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(54) Title: ALKOXY POLYSILOXANES AND METHODS OF MAKING ALKOXY SILANES AND SILOXANES

(57) Abstract: Methods of making alkoxy polysiloxanes, as well as alkoxy-substituted silanes are described. Generally, the methods involve the reaction of an alcohol with a hydrosilane or a hydrosiloxane in the presence of a palladium or platinum catalyst. Alkoxy polysiloxanes, including linear and branched alkoxy polysiloxanes are also described.

ALKOXY POLYSILOXANES AND METHODS OF MAKING ALKOXY SILANES AND SILOXANES

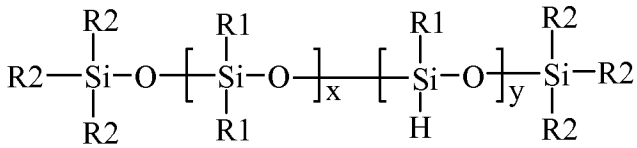
FIELD

[0001] The present disclosure relates to alkoxy polysiloxanes, including linear and branched alkoxy polysiloxanes. Methods of making alkoxy polysiloxanes, as well as alkoxy-substituted silanes are also described. Specifically, the methods involve the reaction of an alcohol with a hydrosilane or a hydrosiloxane in the presence of a palladium or platinum catalyst.

SUMMARY

[0002] Briefly, in one aspect, the present disclosure provides methods of making an alkoxy polysiloxane comprising combining a hydropolysiloxane and an alcohol and reacting the hydropolysiloxane and the alcohol in the presence of at least one of a Pd(0) and Pt(0) catalyst to form the alkoxy polysiloxane. In some embodiments, the hydropolysiloxane comprises a linear hydropolysiloxane. In some embodiments, the hydropolysiloxane comprises a cyclic hydropolysiloxane.

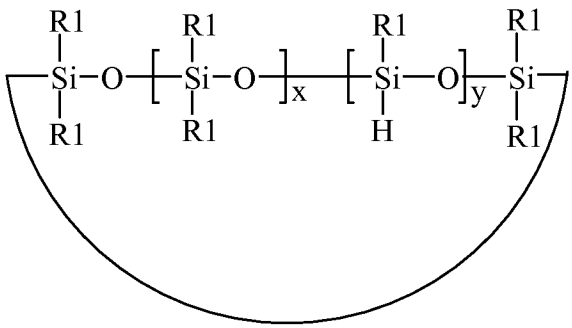
[0003] In some embodiments, the linear hydropolysiloxane comprises



;

wherein x and y are integers, x may be zero, each R1 is independently selected from the group consisting of alkyl groups, aryl groups, siloxanes, and combinations thereof, and each R2 is independently selected from the group consisting of alkyl groups, aryl groups, and hydrogen; wherein the alkyl and aryl groups comprise carbon and hydrogen.

[0004] In some embodiments, the cyclic hydropolysiloxane comprises

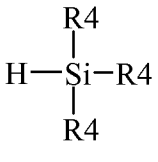


wherein x and y are integers, x may be zero, and each R1 is independently selected from the group consisting of alkyl groups, aryl groups, siloxanes, and combinations thereof; wherein the alkyl and aryl groups comprise carbon and hydrogen.

[0005] In some embodiments, at least one of the alkyl or aryl groups further comprises fluorine. In some embodiments, at least one R1 comprises a linear or branched siloxane. In some embodiments, each R1 is a nonfunctional group, wherein the nonfunctional group consists of carbon and one or more of hydrogen, fluorine, and polysiloxane. In some embodiments, at least one R1 is a functional group comprising an unsaturated carbon-carbon bond. In some embodiments, each R2 is a nonfunctional group, wherein the nonfunctional group consists of carbon and one or more of hydrogen, fluorine, and polysiloxane. In some embodiments, at least one R2 is a functional group. In some embodiments, the functional R2 group is hydrogen and, optionally, y is zero. In some embodiments, the functional group comprises an unsaturated carbon-carbon bond.

[0006] In another aspect, the present disclosure provides a method of making an alkoxy silane comprising combining a hydrosilane and an alcohol and reacting the hydrosilane and the alcohol in the presence of at least one of a Pd(0) and Pt(0) catalyst to form the alkoxy silane.

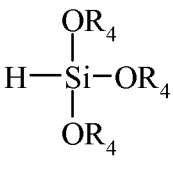
[0007] In some embodiments, the hydrosilane comprises



;

wherein each R4 is independently selected from the group consisting of alkyl groups and aryl groups, wherein the alkyl and aryl groups comprise carbon and hydrogen.

[0008] In some embodiments, the hydrosilane comprises



;

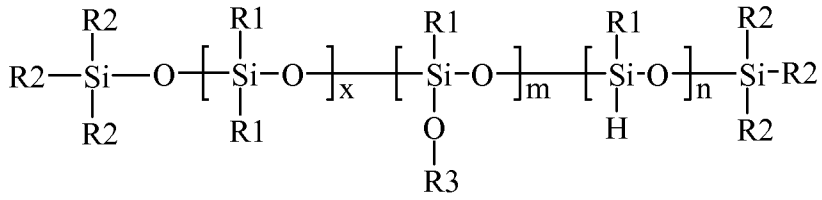
wherein each R4 is independently selected from the group consisting of alkyl groups and aryl groups, wherein the alkyl and aryl groups comprise carbon and hydrogen.

[0009] In some embodiments, the alcohol comprises R3–(OH)p; wherein p is an integer, and R3 is a radical with a valence of p. In some embodiments, p is one. In some embodiments, each R3 is an alkyl group. In some embodiments, at least one R3 is an aryl group.

[0010] In some embodiments, the catalyst comprises Pd(0). In some embodiments, the catalyst comprises Pt(0). In some embodiments, the catalyst is supported on a heterogeneous support, e.g., activated carbon.

