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(54) Title: UREA-SILOXANE COMPOSITIONS AND METHODS OF MAKING THE SAME

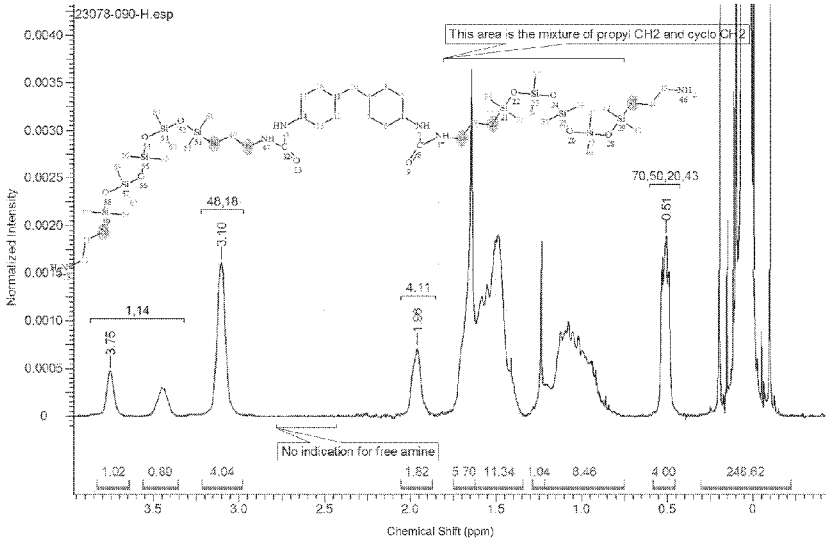


FIG. 1

(57) Abstract: An amphiphilic saccharide-urea-siloxane composition includes an amino-functional prepolymer reacted with saccharide lactone. The composition is prepared by reacting an amino-alkyl functional siloxane with isocyanate to form the amino-functional prepolymer, the molar ratio of amine in the amino-alkyl functional siloxane to cyanate in the isocyanate being greater than 1.

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UREA-SILOXANE COMPOSITIONS AND METHODS OF MAKING THE SAME

BRIEF SUMMARY OF THE INVENTION

[0001] According to one embodiment, an amphiphilic saccharide-urea-siloxane composition includes an amino-functional prepolymer reacted with saccharide lactone. The composition is prepared by reacting an amino-alkyl functional siloxane with isocyanate to form the amino-functional prepolymer, the molar ratio of amine in the amino-alkyl functional siloxane to cyanate in the isocyanate being greater than 1.

[0002] According to another embodiment, an amphiphilic saccharide-urea-siloxane composition includes about 0.01 to about 20 mol% urea, about 0.01 to about 20 mol% saccharide, and about 60 to about 99.8 mol% siloxane.

[0003] According to one process of the present invention, a method of forming an amphiphilic saccharide-urea-siloxane composition includes reacting an amino-alkyl functional siloxane with isocyanate to form an amino-functional prepolymer, the molar ratio of amine in the amino-alkyl functional siloxane to cyanate in the isocyanate being greater than 1. The method further includes reacting the amino-functional prepolymer with saccharide lactone to form the amphiphilic saccharide-urea-siloxane composition.

[0004] Additional aspects of the invention will be apparent to those of ordinary skill in the art in view of the detailed description of various embodiments, a brief description of which is provided below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] Features, aspects and advantages of the disclosed embodiments will become apparent from the following description and the accompanying exemplary embodiments shown in the drawings, which are briefly described below.

[0006] FIG. 1 is a graph showing the proton Nuclear Magnetic Resonance (NMR) of an amphiphilic urea-polyorganosiloxane according to one embodiment.

[0007] FIG. 2 is a graph showing the proton NMR of an amphiphilic urea-polyorganosiloxane according to another embodiment.

[0008] FIG. 3 is a graph showing the proton NMR of an amphiphilic urea-polyorganosiloxane according to another embodiment after a few hours.

[0009] FIG. 4 is a graph showing the proton NMR of an amphiphilic urea-polyorganosiloxane of the embodiment of FIG. 3 after completion.

[0010] FIG. 5 is a graph showing the carbon NMR of an amphiphilic urea-polyorganosiloxane of the embodiment of FIGs. 3 and 4.

[0011] FIG. 6a is a graph showing the physical properties of a urea siloxane film.

[0012] FIG. 6b is a graph showing the physical properties of a sugar urea siloxane film, according to one embodiment.

[0013] While the invention is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and will be described in detail herein. It should be understood, however, that the invention is not intended to be limited to the particular forms disclosed. Rather, the invention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention.

DETAILED DESCRIPTION OF THE INVENTION

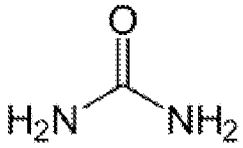
[0014] All amounts, ratios, and percentages are by weight unless otherwise indicated. The articles 'a', 'an', and 'the' each refer to one or more, unless otherwise indicated by the context of specification. The disclosure of ranges includes the range itself and also anything subsumed therein, as well as endpoints. Similarly, the disclosure of Markush groups includes the entire group and also any individual members and subgroups subsumed therein. For example, the Markush group including a hydrogen atom, an alkyl group, an aryl group, or an aralkyl group includes the member alkyl individually; the subgroup alkyl and aryl; and any other individual member and subgroup subsumed therein.

[0015] The embodiments herein describe novel amphiphilic urea-polyorganosiloxane compositions or, more specifically, amphiphilic saccharide-urea-siloxane compositions, and synthesis methods of making the same. The general composition of this novel composition may also be referred to as a urea-siloxane composition or a saccharide-modified urea siloxane composition.

[0016] According to one embodiment, an amphiphilic saccharide-urea-siloxane may be formed by reacting an amino-alkyl functional siloxane (component (a)) with isocyanate (component (b)) to form an amino-functional prepolymer. The reaction may take place at a temperature ranging from about 25°C to about 125°C. In another embodiment, the reaction may take place at a temperature ranging from about 60°C to about 70°C. The amino/isocyanate molar ratio is such that an amino functional prepolymer that can be reacted with sugar/saccharide lactone is obtained. In the embodiments described herein, the molar ratio of amine in the amino-alkyl functional siloxane to cyanate in the isocyanate is greater than 1. In one embodiment, the ratio of amine in the amino-alkyl functional siloxane to cyanate in the isocyanate is from about 1.01 to about 5.

[0017] The resulting amino-functional prepolymer is then reacted with sugar/saccharide lactone (component (c)) to form the amphiphilic saccharide-urea-siloxane composition. The reaction may take place, for example, in a solvent or a melt. The reaction may take place at a temperature ranging from about 25°C to about 85°C. In another embodiment, the reaction

may take place at a temperature ranging from about 50°C to about 80°C. In yet another embodiment, the reaction may take place at a temperature ranging from about 70°C to about 80°C. The molar ratio of the amino functionality of the prepolymer to the lactone functionality of the saccharide lactone depends on the amino alkyl structure. If the amino-alkyl functionality includes only one amine group, the molar ratio is 1. If the amino alkyl functionality includes two amine groups, the molar ratio is in the range of about 0.5 to 1. In other words, the lactone is intended to react with all of the primary amines, but at least some of the secondary amine may be left un-reacted.

[0018] The urea component of the compositions described herein has the general form HN-CO-NH, or . The urea generally links the siloxane with the isocyanate.

