(54) Title: POLYSILOXANEPOLYAMIDE COPOLYMER, AND METHODS OF MAKING AND USING THE SAME

(57) Abstract: The present invention relates to polysiloxane-polyamide block copolymers. In various embodiments, the present invention provides a polysiloxane-polyamide block copolymer including the repeating unit \( -M^1\cdot M^2 - \), wherein \( M^1 \) is a divalent polydiorganosiloxane, and wherein \( M^2 \) is a divalent polyamide. The present invention also provides methods of making the copolymer, compositions and articles of manufacture including the copolymer, and methods of using the copolymer.
POLYSILOXANE-POLYAMIDE COPOLYMER, AND METHODS OF MAKING AND USING THE SAME

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority to U.S. Provisional Patent Application Serial No. 61/760,783 filed Feb. 5, 2013, the disclosure of which is incorporated herein in its entirety by reference.

[0002] Polyamide based resins, ornyls, are an important class of thermoplastic resins in a variety of industries such as textiles, coatings, molded parts, and the like. A variety of methods and techniques have been developed to improve the physical properties ofnyls for certain applications. Typically, such improvements are based on the addition of certain components to the nylon, either during the processing of the nylon resin, or as a post-processing additive. Silicones, or organopolysiloxanes, have been used as additives in nylon compositions and processing to affect physical properties. However, when silicones, such as polydimethylsiloxanes, are added to nytons during fiber production, the silicone can migrate within the nylon fiber and negatively impact certain physical properties.

SUMMARY OF THE INVENTION

[0003] In various embodiments, the present invention provides a polysiloxane-polyamide block copolymer including the repeating unit -[M1-M2]DP1-. The variable M1 is a divalent polydiorganosiloxane. The variable M2 is a divalent polyamide. The variable DP1 is about 1-200.

[0004] In various embodiments, the present invention provides a polysiloxane-polyamide block copolymer including the repeat unit -[SiR1R2-2(OSiR1R2)DP2-R3-C(O)NH-R4-]

NHC(O)-R5-C(O))DP3-NH-R4-NHC(O)-R3-JDP1-. Each of R3, R4, and R5 can be independently at each occurrence at least one of straight-chain, branched, and cyclic, divalent (C1-C30)alkylene group. The variable DP2 can be about 1-500. Also, the variable DP3 can be about 0-50.

[0005] In various embodiments, the present invention provides a polysiloxane-polyamide block copolymer having the structure E1-[SiR1R2-2(OSiR1R2)DP2-R3-C(O)NH-R4-

NHC(O)-R5-C(O))DP3-NH-R4-NHC(O)-R3-JDP1-E2-. The variable E1 can be HR3-

C(O)[NH-R4-NHC(O)-R5-C(O)]DP3-NH-R4-NHC(O)-R3-, or HSiR1R2-2(OSiR1R2)DP2-R3-

C(O)[NH-R4-NHC(O)-R5-C(O)]DP3-NH-R4-NHC(O)-R3-. The variable E2 can be -SiR1R2-

[OSiR1R2]DP2H, or -SiR1R2-2(OSiR1R2)DP2-R3-C(O)[NH-R4-NHC(O)-R5-C(O)]DP3NH-
R$^4$-NHC(O)-R$^5$H. The variable R$^3$ can be an n-undecylene group. Each of R$^4$ and R$^5$

 can independently be a straight chain (C$_{4-15}$)alkylene group. The variable DP1 can be

 about 2-20. The variable DP2 can be about 10 to about 200. The variable DP3 can be

 about 0-10.

5 [0006] In various embodiments, the present invention provides a method of making the polylsioxane-polyamide block copolymer. The method includes obtaining or providing a mixture that includes an Si-H-terminated polydiorganosiloxane having the formula

 HSiR$^1$R$^2$-[OSiR$^1$R$^2$]$_{DP2}$H. Each of R$^1$ and R$^2$ at each occurrence can be an organic

 functional group. The variable DP2 can be about 1 to about 500. The mixture also

 includes an alkenyl-terminated polyamide having the formula R$^6$-C(O)[NH-R$^4$-NHC(O)-R$^5$-

 C(O)]$_{DP3}$NH-R$^4$-NHC(O)-R$^6$. The variable R$^6$ at each occurrence can be independently a

 monovalent (C$_{1-30}$)hydrocarbyl group having at least one nonaromatic unsaturated

 carbon-carbon bond. Each of R$^4$ and R$^5$ can be independently a divalent (C$_{1-}

 C_{30}$)alkylene group. The variable DP3 can be about 0-50. The mixture also includes a

 hydroisilylation catalyst. The method also includes subjecting the mixture to reaction

 conditions to give the polylsioxane-polyamide block copolymer.

[0007] In various embodiments, the present invention provides a personal care

 composition including the polylsioxane-polyamide block copolymer. In some embodiments,

 the present invention provides a thermoplastic composition including the polylsioxane-

 polyamide block copolymer and at least one organic polymer, and also provides a

 thermoplastic film including the thermoplastic composition and methods of forming the film.

 In other embodiments, the present invention provides a coated substrate wherein the

 coating includes a composition that includes the polylsioxane-polyamide block copolymer,

 and also provides methods of coating substrates with the composition. In various

 embodiments, the present invention provides an article of manufacture that includes the

 polylsioxane-polyamide block copolymer such as at least one of sheet product, a molded

 article, a fiber, a spun yarn, a textile, and a nonwoven fabric.

[0008] Various embodiments of the present invention have certain advantages over other

 nylons, nylon copolymers, and compositions including the same. For example, in some

 embodiments, the polylsioxane has a higher melting point than other polylsioxane polymers

 and copolymers, including as compared to diamide-polylsioxane block copolymers. The

 higher melting point of various embodiments can allow for more facile use as a surface

 modifier in various applications, such as plastics applications. Some polylsioxane

 polymers and copolymers, for example diamide-polylsioxane block copolymers, have a

 melting point that is so different from the melting point of other thermoplastic materials that

 it is difficult to use the polylsioxane polymer or copolymer as a surface treatment, for
example, due to difficulty in applying the polysiloxane polymer or copolymer uniformly. In some embodiments, the melting point of the polysiloxane-polyamide block copolymer can be closer to the melting point of some organic thermoplastic polymers, making it easier to use the polysiloxane-polyamide block copolymer as a surface treatment for the thermoplastic polymers, for example, easier to apply the polysiloxane-polyamide block copolymer uniformly.

[0009] In various embodiments, as compared to other polyamide polymers and copolymers, the polysiloxane-polyamide block copolymer can be more hydrophobic due at least to the presence of the polysiloxane units in the polymer. The increased hydrophobicity of various embodiments can result a lower contact angle with water, and can give advantages such as less moisture pick up in fabrics, lower coefficients of friction, improved softening, and improved water repellency. In some embodiments, the increased hydrophobicity can result in advantages in the fiber production, processing, and weaving process. For example, in the production of nylon fibers by extrusion, extruder pressure can be reduced for polyamides and polyamide compositions having a reduced hydrophilic nature, which can result in easier processing, faster throughput, and ultimately a lower cost of production. In some examples, the reduced hydrophilic nature of various embodiments can reduce or eliminate the use of sizing finishes in fiber weaving production. In some examples, the reduced hydrophilic nature of various embodiments can result in greater resiliency to adhesion by soiling materials such as dirt and aqueous solutions or suspensions of soiling material. In some examples, the polysiloxane-polyamide block copolymer can have a softer feel than other polyamide polymers and copolymers, due at least to the presence of the polysiloxane units in the polymer.

[0010] In some examples, the advantageous properties of the polysiloxane-polyamide block copolymer make it valuable as a surface modification agent, such as for use as a coating on various materials, such as on organic thermoplastic polymers, nyans, and the like, or on any material for which reduced adhesion of water or soiling materials is desired. In other examples, the polysiloxane-polyamide block copolymer can be blended with various materials to produce compositions with valuable and advantageous properties.

Various embodiments can advantageously be used as gellants for personal care applications.

**BRIEF DESCRIPTION OF THE FIGURES**

[0011] In the drawings, which are not necessarily drawn to scale, like numerals describe substantially similar components throughout the several views. Like numerals having different letter suffixes represent different instances of substantially similar components. The drawings illustrate generally, by way of example, but not by way of limitation, various embodiments discussed in the present document.
[0012] FIG. 1 illustrates the normalized response versus time for various polysiloxane-polyamide block copolymers, in accordance with various embodiments.

[0013] FIG. 2 illustrates the percent moisture weight gain for fabric samples having varying amounts of polysiloxane-polyamide copolymer thereon, in accordance with various embodiments.

DETAILED DESCRIPTION OF THE INVENTION

[0014] Reference will now be made in detail to certain embodiments of the disclosed subject matter, examples of which are illustrated in part in the accompanying drawings. While the disclosed subject matter will be described in conjunction with the enumerated claims, it will be understood that the exemplified subject matter is not intended to limit the claims to the disclosed subject matter.

[0015] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. For example, a range of “about 0.1% to about 5%” or “about 0.1% to 5%” should be interpreted to include not just about 0.1% to about 5%, but also the individual values (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range. The statement “about X to Y” has the same meaning as “about X to about Y,” unless indicated otherwise. Likewise, the statement “about X, Y, or about Z” has the same meaning as “about X, about Y, or about Z,” unless indicated otherwise.

