hard crystalline solid with a Tg of about 83°C.

Example 3

A polymerization starting with a set of reactants as described above is performed in a reactor able to handle high viscosity material, able to generate a vacuum of less than 1 mm Hg, and able to remove frictional heat from mixing a viscous material. In such a reactor, the monomers are added and heated to 160°C to remove 85-90% of the water of condensation. The vessel contents are then put under vacuum by gradually going from atmospheric pressure to 1 mm Hg over a 1 hour period while maintaining the temperature at 160°C. As the viscosity builds during the course of the reaction, the temperature increases due to frictional heating by the stirrer. However, as stated above, the reactor removes the excess heat and maintains the internal polymerization temperature between 163-165°C until the desired viscosity is reached.

All of the compositions and methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and methods and in the steps or in the sequence of steps of the methods described herein without departing from the concept, spirit and scope of the invention. More

specifically, it will be apparent that certain agents which are both chemically and physiologically related may be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention as defined by the appended claims.

WHAT IS CLAIMED IS:

1. A composition, comprising:

a polyester comprising about 1 mole part polyol units derived from a polyol having m –OH groups, wherein m is an integer from 3 to 8, and from about 0.98 mole parts fumaric acid units to about 3.03 mole parts fumaric acid units.

2. The composition of claim 1, wherein the polyol units are sorbitol units.

3. The composition of claim 2, wherein the polyester has a Tg of at least about 50°C.

4. The composition of claim 1, wherein the polyester is present at from about 5 weight parts to about 90 weight parts, and the composition further comprises at least one component selected from the group consisting of from about 0.1 weight parts to about 20 weight parts of a plasticizer, from about 0.1 weight parts to about 1 weight part of a pigment, and from about 0.1 weight parts to about 1 weight part of an oxidation inhibitor.

5. The composition of claim 4, wherein the plasticizer is a polyethylene glycol or the oxidation inhibitor is 2,5-di-*tert*-butyl hydroquinone.

6. The composition of claim 1, wherein the polyester is present at from about 5 weight parts to about 90 weight parts, and the composition further comprises from about 10 weight parts to about 95 weight parts of a second polymer selected from the group consisting of starch or polylactic acid.

7. The composition of claim 1, wherein the polyol units and the fumaric acid units are derived from biomass.

8. The composition of claim 1, in a form selected from the group consisting of a plate, a tray, a bowl, a cup, a bowl lid, a cup lid, a fork, a spoon, a knife, a jewel case, and a packaging article.

9. A packaging article, comprising:

a composition comprising a polyester comprising about 1 mole part polyol units derived from a polyol having m –OH groups, wherein m is an integer from 3 to 8, and from about 0.98 mole parts fumaric acid units to about 3.03 mole parts fumaric acid units.

10. The packaging article of claim 9, wherein the polyol units are sorbitol units.

11. The packaging article of claim 10, wherein the polyester has a Tg of at least about 50°C.

12. The packaging article of claim 9, wherein the polyester is present at from about 50 weight parts to about 80 weight parts, and the composition further comprises at least one component selected from the group consisting of from about 0.1 weight parts to about 20 weight parts of a plasticizer, from about 0.1 weight parts to about 1 weight part of a pigment, and from about 0.1 weight parts to about 1 weight part of an oxidation inhibitor.

13. The packaging article of claim 9, wherein the packaging article is selected from the group consisting of a plate, a tray, a bowl, a cup, a bowl lid, a cup lid, a fork, a spoon, a knife, a jewel case, and a packaging article.

14. A method of manufacturing a composition comprising a polyester comprising about 1 mole part polyol units derived from a polyol having m –OH groups, wherein m is an integer from 3 to 8, and from about 0.98 mole parts fumaric acid units to about 3.03 mole parts fumaric acid units, the method comprising:

combining about 1 mole part polyol, from about 0.98 mole parts fumaric acid to about 3.03 mole parts fumaric acid, and from about 0.0002 mole parts to about 0.0020 mole parts of a polyesterfication catalyst, to yield a combination of polyol and fumaric acid;

maintaining the combination of polyol and fumaric acid under an inert atmosphere at a temperature from about 130°C to about 190°C for at least about 2 hr, to yield a molten polyester; and

cooling the molten polyester, to yield the polyester.

15. The method of claim 14, wherein the polyol is sorbitol.

16. The method of claim 14, wherein the polyesterification catalyst is selected from the group consisting of tin(II) chloride, tin(II) octonate, n-butyl stannoic acid, sulfuric acid, p-toluene sulfonic acid, and mixtures thereof.

17. The method of claim 14, further comprising extruding the polyester, to yield a sheet of the composition.

18. The method of claim 17, wherein the extruding step further comprises coextruding with the polyester a second polymer selected from the group consisting of starch or polylactic acid.

19. The method of claim 17, wherein the extruding step further comprises coextruding with the polyester at least one component selected from the group consisting of a plasticizer, a pigment, and an oxidation inhibitor.

20. The method of claim 17, further comprising molding the sheet of the composition, wherein the sheet is molded to a form selected from the group consisting of a plate, a tray, a bowl, a cup, a bowl lid, a cup lid, a fork, a spoon, a knife, a jewel case, and a packaging article.

21. The method of claim 14, wherein the polyol and the fumaric acid are derived from biomass.

22. The method of claim 17, further comprising reacting the molten polyester with a chain extending agent selected from the group consisting of isocyanates, epoxides, acyl chlorides, anhydrides, acrylics, aziridines, phosphate esters, multivalent metals, polyacids, polyols, oxazolines, polymers or copolymers containing any of the foregoing functional groups, and mixtures thereof.

23. The method of claim 22, wherein the chain extending agent is selected from the group consisting of 4,4'-methylene diphenyl diisocyanate (MDI), toluene diisocyanate (TDI), hexamethylene diisocyanate (HDI or HDMI), isophorone diisocyanate (IPDI), lysine diisocyanate (LDI), trimethylxylene diisocyanate (TMDI or TMXDI), polyisocyanate compounds, and mixtures thereof.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/031540

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G63/12 C08G63/52 C08K3/00 C08K5/00 C08K5/053
C08K5/13 C08K13/02 C08L3/02 C08L67/02 C08L67/06
ADD. C08L67/04 C08L71/02

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)
C08G C08K C08L

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WERRY B ET AL: "Hyperbranching polymerization of glycerol and fumaric acid" POLYMER PREPRINTS, AMERICAN CHEMICAL SOCIETY, US, vol. 48, no. 1, 1 January 2007 (2007-01-01), pages 426-427, XP009114548 ISSN: 0032-3934 column 1; figure 1 ----- -/--	1,7,9, 14,16,21

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

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 March 2009	22/04/2009

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/031540

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