[0019] In one embodiment, an amphiphilic saccharide-urea-siloxane composition includes about 0.01 to about 20 mol% urea, about 0.01 to about 20 mol% saccharide, and about 60 to about 99.8 mol% siloxane. In another embodiment, the amphiphilic saccharide-urea-siloxane composition includes about 4 to about 10 mol% urea, about 0.4 to about 10 mol% saccharide, and about 80 to about 95.6 mol% siloxane.

[0020] The amino-alkyl functional siloxane component (component (a)) used to form the amphiphilic saccharide-urea-siloxane compositions described herein may include any amino-alkyl functional siloxane component known in the art. In one embodiment, the amino-alkyl functional siloxane component includes a terminal and/or pendant functional polydiorganosiloxane with at least 2 amino functionality. The polydiorganosiloxane may have one of the following general structures: (a) $(R^1_mR^2_n\text{-}Si(R^2)_2\text{-}O\text{-}[Si(R^2)_2\text{-}O]_y\text{-}Si(R^2)_2\text{-}(R^1_mR^2_n)$ or (b) $Si(R^2)_3\text{-}O\text{-}[Si(R^2R^1)\text{-}O]_x\text{-}[Si(R^2)_2\text{-}O]_y\text{-}Si(R^2)_3$ where m+n=1, m is from 0.1 to 1, x is from 1 to 2, y is from 1 to 1000, R^2 is an alkyl chain with 1-18 carbons, and R^1 is selected from $-CH_2CH_2NH_2$, $-CH_2CH_2\ CH_2NH_2$, $-CH_2CH_2CH_2CH_2NH_2$, $-CH_2CH(CH_3)CH_2NH2$, $-CH_2CH_3CH_2NHCH_2CH_2NH_2-\ CH_2CH_2NHCH_2CH_2NH_2$, $-CH_2CH_2CH_2NHCH_2CH_2CH_2NH_2$, $-CH_2CH_2CH_2CH_2NHCH_2CH_2CH_2CH_2NH_2$, $-CH_2CH_2CH_2NHCH_2CH_2NH_2$, $-CH_2CH(CH_3)CH_2NHCH_2CH_2NH_2$, $-CH_2CH_2CH_2CH_2CH_2NH_2$, $-CH_2CH_2CH_2CH_2CH_2CH_2NH_2$, $-CH_2CH_2NHCH_3$, $-CH_2CH_2CH_2NHCH_3$, $-CH_2CH_2CH_2CH_2NHCH_3$, $-CH_2CH(CH_3)CH_2NHCH_3$, $-CH_2CH_2NHCH_2CH_2NHCH_3$, $-CH_2CH_2CH_2NHCH_2CH_2CH_2NH\ CH_3$, $-CH_2CH_2CH_2CH_2NHCH_2CH_2CH_2CH_2NHCH_3$, $-CH_2CH_2CH_2NHCH_2CH_2NH\ CH_3$, $-CH_2CH(CH_3)CH_2NHCH_2CH_2NHCH_3$, $-CH_2CH_2CH_2CH_2CH_2NHCH_3$, or $-CH_2CH_2CH_2CH_2CH_2CH_2NHCH_3$. When m is 1, some of the terminals of the polydiorganosiloxane chains will not have amino alkyl functionality but, rather, alkyl functionality.

[0021] The isocyanate component (component (b)) may be any isocyanate component known in the art. Examples of suitable isocyanate components for forming the amphiphilic saccharide-urea-siloxane composition include, but are not limited to, organic polyisocyanates, which may have two or more isocyanate functionalities, and include conventional aliphatic, cycloaliphatic, araliphatic and aromatic isocyanates. The isocyanate component may include, but is not limited to, diphenylmethane diisocyanates (MDI), polymeric diphenylmethane diisocyanates (pMDI), toluene diisocyanates (TDI), hexamethylene diisocyanates (HDI), dicyclohexylmethane diisocyanates (HMDI), isophorone diisocyanates (IPDI), cyclohexyl diisocyanates (CHDI), and combinations thereof. In one embodiment, the isocyanate component is of the formula OCN--R--NCO, wherein R is selected from one of an alkyl moiety, an aryl moiety, and an arylalkyl moiety. In this embodiment, the isocyanate component can include any number of carbon atoms, typically from 4 to 20 carbon atoms.

[0022] Specific examples of suitable isocyanate components include: alkylene diisocyanates with 4 to 12 carbons in the alkylene radical such as 1,12-dodecane diisocyanate, 2-ethyl-1,4-tetramethylene diisocyanate, 2-methyl-1,5-pentamethylene diisocyanate, 1,4-tetramethylene diisocyanate and preferably 1,6-hexamethylene diisocyanate; cycloaliphatic diisocyanates such as 1,3- and 1,4-cyclohexane diisocyanate as well as any mixtures of these isomers, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane, 2,4- and 2,6-hexahydrotoluene diisocyanate as well as the corresponding isomeric mixtures, 4,4'- 2,2'-, and 2,4'-dicyclohexylmethane diisocyanate as well as the corresponding isomeric mixtures, and aromatic diisocyanates and polyisocyanates such as 2,4- and 2,6-toluene diisocyanate and the corresponding isomeric mixtures, 4,4'-, 2,4'-, and 2,2'-diphenylmethane diisocyanate and the corresponding isomeric mixtures, mixtures of 4,4'-, 2,4'-, and 2,2-diphenylmethane diisocyanates and polyphenylenepolymethylene polyisocyanates, as well as mixtures of MDI and toluene diisocyanates.

[0023] The isocyanate component may include modified multivalent isocyanates, i.e., products obtained by the partial chemical reaction of organic diisocyanates and/or polyisocyanates. Examples of suitable modified multivalent isocyanates include diisocyanates and/or polyisocyanates containing ester groups, urea groups, biuret groups, allophanate groups, carbodiimide groups, isocyanurate groups, and/or urethane groups. Specific examples of suitable modified multivalent isocyanates include organic polyisocyanates containing urethane groups and having an NCO content of 15 to 33.6 parts by weight based on the total weight, e.g. with low molecular weight diols, triols, dialkylene glycols, trialkylene glycols, or polyoxyalkylene glycols with a molecular weight of up to 6000; modified 4,4'-diphenylmethane diisocyanate or 2,4- and 2,6-toluene diisocyanate, where

examples of di- and polyoxyalkylene glycols that may be used individually or as mixtures include diethylene glycol, dipropylene glycol, polyoxyethylene glycol, polyoxypropylene glycol, polyoxyethylene glycol, polyoxypropylene glycol, and polyoxypropylene polyoxyethylene glycols or -triols. Prepolymers containing NCO groups with an NCO content of from 3.5 to 29 parts by weight based on the total weight of the isocyanate and produced from the polyester polyols and/or polyether polyols; 4,4'-diphenylmethane diisocyanate, mixtures of 2,4'- and 4,4'-diphenylmethane diisocyanate, 2,4- and/or 2,6-toluene diisocyanates or polymeric MDI are also suitable. Furthermore, liquid polyisocyanates containing carbodiimide groups having an NCO content of from 15 to 33.6 parts by weight based on the total weight of the isocyanate component, may also be suitable, e.g. based on 4,4'- and 2,4'- and/or 2,2'-diphenylmethane diisocyanate and/or 2,4'- and/or 2,6-toluene diisocyanate. The modified polyisocyanates may optionally be mixed together or mixed with unmodified organic polyisocyanates such as 2,4'- and 4,4'-diphenylmethane diisocyanate, polymeric MDI, 2,4'- and/or 2,6-toluene diisocyanate.