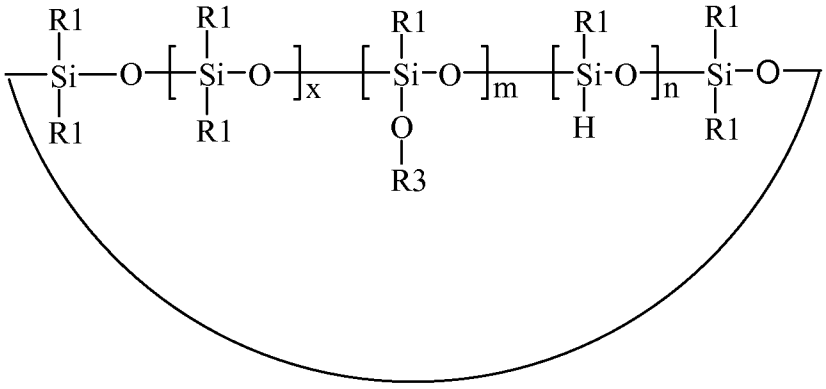
[0011] In another aspect, the present disclosure provides a compound made by a process of the present disclosure.

[0012] In yet another aspect, the present disclosure provides an alkoxy polysiloxane comprising



wherein x, m, and n are integers, wherein x and n may be zero; each R1, R2, and R3 is independently selected from the group consisting of alkyl and aryl groups, wherein the alkyl and aryl groups comprise carbon and hydrogen.

[0013] In yet another aspect, the present disclosure provides an alkoxy polysiloxane comprising



wherein x, m, and n are integers, wherein x and n may be zero, and each R1 and R3 is independently selected from the group consisting of alkyl and aryl groups, wherein the alkyl and aryl groups comprise carbon and hydrogen.

[0014] In some embodiments, x is zero. In some embodiments, the ratio of m:n is at least 15:85. In some embodiments, n is zero. In some embodiments, the ratio of m:n is no greater than 95:5.

[0015] In some embodiments, at least one of the alkyl or aryl groups further comprises fluorine. In some embodiments, at least one R1 comprises a linear or branched siloxane. In some embodiments, each R1 is a nonfunctional group, wherein the nonfunctional group consists of carbon and one or more of hydrogen, fluorine, and polysiloxane. In some embodiments, at least one R1 is a functional group other than hydrogen.

[0016] The above summary of the present disclosure is not intended to describe each embodiment of the present invention. The details of one or more embodiments of the invention are also set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and from the claims.

DETAILED DESCRIPTION

[0017] Alkoxy-functional silicones are an important class of curable materials used in a number of formulations, such as in moisture-curable room temperature vulcanates (RTVs); primers and adhesion promoter for binders, coatings and sealants; coupling agents for siliceous surfaces; and hydrophobes.

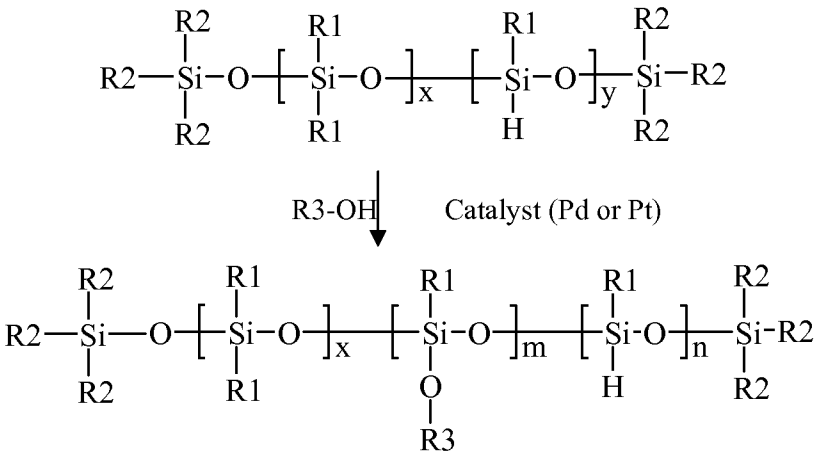
Alkoxy-functional silanes and silicones are also used as precursors to the sol-gel process commonly used for making thin-inorganic films.

[0018] The common method of preparing alkoxy silicones is via hydrolysis of chlorosilanes with alcohols. (See, e.g., U.S. Patent Nos. 3,435,001; 3,668,180; 3,792,071; and 8,076,438.) One drawback of this method is that the hydrolysis of chlorosilanes generates corrosive hydrochloride gas that not only is toxic but can also cause the degradation of silicone chains. Other drawbacks of this currently used process are that it requires multiple steps including costly distillation steps, it is not selective resulting in unwanted by-products, and it is inefficient resulting in low yields.

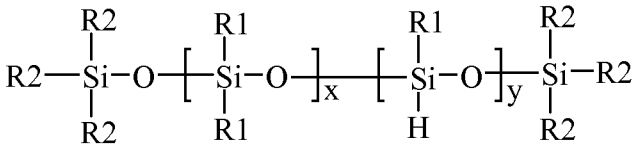
[0019] The present inventors have discovered an alternative process by which polyalkoxy silicones can be produced from hydrosilicones. In contrast to the prior approach, this process is simple, involves mild room temperature reactions, and is high in selectivity with almost quantitative yield. In addition, using the inventive process a new class of bis-functional polyalkoxy containing alkylhydrosiloxanes can be made. Furthermore, these materials can be cured under different conditions corresponding to RO-Si and H-Si functional groups.

[0020] Generally, the methods of the present disclosure provide a convenient catalytic route to provide curable polyalkoxy-substituted silicones. In some embodiments, the methods can be one-step, room-temperature, high yield (>98%), no side-reaction, non-acidic, and solvent-free processes.

[0021] More specifically, the methods of the present disclosure use a precious metal to catalyze the reaction of a hydropolysiloxane and an alcohol to produce alkoxy polysiloxanes. The general reaction scheme is illustrated below.

