

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
17 November 2005 (17.11.2005)

PCT

(10) International Publication Number
WO 2005/108457 A1

(51) International Patent Classification⁷: **C08G 18/30**,
63/02, 64/00

(21) International Application Number:
PCT/US2005/015376

(22) International Filing Date: 4 May 2005 (04.05.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/567,816 5 May 2004 (05.05.2004) US

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: DIHYDROXYACETONE-BASED POLYMERS

(57) Abstract: Chemically protected dihydroxyacetone and/or dimers are used to make polycarbonates, poly(acetal carbonate)s, poly(spiroacetal)s, polyesters and polyurethanes.



WO 2005/108457 A1

DIHYDROXYACETONE-BASED POLYMERS

Cross-Reference to Related Applications

This application claims the benefit of U.S. Provisional Application No. 60/567,816, filed May 5, 2004, the whole of which is incorporated herein by reference.

Technical Field

The invention is directed to dihydroxyacetone (DHA)-based polymers and methods for making them.

Background of the Invention

Polymeric biomaterials are in high demand for a number of biomedical and consumer applications. Two of the most prominent biomaterials are the polyesters of lactic and/or glycolic acid, and the polyanhydrides based on sebacic acid and 1,3-bis (carboxyphenoxy) propane. The number of applications for polymeric biomaterials is rapidly growing, leading to a corresponding need for the development of new kinds of biomaterials. DHA-based polymers should be an ideal candidate for this purpose. DHA is a precursor for the synthesis of glucose in humans and is also an intermediate in the metabolism of glucose in humans and is FDA-approved for topical use as the active ingredient in sunless tanning lotions. These characteristics suggest that polymers based on DHA would be advantageous materials since DHA degradation product will enter the normal metabolic pathway and minimize toxicity. However, DHA is not subject to facile polymerization because in solution its monomer is in equilibrium with its dimer, and is also reactive to primary amines. The difficulty of polymerizing DHA is evidenced by there being no publication or patent reports of a characterized polymer based on DHA.

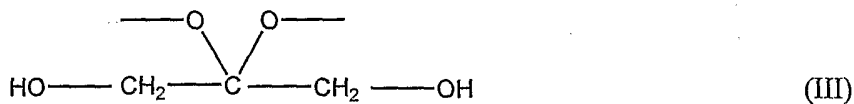
Summary of the Invention

It has been discovered herein that polymers can be made from DHA by proceeding from DHA monomer and/or dimer that have been chemically protected and, if desired, deprotecting after polymerization.

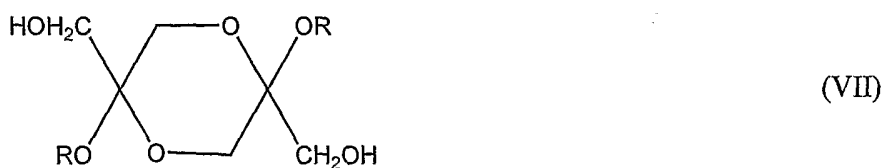
In its broad aspects the invention is directed to polymer comprising dihydroxy acetone monomer and/or dimer, having a number average molecular weight ranging from 500 to 1,000,000.

In narrower aspects the invention is directed to polycarbonates, poly(acetal carbonate)s, poly(acetal ester)s, poly(acetal urethane)s, poly(spiroacetal)s, polyesters, polyurethanes and combinations of said polymer types which meet the broad definition of polymer set forth in the above paragraph. In one embodiment the polycarbonate is functionalized by one or more nucleophiles.

One method for making herein involves the converting DHA to protected monomer, e.g., 2,2-dimethoxy-propane-1,3-diol having the structure:



or to protected dimer, e.g., having the structure:



where R is C₁-C₁₀ straight chain or branched alkyl.

A method for making the polycarbonates comprises converting (III) to 2,2-dimethoxy-propylene carbonate (IV), then polymerizing (IV) in the presence of a ring

opening polymerization catalyst or initiator to produce protected polymer (V) and if desired deprotecting to convert dimethoxy to carbonyl and produce deprotected polycarbonate (VI). Structures for (IV), (V) and (VI) are set forth in the detailed description. Functionalization of (VI) with one or more nucleophiles is readily carried out by incubating the polycarbonate with a solution of nucleophile functionalizing agent.

A method herein for making the poly(acetal carbonate)(s) of the invention comprises converting (VII) to poly(acetal carbonate).

A method herein for producing the poly(spiroacetal)s of the invention comprises subjecting (III) or (VII) to dealcoholysis.

A method herein for producing the polyesters of the invention comprises subjecting (III) or (VII) and a dicarboxylic acid to dehydration.

A method for producing the polyurethanes of the invention comprises reacting (III) or (VII) with diisocyanate $\text{OCN}R\text{NCO}$ where R is $\text{C}_1\text{-C}_{10}$ straight chain or branched alkyl, cyclohexyl, dicyclohexyl, norbornyl, toluene, diphenyl methane, naphthalene or other aromatic or converting (III) or (VII) to the corresponding bischloroformate and reacting the bischloroformate with a diamine.

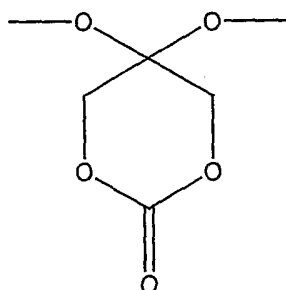
The number average molecular weights herein are determined by gel permeation chromatography using polystyrene standards.