[0016] In this document, the terms “a,” “an,” or “the” are used to include one or more than one unless the context clearly dictates otherwise. The term “or” is used to refer to a nonexclusive “or” unless otherwise indicated. In addition, it is to be understood that the phraseology or terminology employed herein, and not otherwise defined, is for the purpose of description only and not of limitation. Any use of section headings is intended to aid reading of the document and is not to be interpreted as limiting; information that is relevant to a section heading may occur within or outside of that particular section. Furthermore, all publications, patents, and patent documents referred to in this document are incorporated by reference herein in their entirety, as though individually incorporated by reference. In the event of inconsistent usages between this document and those documents so incorporated by reference, the usage in the incorporated reference should be considered supplementary to that of this document; for irreconcilable inconsistencies, the usage in this document controls.

[0017] In the methods of manufacturing described herein, the steps can be carried out in any order without departing from the principles of the invention, except when a temporal or operational sequence is explicitly recited.
[0018] Furthermore, specified steps can be carried out concurrently unless explicit claim language recites that they be carried out separately. For example, a claimed step of doing X and a claimed step of doing Y can be conducted simultaneously within a single operation, and the resulting process will fall within the literal scope of the claimed process.

[0019] The term “about” as used herein can allow for a degree of variability in a value or range, for example, within 10%, within 5%, or within 1% of a stated value or of a stated limit of a range.

[0020] The term “substantially” as used herein refers to a majority of, or mostly, as in at least about 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98%, 99%, 99.5%, 99.9%, 99.99%, or at least about 99.99% or more.

[0021] The term “organic group” as used herein refers to but is not limited to any carbon-containing functional group. For example, an oxygen-containing group such as alkoxy groups, aryloxy groups, aralkyloxy groups, oxo(carbonyl) groups, carboxyl groups including carboxylic acids, carboxylates, and carboxylate esters; a sulfur-containing group such as alkyl and aryl sulfide groups; and other heteroatom-containing groups. Non-limiting examples of organic groups include OR', OC(O)N(R')2, CN, CF3, OCF3, R', C(O), methylenedioxy, ethylenedioxy, N(R')2, SR', SOR', SO2R', SO2N(R')2, SO3R', C(O)R', C(O)C(O)R', C(O)CH2C(O)R', C(S)R', C(O)OR', OC(O)R', C(O)N(R')2, OC(O)N(R')2, C(S)N(R')2, (CH2)0.2N(R')C(O)R', (CH2)0.2N(R')N(R')2, N(R')N(R')C(O)R', N(R')N(R')C(O)OR', N(R')N(R')CON(R')2, N(R')SO2R', N(R')SO2N(R')2, N(R')C(O)OR', N(R')C(O)R', N(R')C(S)R', N(R')C(O)N(R')2, N(R')C(S)N(R')2, N(COR')COR', N(OR')R', C(=NH)N(R')2, C(O)N(OR')R', or C(=NOR')R' wherein R' can be hydrogen (in examples that include other carbon atoms) or a carbon-based moiety, and wherein the carbon-based moiety can itself be further substituted; for example, wherein R' can be hydrogen (in examples that include other carbon atoms), alkyl, acyl, cycloalkyl, aryl, aralkyl, heterocyclyl, heteroaryl, or heteroarylalkyl, wherein any alkyl, acyl, cycloalkyl, aryl, aralkyl, heterocyclyl, heteroaryl, or heteroarylalkyl, or R' can be independently mono- or multi-substituted with J; or wherein two R' groups bonded to a nitrogen atom or to adjacent nitrogen atoms can together with the nitrogen atom or atoms form a heterocyclyl, which can be mono- or independently multi-substituted with J. The term “substituted” as used herein refers to an organic group as defined herein or molecule in which one or more hydrogen atoms contained therein are replaced by one or more non-hydrogen atoms. The term “functional group” or “substituent” as used herein refers to a group that can be or is substituted onto a molecule, or onto an organic group. Examples of substituents or functional groups include, but are not limited to, a halogen (e.g., F, Cl, Br, and I); an oxygen atom in groups such as hydroxyl groups, alkoxy groups, aryloxy groups, aralkyloxy groups, oxo(carbonyl) groups,
carboxyl groups including carboxylic acids, carboxylates, and carboxylate esters; a sulfur atom in groups such as thiol groups, alkyl and aryl sulfide groups, sulfoxide groups, sulfone groups, sulfonyl groups, and sulfonamide groups; a nitrogen atom in groups such as amines, hydroxylamines, nitriles, nitro groups, N-oxides, hydrazides, azides, and enamines; and other heteroatoms in various other groups. Non-limiting examples of substituents \( J \) that can be bonded to a substituted carbon (or other) atom include \( F, Cl, Br, I, OR', OC(O)N(R')_2, CN, NO, NO_2, ONO_2, azido, CF_3, OCF_3, R', O (oxo), S (thiono), C(O), S(O), methylenedioxy, ethylenedioxy, N(R')_2, SR', SOR', SO_2R', SO_2N(R')_2, SO_3R', C(O)R', C(O)C(O)R', C(O)CH_2C(O)R', C(S)R', C(O)OR', OC(O)R', C(O)N(R')_2, OC(O)N(R')_2, C(S)N(R')_2, (CH_2)_0-2N(R')C(O)R', (CH_2)_0-2N(R')N(R')_2, N(R')N(R')C(O)R', N(R')N(R')CON(R')_2, N(R')SO_2R', N(R')SO_2N(R')_2, N(R')C(O)OR', N(R')C(O)R', N(R')C(S)R', N(R')C(O)N(R')_2, N(R')C(S)N(R')_2, N(COR')COR', N(OR')R', C(=NH)N(R')_2, C(O)N(OR')R', or C(=NOR')R' wherein R' can be hydrogen or a carbon-based moiety, and wherein the carbon-based moiety can itself be further substituted; for example, wherein R' can be hydrogen, alkyl, acyl, cycloalkyl, aryl, aralkyl, heterocyclyl, heteroaryl, or heteroaryalkyl, wherein any alkyl, acyl, cycloalkyl, aryl, aralkyl, heterocyclyl, heteroaryl, or heteroaryalkyl or R' can be independently mono- or multi-substituted with J; or wherein two R' groups bonded to a nitrogen atom or to adjacent nitrogen atoms can together with the nitrogen atom or atoms form a heterocyclyl, which can be mono- or independently multi-substituted with J.

[0022] The term “alkyl” as used herein refers to straight chain and branched alkyl groups and cycloalkyl groups having from 1 to 40 carbon atoms, 1 to about 20 carbon atoms, 1 to 12 carbons or, in some embodiments, from 1 to 8 carbon atoms. Examples of straight chain alkyl groups include those with from 1 to 8 carbon atoms such as methyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, and n-octyl groups. Examples of branched alkyl groups include, but are not limited to, isopropyl, iso-butyl, sec-butyl, t-butyl, neopentyl, isopentyl, and 2,2-dimethylpropyl groups. As used herein, the term “alkyl” encompasses n-alkyl, isoalkyl, and antiisoalkyl groups as well as other branched chain forms of alkyl. Representative substituted alkyl groups can be substituted one or more times with any of the groups listed herein, for example, amino, hydroxy, cyano, carboxy, nitro, thio, alkxy, and halogen groups.

[0023] The term “alkenyl” as used herein refers to straight and branched chain and cyclic alkyl groups as defined herein, except that at least one double bond exists between two carbon atoms. Thus, alkenyl groups have from 2 to 40 carbon atoms, or 2 to about 20 carbon atoms, or 2 to 12 carbons or, in some embodiments, from 2 to 8 carbon atoms. Examples include, but are not limited to vinyl, -CH=CH(CH_3), -CH=C(CH_3)_2, -.
C(CH₃)₂CH₂, -C(CH₃)₂CH(CH₃), -C(CH₂CH₃)₂CH₂, cyclohexenyl, cyclopentenyl, cyclohexadienyl, butadienyl, pentadienyl, and hexadienyl among others.

[0024] The term “alkynyl” as used herein refers to straight and branched chain alkyl groups, except that at least one triple bond exists between two carbon atoms. Thus, alkynyl groups have from 2 to 40 carbon atoms, 2 to about 20 carbon atoms, or from 2 to 12 carbons or, in some embodiments, from 2 to 8 carbon atoms. Examples include, but are not limited to -C≡CH, -C≡C(CH₃), -C≡C(CH₂CH₃), -CH₂C≡CH, -CH₂C≡C(CH₃), and -CH₂C≡C(CH₂CH₃) among others.

[0025] The term “acyl” as used herein refers to a group containing a carbonyl moiety wherein the group is bonded via the carbonyl carbon atom. The carbonyl carbon atom is also bonded to another carbon atom, which can be part of an alkyl, aryl, aralkyl cycloalkyl, cycloalkylalkyl, heterocyclyl, heterocyclylalkyl, heteroaryl, heteroarylalkyl group or the like. In the special case wherein the carbonyl carbon atom is bonded to a hydrogen, the group is a “formyl” group, an acyl group as the term is defined herein. An acyl group can include 0 to about 12-20 or 12-40 additional carbon atoms bonded to the carbonyl group. An acyl group can include double or triple bonds within the meaning herein. An acryloyl group is an example of an acyl group. An acyl group can also include heteroatoms within the meaning here. A nicotinoyl group (pyridyl-3-carbonyl) group is an example of an acyl group within the meaning herein. Other examples include acetyl, benzoyl, phenylacetyl, pyridylacetyl, cinnamoyl, and acryloyl groups and the like. When the group containing the carbon atom that is bonded to the carbonyl carbon atom contains a halogen, the group is termed a “haloacyl” group. An example is a trifluoroacetyl group.