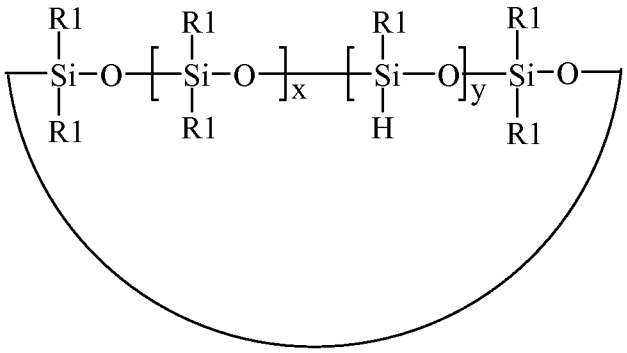


[0022] Exemplary hydropolysiloxanes suitable for use in the present disclosure can be described by the following illustration of a linear siloxane backbone with a variety of pendant and terminal groups (Formula 1):



(1)

[0023] In some embodiments, the polysiloxane backbone may be cyclic, as illustrated below in Formula 2:



(2)

[0024] In either case, R1 represents pendant groups extending from the siloxane backbone, while R2 represents terminal groups, and subscripts x and y are integers, wherein x may be zero. As used herein, R-group refers collectively to R1 and R2 groups.

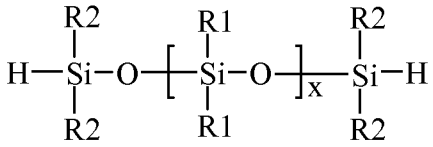
[0025] Each R1 and R2 group may be independently selected. In some embodiments, the R1 and R2 groups are nonfunctional groups. As used herein, "nonfunctional groups" are alkyl groups, aryl groups, or linear and branched siloxanes having alkyl or aryl pendant and terminal groups, wherein the alkyl and aryl groups consist of carbon, hydrogen, and in some embodiments, fluorine atoms. In some embodiments, each R1 is independently selected from the group consisting of an alkyl group and an aryl group. In some embodiments, one or more of the alkyl or aryl groups may contain fluorine. If fluorine is present, the groups may be partially fluorinated or perfluorinated.

[0026] In some embodiments, at least one R2 is an aryl group. In some embodiments, each R2 is an alkyl group, e.g., in some embodiments, each R2 is a methyl group, i.e., the hydropolysiloxane material is terminated by trimethylsiloxy groups. In some embodiments, one or more of the alkyl or aryl groups may contain fluorine. If fluorine is present, the groups may be partially fluorinated or perfluorinated.

[0027] Exemplary R-groups include, e.g., CH_3, CH_3CH_2, n-C_4H_9, n-C_6H_{13}, $C_6H_5C_2H_4$ and phenyl groups. Exemplary fluorinated R-groups include, e.g., $CH_2CH_2C_4F_9$, $C_4F_9C_2H_4$, $C_6F_{13}C_2H_4$, and $CF_3C_2H_4$. As will be recognized by one of ordinary skill in the art, a wide variety of other R-groups may be used. Although some R-groups may inhibit the desired reaction through, e.g., steric hindrance, such potential concerns can be rapidly screened through routine experimentation using the methods of the present disclosure. In addition, one of ordinary skill in the art could readily limit or eliminate the use of such R-groups depending on the desired end product.

[0028] In some embodiments, the polysiloxane backbone may be branched. For example, one or more of the R1 groups may be a linear or branched siloxane with, e.g., alkyl or aryl, including fluorinated alkyl or aryl, pendant and terminal groups.

[0029] In some embodiments, at least one R2 group of the hydropolysiloxane may be hydrogen, i.e., the hydropolysiloxane may include terminal hydrogen groups. In some embodiments, wherein at least one R2 group is hydrogen, the linear polysiloxanes of Formula 1 may contain only terminal hydride groups, i.e., y =0, as shown in Formula 3:



(3)

[0030] In some embodiments, the hydropolysiloxane material may include functional groups other than the hydride groups. For example, in some embodiments, at least one of the R-groups may include an unsaturated carbon-carbon bond such as alkene-containing groups (e.g., vinyl groups and allyl groups) and alkyne-containing groups. In some embodiments, at least two of the R-groups are functional groups other than hydrogen.

[0031] Generally, the hydropolysiloxane materials may be oils, fluids, gums, elastomers, or resins, e.g., friable solid resins. Generally, lower molecular weight, lower viscosity materials are referred to as fluids or oils, while higher molecular weight, higher viscosity materials are referred to as gums; however, there is no sharp distinction between these terms. Elastomers and resins have even higher molecular weights than gums and typically do not flow. As used herein, the terms "fluid" and "oil" refer to materials having a dynamic viscosity at 25 °C of no greater than 1,000,000 mPa•sec (e.g., less than 600,000 mPa•sec), while materials having a dynamic viscosity at 25 °C of greater than 1,000,000 mPa•sec (e.g., at least 10,000,000 mPa•sec) are referred to as "gums".

[0032] In the methods of the present disclosure, the hydropolysiloxane is reacted with an alcohol to produce an alkoxy polysiloxane. Generally, any known alcohol may be used, including those of Formula 4:

$$R3 - (OH)_p \qquad (4)$$

wherein R3 is a radical with a valence of p. In some embodiments, p equals 1. Generally, R3 may be linear or branched, cyclic or acyclic or aromatic. Exemplary R3 groups include alkyl groups, including C1 to C12 alkyl groups such as methyl, ethyl, isopropyl, n-butyl, and t-butyl groups. Exemplary R3 groups also include aryl groups such as phenyl groups. In some embodiments, methyl alcohol and ethyl alcohol may be preferred.

[0033] Generally, the hydropolysiloxane is reacted with the alcohol in the presence of a group 10 precious metal, i.e., palladium and platinum, e.g., Pd(0) and Pt(0). In some embodiments, Pd(0) may be preferred.