Detailed Description

The broadly described polymer is appropriately made using dihydroxyacetone monomer and/or dimer that are chemically protected, e.g., from protected dihydroxyacetone monomer where the carbonyl group of the monomer is protected, e.g., from 2,2-di- $\text{C}_1\text{-C}_{10}$ alkoxy-propane-1,3-diol, e.g., from 2,2-dimethoxy-propane-1,3-diol (protected monomer, denoted (III)), or, for example, where the carbonyl group of the monomer is protected with methoxybenzyl or benzyloxy or allyloxy, or from protected dimer where the hydroxyl groups of the dimer are protected, e.g., from 2,5-di- $\text{C}_1\text{-C}_{10}$ alkoxy-2,5-bis(hydroxymethyl)-[1,4]-dioxane (protected dimer denoted (VII)). The 2,2-dimethoxy-propane-1,3 diol is readily made from combination of DHA monomer and dimer as described in Ferroni, E.L., et al, J.

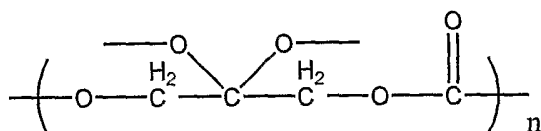
Org. Chem 64, 4943-4945 (1999); a detailed synthesis of (III) is set forth in Example 1 hereinafter. Detailed syntheses of (VII) are set forth in Examples 2 and 3 hereinafter.

The polycarbonates herein in protected form are poly(2,2-dimethoxy-propylene carbonate) and in deprotected form are poly(2-oxypropylene carbonate). The protected form can be made by converting (III) to



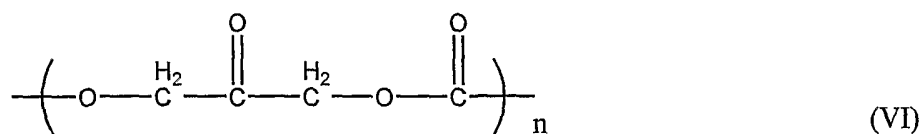
(IV)

e.g., by treating (III) with either triphosgene/pyridine or ethylchloroformate/triethylamine and subjecting (IV) to ring opening polymerization using a coordination catalyst or initiator (e.g. an organotin catalyst, e.g. stannous octoate (preferred), dibutyl tin laurate, dibutyltin diacetate or dibutyltin hexoate; or antimony; or zinc), to produce poly(2,2-dimethoxy-propylene carbonate), that is



(V)

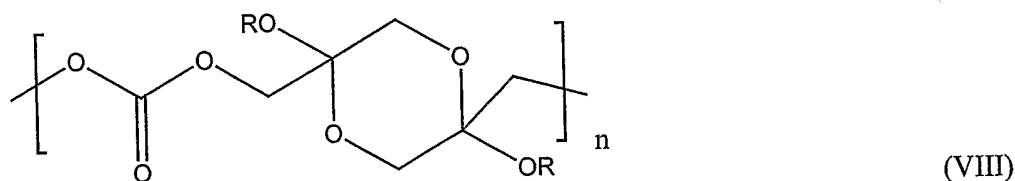
where n is a number such as to provide a number average molecular weight ranging from 500 to 1,000,000. A detailed synthesis of (V) from (III) is given in Example 4 hereinafter. The protected polymer (V) is readily converted to deprotected form poly (2-oxypropylene carbonate), that is



where n is a number such as to provide a weight average molecular weight ranging from 500 to 1,000,000. A detailed synthesis of (VI) from (V) is given in Example 5 hereinafter. The compound (VI) can be functionalized by one or more nucleophiles by suspending or dissolving (VI) in a liquid such as water and adding functionalizing agent. Functionalization of (VI) can also be performed by placing a functionalizing agent onto a surface consisting of (VI). Functionalizing agent can be, for example, an amine. Another way to make a functionalized form of (VI) is to create (VI) *in situ* from a deprotection of (V) in the presence of functionalizing nucleophile; this reaction can also be performed in two steps rather than *in situ*. A detailed example of functionalizing (VI) using 2,2,-dimethyl-1-methyl ethyl diamine as the functionalizing agent is given in Example 6 hereinafter. A detailed route of functionalizing using phenethylamine is given in Example 7. Other useful functionalizing amines include, for example, aliphatic and cycloaliphatic monoamines, e.g., amino sugars, amino lipids, amino acids, methylamine, ethylamine, propylamine, butylamine, tert-butylamine, allylamine, dimethylamine, diethylamine, diallylamine, cyclohexylamine; aromatic monamines, e.g., aniline, o-toluidine, 2,3-xylylidine, 3,4-xylylidine, o-aminophenol m-aminophenol, m-phenetidine, m-aminobenzaldehyde, aminobenzaldehyde, aminobenzonitrile, 2-aminobiphenyl, 4-aminobiphenyl, 2-aminophenyl phenyl ether, 3-aminophenyl phenyl ether, 2-aminobenzophenone, 3-aminobenzophenone, 3-aminophenyl phenyl sulfide, naphthylamine, amino-2-naphthol, 2-amino-1-naphthol; aliphatic and cycloaliphatic diamines, e.g., 1,2-diaminoethane, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, 1,6-diaminohexane, 1,6-diamino-2,2,4-trimethylhexane, 1,6-diamino-2,4,4-trimethylhexane, 1,4- and 1,5-diaminohexane, 2,4- and 2,6-diamino-1-methylcyclohexane, 1-amino-3,3,5-trimethyl-5-aminomethylcyclohexane, 1,3- and 1,4-bis(aminomethyl)cyclohexane, 4,4'-diaminodicyclohexylmethane and α , ω -diamino polyethers prepared by amination of polyalkylene oxides with ammonia; aromatic diamines,

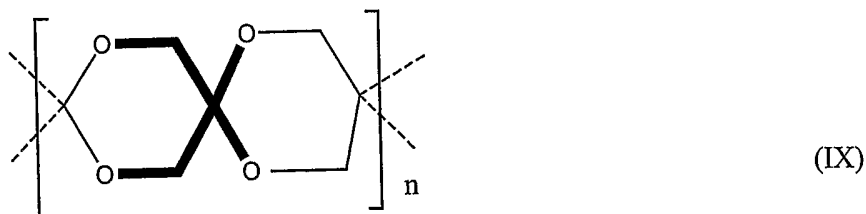
e.g., para-phenylenediamine, 4,4'-diamino-diphenylpropane, 4,4'-diamino-diphenylmethane, phenylene diamine, 1,5-diamino-naphthalene, bisaniline-p-xylylene, 3,3'-diaminobenzophenone, 4,4'-diaminobenzophenone, 3,3'-diaminodiphenylether, 4,4'-diaminodiphenylmethane, 3,3'-dimethyl benzidine; and triamines, e.g., 1,3,5-triaminobenzene, 4,4',4''-triaminotriphenylmethane, 4,4',4''-triaminotriphenylcarbinol and triaminophenyl benzene. The monamines can give functionality to the surface. The diamines and triamines can be crosslinkers.