[0026] The term “cycloalkyl” as used herein refers to cyclic alkyl groups such as, but not limited to, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, and cyclooctyl groups. In some embodiments, the cycloalkyl group can have 3 to about 8-12 ring members, whereas in other embodiments the number of ring carbon atoms range from 3 to 4, 5, 6, or 7. Cycloalkyl groups further include polycyclic cycloalkyl groups such as, but not limited to, norbornyl, adamantyl, bornyl, camphenyl, isocamphenyl, and carenyl groups, and fused rings such as, but not limited to, decahydro, and the like. Cycloalkyl groups also include rings that are substituted with straight or branched chain alkyl groups as defined herein. Representative substituted cycloalkyl groups can be mono-substituted or substituted more than once, such as, but not limited to, 2,2-, 2,3-, 2,4-, 2,5- or 2,6-disubstituted cyclohexyl groups or mono-, di- or tri-substituted norbornyl or cycloheptyl groups, which can be substituted with, for example, amino, hydroxy, cyano, carboxy, nitro, thio, alkoxy, and halogen groups. The term “cycloalkenyl” alone or in combination denotes a cyclic alkenyl group.
[0027] The term "aryl" as used herein refers to cyclic aromatic hydrocarbons that do not contain heteroatoms in the ring. Thus aryl groups include, but are not limited to, phenyl, azulenyl, heptaleny1, biphenyl, indacenyl, fluorenyl, phenanthrenyl, triphenylenyl, pyrenyl, naphthacenyl, chrysenyl, biphenylenyl, anthracenyl, and naphthyl groups. In some embodiments, aryl groups contain about 6 to about 14 carbons in the ring portions of the groups. Aryl groups can be unsubstituted or substituted, as defined herein. Representative substituted aryl groups can be mono-substituted or substituted more than once, such as, but not limited to, 2-, 3-, 4-, 5-, or 6-substituted phenyl or 2-8 substituted naphthyl groups, which can be substituted with carbon or non-carbon groups such as those listed herein.

[0028] The term "aralkyl" as used herein refers to alkyl groups as defined herein in which a hydrogen or carbon bond of an alkyl group is replaced with a bond to an aryl group as defined herein. Representative aralkyl groups include benzyl and phenylethyl groups and fused (cycloalkylary1)alkyl groups such as 4-ethyl-indanyl. Aralkenyl group are alkenyl groups as defined herein in which a hydrogen or carbon bond of an alkyl group is replaced with a bond to an aryl group as defined herein.

[0029] The term "heterocyclyl" as used herein refers to aromatic and non-aromatic ring compounds containing 3 or more ring members, of which, one or more is a heteroatom such as, but not limited to, N, O, and S. Thus a heterocyclyl can be a cycloheteroalkyl, or a heteroaryl, or if polycyclic, any combination thereof.

[0030] The term "heteroaryl" as used herein refers to aromatic ring compounds containing 5 or more ring members, of which, one or more is a heteroatom such as, but not limited to, N, O, and S; for instance, heteroaryl rings can have 5 to about 8-12 ring members. A heteroaryl group is a variety of a heterocyclyl group that possesses an aromatic electronic structure.

[0031] The term "heterocyclylalkyl" as used herein refers to alkyl groups as defined herein in which a hydrogen or carbon bond of an alkyl group as defined herein is replaced with a bond to a heterocyclyl group as defined herein. Representative heterocyclyl alkyl groups include, but are not limited to, furan-2-yl methyl, furan-3-yl methyl, pyridine-3-yl methyl, tetrahydrofuran-2-yl ethyl, and indol-2-yl propyl.

[0032] The term "heteroarylalkyl" as used herein refers to alkyl groups as defined herein in which a hydrogen or carbon bond of an alkyl group is replaced with a bond to a heteroaryl group as defined herein.

[0033] The term "alkoxy" as used herein refers to an oxygen atom connected to an alkyl group, including a cycloalkyl group, as are defined herein. Examples of linear alkoxy groups include but are not limited to methoxy, ethoxy, propoxy, butoxy, pentyloxy, hexyloxy, and the like. Examples of branched alkoxy include but are not limited to
isopropoxy, sec-butoxy, tert-butoxy, isopentyl oxy, isohexyloxy, and the like. Examples of cyclic alkoxy include but are not limited to cyclopropyl oxy, cyclobutyl oxy, cyclopentyl oxy, cyclohexyl oxy, and the like. An alkoxy group can include one to about 12-20 or about 12-40 carbon atoms bonded to the oxygen atom, and can further include double or triple bonds, and can also include heteroatoms. For example, an allyloxy group is an alkoxy group within the meaning herein. A methoxyethoxy group is also an alkoxy group within the meaning herein, as is a methylenedioxy group in a context where two adjacent atoms of a structures are substituted therewith.

[0034] The term "amine" as used herein refers to primary, secondary, and tertiary amines having, e.g., the formula N(group)₃ wherein each group can independently be H or non-H, such as alkyl, aryl, and the like. Amines include but are not limited to R-NH₂, for example, alkylamines, arylamines, alkylarylamines; R₂NH wherein each R is independently selected, such as dialkylamines, diarylamines, aralkylamines, heterocyclylamines and the like; and R₃N wherein each R is independently selected, such as trialkylamines, dialkylarylamines, alkylarylines, triarylamines, and the like. The term "amine" also includes ammonium ions as used herein.

[0035] The term "amino group" as used herein refers to a substituent of the form -NH₂, -NHR, -NR₂, -NR₃⁺, wherein each R is independently selected, and protonated forms of each, except for -NR₃⁺, which cannot be protonated. Accordingly, any compound substituted with an amino group can be viewed as an amine. An "amino group" within the meaning herein can be a primary, secondary, tertiary or quaternary amino group. An "alkylamino" group includes a monoalkylamino, dialkylamino, and trialklamino group.

[0036] The terms "halo" or "halogen" or "halide", as used herein, by themselves or as part of another substituent mean, unless otherwise stated, a fluorine, chlorine, bromine, or iodine atom, preferably, fluorine, chlorine, or bromine.

[0037] The term "haloalkyl" group, as used herein, includes mono-halo alkyl groups, poly-halo alkyl groups wherein all halo atoms can be the same or different, and per-halo alkyl groups, wherein all hydrogen atoms are replaced by halogen atoms, such as fluoro. Examples of haloalkyl include trifluoromethyl, 1,1-dichloroethyl, 1,2-dichloroethyl, 1,3-dibromo-3,3-difluoropropyl, perfluorobutyl, and the like.

[0038] The term "monovalent" as used herein refers to a substituent connecting via a single bond to a substituted molecule. When a substituent is monovalent, such as, for example, F or Cl, it is bonded to the atom it is substituting by a single bond.

[0039] The term "hydrocarbon" as used herein refers to a functional group or molecule that includes carbon and hydrogen atoms. The term can also refer to a functional group or
molecule that normally includes both carbon and hydrogen atoms but wherein all the hydrogen atoms are substituted with other functional groups.

[0040] The term “resin” as used herein refers to polysiloxane material of any viscosity that includes at least one siloxane monomer that is bonded via a Si-O-Si bond to three or four other siloxane monomers. In one example, the polysiloxane material includes T or Q groups, as defined herein.

[0041] The term “solvent” as used herein refers to a liquid that can dissolve a solid, liquid, or gas. Nonlimiting examples of solvents are silicones, organic compounds, water, alcohols, ionic liquids, and supercritical fluids.

[0042] The term “coating” as used herein refers to a continuous or discontinuous layer of material on the coated surface, wherein the layer of material can penetrate the surface and can fill areas such as pores, wherein the layer of material can have any three-dimensional shape, including a flat or curved plane. In one example, a coating can be formed on one or more surfaces, any of which may be porous or nonporous, by immersion in a bath of coating material.

[0043] The term “room temperature” as used herein refers to a temperature of about 15 °C to 28 °C.

[0044] The term “number-average molecular weight” as used herein refers to the ordinary arithmetic mean of the molecular weight of individual molecules in a sample. It is defined as the total weight of all molecules in a sample divided by the total number of molecules in the sample. Experimentally, the number average molecular weight (Mn) is determined by analyzing a sample divided into molecular weight fractions of species i having ni molecules of molecular weight Mi through the formula Mn = ΣMi·ni / Σni. The number average molecular weight can be measured by a variety of well-known methods including gel permeation chromatography, spectroscopic end group analysis and osmometry.

[0045] The term “weight-average molecular weight” as used herein refers (Mw), which is equal to ΣMi·ni / Σni, where ni is the number of molecules of molecular weight Mi. In various examples, the weight average molecular weight can be determined using light scattering, small angle neutron scattering, X-ray scattering, and sedimentation velocity.

[0046] As used herein, the term “hydrocarbyl” refers to a functional group derived from a straight chain, branched, or cyclic hydrocarbon, such as an alkyl, alkenyl, alkynyl, aryl, cycloalkyl, acyl, or a combination thereof.

Copolymer.