[0024] In one embodiment, the isocyanate component is a diisocyanate. As known to those of ordinary skill in the art, diisocyanates include two isocyanate functional groups, i.e., two NCO groups.

[0025] In another embodiment, the isocyanate component is a polyisocyanate. As known to those of ordinary skill in the art, polyisocyanates include three or more isocyanate functional groups.

[0026] In other embodiments, the isocyanate component can include a combination of one or more diisocyanates and one or more polyisocyanates. The isocyanated intermediary includes a plurality of the isocyanate functional groups.

[0027] The saccharide lactone component (component (c)) may include any saccharide and/or saccharide lactone known in the art. Non-limiting examples of the ssaccharide lactone component may include gluconolactone, lactobionolactone, combinations thereof, or the like.

[0028] According to one embodiment, an amphiphilic saccharide-urea-siloxane composition includes an amino-functional prepolymer reacted with saccharide lactone, wherein the composition is prepared by reacting an amino-alkyl functional siloxane with isocyanate to form the amino-functional prepolymer. The molar ratio of amine in the amino-alkyl functional siloxane to cyanate in the isocyanate is greater than 1 (e.g., about 1.01 to about 5). The amino-functional prepolymer may be reacted with the saccharide lactone in a solvent or a melt. The amino-functional prepolymer may react with the saccharide lactone at a temperature ranging from about 25°C to about 85°C, about 50°C to about 80°C, or about 70°C to about 80°C. The composition may be a film, which may be formed in the absence of

further catalysis or chemical reaction. The composition may be tacky, sticky, rubbery, a plastic, or an elastomer.

[0029] The amphiphilic saccharide-urea-siloxane compositions of the embodiments described herein may form a film by forming one or more networks via secondary bonding, without further catalysis or chemical reaction. The amphiphilic saccharide-urea-siloxane composition can be easily customized by varying one or more parameters including, but not limited to the following: chain type and/or length of the amino-alkyl functional siloxane, amine content, type of isocyanate, type of isocyanate terminal prepolymer, type of amino-alkyl functional siloxane, saccharide and/or saccharide lactone type, any combination thereof, and the like. These variations allow for a wide range of characteristics to be obtained, including, but not limited to, tacky, sticky, rubbery, elastomeric, plastic, and the like.

[0030] The novel amphiphilic urea-polyorganosiloxanes described herein may be useful, in particular, in the health care industry. Applications within the health care industry include, but are not limited to, medical devices for wound care or drug delivery, such as pressure sensitive adhesives, soft skin adhesives, film formers, or medical tubing such as catheters, pharmaceutical processing, or diagnostic devices. In each of these applications, the ability to load and controllably release various drugs or active agents can be especially beneficial. Active agents can be any component suitable for transdermal delivery. Examples include, but are not limited to, cardioactive medications, androgenic stereoids, estrogens, hormones, proestational agents, drugs having an action on the central nervous system, nutritional agents, anti-inflammatory agents, antihistamines, respiratory agents, sympathomimetics, miotics, cholinergic agonists, antimuscarinic or muscarinic cholinergic blocking agents, mydriatics, psychicenergizers, anti-infectives, dermatological agents, humoral agents, antispasmodics, antidepressant drugs, anti-diabetic, anorectic drugs, anti-allergenics, tranquilizers, antipsychotics, decongestants, antipyretics, antimigrane agents, drugs for treating nausea and vomiting, anti-malarials, anti-ulcerative agents, peptides, drugs for Parkinson's disease, drugs for spasticity, drugs for acute muscle spasms, anti-estrogen, anti-hormone agents, therapeutic agents, and combinations thereof.

EXAMPLES

[0031] The examples below are intended to illustrate the embodiments of the present invention to one of ordinary skill in the art and should not be interpreted as limiting the scope of the invention set forth in the claims.

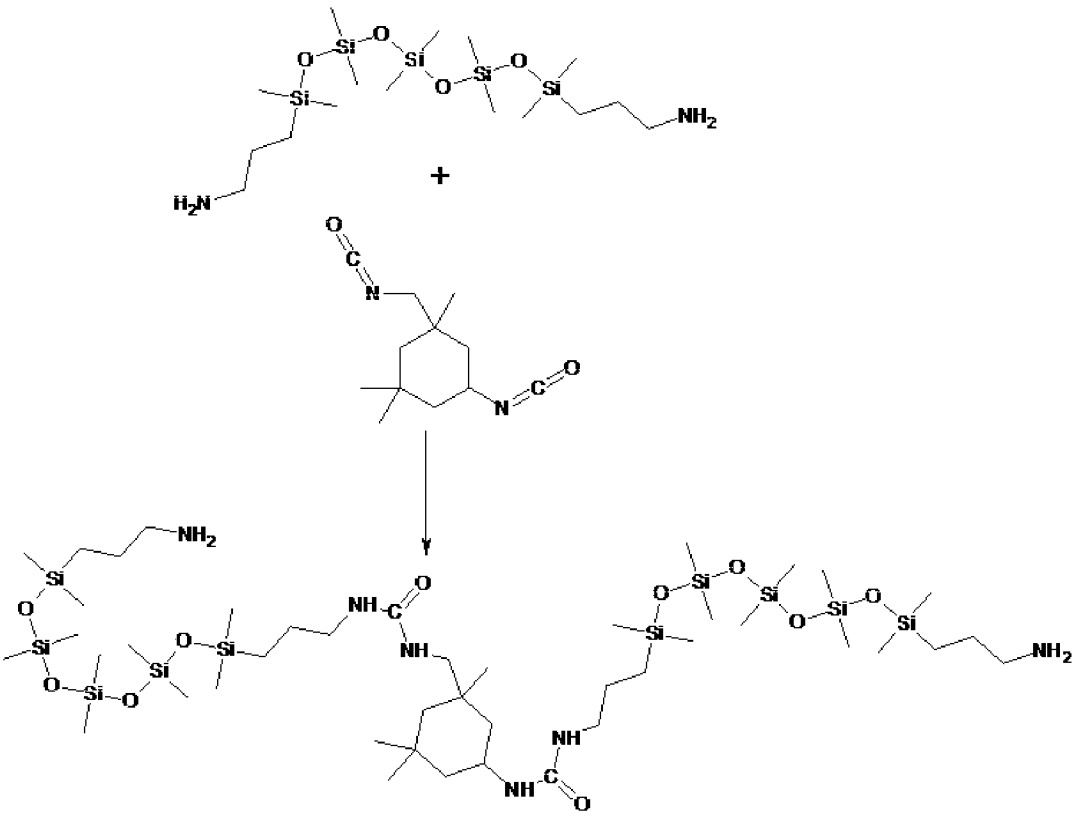
Example 1

[0032] An amphiphilic saccharide-urea-siloxane was prepared according to one embodiment, as described below. The molar ratio or amine to isocyanate was about one-to-one. Theoretically, there was no isocyanate or amine left in the system. Therefore, there

was no way to attach sugar functionality. The structure was also confirmed by proton Nuclear Magnetic Resonance (NMR), as shown in FIG. 1.