The poly(acetal carbonate)s herein have the formula

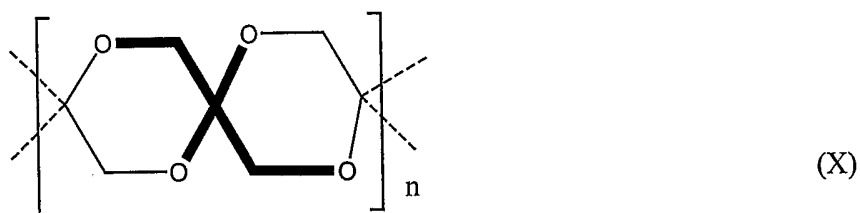


where R is C₁-C₁₀ straight chain or branched alkyl and n is a number such as to provide a number average molecular weight ranging from 500 to 1,000,000. The poly(acetal carbonate)s (VIII) can be prepared by adding triphosgene to a solution of (VII) in pyridine/methylene chloride and recovering product. Two examples of poly(acetal carbonate) synthesis are given in Example 9 hereinafter, one where (VII) is 2,5-diethoxy-2,5-bis(hydroxy methyl)-[1,4]-dioxane and the other where (VII) is 2,5-diisopropoxy-2,5-bis(hydroxy methyl)-[1,4]-dioxane.

The poly(spiroacetal)s here have the formulas

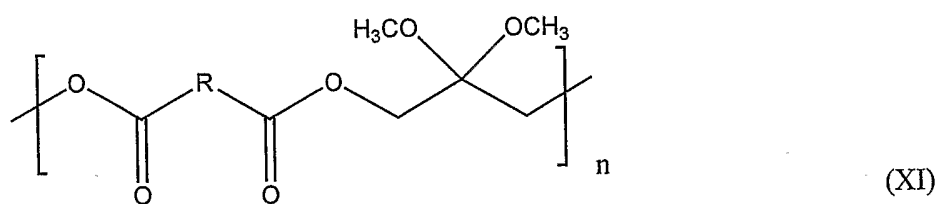


and

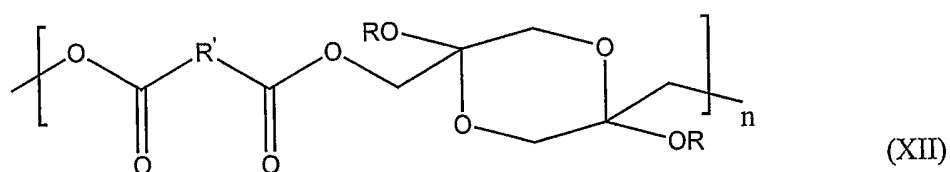


where n is a number such as to provide a number average molecular weight ranging from 500 to 1,000,000. Compound (IX) is prepared by subjecting (III) to dealcoholysis, and compound (X) is prepared by subjecting (VII) to dealcoholysis. Detailed examples of synthesis of (IX) and synthesis of (X) are given in Example 10 hereinafter.

The polyesters herein have the structural formulas



where R is C_1 - C_{10} straight chain or branched alkyl, cyclohexyl, dicyclohexyl, norbornyl, toluene, diphenylmethane, naphthalene or other aromatic and n is a number such that the number average molecular weight ranges from 500 to 1,000,000; and



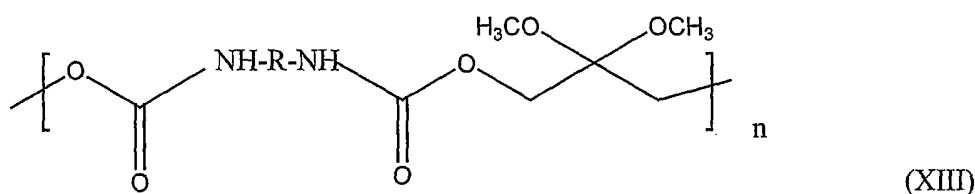
where R is C_1 - C_{10} straight chain or branched alkyl and R' is C_1 - C_{10} straight chain or branched alkyl, cyclohexyl, dicyclohexyl, norbornyl, toluene, diphenylmethane, naphthalene or other

aromatic and n is a number such that the number average molecular weight ranges from 500 to 1,000,000.

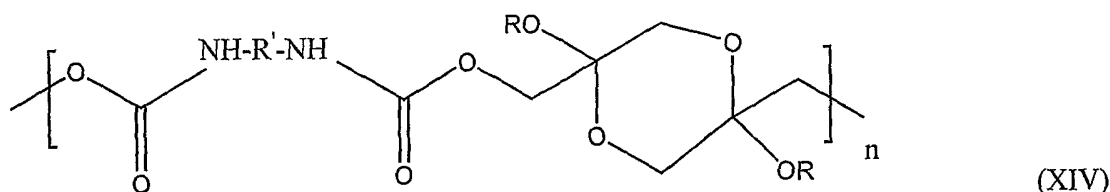
Compound (XI) can be prepared by subjecting (III) and a dicarboxylic acid to dehydration. Suitable dicarboxylic acids include, for example, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, sebacic acid, phthalic acid, isophthalic acid and terephthalic acid. A detailed synthesis of (XI) from (III) and succinic acid is given in Example 11 hereinafter. Compound (XI) except that dimethoxy is converted to carbonyl, is prepared by treating (XI) with trifluoroacetic acid. Functionalizing of (XI) where dimethoxy is converted to carbonyl, with one or more nucleophiles can be carried out, e.g., by suspending or dissolving the compound in water and adding functionalizing agent or by placing functionalizing agent onto a surface consisting of the compound; the functionalizing agent can be an amine, e.g., selected from the group consisting of those listed in conjunction with functionalizing (VI) or mixtures thereof.