[0047] In various embodiments, the present invention provides a polysiloxane-polyamide block copolymer including the repeating unit -[M1-M2]DP1-. The variable M1 can be a divalent polydiorganosiloxane. The variable M2 can be a divalent polyamide. The variable
DP1 can be about 1-1000, 1-200, 2-200, 2-100, 2-50, or about 2-20. The copolymer can be terminated by any suitable functional group or combination of functional group. The copolymer can include any other suitable unit, such as any other suitable repeating unit, in addition to the repeating unit \([-M^1-M^2]_{DP1}\). Embodiments of the present invention encompass a plurality of block copolymers including the repeating unit \([-M^1-M^2]_{DP1}\), a single block copolymer including the repeating unit \([-M^1-M^2]_{DP1}\), and any composition including the same.

In some embodiments, polysiloxane-polyamide block copolymer can have the following structure \(E^1\cdot[-M^1-M^2]_{DP1}\cdot E^2\). The variable \(E^1\) can be \(Y^-\) or \(X-M^2^-\). The variable \(E^2\) can be \(-X\) or \(-M^1^-Y\). The variable \(X\) is a monovalent polydiorganosiloxane corresponding to \(M^1\); e.g., \(X\) is divalent polysiloxane \(M^1\) having an \(-H\) substituent at one of the locations of valency. For example, \(X\) is \(M^1^-H\). The variable \(Y\) is a monovalent polyamide corresponding to \(M^2\); \(Y\) is a divalent amide having an \(-H\) substituent at one of the locations of valency. For example, \(Y\) is \(M^2^-H\). In some embodiments, the polysiloxane-polyamide block copolymer has the structure \(Y\cdot[-M^1-M^2]_{DP1}\cdot X\), \([-M^1-M^2]_{DP1}\cdot Y\), \(-X\cdot[-M^1-M^2]_{DP1}\cdot X\), or \(-X\cdot[-M^1-M^2]_{DP1}\cdot M^2^-Y\).

The polysiloxane-polyamide block copolymer can have any suitable molecular weight. In some examples, the copolymer has a molecular weight of about 5,000 Daltons to 500,000 Daltons, 10,000 Daltons - 100,000 Daltons, or about 15,000 Daltons to 90,000 Daltons.

The polysiloxane-polyamide block copolymer can have any suitable properties, consistent with the structure as described herein. The block copolymer can have any suitable polydispersity. For example, in various embodiments, the block copolymer can have a polydispersity relative to polystyrene strands in THF of about 1 to 20, 2 to 10, or about 2.7 to 7. The block copolymer can have any suitable melt viscosity. For example, in various embodiments, the block copolymer can have a melt viscosity at about 190 °C of about 1,000 cP to 50,000 cP, 5,000 cP - 20,000 cP, or about 7,500 to 18,000 cP. The block copolymer can have any suitable melting point. For example, the block copolymer can have a melting point of about 100 °C to about 300 °C, 130 °C - 220 °C, or about 140 °C to 200 °C.

Polysiloxane.

In the polysiloxane-polyamide block copolymer, the polysiloxane units can have any suitable polysiloxane structure consistent with the properties of the block copolymer described herein. In various embodiments, in the polysiloxane-polyamide block copolymer,
the divalent polysiloxane M¹ can have the structure -SiR¹R²-[OSiR¹R²]DP₂⁻. Each of R¹ and R² at each occurrence can be an organic functional group. The variable DP₂ can be about 1 to about 500, or 10-200, or about 20-120. In some examples, each of R¹ and R² can be at each occurrence independently at least one of straight chain, branched, and cyclic, substituted or unsubstituted (C₁-C₂₀)hydrocarbyl, with the proviso that R¹ and R² do not include an aliphatic unsaturated carbon-carbon bond such as alkenyl (e.g., vinyl) or alkynyl. Each of R¹ and R² can be at each occurrence independently at least one of straight chain and branched unsubstituted (C₁-C₁₀)hydrocarbyl. In some examples, each of R¹ and R² are methyl.

Polyamide.

[0052] In the polysiloxane-polyamide block copolymer, the polyamide units can have any suitable polyamide structure consistent with the properties of the block copolymer described herein. In various embodiments, in the polysiloxane-polyamide block copolymer, the divalent polyamide M² can have the structure -R³-C(O)[NH-R⁴-NHC(O)]-R⁵⁻. Each of R³, R⁴, and R⁵ at each occurrence can be independently at least one of straight-chain, branched, and cyclic, divalent (C₁-C₃₀)alkylene group. In some examples, the variable DP₃ can be about 0-50, 0-10, 0-5, or about 0-1. In some examples, the variable DP₃ can be about 1-50, 1-10, 1-5, or about 1. Various embodiments provide a plurality of the copolymers wherein DP₃ has an average value of about 0-50, 0.001-10, 0.01-5, or about 0.1-1. In some examples, each of R³, R⁴, and R⁵ is independently a divalent (C₁-C₁₅) alkylene group. The variable R³ can be an n-undecylene group. Each of R⁴ and R⁵ can be a straight chain alkylene group independently selected from a (C₄-1₅)alkylene group, or from a (C₄)alkylene group, a (C₆)alkylene group, and a (C₉)alkylene group. For example, the divalent polyamide can correspond to a nylon-6,6 structure, a nylon-4,6 structure, a nylon-6,9 structure, a nylon-4,9 stucture, a nylon-9,4 structure, or a nylon-6,4 structure.

Method of making the copolymer.

[0053] Various embodiments of the present invention provide a method of making the polysiloxane-polyamide block copolymer. The method can be any suitable chemical synthetic method that produces the polysiloxane-polyamide block copolymer. In some examples, the method includes combining an Si-H terminated polydiorganosiloxane with a polyamide having terminal groups that include at least one aliphatic unsaturated carbon-carbon bond in the presence of a hydroisilylation catalyst, and subjecting the mixture to conditions suitable for hydroisilylation, thereby forming the block copolymer. For example,
in various embodiments, the method can include obtaining or providing a mixture that includes an Si-H-terminated polydiorganosiloxane having the formula HSiR\(^1\)R\(^2\)-[OSiR\(^1\)R\(^2\)]\(_{DP2}\)H. Each of R\(^1\) and R\(^2\) at each occurrence can be an organic functional group. The variable DP2 can be about 1 to about 500. The mixture also includes an alkenyl-terminated polyamide having the formula R\(^6\)-C(O)[NH-R\(^4\)-NHC(O)-R\(^5\)]-C(O)]\(_{DP3}\)NH-R\(^4\)-NHC(O)-R\(^6\). The variable R\(^6\) at each occurrence can be independently a monovalent (C\(_1\) - C\(_{30}\)) hydrocarbyl group having at least one nonaromatic unsaturated carbon-carbon bond. Each of R\(^4\) and R\(^5\) can be independently a divalent (C\(_1\) - C\(_{30}\)) alkenylene group. The variable DP3 can be about 0-50. The mixture also can include a hydrosilylation catalyst. The method also can include subjecting the mixture to reaction conditions to give the polysiloxane-polyamide block copolymer.

[0054] The hydrosilylation catalyst can be any suitable hydrosilylation catalyst. In some embodiments, the hydrosilylation catalyst can be any hydrosilylation catalyst including a platinum group metal or a compound containing a platinum group metal. Platinum group metals can include platinum, rhodium, ruthenium, palladium, osmium and iridium. Examples of hydrosilylation catalysts include the complexes of chloroplatinic acid and certain vinyl-containing organosiloxanes disclosed by Willing in U.S. Pat. No. 3,419,593, such as the reaction product of chloroplatinic acid and 1,3-divinyl-1,1,3,3-tetramethyldisiloxane; microencapsulated hydrosilylation catalysts including a platinum group metal encapsulated in a thermoplastic resin, as exemplified in U.S. Pat. No. 4,766,176 and U.S. Pat. No. 5,017,654; and photoactivated hydrosilylation catalysts, such as platinum(II) bis(2,4-pentanedioate), as exemplified in U.S. Patent No. 7,799,842. An example of a suitable hydrosilylation catalyst can include a platinum(IV) complex of 1,3-diethylen-1,1,3,3-tetramethyldisiloxane. In another embodiment, the hydrosilylation catalyst can be at least one photoactivated hydrosilylation catalyst. The suitability of a particular hydrosilylation catalyst for use in a reaction mixture of the present invention can be readily determined by routine experimentation. The concentration of the hydrosilylation catalyst can be sufficient to catalyze hydrosilylation of the polysiloxane having terminal Si-H groups and the polyamide having terminal unsaturated aliphatic carbon-carbon bond-containing groups. Typically, the concentration of the hydrosilylation catalyst is sufficient to provide from about 0.1 to about 1000 ppm of a platinum group metal, from about 0.5 to about 500 ppm of a platinum group metal, and more preferably from about 1 to about 100 ppm of a platinum group metal, based on the total weight of the uncured composition. The rate of cure can be very slow below about 0.1 ppm of platinum group metal. The use of more than 1000 ppm of platinum group metal is possible, but is generally undesirable because of catalyst cost.
Compositions including the copolymer.

[0055] Various embodiments of the present invention provide compositions that include one or more of the polysiloxane-polyamide copolymers described herein. The composition that includes that copolymer can be any suitable composition that is used for any suitable purpose consistent with the properties of the copolymer or composition including the same. In some examples, the present invention provides a personal care composition including the polysiloxane-polyamide block copolymer. The personal care composition can be any suitable personal care composition, such as a cosmetic composition or a deodorant composition.