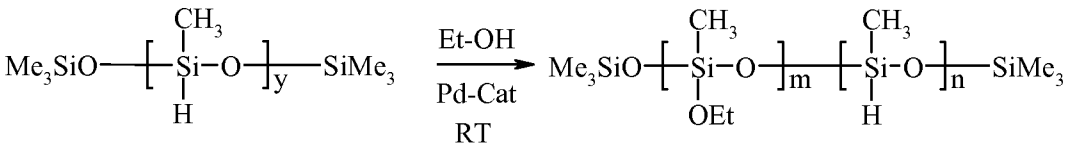
[0034] The use of acidic or basic catalysts can result in side reactions and undesirable by-products. In contrast, the use of neutral catalysts such as Pd(0) can provide a very clean product with no side reactions. Thus, in some embodiments, the catalyst is supported on an insoluble or heterogeneous media, such as carbon, alumina, and silica. For example, the use of activated carbon, allows reusability providing additional benefits.

[0035] The following examples illustrate the features and advantages of various embodiments of the present disclosure. Based on the following examples, in the context of the present disclosure, one of ordinary skill in the art could readily extend this method to include, e.g., other hydropolysiloxanes and/or alcohols through routine experimentation.

Table 1: Summary of materials used in the preparation of the examples.

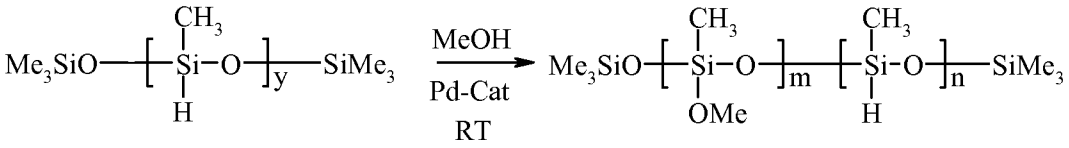
Name	Description	Trade Name and Source
HPS-1	100 weight percent solids silane crosslinker (said to comprise methylhydrogen siloxane)	SYL-OFF 7048 Dow Corning Corp. Midland, Michigan
HPS-2	100 weight percent solids silane crosslinker (said to comprise dimethyl, methylhydrogen siloxane	SYL-OFF 7678 Dow Corning Corp.
HPS-3	100 weight percent solids crosslinker (comprising –(SiMeC2H4C4F9-O)- and –(SiMeH-O)-)	SYL-OFF Q2-7560 Dow Corning Corp.
HT-PDMS-1	Hydride-terminated polydimethylsiloxane	DMS-H03 Gelest, Inc. Morrisville, Pennsylvania
HT-PDMS-2	Hydride-terminated polydimethylsiloxane	DMS-H11 Gelest, Inc.
Silicone-A	30 weight percent solids silicone in xylene (said to comprise hydroxyl-terminated polydimethylsiloxane)	SYL-OFF 2792 Dow Corning Corp.
Silicone-B	100 weight percent silicone (said to comprise vinyl-terminated polydimethylsiloxane)	DMS-V52 Gelest Inc.
XL-1	bis(triethoxysilyl)octane crosslinker	SIB 1817.0 Gelest Inc.
XL-2	Tetraethoxysilane crosslinker	Gelest Inc.
Pd-Cat	Pd(0) supported on activated charcoal	
Pt-Cat	bis(1,3-divinyl-1,1,3,3-tetrametyldisiloxane) platinum(0) (2 wt.% Pt in xylene)	Sigma-Aldrich Chemical Company
Ti-Cat	titanium (IV)-2-ethylhexoxide (alternatively known as tetraoctyltitanate)	Gelest Inc.

[0036] Example EX-1: Poly(ethoxymethyl-co-methylhydro)siloxane.



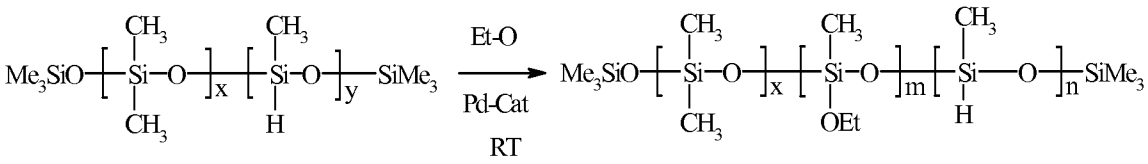
[0037] HPS-1 hydropolysiloxane (10 g, 166.7 mmol of SiH) was mixed with ethanol (3.8 g, 82.6 mmol) in a 100 mL round bottom flask followed by the addition of 5 wt% Pd/charcoal (0.008 g) at room temperature under nitrogen. The addition of the Pd-Cat resulted in rapid evolution of hydrogen gas signifying the substitution of ethoxy groups. After 4-5 hours of stirring at room temperature, the completion of reaction was confirmed by FT-IR analysis of the reaction mixture (Si-H at about 2160 cm^{-1} reduced) and ^1H NMR analysis (Si-H at δ 4.5 reduced. To isolate the product, Pd/charcoal was filtered through a one micron-glass filter and any unreacted/residual ethanol was then evaporated using vacuum. Yield was 99% and the ratio of m:n was 49:51. Chemical shift of ^1H-NMR: 4.57 (-SiH); 3.66 (q, $-OCH_2$); 1.09 (t, $-OCH_2CH_3$); 0.06 (m, $-SiCH_3$).

[0038] Example EX-2: Poly(methoxymethyl)-co-poly(methylhydro)siloxane.



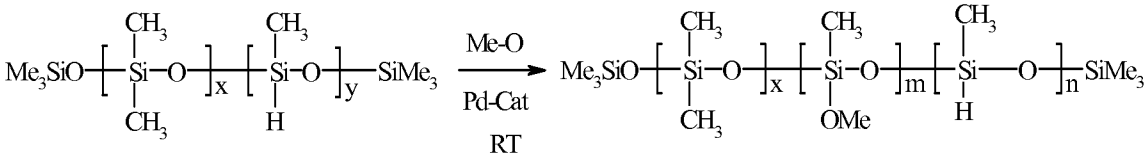
[0039] The procedure of Example EX-1 was followed except the HPS-1 hydropolysiloxane (10 g, 166.7 mmol of SiH) was mixed with methanol (2.5 g, 54.3 mmol). The yield was 99% and the ratio of m:n was 33:67. Chemical shift of ^1H-NMR: 4.59 (-SiH); 3.37 ($-OCH_3$); 0.03 (m, $-SiCH_3$).