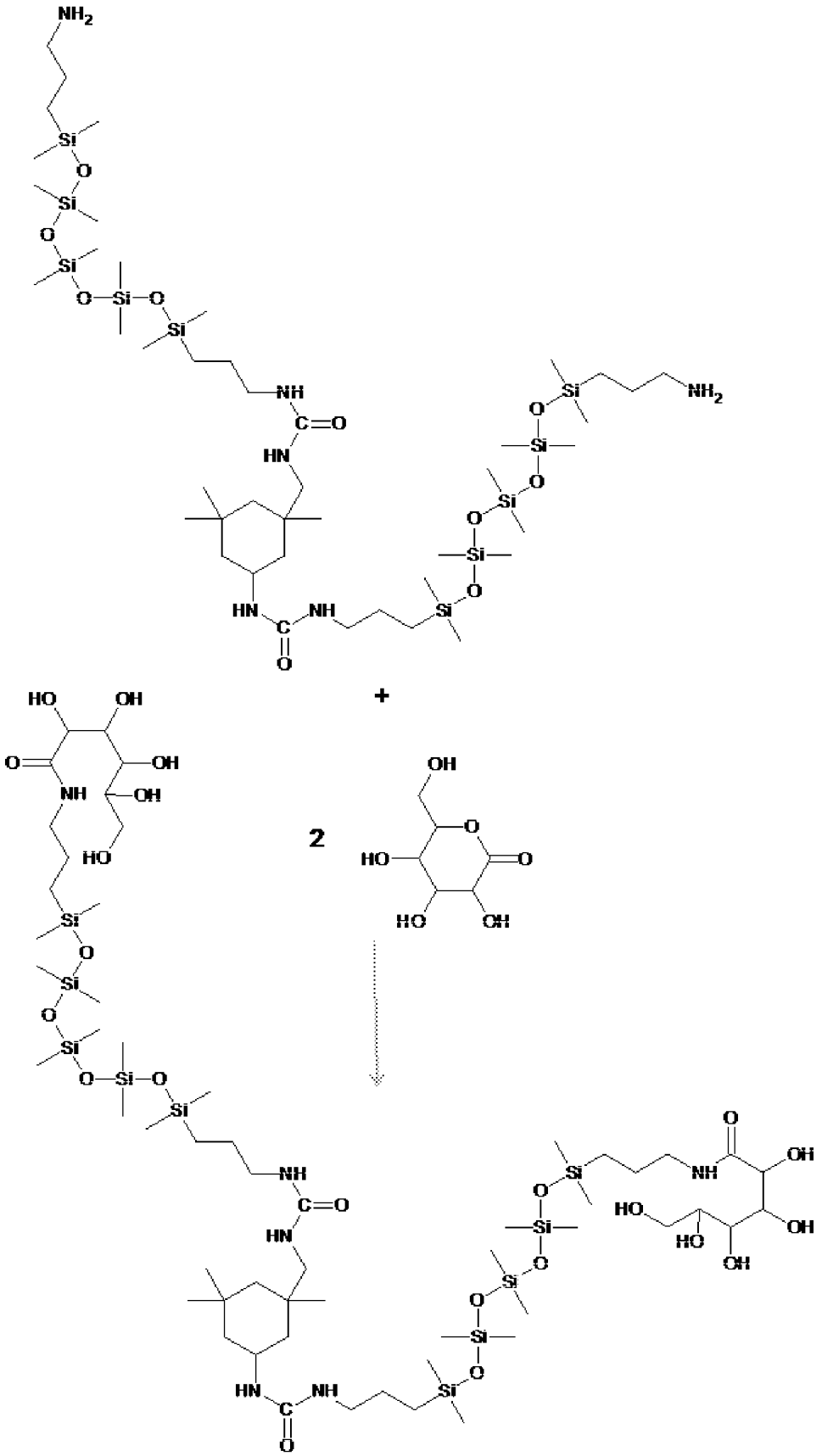
Example 2

[0033] In this example, the molar ratio of amine to isocyanate for the reaction of aminosiloxane and isocyanate was modified to about 1.15. The molecular weight decreased, and resulting prepolymer was amino-functional. The reaction is shown below:



The presence of amino functionality is indirectly shown in the proton NMR of FIG. 2, where the CH_2 protons adjacent to the unreacted primary amine appear at about 2.66 ppm.

[0034] The amino-functional prepolymer was then further reacted with saccharide lactone. This reaction occurred in solvent, and was generally run at about 70°C to about 80°C. The reaction is shown below:



[0035] The reaction completion was proven by proton and carbon NMR. In the proton NMR, shown in FIG. 3, the reaction completion is evidenced by the disappearance of the CH_2 peak next to the unreacted primary amine at about 2.66 ppm and the appearance of a peak at about 4.16 ppm, indicating saccharide CH next to an amide. FIG. 3 shows the reaction after a few hours, and FIG. 4 shows the reaction after completion. Additional evidence of the reaction completion includes the appearance of an amide peak in the carbon NMR, as shown in FIG. 5.

[0036] The obtained amphiphilic saccharide-urea-siloxane formed a clear film when the solvent was evaporated. It is contemplated that the amphiphilic saccharide-urea-siloxane could also or alternatively be processed with heat.

[0037] The saccharide not only provided hydrophilic groups, but it also enhanced the physical properties of the film, as shown in FIGs. 6a and 6b and Table 1 below. As evidenced in Table 1, increasing the saccharide content by only about 1% nearly doubled the strength property of the amphiphilic urea-polyorganosiloxane.

Table 1

Material	Saccharide Content, %	Molecular Weight	Peak Stress, psi
Sugar urea siloxane	~1	32,350	6.9
Urea siloxane	0	32,000	3.9

[0038] While the invention is susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the examples and described in detail herein. It should be understood, however, that the invention is not intended to be limited to the particular forms disclosed. Rather, the invention is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the invention as defined by the appended claims.

CLAIMS

1. An amphiphilic saccharide-urea-siloxane composition comprising:

an amino-functional prepolymer reacted with saccharide lactone,

wherein the composition is prepared by reacting an amino-alkyl functional siloxane with isocyanate to form the amino-functional prepolymer, the molar ratio of amine in the amino-alkyl functional siloxane to cyanate in the isocyanate being greater than 1.

2. The composition of claim 1, wherein the amino-functional prepolymer is reacted with the saccharide lactone in a solvent or a melt.

3. The composition of any of claims 2-3, wherein the composition is a film, the film being formed by evaporating the solvent in the absence of further catalysis or chemical reaction.

4. The composition of any of claims 1-6, wherein the ratio of amine to cyanate is from about 1.01 to about 5.

5. The composition of claim 1, wherein the composition comprises

about 0.01 to about 20 mol% urea;

about 0.01 to about 20 mol% saccharide; and

about 60 to about 99.8 mol% siloxane.

6. An amphiphilic saccharide-urea-siloxane composition comprising:

about 0.01 to about 20 mol% urea;

about 0.01 to about 20 mol% saccharide; and

about 60 to about 99.8 mol% siloxane.

7. The composition of any of claims 8-10, wherein the composition is a film, plastic, or elastomer.

8. The composition of any of claims 1-12, wherein the composition is used to form a skin adhesive, a film former, or a medical tubing.

9. The composition of any of claims 1-13, further comprising one or more drugs or active agents, the composition being configured to controllably release the one or more drugs.