[0056] In some examples, the present invention provides a thermoplastic composition including the polysiloxane-polyamide block copolymer and at least one organic polymer. The organic polymer can be any organic polymer that can be suitably combined with the block copolymer, such that it is useful for its intended use. For example, the organic copolymer can be a thermoplastic nylon resin. The nylon resin can be any high molecular weight solid homopolymer, copolymer or terpolymer having recurring amide units within the polymer chain (e.g. polyamides or copolymers thereof) having thermoplastic properties. The nylon resin can be crystalline or amorphous. The nylon resin can have a melting point greater than about 25 °C. In copolymer and terpolymer systems, more than 50 mole percent of the repeat units can be amide-containing units. Examples of suitable polyamides include polylactams such as nylon 6, polyenantholactam (nylon 7), polycapryllactam (nylon 8), polylauryllactam (nylon 12), and the like; homopolymers of aminoacids such as polypyrrolidinone (nylon 4); copolymides of dicarboxylic acid and diamine such as nylon 6,6, polyhexamethyleneazetamide (nylon 6,9), polyhexamethylene-sebacamide (nylon 6,10), polyhexamethyleneisophthalamide (nylon 6,IP), polyhexamethylenedodecanolic acid (nylon 6,12) and the like; aromatic and partially aromatic polyamides; copolyamides such as copolymers of caprolactam and hexamethyleneadipamide (nylon 6,6/6), or a terpolyamide (e.g., nylon 6,6/6,6); block copolymers such as polyether polyamides; or mixtures thereof. Representative examples of siloxane-based polyamides useful in the compositions of the present invention are disclosed in U.S. Pat. No. 6,051,216 and U.S. Pat. No. 6,353,076 B1, which are hereby incorporated by reference.

[0057] In some examples, the compositions of the present invention can be prepared by melt mixing the polysiloxane-polyamide block copolymer with the organic polymer. The organic polymer can be melted and then the polysiloxane-polyamide block copolymer can be mixed with the organic polymer melt. The mixing can occur via any known mixing techniques in the art for processing and mixing thermoplastic resins at elevated temperatures. For example, the components may be mixed in a twin screw extruder, a
Banbury mixer, a two roll mill or a single screw extruder, with or without a mixing gear. The mixing can occur in an extrusion process. The amount of the polysiloxane-polyamide block copolymer used per 100 parts of the organic polymer can be about 0.1 to 20 weight parts, 0.2-20 weight parts, 0.5-10 weight parts, or about 0.5-5 weight parts of the polysiloxane-polyamide block copolymer per 100 weight parts of the organic polymer. Other components, such as those commonly added to nylon compositions or processes, can be added to the melt mixture. In some examples, the additional components are not equal to or exceed 20 weight percent of the total composition. The other components can be, but not limited to, processing additives, fillers, flame retardants, UV stabilizers, antioxidants, antiblock agents, catalyst stabilizers, lubricants, colorants, impact modifiers, foaming agents, mold release agents, matt/gloss additives, plasticizers, and combinations thereof.

In various examples, the compositions can be further compounded or mixed with additional components. These additional components can be illustrated by, but not limited to, reinforcing fillers for polyamide resins, such as glass fibers and carbon fibers; extending fillers such as quartz, calcium carbonate, and diatomaceous earth; pigments such as iron oxide and titanium oxide, electrically conducting fillers such as carbon black and finely divided metals, heat stabilizers such as hydrated cerium oxide, antioxidants, flame retardants such as halogenated hydrocarbons, alumina trihydrate, magnesium hydroxide, organophosphorous compounds and other fire retardant (FR) materials; adhesion promoters; and combinations thereof. In various embodiments, the composition can be a mixture of adhesion promoter and the polysiloxane-polyamide copolymer having any suitable amount of adhesion promoter present, such as about 0.001 wt% or less, about 0.01 wt%, 0.1 wt%, 0.2 wt%, 0.3 wt%, 0.4 wt%, 0.5 wt%, 0.6 wt%, 0.7 wt%, 0.8 wt%, 0.9 wt%, 1 wt%, 2 wt%, 3 wt%, 4 wt%, 5 wt%, 6 wt%, 8 wt%, 9 wt%, 10 wt%, 20 wt%, 30 wt%, 40 wt%, or about 50 wt% or more of the polysiloxane-polyamide copolymer composition.

Embodiments of the composition including the polysiloxane-polyamide block copolymer can have any suitable application. For example, a thermoplastic composition can be extruded and blown into sheet products or molded or cast into articles of manufacture. In other examples, they can be drawn into fiber and made into nonwoven fabrics or spun to produce yarns from which fabrics may be woven. In some examples, the compositions can be used to coat or treat the surface of another material, such as a nylon-based material (e.g. a film) or any suitable material.

Article of manufacture including the copolymer.

In various embodiments, the present invention provides an article of manufacture including the polysiloxane-polyamide copolymer described herein. The article of manufacture can be any suitable article of manufacture that can benefit from the inclusion
of the copolymer. For example, the article of manufacture can be at least one of a sheet product (e.g., a film), a molded article, a fiber, a spun yarn, a textile, and a nonwoven fabric. The article of manufacture can include the copolymer alone or as a component of a mixture of other components. In one example the article of manufacture is a thermoplastic film that includes a composition that includes the copolymer. The article of manufacture can include a coating or surface treatment that includes the copolymer or that includes a composition that includes the copolymer. In some embodiments, the article of manufacture can include any suitable substrate that is coated with the polysiloxane-polyamide copolymer, such as a coated fiber, a coated film, a coated spun yarn. The article of manufacture can include any suitable amount of the copolymer, or of a composition including the copolymer, such as about 0.001-1000 g/m², or about 20-200 g/m². In various examples, the article of manufacture can include an adhesion promoter underneath a coating or treatment of the polysiloxane-polyamide copolymer, or the article of manufacture can include a coating of a composition including the polysiloxane-polyamide copolymer and an adhesion promoter.

**Method of using the copolymer.**

[0061] In various examples, the present invention provides a method of using the copolymer, or a method of using a composition that includes the copolymer, or a method of using an article of manufacture that includes the copolymer. The method can be any suitable method of using the copolymer consistent with the structure and properties of the block copolymer and compositions including the same as described herein.

[0062] For example, some embodiments provide a method of coating a substrate. The method can include obtaining or providing a substrate. The method also can include coating the substrate with a composition including the polysiloxane-polyamide block copolymer. The coating can be performed using any suitable method, such as knife-over-air or knife-over-roller. In some examples, the substrate can include a fiber, a film, and the like. The method can include applying any suitable amount of the copolymer, such as about 0.001-1000 g/m², or about 20-200 g/m².

[0063] In some embodiments, the present invention provides a method of forming a film. The method can include obtaining or providing a thermoplastic composition including the polysiloxane-polyamide block copolymer. The method can also include forming the thermoplastic composition into a film. In another embodiment, the method of forming a film includes generating a film, and then coating or otherwise treating at least some part of the surface of the film with the copolymer or with a composition including the copolymer.

[0064] The present invention can be better understood by reference to the following examples which are offered by way of illustration. The present invention is not limited to the examples given herein. In the Examples, “DP” refers to degree of polymerization.
[0065] General. The 244 fluid used was a mixture of about 85-100 wt% octamethyicyclotetracyclosiloxane and ≤ 0.5% hexamethyicyclotrisiloxane. Sylof 4000 Pt catalyst used was about 85-100 wt% dimethylvinyl-terminated dimethylsiloxane, 5-10 wt% tetramethylenevinylsiloxane, and 1-5 wt% diethyleneyl tetramethyl disiloxane platinum complex.

[0066] The samples were prepared in certified grade THF, filtered with a 0.45μm PTFE syringe filter, and analyzed against polystyrene standards. The relative calibration (third order fit) used for molecular weight determination was based on 16 polystyrene standards ranging in molecular weights from 580 to 2,320,000 Daltons.

[0067] The chromatographic equipment included a Waters 2695 Separations Module equipped with a vacuum degasser, a Waters 2410 differential refractometer and two (300 mm x 7.5 mm) Polymer Laboratories Mixed C columns (molecular weight separation range of 200 to 3,000,000) preceded by a guard column.

[0068] The separations were performed using certified grade THF programmed to flow at 1.0 mL/min., injection volume was set at 100μL and columns and detector were heated to 35 °C. Data collection was 25 minutes and processing was performed using Atlas/Cirrus software.

Example 1. Adipic Acid Diamide, 11.1 mol%.

[0069] A 70 wt% solution of hexamethylenediamine (HMDA, 339.5 g) was loaded into a 2000 mL three-neck round bottom flask equipped with thermocouple, electrical stirrer, condenser, and nitrogen sweep. The flask was allowed to purge with nitrogen for a minimum of 5 minutes prior to heating or adding other reagents to ensure an inert atmosphere. The mixing apparatus was turned on and adipic acid (29.8 g) was added to the flask. A small exotherm was observed and recorded, and then the mixture was heated to 60°C. The mixture was held at 60°C until it became clear (approximately 1 hour).

[0070] Once the reaction mixture became clear, undecylenic acid (UDA, 679.0 g) was added streamwise via an addition funnel and the highest temperature reached due to exotherm was observed (95°C). Once the addition was complete, a distillation apparatus was set up and the temperature was increased to 120°C to remove water from the starting materials. The temperature of 120°C was held for 1 hour, then the temperature was ramped up to 175°C to remove the water formed as a byproduct of the acid-base reaction, thus driving the reaction forward. The temperature of 175°C was held for 1 hour, then vacuum was applied and temperature was increased to 220°C to remove excess UDA from the product. A reaction temperature of 220°C was maintained while under full vacuum (< 20 mmHg) for at least 2 hours.