Compound (XII) can be prepared by subjecting (VII) and a dicarboxylic acid to dehydration. The dicarboxylic acids named above for synthesis of (XI) are also suitable for synthesis of (XII). The procedure is analogous to the detailed procedure for synthesis of (XI) in Example 11.

The polyurethanes herein have the structure formulas



where R is C_1 - C_{10} straight chain or branched alkyl, cyclohexyl, dicyclohexyl, norbornyl, toluene, diphenylmethane, naphthalene or other aromatic and n is a number such that the number average molecular weight ranges from 500 to 1,000,000; and



where R is C₁-C₁₀ straight chain or branched alkyl and R' is C₁-C₁₀ straight chain or branched alkyl, cyclohexyl, dicyclohexyl, norbornyl, toluene, diphenylmethane, naphthalene or other aromatic and n is a number such that the number average molecular weight ranges from 500 to 1,000,000. Structure (XIV) is of a poly(acetal urethane).

The compound (XIII) can be made by reacting (III) with a diisocyanate OCN-R-NCO where R is the same as for (XIII) or by converting (III) to the corresponding bischloroformate and reacting the bischloroformate with a diamine. Suitable diisocyanates include, for example, 1,4-diisocyanatobutane, 1,6-diisocyanatohexane (HDI), 2-methyl-1,5-diisocyanatopentane, 1,5-diisocyanato-2,2-dimethylpentane, 2,2,4- or 2,4,4-trimethyl-1,6-diisocyanatocyclohexane, 1,10-diisocyanatodecane, 1,3 and 1,4-diisocyanato-cyclohexane, 1,3- and 1,4-bis(isocyanatomethyl)-cyclohexane, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI), 4,4'-diisocyanatodicyclohexylmethane, 1-isocyanato-1-methyl-4(3)-isocyanato-methylcyclohexane, bis-(isocyanatomethyl)-norbornene, 1,3- and 1,4-bis-(1-isocyanato-1-methylethyl)-benzene (TMXDI), 2,4- and 2,6-diisocyanatotoluene (TDI), 2,4' and 4,4'-diisocyanato-diphenylmethane (MDI), 1,5-diisocyanatonaphthalene or any mixture of such diisocyanates. Suitable diamines are, for example, those recited above as functionalizing agents. The compound (XIII) except that dimethoxy is converted to carbonyl is prepared by reacting (XIII) with trifluoroacetic acid. (XIII) where dimethoxy is converted to carbonyl can be functionalized with one or more nucleophiles by suspending or dissolving the compound in water and adding functionalizing agent or by placing functionalizing agent onto a surface consisting of the compound; the functionalizing agent can be an amine, e.g., selected from the group consisting on those listed in conjunction with functionalizing (VI) or mixtures thereof.

The compound (XIV) can be prepared by reacting (VII) with diisocyanate $\text{OCN-R}^1\text{-NCO}$ where R^1 is the same as R^1 for (XIV) or by converting (VII) to the corresponding bischloroformate and reacting the bischloroformate with a diamine. Exemplary diisocyanates and diamines are the same as those in the paragraph directly above.

The synthesis of intermediates of polymers of the invention and polymers of the invention are illustrated by the following examples.

Example 1

Synthesis of 2,2-dimethoxy-propane-1,3-diol (III)

2,2-dimethoxy-propane-1,3-diol (III) was synthesized according to the method of Ferroni, E.L., et al., J. Org. Chem., 64, 4943-4945 (1999). DHA dimer (25 g, 0.139 mole), trimethylorthoformate (30.4 ml, 0.278 mole) and p-toluenesulfonic acid (100 mg) were combined in 300 mL of methanol and stirred for 12h. At this time 300 mg of Na_2CO_3 were added and the reaction mixture was stirred for an additional 12h, after which the mixture was filtered and solvent was removed in vacuo. The resulting solid was recrystallized from ethyl ether to give 17.5 g of III (47%). ^1H NMR (D_2O) δ 3.58 (s; 4H), 3.24 (s; 6H). Anal. Calc.: C, 44.12; H, 8.82. Found: C, 44.50; H, 8.78.

Example 2

Synthesis of 2,5-di-ethoxy-2,5-bis(hydroxymethyl)-[1,4]-dioxane (VII)

Synthesis of 2,5-diethoxy-2,5-bis(hydroxymethyl)-[1,4]-dioxane (VII) was carried out as follows: DHA (32 g, 177.8 mmole), triethylorthoformate (60 ml, 360 mmole), p-TsOH (128 mg) were combined in 300 mL of ethyl alcohol and stirred for 24 hours, after which time 400 mg of Na_2CO_3 were added and the reaction mixture was stirred for an additional 30 minutes and filtered. Removal of the solvent and residual triethylorthoformate *in vacuo* and recrystallization of the product from ethyl acetate resulted in title compound (31 g, 74%). ^1H NMR (CDCl_3) δ 1.14-1.24 (6H), 3.4-3.9 (12H). Anal Calc: C, 50.85; H, 8.47. Found: C, 50.89; H, 8.69.