10. A method of forming an amphiphilic saccharide-urea-siloxane composition, the method comprising:

reacting an amino-alkyl functional siloxane with isocyanate to form an amino-functional prepolymer, the molar ratio of amine in the amino-alkyl functional siloxane to cyanate in the isocyanate being greater than 1; and

reacting the amino-functional prepolymer with saccharide lactone to form the amphiphilic saccharide-urea-siloxane composition.

11. The method of claim 15, wherein the amino-functional prepolymer is reacted with the saccharide lactone in a solvent or a melt.

12. The method of any of claims 16-17, further comprising evaporating the solvent to form a film of the amphiphilic saccharide-urea-siloxane composition in the absence of further catalysis or chemical reaction.

13. The method of any of claims 15-20, wherein the amino-alkyl functional siloxane includes one or more amino-alkyl functional siloxane chains, wherein the one or more amino-alkyl functional siloxane chains is linear and/or pendant functional with at least 2 amino functionality and has a general structure selected from

(a) $(R^1_mR^2_n\text{-}Si(R^2)_2\text{-}O\text{-}[Si(R^2)_2\text{-}O]_y\text{-}Si(R^2)_2\text{-}(R^1_mR^2_n)$ or

(b) (b) $Si(R^2)_3\text{-}O\text{-}[Si(R^2R^1)\text{-}O]_x\text{-}[Si(R^2)_2\text{-}O]_y\text{-}Si(R^2)_3$

where m+n=1, m is from 0.1 to 1, x is from 1 to 2, y is from 1 to 1000, R^2 is an alkyl chain with 1-18 carbons, and R^1 is selected from $-CH_2CH_2NH_2$, $-CH_2CH_2\ CH_2NH_2$, $-CH_2CH_2CH_2CH_2NH_2$, $-CH_2CH(CH_3)CH_2NH2$, $-CH_2CH_3CH_2NHCH_2CH_2NH_2-CH_2CH_2NHCH_2CH_2NH_2$, $-CH_2CH_2CH_2NHCH_2CH_2CH_2NH_2$, $-CH_2CH_2CH_2CH_2NHCH_2CH_2CH_2CH_2NH_2$, $-CH_2CH_2CH_2NHCH_2CH_2NH_2$, $-CH_2CH(CH_3)CH_2NHCH_2CH_2NH_2$, $-CH_2CH_2CH_2CH_2CH_2NH_2$, $-CH_2CH_2CH_2CH_2CH_2CH_2NH_2$, $-CH_2CH_2NHCH_3$, $-CH_2CH_2CH_2NHCH_3$, $-CH_2CH_2CH_2CH_2NHCH_3$, $-CH_2CH(CH_3)CH_2NHCH_3$, $-CH_2CH_2NHCH_2CH_2NHCH_3$, $-CH_2CH_2CH_2NHCH_2CH_2CH_2NH\ CH_3$, $-CH_2CH_2CH_2CH_2NHCH_2CH_2CH_2CH_2NHCH_3$, $-CH_2CH_2CH_2NHCH_2CH_2NH\ CH_3$, $-CH_2CH(CH_3)CH_2NHCH_2CH_2NHCH_3$, $-CH_2CH_2CH_2CH_2CH_2NHCH_3$, or $-CH_2CH_2CH_2CH_2CH_2CH_2NHCH_3$.

14. The method of any of claims 15-21, wherein the ratio of amine to cyanate is from about 1.01 to about 5.

15. An amphiphilic saccharide-urea-siloxane composition formed using the method of any of claims 15-22.

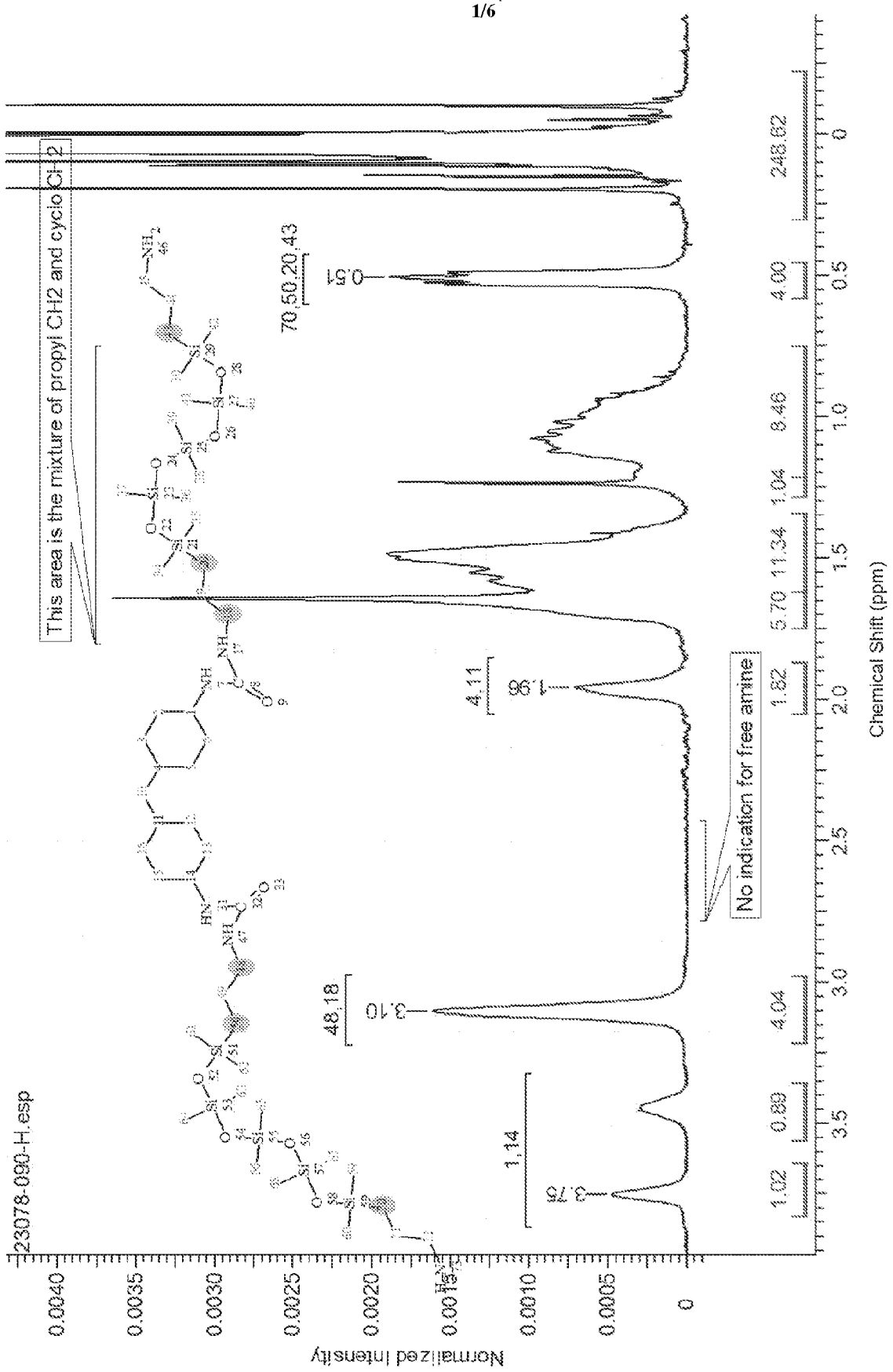

23078-090-H.esp
Normalized Intensity
Chemical Shift (ppm)
This area is the mixture of propyl CH2 and cyclo CH2
No indication for free amine
3.75
1.14
3.10
48.18
1.96
4.11
0.51
70.50.20.43
1.02
0.89
4.04
1.82
5.70
11.34
1.04
8.46
4.00
248.62