[0071] The mixture was allowed to cool down to 175°C and then the vacuum was broken with nitrogen. The hot mixture was poured off into dry ice-cooled aluminum foil-covered
trays. The material was allowed to cool sufficiently prior to handling and characterization. The melt point was determined to be 155-160°C according to the Fisher-Johns melt point apparatus.

**Example 2. Adipic Acid Diamide, 17.6 mol%**.

[0072] A 70 wt% solution of hexamethylenediamine (HMDA, 166.03 g) was loaded into a 2000 mL three-neck round bottom flask equipped with thermocouple, electrical stirrer, condenser, and nitrogen sweep. The flask was purged with nitrogen for a minimum of 5 minutes prior to heating or adding other reagents to ensure an inert atmosphere. The mixing apparatus was turned on and adipic acid (21.94 g) was added to the flask. A small exotherm was observed, and then the mixture was heated to 60°C. The mixture was held at 60°C until it became clear (approximately 1 hour).

[0073] Once the reaction mixture became clear, undecylenic acid (UDA, 319.67 g) was added streamwise via an addition funnel and the highest temperature reached due to exotherm was recorded (95°C). Once the addition was complete, a distillation apparatus was set up and the temperature was increased to 120°C to remove water from the starting materials. The temperature was held at 120°C for 1 hour, then the temperature was ramped up to 175°C to remove the water formed as a byproduct of the acid-base reaction, thus driving the reaction forward. The temperature was held at 175°C for 1 hour, and then vacuum was applied and the temperature was increased to 220°C to remove excess UDA from the product. A reaction temperature of 220°C was maintained while under full vacuum (<20 mmHg) for at least 2 hours.

[0074] The mixture was allowed to cool down to 175°C and then the vacuum was broken with nitrogen. The hot mixture was poured off thinly into dry ice-cooled aluminum foil-covered trays. The material was allowed to cool sufficiently prior to handling and characterization. The melt point was determined to be 170-175°C according to the Fisher-Johns melt point apparatus.

**Example 3. Siloxane Equilibration, 80 dp.**

[0075] Into a 12 liter three-neck round bottom flask equipped with thermocouple, electrical stirrer, condenser, and nitrogen sweep was added a mixture of 244 fluid (2833.5 g) and 73.33 g of 1,1,3,3-tetramethyldisiloxane. The flask was purged with nitrogen for a minimum of 5 minutes prior to heating or catalyzing to ensure an inert atmosphere. The mixing apparatus was turned on and 1.6 mL of trifluoromethanesulfonic acid was added as a catalyst. The reaction temperature was increased to 70°C and the temperature was held overnight (16 hours).

[0076] The mixture was neutralized with 43.7 g of sodium bicarbonate and cooled to room temperature. Once the materials cooled, the materials were pressure filtered using 0.45 µm filter paper and celite filtration aid.
[0077] The filtered siloxane was loaded into a 12 liter three-neck round bottom flask equipped with thermocouple, electrical stirrer, condenser, and nitrogen sweep in a vacuum strip setup. The flask was purged for 5 minutes with nitrogen, and then mixing was turned on and heating to 100°C was initiated. Once at temperature, gradually full vacuum was applied (20 mmHg) and then the temperature was incrementally ramped up to 150°C. The temperature was held at 150°C under full vacuum for five hours. The reaction was allowed to cool to less than 100°C prior to breaking the vacuum with nitrogen. The material was allowed to cool down to room temperature prior to characterization. The stripped siloxane was poured into a plastic lined container, from which 270 g of overheads (8.9 wt%) was collected. The SiH concentration of the stripped siloxane was determined to be 321 ppm using FT-IR, which corresponds to approximately an 84 DP terminal SiH siloxane.


[0078] Into a 500 mL resin kettle equipped with thermocouple, electrical stirrer, condenser, and nitrogen sweep was loaded 240.49 g of 84 DP terminal SiH siloxane (SiH=321 ppm, from Example 3) and 22.65 g of 17.6 mol% adipic diamide (from Example 2). The kettle was purged with nitrogen for a minimum of 5 minutes prior to heating to ensure an inert atmosphere. The kettle was mixed at 100 rpm and the temperature was increased to 190°C. Once at temperature and diamide was fully melted, the mixing rate was increased to 300 rpm and the reaction was catalyzed with three doses of Sylof 4000 Pt catalyst (0.21 g, 0.24 g, 0.07 g, respectively) over a 15 minute time frame. Following the third dose of catalyst, the reaction was held at 190°C for 2 hours and then poured off hot into a glass tray. The material was allowed to cool to room temperature prior to handling and characterization. The melt point was determined to be 142-144°C according to a Fisher-Johns melt point apparatus, and the molecular weight (Mw) was determined to be 81,000 daltons with a polydispersity of 5.03 relative to polystyrene standards in THF using conventional GPC analysis.

Example 5. Nylon 6.6 Modified Diamide, 16.75 mol%.

[0079] Into a 3L three-neck round bottom flask equipped with thermocouple, motorized stirrer, condenser, and nitrogen sweep was loaded 474.22 g of a 70 wt% solution of hexamethylenediamine (HMDA). The flask was purged with nitrogen for a minimum of 5 minutes prior to heating or adding other reagents to ensure an inert atmosphere. The mixing apparatus was turned on and 62.65 g of adipic acid was added to the flask. The highest temperature observed due to exotherm was observed, then the mixture was heated to 60°C. The mixture was held at 60°C until it became transparent (approximately 1 hour).

[0080] Once reaction mixture became clear, 913.13 g of undecylenic acid (UDA) was added streamwise via an addition funnel and the highest temperature reached due to exotherm was observed (94°C). Once the addition was complete, a distillation apparatus
was set up and the temperature was increased to 120°C to remove water from the starting materials. The temperature of 120°C was held for 1 hour, then the temperature was ramped up to 175°C to remove the water formed as a byproduct of the acid-base reaction, thus driving the reaction forward. The temperature of 175°C was held for 1 hour, and then vacuum was applied and the temperature was increased to 220°C to remove excess UDA from the product. A reaction temperature of 220°C was maintained while under full vacuum (<20 mmHg) for at least 2 hours.

[0081] The mixture was allowed to cool down to 175°C and then the vacuum was broken with nitrogen. The mixture was poured off thinly into dry ice-cooled aluminum foil-covered trays. The material was allowed to cool sufficiently prior to handling and characterization. The melt point was determined to be 181.9°C based upon measurements obtained using a Buchi Melting Point M-565 instrument.

Example 6. Nylon 6,6 Modified Diamide, 25.0 mol%.

[0082] Into a 5L three-neck round bottom flask equipped with thermocouple, motorized stirrer, water chilled condenser, and nitrogen sweep was loaded 335 g of a 70 wt% solution of hexamethylenediamine (HMDA). The flask was purged with nitrogen for a minimum of 5 minutes prior to heating or adding other reagents to ensure an inert atmosphere. The mixing apparatus was turned on and 59 g of adipic acid was added to the flask. The highest temperature due to exotherm was observed, then the mixture was heated to 60°C. The mixture was held at 60°C until it became transparent (approximately 1 hour).

[0083] Once reaction mixture became clear, 606 g of undecylenic acid (UDA) was added streamwise via an addition funnel and the highest temperature reached due to exotherm was observed (95.5°C). Once the addition was complete, a distillation apparatus was set up and the temperature was increased to 120°C to remove water from the starting materials. The temperature of 120°C was held for 1 hour, then the temperature was ramped up to 175°C to remove the water formed as a byproduct of the acid-base reaction, thus driving the reaction forward. The temperature of 175°C was held for 1 hour, and then vacuum was applied and the temperature was increased to 220°C to remove excess UDA from the product. A reaction temperature of 220°C was maintained while under full vacuum (<20 mmHg) for at least 2 hours.

[0084] The mixture was allowed to cool down to 175°C and then the vacuum was broken with nitrogen. The hot mixture was poured off thinly into dry ice-cooled aluminum foil-covered trays. The material was allowed to cool sufficiently prior to handling and characterization. The melt point was determined to be 188.8°C based upon measurements obtained using a Buchi Melting Point M-565 instrument.

Example 7. Nylon 6,6 Modified Diamide, 27.5 mol%.
[0085] Into a 500 mL three-neck round bottom flask equipped with thermocouple, motorized stirrer, water chilled condenser, and nitrogen sweep was loaded 67.41 g of a 70 wt% solution of hexamethylenediamine (HMDA). The flask was purged with nitrogen for a minimum of 5 minutes prior to heating or adding other reagents to ensure an inert atmosphere. The mixing apparatus was turned on 12.81 g of adipic acid was added to the flask. The highest temperature observed due to exotherm was observed, then the mixture was heated to 60°C. The mixture was held at 60°C until it became transparent (approximately 1 hour).

[0086] Once reaction mixture became clear, 119.78 g of undecylenic acid (UDA) was added streamwise via an addition funnel and the highest temperature reached due to exotherm was observed (82°C). Once the addition was complete, a distillation apparatus was set up and the temperature was increased to 120°C to remove water from the starting materials. The temperature of 120°C was held for 1 hour, then the temperature was ramped up to 175°C to remove the water formed as a byproduct of the acid-base reaction, thus driving the reaction forward. The temperature of 175°C was held for 1 hour, and then vacuum was applied and the temperature increased to 220°C to remove excess UDA from the product. A reaction temperature of 220°C was maintained while under full vacuum (< 20 mmHg) for at least 2 hours.