[0040] Example EX-3: Poly(ethoxymethyl)-co-poly(dimethyl)-co -poly(methylhydro)siloxane.



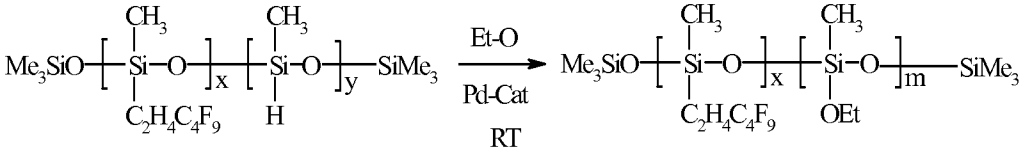
[0041] The procedure of Example EX-1 was followed except HPS-2 hydropolysiloxane (10 g, 116.9 mmol of SiH) was mixed with ethanol (1.0 g, 21 mmol). Yield was 99% and the ratio of m:n was 18:82 Chemical shift of ^1H-NMR: 4.57 (-SiH); 3.66 (q, $-OCH_2$); 1.09 (t, $-OCH_2CH_3$); 0.06 (m, $-SiCH_3$).

[0042] Example EX-4: Poly(methoxymethyl)-co-poly(dimethyl)-co-poly(methylhydro)siloxane.



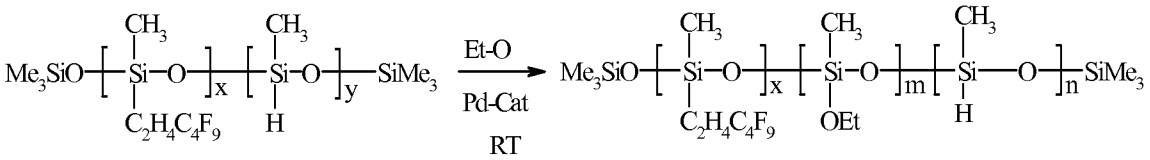
[0043] The procedure of Example EX-3 was followed except methanol (0.8 g, 25 mmol) was mixed with the HPS-2 hydropolysiloxane (10 g, 116.9 mmol of SiH). Yield was 99% and the ratio of n:m was 21:79 Chemical shift of ^1H-NMR: 4.59 (-SiH); 3.37 ($-OCH_3$); 0.03 (m, $-SiCH_3$).

[0044] Example EX-5: linear poly(methylperfluorobutylethyl)-co-poly(methylethoxy)siloxane.



[0045] The procedure of Example EX-1 was followed except HPS-3 fluorinated hydropolysiloxane (10 g, 100 mmol of SiH) was mixed with an excess of ethanol (5 g, 108 mmol). After 4-5 hrs of stirring at room temperature, the completion of reaction was confirmed by the FT-IR (Si-H at about2174 cm^{-1} disappeared) and ^1H NMR (Si-H at δ 4.5 disappeared). Yield was 99%. Chemical shift of ^1H-NMR: 3.65 (q,-OCH_2); 2.1 (t,-$SiCH_2CH_2C_4F_9$), 1.1 (t, -OCH_2CH_3)); 0.63 (t, -$SiCH_2CH_2C_4F_9$), -0.04 (m, -$SiCH_3$).

[0046] Example EX-6: Poly(methylperfluorobutylethyl)-co-poly(methylethoxy)-co-poly(methylhydro)siloxane.



[0047] The procedure of Example EX-5 was followed except that only 1 g (21 mmol) of ethanol was mixed with the HPS-3 fluorinated hydropolysiloxane (10 g, 100 mmol of SiH). After 4-5 hrs of stirring at room temperature, the completion of reaction was confirmed by the FT-IR (Si-H at about 2160 cm^{-1} reduced) and ^1H NMR (Si-H at δ 4.5 reduced) analyses of the reaction mixture. Yield was 99% and the ratio of m:n was 21:79 Chemical shift of ^1H-NMR: 4.55 (-SiH); 3.65 (q, -OCH_2); 2.1 (t, -$SiCH_2CH_2C_4F_9$), 1.1 (t, -OCH_2CH_3)); 0.63 (t, -$SiCH_2CH_2C_4F_9$), -0.04 (m, -$SiCH_3$).

[0048] Ethoxy-terminated poly(dimethyl)siloxane.

[0049] Example 7a: HT-PDMS-1 (10 g) was mixed with ethanol (5 g) in 100 mL round bottom flask followed by the addition of 5 wt% Pd/charcoal (0.008 g) at room temperature under nitrogen. The addition of Pd(0) on charcoal resulted in rapid evolution of hydrogen signifying the substitution of ethoxy groups. After 4-5 hours of stirring at room temperature, the completion of reaction was confirmed by the FT-IR (Si-H at about 2160 cm^{-1} disappeared) and 1H NMR (Si-H at δ 4.5 disappeared) of the reaction mixture. To isolate the product, Pd/charcoal was allowed to settle (typically 30 minutes) and the reaction mixture decanted; excess ethanol was then evaporated using a vacuum. The yield was 99%.

[0050] Example 7b: Example 7a was repeated using HT-PDMS-2. The yield was 99%.

[0051] Butoxy-terminated poly(dimethyl)siloxane.

[0052] Example 8a: The procedure of Example 7 was followed, except that 5 g of butanol was added to the 10 g of HT-PDMS-1 and the reaction mixture was stirred for 6-8 hours at room temperature. The yield was 99%.

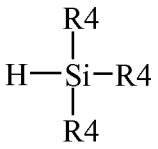
[0053] Example 8b: Example 8a was repeated, except HT-PDMS-2 was used. Yield was 99%.

[0054] Isopropoxy-terminated poly(dimethyl)siloxane.