Example 3

Synthesis of 2,5-diisopropoxy-2,5-bis(hydroxymethyl)-[1,4]-dioxane (VII)

2,5-diisopropoxy-2,5-bis(hydroxymethyl)-[1,4]-dioxane was synthesized from DHA and triisopropylorthoformate in 2-propanol with *p*-TsOH as catalyst using the same protocol described in Example 2 for compound diethoxy derivative. ^1H NMR (CDCl_3) δ 1.18-1.26 (12H); 3.4-4.2 (10H). Anal. Calc. C, 54.53; H, 9.15. Found: C, 54.45; H, 9.06.

Example 4

Synthesis of poly(2,2-dimethoxypropylene carbonate) (V)

2,2-dimethoxypropylene carbonate (IV) was synthesized as follows: a) A solution of triethylamine (14.7 ml, 0.1 mole) in 30 mL of THF was added dropwise to a solution of III (7.15 g, 52.5 mmole) and ethylchloroformate (10 ml, 0.1 mole) in 100 mL of THF at 0°C. After addition was complete, the reaction mixture was stirred at room temperature for 3 hours, after which time the mixture was filtered and THF was removed *in vacuo*. The product was recrystallized from THF-ethyl ether to yield IV (2.5 g, 30%). b) To a solution of III (5 g, 36.76 mmole) and pyridine (18 ml, 0.2 mole) in 100 mL of CH_2Cl_2 at -70°C was added a solution of triphosgene (5.5 g, 18.5 mmole) in 70 mL of CH_2Cl_2 . After addition was complete, the mixture was allowed to warm to room temperature and stirred overnight, after which time the reaction mixture was subsequently washed with ammonium acetate, aq. HCl; aq. NaHCO_3 and brine and dried over sodium sulfate. After removal of the solvent, the product was isolated by flash chromatography on silica gel (eluent – ethyl acetate) and recrystallized from ethanol-hexanes to yield IV (4.5 g, 75%).

^1H NMR (CDCl_3): δ 4.28 (s; 4H), 3.30 (s; 6H). Anal. Calc.: C, 44.44; H, 6.17. Found: C, 44.58; H, 6.29.

Poly(2,2-dimethoxypropylene carbonate) (V) was synthesized as follows: 2,2-dimethoxypropylene carbonate (IV) and $\text{Sn}(\text{Oct})_2$ at varied monomer to initiator ratio (100:1 – 400:1) were placed into a glass vessel and evacuated. The reaction was carried out at 100°C for as long as efficient magnetic stirring was possible (1-2 h), after which time the

mixture was dissolved in methylene chloride and the polymer was obtained by precipitation into methanol. Average polymerization yield was 65%. Molecular weights M_n were determined by GPC with THF as eluent and polystyrene standards and ranged from 6000 to 25000 with polydispersities ranging from 1.4 to 1.5. ^1H NMR (CDCl_3): δ 4.28 (s; 4H), 3.30 (s; 6H). ^{13}C NMR (CDCl_3): δ 154 (-O-CO-O-), 99 (acetal carbon), 63 (-CH₂-), 49 (-OCH₃). Anal. Calc.: C, 44.44; H, 6.17. Found: C, 44.26; H, 6.04.

Example 5

Synthesis of Poly(2-oxypropylene carbonate) (VI)

Poly(2-oxypropylene carbonate) (VI) was synthesized as follows: Deacetalization of poly(2,2-dimethoxypropylene carbonate) (V) was carried out in trifluoroacetic acid – water mixture (4:1 v/v) at polymer concentration of 0.1 mg/ml for 15 minutes during which time the title polymer precipitated. The solid product was collected, washed several times with methanol and dried under vacuum. Anal. Calc.: C, 41.39; H, 3.47. Found: C, 41.34; H, 3.33.

To determine whether the trifluoroacetic acid degraded the polymer backbone, two infrared spectroscopy scans were carried out, one on (V) and one on (VI). The presence of the C-O stretch at 1700 which is distinctive for carbonyl groups, in the IR scan on (VI) showed the polymer carbonyl remains intact following deprotection with TFA:H₂O.

Example 6

Nucleophilic functionalization of (VI) using 2,2-dimethyl-1-methylethyldiamine

2,2-dimethyl-1-methylethyldiamine was added in excess to a suspension of (VI) in unbuffered water at room temperature. The solid (I) dissolved in the water within 1 hour and the functionalized polymer was analyzed by NMR spectroscopy. Modification of VI was also carried out by mixing (VI) with amine and precipitating the formed clear solution into hexane; precipitated polymer was dried, dissolved in water and analyzed by NMR spectroscopy. ^{13}C NMR revealed the absence of the characteristic C2 ketone located between

180 and 220 ppm demonstrating that no unreacted C2 ketone groups remained in the polymer (i.e., functionalization was complete.)

Example 7

Functionalization with Phenethylamine

To a suspension of (VI) (500 mg) in THF was added phenethylamine (0.27 microliters) and NaBH₃CN (670 mg) and the mixture was stirred overnight at 0°C whereupon the polymer dissolved. NMR spectroscopy did not allow a definitive determination of the final polymer structure. To show that the polymer dissolved due to reaction with the carbonyl, a polymer analogue, carbonic acid 3-ethoxycarbonyloxy-2-oxo-propyl ester ethyl ester, was synthesized and reacted (500 mg) with phenylethylamine (0.27 microliters) at 0°C for 1 hr, after which NaBH₃CN (670 mg) were added and the mixture stirred for another 3 hours at room temperature. The isolated product was subjected to ¹³C NMR, showing a quantitative elimination of the carbonyl, and the addition of the phenylethylamine.

Example 8

Amine-containing Polymer Binds to (VI) But Not to (V)

(V) was spin coated onto glass slides. Half of the coatings were deprotected using TFA/H₂O over 15 minutes. The slides were washed with deionized water and dried, then covered with a phosphate-buffered saline solution of a fluorescently labeled amine-containing polymer, namely polylysine conjugated with fluorescein (polylysine-FTIC), for 30 minutes, washed with deionized water again, and dried under N₂ gas. Images were obtained using a fluorescent microscope, and bright fields indicate that the polylysine-FTIC reacts with (VI), the unprotected form, but not with (V) the protected form. This characteristic is associated with, but not limited to, usefulness as a bioadhesive for surgical sutures or wound closure dressings.