FIG. 1

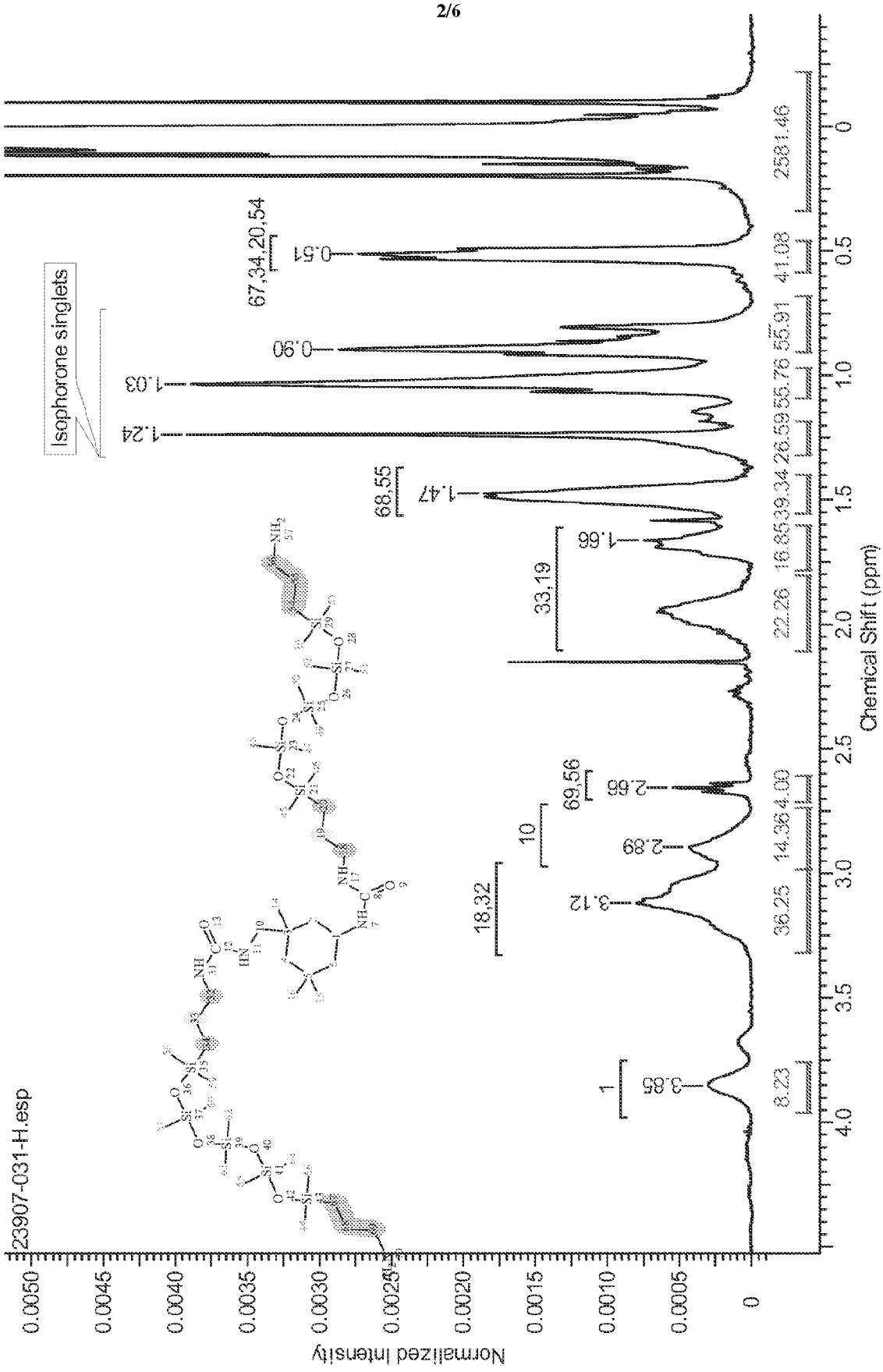

23907-031-H.esp
Normalized Intensity
Chemical Shift (ppm)
Isophorone singlets
3.85
3.12
2.89
2.66
1.66
1.47
1.24
1.03
0.90
0.51
1
10
18.32
33.19
68.55
67.34.20.54
69.56
8.23
36.25
14.36
4.00
22.26
16.85
39.34
26.59
55.76
55.91
41.08
2581.46