[0055] Example 9a: The procedure of Example 7 was followed, except that 5 g of isopropanol was added to the 10 g of HT-PDMS-1 and the reaction mixture was stirred for 6-8 hours at 60 °C. The yield was 99%.

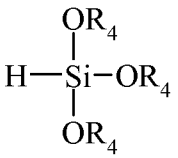
[0056] Example 9b: Example 9a was repeated using HT-PDMS-2. The yield was 99%.

[0057] The methods of the present disclosure may also be used with silanes such as those according to Formula 5:



(5)

or Formula 6:



(6)

wherein each R4 is independently selected from the group consisting of alkyl and aryl groups.

[0058] Ethyoxy-substituted triethyl silane.

[0059] Example 10: Triethylsilane (5 g) was mixed with ethanol (5 g) in 100 mL round bottom flask followed by the addition of 5 wt% Pd on charcoal (0.001 g). The addition of Pd(0) on charcoal resulted in the rapid evolution of hydrogen gas signifying the substitution of ethoxy groups. After 6 hours of stirring at room temperature, the completion of reaction was confirmed by the FT-IR (Si-H at about 2164 cm^{-1} disappeared) and ^{1}H NMR (Si-H at δ 3.6 disappeared) of the reaction mixture. To isolate the product, Pd/charcoal was allowed to settle (typically 30 minutes) and the reaction mixture was decanted. Excess ethanol was then evaporated using mild-vacuum. The yield was 99%.

[0060] Example 11: Butoxy-substituted triethyl silane. Example 10 was repeated except 5 g of butanol was added to the triethylsilane and the reactants were mixed for 12 hours at room temperature. The yield was 99%.

[0061] Phenoxy-substituted triethoxysilane.

[0062] Example 12: Triethoxysilane (5 g) was mixed with phenol (5 g) in 100 mL round bottom flask followed by the addition of 5 wt% Pd on charcoal (0.008 g). The reaction mixture was stirred at 100 °C for 20 hours. The completion of reaction was confirmed by the FT-IR (Si-H at about 2185 cm^{-1} disappeared) and ^{1}H NMR (Si-H at δ 4.45 disappeared) of the reaction mixture. To isolate the product,

Pd/charcoal was allowed to settle (typically 30 minutes) and the reaction mixture was decanted. Excess phenol was then crystallized out by adding 25 mL of heptanes to the reaction mixture and product was isolated by evaporating the heptanes. The yield was 99%.

[0063] Example 13: ethylene glycol-substituted triethoxysilane. Example 12 was repeated except 5 g ethylene glycol was added to 8 g of the triethoxysilane. The reaction mixture was stirrer for 20 hours at 100 °C. Yield was 99%.

[0064] The alkoxy siloxanes and silanes of the present disclosure may be used in a wide variety of applications, either alone or in combination with other reactants. For example, in some embodiments, the alkoxy siloxanes and silanes may be used as co-reactants, e.g., crosslinkers, in a silicone system.

[0065] Silicone Coat Weight Procedure. Silicone coat weights were determined by comparing approximately 3.69 centimeter diameter samples of coated and uncoated substrates using an EDXRF spectrophotometer (obtained from Oxford Instruments, Elk Grove Village, IL under trade designation OXFORD LAB X3000).

[0066] Silicone Extractables Procedure. Unreacted silicone extractables were measured on cured thin film formulations to ascertain the extent of silicone crosslinking immediately after the coatings were cured. The percent extractable silicone, (i.e., the unreacted silicone extractables), a measure of the extent of silicone cure on a release liner, was measured by the following method.

[0067] The silicone coat weight of a 3.69 centimeter diameter sample of coated substrate was determined according to the Silicone Coat Weight Procedure. The coated substrate sample was then immersed in and shaken with methyl isobutyl ketone (MIBK) for 5 minutes, removed, and allowed to dry. The silicone coating weight was measured again according to the Silicone Coat Weight Procedure. Silicone extractables were attributed to the weight difference between the silicone coat weight before and after extraction with MIBK as a percent using the following formula:

$$\text{Extractable Silicone\%} = (a - b) / a * 100\%$$

wherein a = initial coating weight (before extraction with MIBK); and

b = final coating weight (after extraction with MIBK).

[0068] Release Procedure. This test was used to measure the effectiveness of release liners prepared using the compositions according to the examples and comparative examples described below that had been aged for a period of time at a constant temperature and relative humidity. The aged release value is a quantitative measure of the force required to remove a flexible adhesive from the release liner at a specific angle and rate of removal. The 180 degree angle peel adhesion strength of a release liner to an adhesive sample was measured in the following manner, which is generally in accordance with the test method described in Pressure Sensitive Tape Council PSTC-101 method D (Rev 05/07) "Peel Adhesion of Pressure Sensitive Tape."

[0069] The example and comparative example release liners prepared as described below were dry laminated with acrylic adhesive coating using an adhesive transfer tape. A sample of the adhesive transfer tapes was cut 2.54 cm wide and approximately 20 cm in length using a specimen razor cutter. The cut sample was applied with its exposed adhesive side down and lengthwise onto the platen surface of a peel adhesion tester (Slip/Peel Tester, Model 3M90, obtained from Instrumentors, Incorporated, Strongsville, Ohio). The applied sample was rubbed down on the test panel using light thumb pressure. The adhesive transfer tape on the platen surface was then rolled twice with a 2 kg rubber roller at a rate of 61 cm/minute. The release liner was carefully lifted away from the adhesive transfer tape on the platen surface, doubled-back at an angle of 180 degrees, and secured to clamp of the peel adhesion tester. The 180 degree angle release liner peel adhesion strength was then measured at a peel rate of 38.1 mm/s. A minimum of two test specimens were evaluated with results obtained in g/inch which were used to calculate the average peel force. All release tests were carried out in a facility at constant temperature (23 °C) and constant relative humidity (50 percent).