Example 9

Synthesis of Poly(acetal carbonates) (VIII)

The polycondensation protocol for precondensing these was as follows: To a solution of diol (y mmole) in 3.5×y mmole of pyridine and z ml of CH₂Cl₂ was added dropwise a solution of triphosgene (5-z ml per gram of diol) at varied temperature and rate of addition. After complete addition, the mixture was allowed to stir for an additional 5 minutes and directly precipitated into methanol. The resulting polymer was collected by filtration, washed with methanol and dried under vacuum. The diol starting materials were compounds (VII) of Examples 2 and 3.

pEAC (R = -Et): ¹H NMR (CDCl₃) δ 1.10-1.25 (6H), 3.40-3.90 (8H), 4.0-4.4 (4H). ¹³C NMR (CDCl₃) δ 154 (-O-CO-O-), 94-98 (apical C), 64-67 (ring -CH₂- and -CH₂-OCOO-), 57 (-CH₂-CH₃), 15 (-CH₃). Anal. Calc. C, 50.38; H, 6.92. Found: C, 49.71; H, 7.23.

pPAC (R = -i-Pr): ¹H NMR (CDCl₃) δ 1.1-1.3 (12H), 3.5-4.3 (10H). ¹³C NMR (CDCl₃) δ 154 (-O-CO-O-), 94-98 (apical C), 63-67 (ring -CH₂- ; -CH₂-OCOO- and -CH-), 24 (-CH₃). Anal. Calc. C, 53.78; H, 7.64. Found: C, 55.05; H, 7.91.

Example 10

Synthesis of Poly(Spiroacetal) (IX) and (X)

Typical protocol for the synthesis of poly(spiroacetals) were as follows: Monomer, 2,2-dimethoxy-propane-1,3-diol (for producing IX) or 2,5-diethoxy-2,5-bis(hydroxymethyl)-[1,4]-dioxane (for producing X), (1 g) with diluent, DMSO or dimethoxytetraoxyethylene, 0 to 400 μl, were heated up to 100°C and stirred to form clear solution. *p*-Toluenesulfonic acid (5 mg) was added to reaction mixture, after which time it was stirred at 100°C under vacuum for 15 minutes or until efficient stirring was possible. The mixture was cooled to room temperature, dissolved in methylene chloride (1 ml) and precipitated from ethyl ether.

Poly(2,6-spiroacetal) (IX). ¹H NMR (CDCl₃ or DMSO) δ 3.0-4.2 (br). ¹³C NMR (CDCl₃ or DMSO) δ 89-99 (ring apex carbons), 62-64 (ring -CH₂- groups), 49 (terminal -OCH₃). Anal Calc: C, 47.37; H, 5.26. Found: C, 50.02; H, 7.26. M_w (0.9 - 3.0)×10³; typical M_w/M_n 1.5.

Poly (2,5-spiroacetal) (X). ^1H NMR (CDCl_3 or DMSO) δ 3.0-4.2 (br), 1.2 ($-\text{CH}_3$). ^{13}C NMR (CDCl_3 or DMSO) δ 89-99 (ring apex carbons), 56-71 (ring $-\text{CH}_2-$ groups, $-\text{OCH}_2\text{CH}_3$ and terminal $-\text{CH}_2\text{OH}$), 16 (terminal $-\text{OCH}_2\text{CH}_3$). Anal Calc: C, 47.37; H, 5.26. Found: C, 50.45; H, 7.12. M_w $(0.9 - 3.3) \times 10^3$; typical M_w/M_n 1.5.

Example 11

Synthesis of Polyester (XI)

Poly(2,2-dimethoxypropylene succinate) (XI) was synthesized as follows: 2,2-dimethoxy-1,3-propane diol (III) (1g, 7.35 mmole) and succinic acid (0.867 g, 7.35 mmole) were combined in 5 ml of methylene chloride. To this mixture dicyclohexylcarbodiimide (3.03 g, 14.70 mmole) and (dimethylamino)pyridine (10 mg) were added and reaction mixture was stirred for 24 h. After this, reaction mixture was diluted with methylene chloride to appr. 10 ml and filtered; excess of solvent was removed in vacuo, polymer was obtained by precipitating into methanol to yield 0.9 g (56%) of title polymer. M_w 6.0×10^3 ; M_w/M_n 1.4.

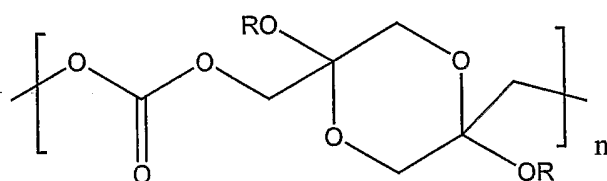
When 2,5-di- C_1 - C_{10} alkoxy-2,5-bis(hydroxymethyl)-[1,4]-dioxane (VII) is substituted for (III) in the above synthesis, poly(acetal ester) is produced.

Variations

The foregoing description of the invention has been presented describing certain operable and preferred embodiments. It is not intended that the invention should be so limited since variations and modifications thereof will be obvious to those skilled in the art, all of which are within the spirit and scope of the invention.