FIG. 2

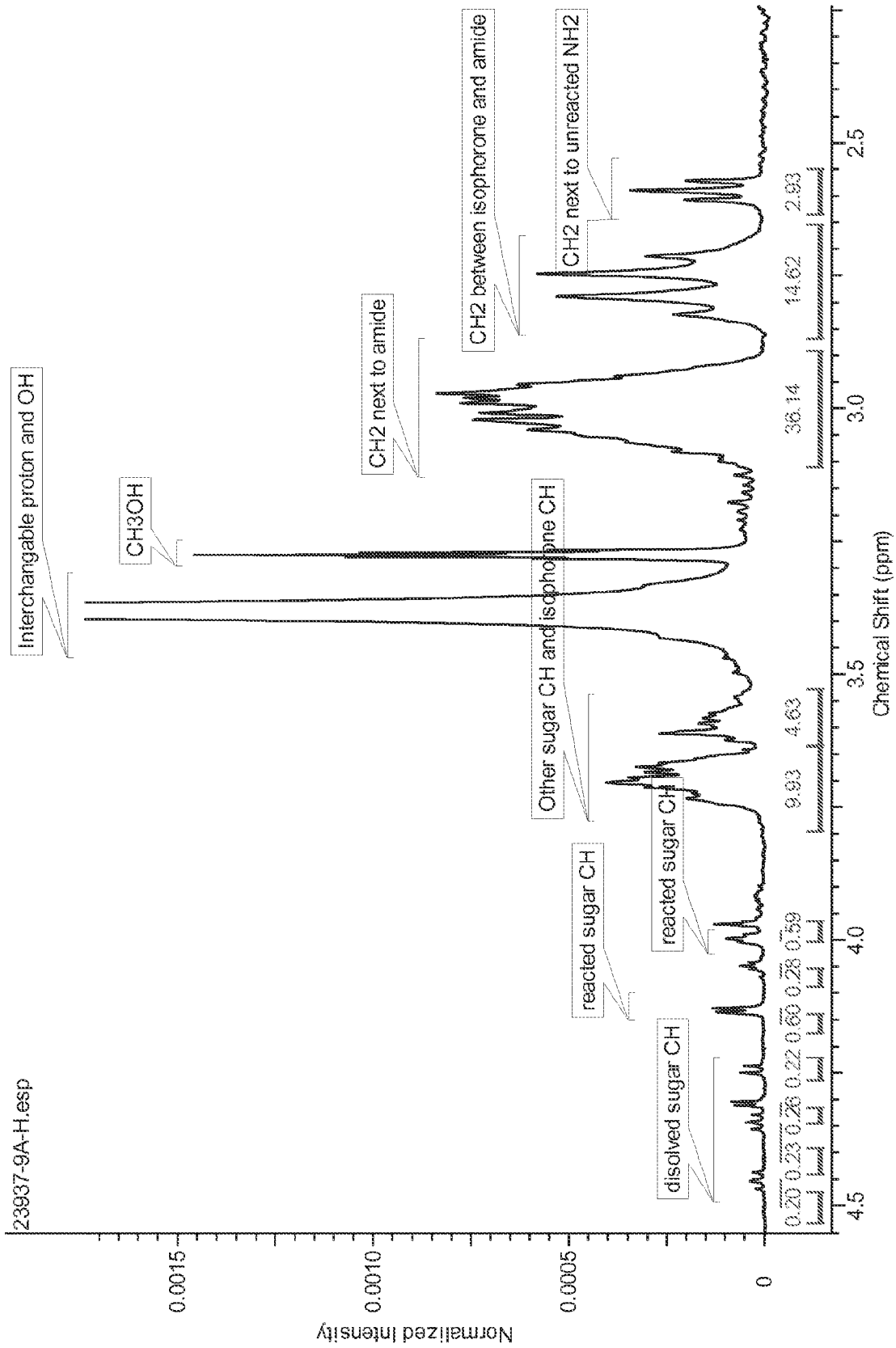

23937-9A-H.esp
Normalized Intensity
0.0015
0.0010
0.0005
0
Interchangable proton and OH
CH3OH
CH2 next to amide
CH2 between isophorone and amide
CH2 next to unreacted NH2
Other sugar CH and isophorone CH
reacted sugar CH
reacted sugar CH
disolved sugar CH
0.20 0.23 0.26 0.22 0.60 0.28 0.59
9.93
4.63
36.14
14.62
2.93
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

FIG. 3

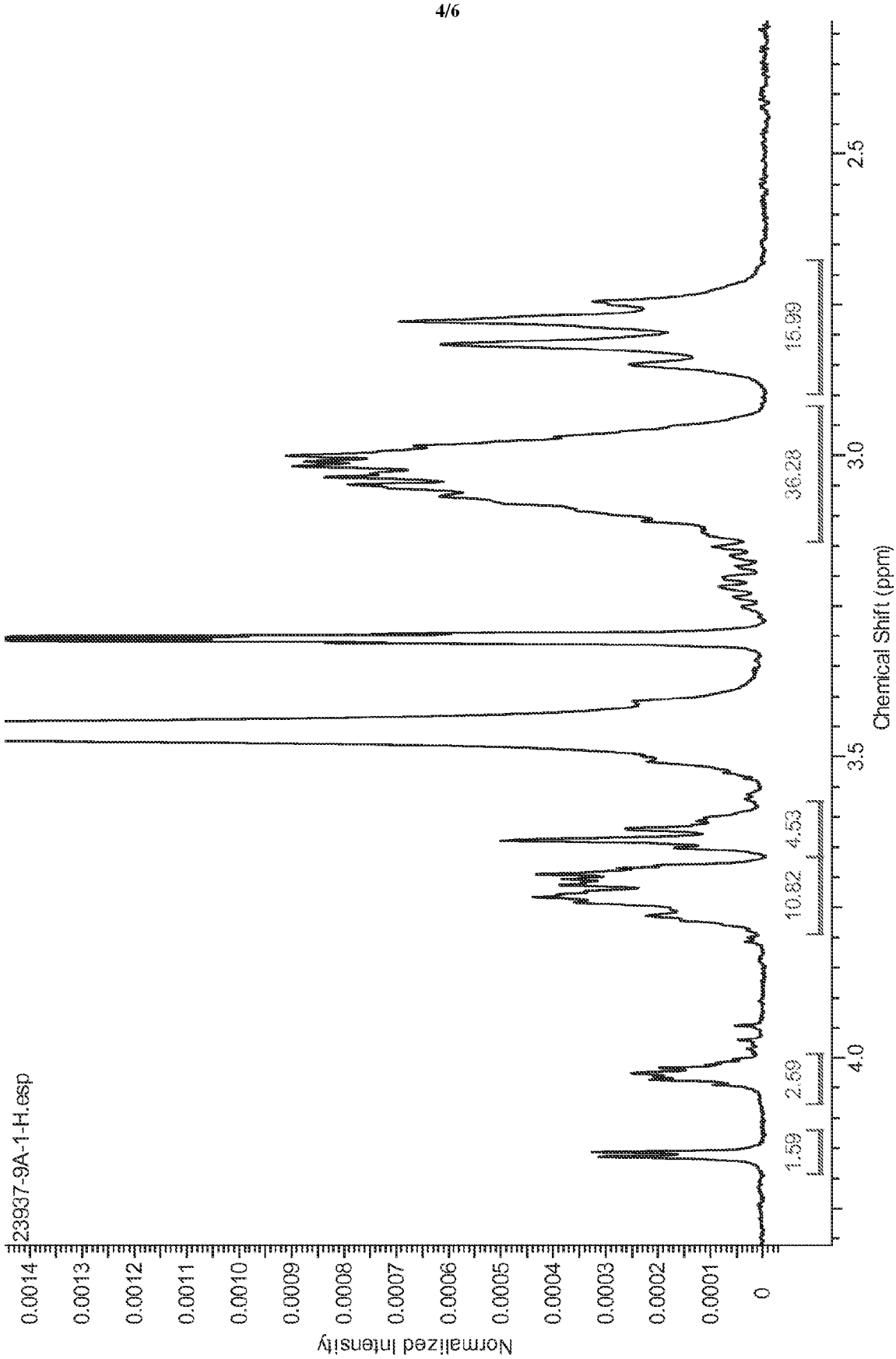

23937-9A-1-H.esp
Normalized Intensity
0.0014
0.0013
0.0012
0.0011
0.0010
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
1.59
2.59
10.82
4.53
36.28
16.99
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