[0070] Comparative Example CE-A1. Silicone-A (6.88 g) was diluted with heptane (12.80 g) followed by addition of diallyl maleate (0.15 g), Pt-Cat (150 parts per million of Pt(0)) and HPS-1 (0.176 g). Then, XLINK-1 and Ti-Cat were added to the aforementioned mixture, each at 3 wt% with respect to total amount of solids in the final formulation. The formulation was thoroughly mixed and coated on a corona-treated, polyethylene-coated, kraft paper ("PCK", obtained from Jen-Coat, Inc., Westfield, MA) with a # 3 Mayer bar. The coated layer was cured at 110 °C for 60 seconds in an oven equipped with solvent exhaust.

[0071] Comparative Example CE-A2. The procedure for comparative example CE-A1 was repeated, except that XLINK-2 was used.

[0072] Comparative Example CE-B. Silicone-A (3.44 g) and Silicone-B (1.03 g) were diluted with heptane (15 g) followed by addition of diallyl maleate (0.15 g), Pt-Cat (150 parts per million of Pt(0)) and HPS-1 (0.176 g). Then, XLINK-1 and Ti-Cat were added to the aforementioned mixture, each at 3 wt% with respect to total amount of solids in the final formulation. The formulation was thoroughly mixed and coated on a PCK with a # 3 Mayer bar. The coated layer was cured at 110 °C for 60 seconds in an oven equipped with solvent exhaust.

[0073] Example EX-A1. The procedure of comparative example CE-A1 was repeated except that the poly(ethoxymethyl-co-methylhydro)siloxane of Example EX-1 was added instead of XLINK-1. The amount HPS-1 was unchanged (0.176 g).

[0074] Example EX-A2. The procedure of comparative example CE-A1 was repeated except that 0.176 g of the poly(ethoxymethyl-co-methylhydro)siloxane of Example EX-1 was added instead of XLINK-1, and no HPS-1 was present.

[0075] Example EX-A3. The procedure of comparative example CE-A1 was repeated except that 0.176 g of the poly(methoxymethyl)-co-poly(methylhydro)siloxane of Example EX-2 was added instead of XLINK-1, and no HPS-1 was present.

[0076] Example EX-A4. The procedure of comparative example CE-A1 was repeated except that the poly(ethoxymethyl)-co-poly(dimethyl)-co -poly(methylhydro)siloxane of Example EX-3 was added instead of XLINK-1. The amount of HPS-1 was unchanged (0.176 g).

[0077] Example EX-B1. The procedure of comparative example CE-B was repeated except that the poly(ethoxymethyl)-co-poly(dimethyl)-co -poly(methylhydro)siloxane of Example EX-3 was added instead of XLINK-1. The amount HPS-1 was unchanged (0.176 g).

[0078] Example EX-B2. The procedure of comparative example CE-B was repeated except that the poly(ethoxymethyl)-co-poly(dimethyl)-co -poly(methylhydro)siloxane of Example EX-3 was added instead of XLINK-1, and no HPS-1 was present.

[0079] Each of the comparative examples and examples were evaluated using the Silicone Extractables Procedure and the Release Procedure. The results are summarized in Table 2.

Table 2: Compositions and results for silicone systems prepared using Silicone-A.

I.D.	Silicone-B present	Crosslinker(s)		Extractable Silicone%	Ave. Release (g/2.5 cm)
		HPS-1	Other		
CE-A1	no	yes	XLINK-1	9.7	46
CE-A2	no	yes	XLINK-2	12.1	37
CE-B	yes	yes	XLINK-1	10.2	43
EX-A1	no	yes	EX-1	6.9	43
EX-A2	no	no	EX-1	7.0	42
EX-A3	no	no	EX-2	6.5	35
EX-A4	no	yes	EX-3	6.1	31
EX-B1	yes	yes	EX-3	8.7	42
EX-B2	yes	no	EX-3	7.5	40

[0080] Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention.

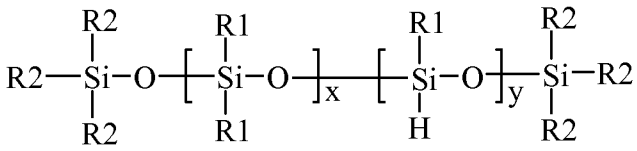
What is Claimed is:

1. A method of making an alkoxy polysiloxane comprising combining a hydropolysiloxane and an alcohol and reacting the hydropolysiloxane and the alcohol in the presence of at least one of a Pd(0) and Pt(0) catalyst to form the alkoxy polysiloxane.

2. The method of claim 1, wherein the hydropolysiloxane comprises a linear hydropolysiloxane.

3. The method of claim 1 or 2, wherein the hydropolysiloxane comprises a cyclic hydropolysiloxane.

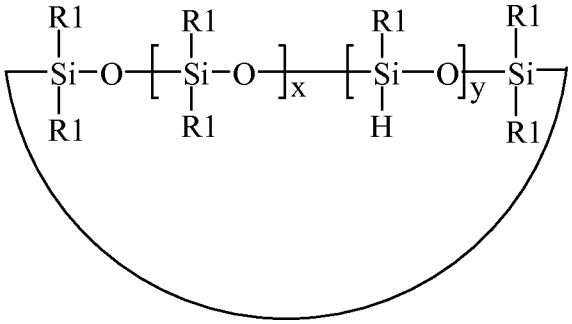
4. The method of claim 2 or 3, wherein the linear hydropolysiloxane comprises



;

wherein x and y are integers, x may be zero, each R1 is independently selected from the group consisting of alkyl groups, aryl groups, siloxanes, and combinations thereof, and each R2 is independently selected from the group consisting of alkyl groups, aryl groups, and hydrogen; wherein the alkyl and aryl groups comprise carbon and hydrogen.

5. The method of claim 3 or 4, wherein the cyclic hydropolysiloxane comprises



wherein x and y are integers, x may be zero, and each R1 is independently selected from the group consisting of alkyl groups, aryl groups, siloxanes, and combinations thereof; wherein the alkyl and aryl groups comprise carbon and hydrogen.