WHAT IS CLAIMED IS

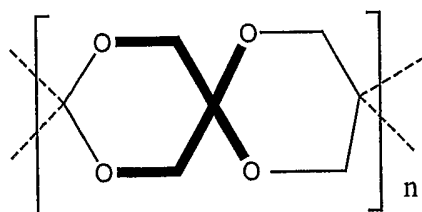
1. Polymer containing dihydroxy acetone monomer and/or dimer having a number average molecular weight ranging from 500 to 1,000,000.
2. The polymer of Claim 1 where the dihydroxyacetone monomer and/or dimer are chemically protected to make the polymer.
3. The polymer of Claim 2 where the carbonyl group of the dihydroxyacetone monomer is chemically protected or the hydroxyl groups of the dihydroxyacetone dimer are chemically protected.
4. The polymer of Claim 2 made from 2,2-di- C_1 - C_{10} alkoxy-propane-1,3-diol or 2,5-di- C_1 - C_{10} alkoxy-2,5-bis(hydroxymethyl)-[1,4]-dioxane.
5. The polymer of Claim 4 which is poly(dimethoxy propylene carbonate).
6. The polymer of Claim 1 which is poly(2-oxypropylene carbonate).
7. The polymer of Claim 4 which is a poly(acetal carbonate) and has the formula:



(VIII)

where R is C_1 - C_{10} straight chain or branched alkyl and n is number such that the number average molecular weight ranges from 500 to 1,000,000.

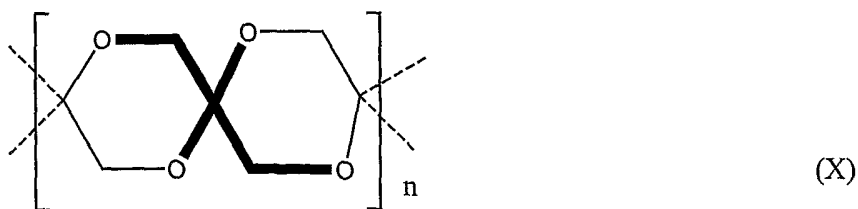
8. The polymer of Claim 4 which is poly(spiroacetal) obtained from 2,2-dimethoxy-propane-1,3-diol and has the structural formula:



(IX)

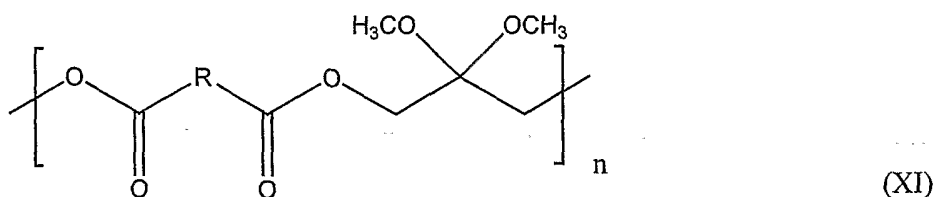
where n is a number such that the number average molecular weight ranges from 500 to 1,000,000.

9. The polymer of Claim 4 which is poly(spiroacetal) obtained from 2,5-diethoxy-2,5-bis(hydroxymethyl)-[1,4]-dioxane and has the structural formula:



where n is a number such that the number average molecular weight ranges from 500 to 1,000,000.

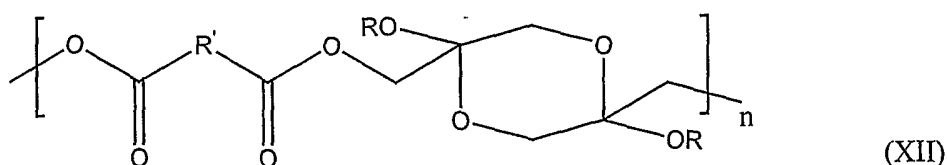
10. The polymer of Claim 4 which is a polyester and has the structural formula:



where R is C₁-C₁₀ straight chain or branched alkyl, cyclohexyl, dicyclohexyl, norbornyl, toluene, diphenylmethane, naphthalene or other aromatic and n is a number such that the number average molecular weight ranges from 500 to 1,000,000.

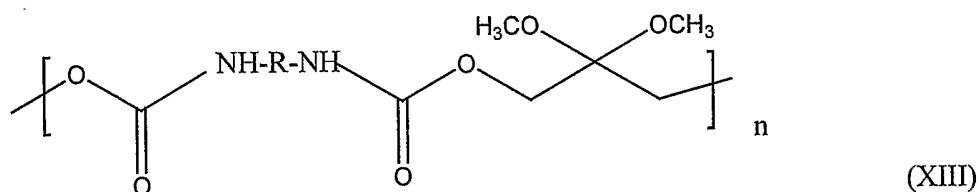
11. The polymer of Claim 10 where the dimethoxy is converted to a carbonyl.

12. The polymer of Claim 4 which is a polyester and has the structural formula:



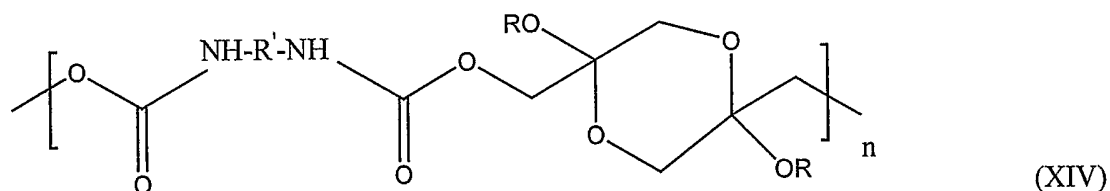
where R is C₁-C₁₀ straight chain or branched alkyl, R' is C₁-C₁₀ straight chain or branched alkyl, cyclohexyl, dicyclohexyl, norbornyl, toluene, diphenylmethane, naphthalene or other aromatic and n is a number such that the number average molecular weight ranges from 500 to 1,000,000.

13. The polymer of Claim 4 which is a polyurethane and has the formula:



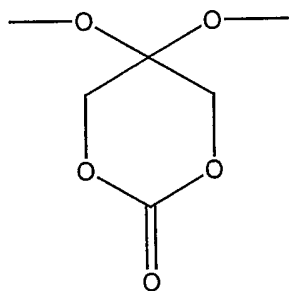
where R is C₁-C₁₀ straight chain or branched alkyl, cyclohexyl, dicyclohexyl, norbornyl, toluene, diphenylmethane, naphthalene or other aromatic and n is number such that the number average molecular weight ranges from 500 to 1,000,000.