FIG. 4

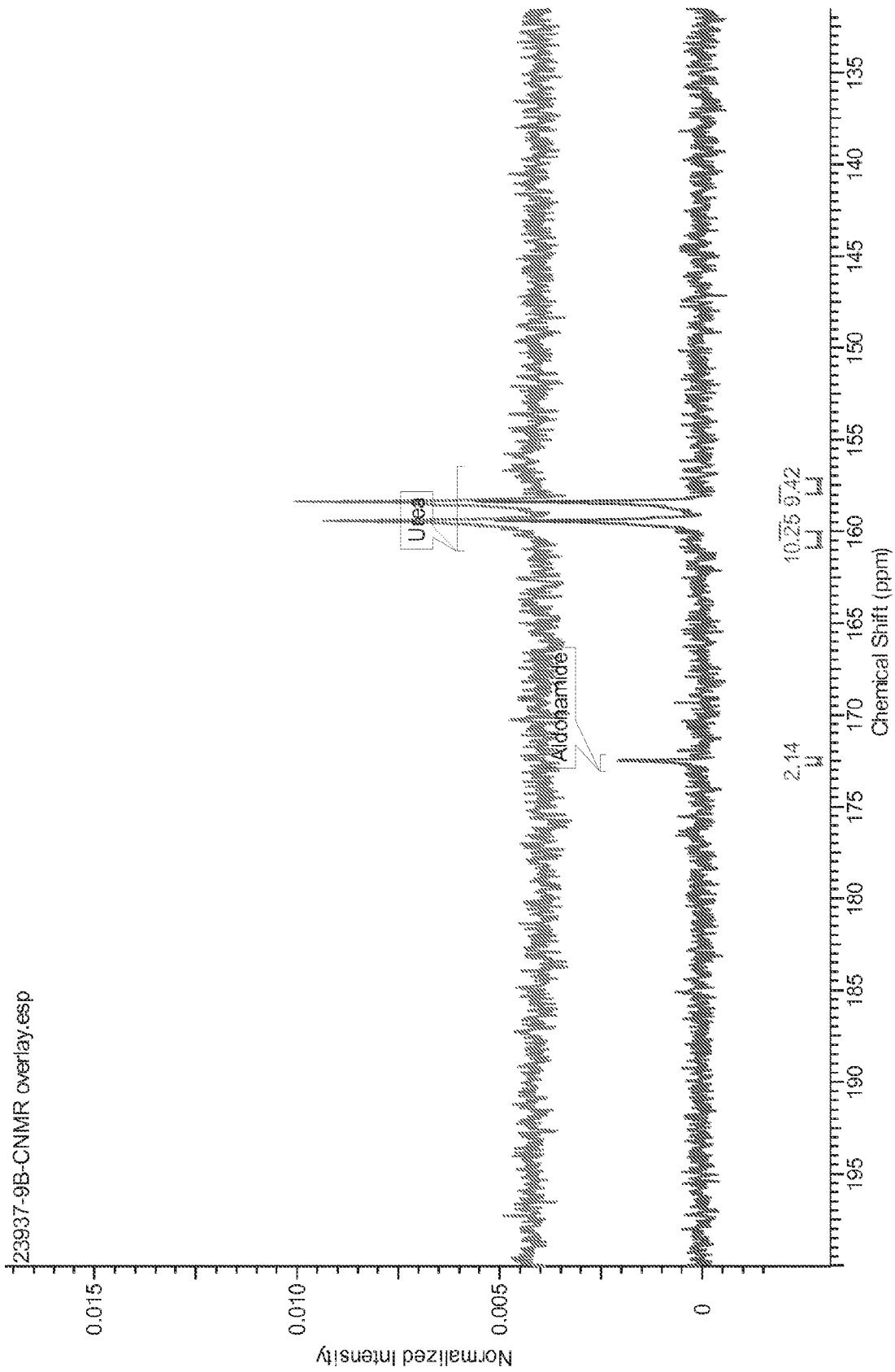

23937-9B-CNMR overlay.esp
Normalized Intensity
0.015
0.010
0.005
0
Urea
Aldohamide
2.14
10.25
9.42
195
190
185
180
175
170
165
160
155
150
145
140
135
Chemical Shift (ppm)

FIG. 5

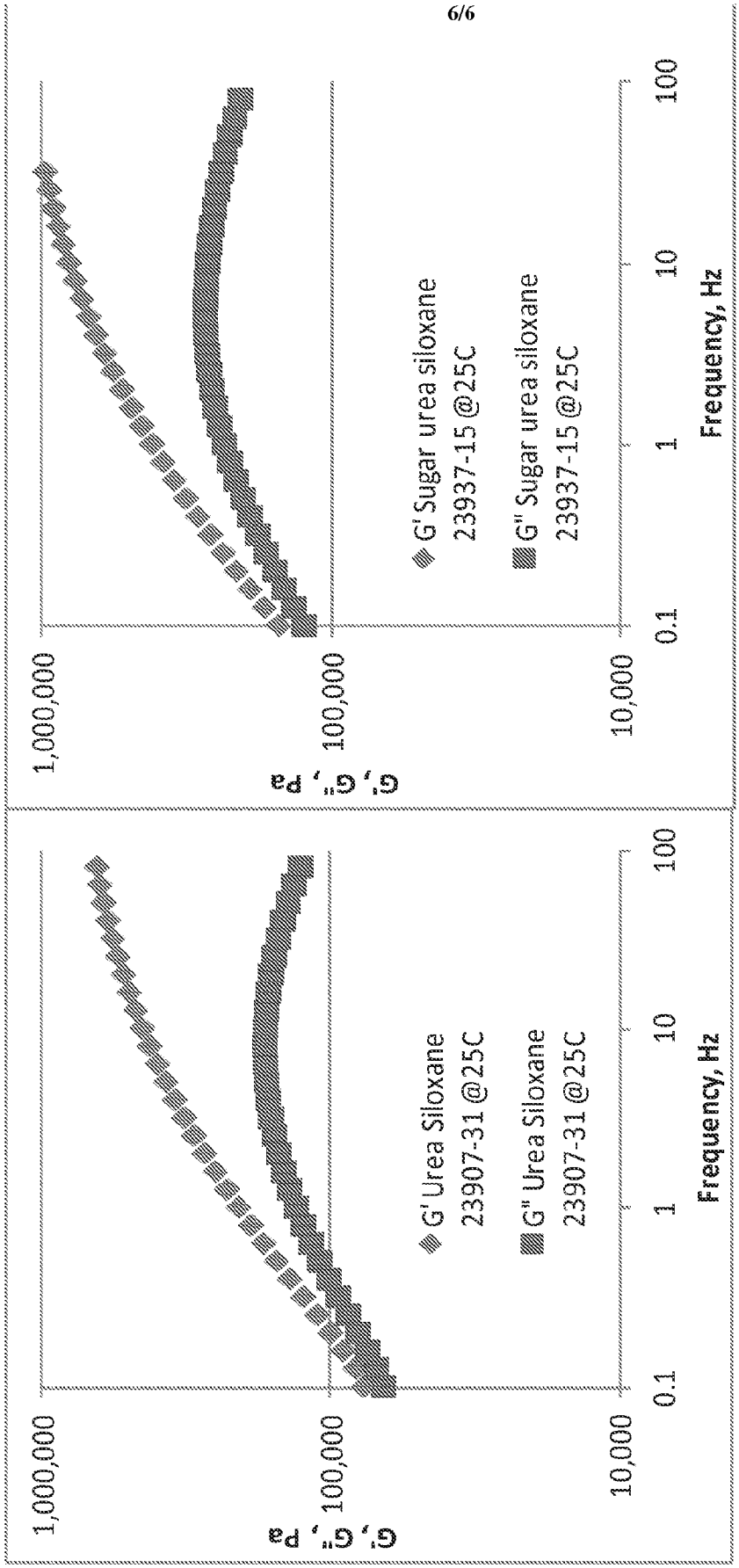

1,000,000
100,000
10,000
G', G", Pa
0.1
1
10
100
Frequency, Hz
G' Urea Siloxane
23907-31 @25C
G" Urea Siloxane
23907-31 @25C
G' Sugar urea siloxane
23937-15 @25C
G" Sugar urea siloxane
23937-15 @25C

FIG. 6a

FIG. 6b

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/025832

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08G77/388 C08L83/08
ADD.

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 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 practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2009/258058 A1 (THOMAS XAVIER [FR] ET AL) 15 October 2009 (2009-10-15) paragraph [0027] - paragraph [0065]	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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"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
2 July 2014	15/07/2014

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

Information on patent family members

International application No
PCT/US2014/025832

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2009258058 A1	15-10-2009	CN 101478973 A	08-07-2009
		EP 2019678 A2	04-02-2009
		JP 5185259 B2	17-04-2013
		JP 2009538370 A	05-11-2009
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		US 2009258058 A1	15-10-2009
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