6. The method according to claim 4 or 5, wherein at least one of the alkyl or aryl groups further comprises fluorine.

7. The method according to any one of claims 4 to 6, wherein at least one R1 comprises a linear or branched siloxane.

8. The method according to any one of claims 4 to 7, wherein each R1 is a nonfunctional group, wherein the nonfunctional group consists of carbon and one or more of hydrogen, fluorine, and polysiloxane.

9. The method according to any one of claims 4 to 7, wherein at least one R1 is a functional group comprising an unsaturated carbon-carbon bond.

10. The method according to any one of claims 4 to 9, wherein each R2 is a nonfunctional group, wherein the nonfunctional group consists of carbon and one or more of hydrogen, fluorine, and polysiloxane.

11. The method according to any one of claims 4 to 9, wherein at least one R2 is a functional group.

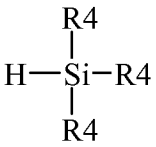
12. The method of claim 11, wherein the functional group is hydrogen.

13. The method of claim 12, wherein y is zero.

14. The method of claim 11, wherein the functional group comprises an unsaturated carbon-carbon bond.

15. A method of making an alkoxy silane comprising combining a hydrosilane and an alcohol and reacting the hydrosilane and the alcohol in the presence of at least one of a Pd(0) and Pt(0) catalyst to form the alkoxy silane.

16. The method of claim 15, wherein the hydrosilane comprises



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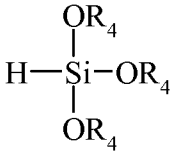
wherein each R4 is independently selected from the group consisting of alkyl groups and aryl groups, wherein the alkyl and aryl groups comprise carbon and hydrogen.

17. The method of claim 15, wherein the hydrosilane comprises



;

wherein each R4 is independently selected from the group consisting of alkyl groups and aryl groups, wherein the alkyl and aryl groups comprise carbon and hydrogen.

18. The method according to any one of the preceding claims, wherein the alcohol comprises R3–(OH)p; wherein p is an integer, and R3 is a radical with a valence of p.

19. The method of claim 18, wherein p is one.

20. The method of claim 18 or 19, wherein each R3 is an alkyl group.

21. The method of claim 18 or 19, wherein at least one R3 is an aryl group.

22. The method according to any one of the preceding claims, wherein the catalyst comprises Pd(0).

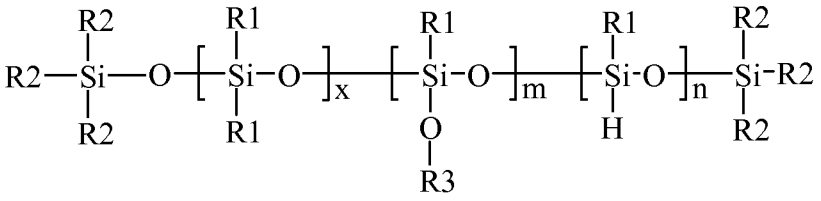
23. The method according to any one of the preceding claims, wherein the catalyst comprises Pt(0).

24. The method according to claim 22 or 23, wherein the catalyst is supported on a heterogeneous support.

25. The method according to claim 24, wherein the heterogeneous support comprises activated carbon.

26. A compound made by the process according to any one of the preceding claims.

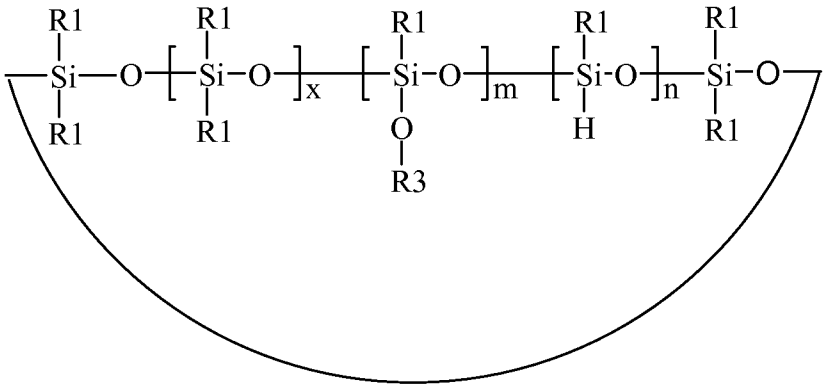
27. An alkoxy polysiloxane comprising



;

wherein x, m, and n are integers, wherein x and n may be zero; each R1, R2, and R3 is independently selected from the group consisting of alkyl and aryl groups, wherein the alkyl and aryl groups comprise carbon and hydrogen.

28. An alkoxy polysiloxane comprising



wherein x, m, and n are integers, wherein x and n may be zero, and each R1 and R3 is independently selected from the group consisting of alkyl and aryl groups, wherein the alkyl and aryl groups comprise carbon and hydrogen.

29. The alkoxy polysiloxane of claim 27 or 28, wherein x is zero.

30. The alkoxy polysiloxane according to any one of claims 27 to 29, wherein the ratio of m:n is at least 15:85.

31. The alkoxy polysiloxane according to claim 30, wherein the ratio of m:n is at least 30:70.

32. The alkoxy polysiloxane of claim 31, wherein the ratio of m:n is at least 50:50.

33. The alkoxy polysiloxane of claim 32, wherein n is zero.

34. The alkoxy polysiloxane according to any one of claims 27 to 32, wherein the ratio of m:n is no greater than 95:5.

35. The alkoxy polysiloxane of claim 34, wherein the ratio of m:n is no greater than 70:30.

36. The alkoxy polysiloxane according to any one of claims 27 to 35, wherein at least one of the alkyl or aryl groups further comprises fluorine.

37. The hydroxy polysiloxane according to any one of claims 27 to 36, wherein at least one R1 comprises a linear or branched siloxane.

38. The hydroxy polysiloxane according to any one of claims 27 to 36, wherein each R1 is a nonfunctional group, wherein the nonfunctional group consists of carbon and one or more of hydrogen, fluorine, and polysiloxane.

39. The hydroxy polysiloxane according to any one of claims 27 to 36, wherein at least one R1 is a functional group other than hydrogen.