[0087] The mixture was allowed to cool down to 175°C and then the vacuum was broken with nitrogen. The hot mixture was poured thinly into dry ice-cooled aluminum foil-covered trays. The material was allowed to cool sufficiently prior to handling and characterization. The melt point was determined to be 199.9°C based upon measurements obtained using a Buchi Melting Point M-565 instrument.

Example 8. Siloxane Equilibration, 80 dp.

[0088] Into a 12 liter three-neck round bottom flask equipped with thermocouple, motorized stirrer, water-cooled condenser, and nitrogen blanket was loaded 8785 g of 244 fluid and 215 g of 1,1,3,3-tetramethyldisiloxane. The mixing apparatus was turned on and the reaction mixture was catalyzed with 4.5 mL of trifluoromethanesulfonic acid, which resulted in an acid concentration of approximately 5 ppm. The reaction temperature was raised to 70°C and the equilibration reaction was allowed to proceed overnight (16 hours).

[0089] The mixture was neutralized with 120 g of sodium bicarbonate and the reaction mixture was cooled to room temperature. Once the reaction kettle temperature had sufficiently cooled, the contents were processed through a pressure filter using 0.45 μm filter paper and celite filtration aid to remove excess sodium bicarbonate, salts, and other particulates.

[0090] The filtered siloxane was loaded into a 12 liter three-neck round bottom flask equipped with thermocouple, electrical stirrer, condenser, and nitrogen sweep in the
vacuum strip setup. The flask was purged for 5 minutes with nitrogen, the mixing was turned on, and the mixture was heated to 100°C. Once at temperature, gradually full vacuum was applied (< 20 mmHg) and then incrementally the temperature was ramped up to 150°C. The temperature was held at 150°C under full vacuum for five hours. The reaction was allowed to cool to less than 100°C prior to breaking the vacuum with nitrogen. The material was allowed to cool down to room temperature prior to decanting and characterization. The stripped siloxane was poured off into a plastic lined container. The overheads removed during the stripping process were 910 g which was 10.11 wt% of the batch size. The SiH concentration of the stripped siloxane was determined to be 327 ppm using FT-IR, which corresponds to approximately an 83 DP terminal SiH siloxane.


[0091] A 2L resin kettle was equipped with a thermocouple, motorized stirrer, condenser, and nitrogen sweep. The kettle was charged with 410 g of an 83 DP terminal SiH siloxane (SiH = 327 ppm, from Example 8) and 48 g of 25.0 mol% nylon 6,6 modified diamide (from Example 6). The kettle was purged with nitrogen for a minimum of 5 minutes prior to heating to ensure an inert atmosphere. The mixture was mixed at 100 rpm and the temperature was increased to 195°C. Once the kettle reached the desired temperature and the diamide was fully melted, the mixing rate was increased to 300 rpm. The reaction was then catalyzed with two doses of Syloff 4000 Pt catalyst (0.53 g + 0.31 g) over a 10 minute time frame to ensure the catalyst was active. Following the second dose of catalyst, the reaction was held at 195-200°C for 2 hours. After the 2 hour hold time, the silicone polyamide was decanted at temperature into a glass tray. The material was allowed to cool to room temperature prior to handling, processing, and characterization.

[0092] The material hardened into a straw colored solid gellant. The melt point was determined to be 160-165°C according to the Fisher-Johns melt point apparatus. The molecular weight (M_w) was 66,800 Daltons with a polydispersity of 3.247 relative to polystyrene standards in THF using conventional GPC analysis. The melt viscosity at 190°C was measured to be 12,100 cP.

Example 10. Nylon 4,6-Modified Diamide, 25.0 mol%.

[0093] Into a 500 mL three-neck round bottom flask equipped with thermocouple, motorized stirrer, water chilled condenser, and nitrogen sweep was loaded 88.15 g of 99% pure 1,4-diaminobutane (putrescine). Deionized water (16.4 g) was added to improve compatibility and dissolve the white crystalline solid. The flask was purged with nitrogen for a minimum of 5 minutes prior to heating or adding other reagents to ensure an inert atmosphere. The mixing apparatus was turned on, and 146.21 g of adipic acid was added to the flask. The highest temperature due to exotherm was observed, then the mixture was
heated to 60°C. The mixture was held at 60°C until it became transparent (approximately 1 hour).

[0094] Once reaction mixture became clear, add 184.28 g of undecylenic acid (UDA) streamwise via an addition funnel and the highest temperature reached due to exotherm was observed (90°C). White particulates formed upon the UDA addition, and the contents of the flask became a thick orange paste. Once the addition was finished, a distillation apparatus was set up and the temperature was increased to 115-120°C to remove water from the starting materials. The temperature was maintained at 120°C for 1 hour to avoid loss of product, then the temperature was ramped up to 175°C to remove the water formed as a byproduct of the acid-base reaction, thus driving the reaction forward. The temperature of 175°C was held for 1 hour, and then vacuum was applied and the temperature was increased to 220°C to remove excess UDA from the product. A reaction temperature of 220°C was maintained while under full vacuum (<20 mmHg) for at least 2 hours.

[0095] The mixture was allowed to cool down to 200°C and then the vacuum was broken with nitrogen. The hot mixture was poured thinly into dry ice-cooled aluminum-foil covered trays. The material was allowed to cool sufficiently prior to handling and characterization. The melt point was determined to be 199.9°C based upon measurements obtained using a Buchi Melting Point M-565 instrument.

Example 11. Nylon 6,9-Modified Diamide, 25.0 mol%.

[0096] Into a 500 mL three-neck round bottom flask equipped with thermocouple, motorized stirrer, water chilled condenser, and nitrogen sweep was loaded 116.21 g of a 70 wt% solution of hexamethylenediamine (HMDA). The flask was purged with nitrogen for a minimum of 5 minutes prior to heating or adding other reagents to ensure an inert atmosphere. The mixing apparatus was turned on, and 188.22 g of a 98% pure solution of azelaic acid (nonanedioic acid) was added to the flask. The highest temperature due to exotherm was observed, then the mixture was heated to 60°C. The mixture was held at 60°C until it became transparent (approximately 1 hour).

[0097] Once reaction mixture became clear, 184.28 g of undecylenic acid (UDA) was added streamwise via an addition funnel and the highest temperature reached due to exotherm was observed (81°C). Once the addition was complete, a distillation apparatus was set up and the temperature was increased to 120°C to remove water from the starting materials. The temperature of 120°C was held for 1 hour, then the temperature was ramped up to 175°C to remove the water formed as a byproduct of the acid-base reaction, thus driving the reaction forward. The temperature of 175°C was held for 1 hour, and then vacuum was applied and the temperature was increased to 220°C to remove excess UDA.
from the product. A reaction temperature of 220°C was maintained while under full vacuum (<20 mmHg) for at least 2 hours.

[0098] The mixture was cooled to 175°C and the vacuum was broken with nitrogen. The hot mixture was decanted thinly into dry ice-cooled aluminum foil-covered trays. The material was allowed to cool sufficiently prior to handling and characterization. The melt point was determined to be 162.2°C based upon measurements obtained using a Buchi Melting Point M-565 instrument.

Example 12. Nylon 6,9-Containing Silicone Polyamide Gellant with 80 DP Si Block.

[0099] A 500 mL resin kettle was equipped with a thermocouple, motorized stirrer, condenser, and nitrogen sweep. The kettle was charged with 153.80 g of a 78 DP terminal SiH siloxane (SiH=346 ppm) and 19.39 g of 25.0 mol% nylon 6,9 modified diamide (from Example 11). The kettle was purged with nitrogen for a minimum of 5 minutes prior to heating to ensure an inert atmosphere. The kettle was mixed at 100 rpm and the temperature was increased to 175°C. Once the kettle reached the desired temperature and the diamide was fully melted, the mixing rate was increased to 300 rpm. Then the reaction was catalyzed with two doses of Syloff 4000 Pt catalyst (0.30 g + 0.20 g, respectively) over a 10 minute time frame to ensure the catalyst was active. Following the second dose of catalyst, the reaction was held at 195-200°C for 2 hours. After the 2 hour hold time, the silicone polyamide was decanted at temperature into a glass tray. The material was allowed to cool to room temperature prior to handling, processing, and characterization.

[0100] The material hardened into a straw colored solid gellant. The pharmacopeia melt point was determined to be 172.6°C based upon measurements obtained using a Buchi Melting Point M-565 instrument. The molecular weight (M_w) was 63,700 Daltons with a polydispersity of 6.67 relative to polystyrene standards in THF using conventional GPC analysis.

Example 13. Nylon 6,9-Containing Silicone Polyamide Gellant with 50 DP Si Block.

[0101] A 500 mL resin kettle was equipped with a thermocouple, motorized stirrer, condenser, and nitrogen sweep. The kettle was charged with 155.70 g of a 50 DP terminal SiH siloxane (SiH=543 ppm) and 30.82 g of 25.0 mol% nylon 6,9 modified diamide (from Example 11). The kettle was purged with nitrogen for a minimum of 5 minutes prior to heating to ensure an inert atmosphere. The kettle was mixed at 100 rpm and the temperature was increased to 180°C. Once the kettle reached the desired temperature and the diamide was fully melted, the mixing rate was increased to 300 rpm. Then the reaction was catalyzed with two doses of Syloff 4000 Pt catalyst (0.33 g + 0.13 g, respectively) over a 10 minute time frame to ensure the catalyst was active. Following the second dose of catalyst, the reaction was held at 195-200°C for 2 hours. After the 2 hour
hold time, the silicone polyamide at temperature was decanted into a glass tray. The material was allowed to cool to room temperature prior to handling, processing, and characterization.