14. The polymer of Claim 13 where the dimethoxy is converted to a carbonyl.
 15. The polymer of Claim 4 which is a polyurethane and has the formula:



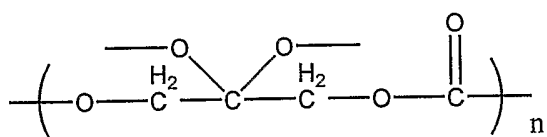
where R is C₁-C₁₀ straight chain or branched alkyl, R' is C₁-C₁₀ straight chain or branched alkyl, cyclohexyl, dicyclohexyl, norbornyl, toluene, diphenylmethane or naphthalene and n is a number such that the number average molecular weight ranges from 500 to 1,000,000.

16. A method for preparing the polymer of Claim 6 comprising the steps of (a) converting dihydroxyacetone monomer to 2,2-dimethoxy-propane-1,3-diol (III), (b) converting (III) to:



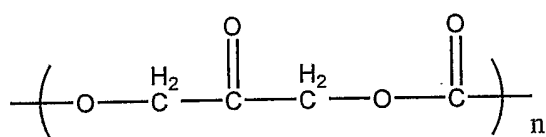
(IV)

(c) converting (IV) to



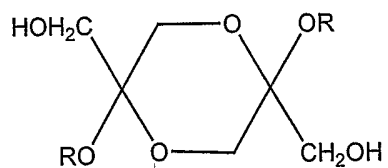
(V)

(d) converting (V) to:



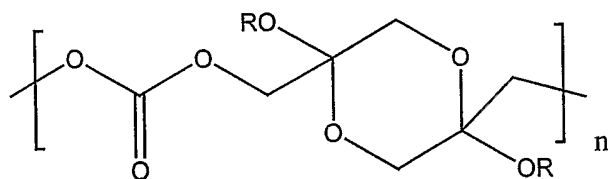
(VI)

17. A method for preparing the polymer of Claim 7 comprising the steps of (a) converting dihydroxyacetone dimer to



(VII)

and (b) converting (VII) to



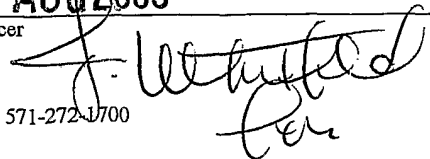
(VIII)

18. A method for preparing the polymer of Claim 8 comprising the step of subjecting (III) to dealcoholysis.
19. A method for preparing the polymer of Claim 9 comprising subjecting (VII) to dealcoholysis.
20. A method for preparing the polymer of Claim 10 which comprises subjecting (III) and a dicarboxylic acid to dehydration.
21. A method for preparing the polymer of Claim 12 which comprises subjecting (VII) and a dicarboxylic acid to dehydration.
22. A method for preparing the polymer of Claim 13 which comprises reacting (III) with a diisocyanate OCN-R-NCO.
23. A method for preparing the polymer of Claim 13 which comprises converting (III) to the corresponding bischloroformate and reacting the bischloroformate with diamine.
24. A method for preparing the polymer of Claim 15 which comprises reacting (VII) with diisocyanate OCN-R'-NCO.
25. A method for preparing the polymer of Claim 15 which comprises converting (VII) to the corresponding bischloroformate and reacting the bischloroformate with a diamine.
26. A method for preparing a dihydroxyacetone based polymer, comprising the steps of chemically protecting a starting material selected from the group consisting of dihydroxyacetone monomer and dihydroxyacetone dimer and converting the protected material to polymer comprising dihydroxyacetone monomer and/or dimer, having a number average molecular weight ranging from 500 to 1,000,000.
27. The polymer of Claim 6 which is functionalized by one or more nucleophiles.
28. The polymer of Claim 11 which is functionalized by one or more nucleophiles.
29. The polymer of Claim 14 which is functionalized by one or more nucleophiles.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US05/15376

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : C08G 18/30, 63/02, 64/00 US CL : 528/85, 272, 370, 403 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) U.S. : 528/85, 272, 370, 403 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 practicable, search terms used)																				
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category *</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>X</td> <td>US 6,037,467A (STAHL et al) 14 March 2000 (14.03.2000), claims 1 and 22</td> <td>1</td> </tr> <tr> <td>X</td> <td>US 6,087,465A (SEPPALA et al) 11 June 2000 (11.06.2000), claims 1 and 6.</td> <td>1</td> </tr> </tbody> </table>			Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 6,037,467A (STAHL et al) 14 March 2000 (14.03.2000), claims 1 and 22	1	X	US 6,087,465A (SEPPALA et al) 11 June 2000 (11.06.2000), claims 1 and 6.	1									
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☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.																				
<table border="1"> <thead> <tr> <th colspan="2">* Special categories of cited documents:</th> <th></th> </tr> </thead> <tbody> <tr> <td>"A"</td> <td>document defining the general state of the art which is not considered to be of particular relevance</td> <td>"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</td> </tr> <tr> <td>"E"</td> <td>earlier application or patent published on or after the international filing date</td> <td>"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</td> </tr> <tr> <td>"L"</td> <td>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)</td> <td>"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</td> </tr> <tr> <td>"O"</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>"P"</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td>"&" document member of the same patent family</td> </tr> </tbody> </table>			* Special categories of cited documents:			"A"	document defining the general state of the art which is not considered to be of particular relevance	"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	"E"	earlier application or patent published on or after the international filing date	"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	"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)	"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	"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	"&" document member of the same patent family
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Date of the actual completion of the international search 25 July 2005 (25.07.2005)		Date of mailing of the international search report 10 AUG 2005																		
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (703) 305-3230		Authorized officer Rachel F. Gorr  Telephone No. 571-272-1700																		