[00102] The material hardened into a straw colored solid gellant. The pharmacopeia melt point was determined to be 174.2°C based upon measurements obtained using a Buchi Melting Point M-565 instrument. The molecular weight (M_w) was 37,800 Daltons with a polydispersity of 4.96 relative to polystyrene standards in THF using conventional GPC analysis.


[00103] A 500 mL resin kettle was equipped with a thermocouple, motorized stirrer, condenser, and nitrogen sweep. The kettle was charged with 102.21 g of a 21 DP terminal SiH siloxane (SiH=1274 ppm) and 47.47 g of 25.0 mol% nylon 6,9 modified diamide (from Example 11). The kettle was purged with nitrogen for a minimum of 5 minutes prior to heating to ensure an inert atmosphere. The kettle was mixed at 100 rpm and the temperature was increased to 180°C. Once the kettle reached the desired temperature and the diamide was fully melted, the mixing rate was increased to 300 rpm. Then the reaction was catalyzed with two doses of Sylof 4000 Pt catalyst (0.24 g + 0.09 g, respectively) over a 10 minute time frame to ensure the catalyst was active. Following the second dose of catalyst, the reaction was held at 180°C for 2 hours. After the 2 hour hold time, the silicone polyamide was decanted at temperature into a glass tray. The material was allowed to cool to room temperature prior to handling, processing, and characterization.

[00104] The material hardened into a straw colored solid gellant. The pharmacopeia melt point was determined to be 171.3°C based upon measurements obtained using a Buchi Melting Point M-565 instrument. The molecular weight (M_w) was 16,000 Daltons with a polydispersity of 3.66 relative to polystyrene standards in THF using conventional GPC analysis.

[00105] Table 1 shows the number average molecular weight, weight average molecular weight, and the polydispersity for the products of Examples 12, 13, and 14.

[00106] Table 1.

<table>
<thead>
<tr>
<th>Sample</th>
<th>M_n</th>
<th>M_w</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 12</td>
<td>9560</td>
<td>63700</td>
<td>6.67</td>
</tr>
<tr>
<td>Example 13</td>
<td>7640</td>
<td>37800</td>
<td>4.96</td>
</tr>
<tr>
<td>Example 14</td>
<td>4380</td>
<td>16000</td>
<td>3.66</td>
</tr>
</tbody>
</table>
[00107] FIG. 1 illustrates the normalized response versus time for Examples 12, 13, and 14. FIG. 1 is a GPC spectrum for various polysiloxane-polyamide block copolymers. The normalized response is also referred to as the intensity, which is directly related to the elution volume of the material. The elution volume is plotted vs. time to yield the spectrum.

Example 15. Hydrophilicity of polyester.

[00108] Samples of treated polyester fabric were prepared using the polysiloxane-polyamide copolymer of Example 9. An adhesion promoter, glycidoxypropyl trimethoxysilane, was added to the polysiloxane-polyamide copolymer in a concentration of 0.2 wt%. The copolymer mixture was applied to the fabric using conventional techniques, followed by curing in a conventional oven.

[00109] The samples were placed in an oven heated at 125° C and allowed to reach equilibrium, driving the majority of the moisture from the fabric. The fabric was then quickly weighed and the basis weight recorded. The fabric was then placed in a heat and humidity chamber at 50° C and 95% relative humidity and allowed to reach equilibrium. The fabric was then taken out of the chamber and immediately reweighed noting the amount of moisture regain from the dried state. The percent of moisture regained by the coated samples was consistently less than the control sample with 0% additive. With higher and higher amounts of coating of the samples, the percent of moisture regained began to plateau. The results are shown in FIG. 2, which illustrates the percent moisture weight gain for fabric samples having varying amounts of polysiloxane-polyamide copolymer thereon.

[00110] Comparing the percent moisture gain of the samples provides evidence of the respective hydrophilicity of the fabric samples. The control sample regained the most moisture, and therefore had a higher hydrophilicity than the treated samples. The lack of a steady increase of hydrophilicity with higher amounts of treatment compound may be due to the concentration of the additive increasing in the middle of the fiber instead of congregating on the surface.


[00111] A polyethylene tetraphthalate (PET)-material was modified with the polysiloxane-polyamide copolymer compound of Example 9. For samples that included adhesion promoter, the adhesion promoter was added to the copolymer prior to the modification of the PET-material in a concentration of about 0.2 wt%. The copolymer mixture was applied to the material using conventional techniques, and the samples were cured in a conventional oven.
[00112] The treated samples were subjected to test method ISO 5981. The number of scrubs (passes) that the material could withstand before reaching a breach or pinhole in the surface of the coating on the fabric was significantly increased when used in combination with the adhesion promoter glycidoxypropyl trimethoxysilane (samples 16a-16d). This was not seen with the samples having no adhesion promoter that depended heavily on SiH bonding on the surface (samples 16e-16h). The results are shown in Table 2.

[00113] Table 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>wt% polysiloxane-polyamide copolymer</th>
<th>With adhesion promoter?</th>
<th>Avg. no scrubs before failure</th>
</tr>
</thead>
<tbody>
<tr>
<td>16a</td>
<td>0</td>
<td>Yes, glycidoxypropyl trimethoxysilane</td>
<td>233</td>
</tr>
<tr>
<td>16b</td>
<td>0.5</td>
<td>Yes, glycidoxypropyl trimethoxysilane</td>
<td>667</td>
</tr>
<tr>
<td>16c</td>
<td>1</td>
<td>Yes, glycidoxypropyl trimethoxysilane</td>
<td>1067</td>
</tr>
<tr>
<td>16d</td>
<td>1.5</td>
<td>Yes, Glycidoxypropyl trimethoxysilane</td>
<td>933</td>
</tr>
<tr>
<td>16e</td>
<td>0</td>
<td>No</td>
<td>233</td>
</tr>
<tr>
<td>16f</td>
<td>0.5</td>
<td>No</td>
<td>33</td>
</tr>
<tr>
<td>16g</td>
<td>1.0</td>
<td>No</td>
<td>133</td>
</tr>
<tr>
<td>16h</td>
<td>1.5</td>
<td>No</td>
<td>83</td>
</tr>
</tbody>
</table>

[00114] The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those of ordinary skill in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

Additional Embodiments.
[00115] The present invention provides for the following exemplary embodiments, the numbering of which is not to be construed as designating levels of importance:

[00116] Embodiment 1 provides a polysiloxane-polyamide block copolymer comprising the following repeating unit: -[M¹-M²]_{DP1} -, wherein M¹ is a divalent polydiorganosiloxane, M² is a divalent polyamide, and DP1 is about 1-200.

[00117] Embodiment 2 provides the polysiloxane-polyamide block copolymer of Embodiment 1, wherein the block copolymer has the following structure: E¹-([M¹-M²]_{DP1} -E², wherein E¹ is Y- or X-M²-, E² is -X or -M¹-Y, X is a monovalent polydiorganosiloxane corresponding to M¹, and Y is a monovalent polyamide corresponding to M².

[00118] Embodiment 3 provides the polysiloxane-polyamide block copolymer of Embodiment 2, wherein the block copolymer has the following structure: Y-[M¹-M²]_{DP1} -X, Y-[M¹-M²]_{DP1} -M²-Y, X-M²-[M¹-M²]_{DP1} -X, or X-M²-[M¹-M²]_{DP1} -M²-Y.

[00119] Embodiment 4 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-3, wherein M¹ is -SiR¹R²-[OSiR¹R²]_{DP2} -, wherein each of R¹ and R² at each occurrence is an organic functional group, and DP2 is about 1 to about 500.

[00120] Embodiment 5 provides the polysiloxane-polyamide block copolymer of Embodiment 4, wherein each of R¹ and R² are at each occurrence independently at least one of straight chain, branched, and cyclic, substituted or unsubstituted (C₁-C₂₀)hydrocarbyl, with the proviso that R¹ and R² do not include an aliphatic unsaturated carbon-carbon bond.

[00121] Embodiment 6 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 4-5, wherein each of R¹ and R² are at each occurrence independently at least one of straight chain and branched unsubstituted (C₁-C₁₀)hydrocarbyl.

[00122] Embodiment 7 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 4-6, wherein each of R¹ and R² are methyl.

[00123] Embodiment 8 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 4-7, wherein DP2 is about 10 to about 200.

[00124] Embodiment 9 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-8, wherein M² is -R³-C(O)[NH-R⁴-NHC(O)-R⁵-C(O)]_{DP3} NH-R⁴ -NHC(O)-R³-, wherein each of R³, R⁴, and R⁵ at each occurrence is independently at least one of straight-chain, branched, and cyclic, divalent (C₁-C₂₀)alkylene group, and DP3 is about 0-50.
Embodiment 10 provides the polysiloxane-polyamide block copolymer of Embodiment 9, wherein each of R³, R⁴, and R⁵ is independently a divalent (C₁-C₁₅) alkyne group.

Embodiment 11 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 9-10, wherein R³ is an n-undecylene group.

Embodiment 12 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 9-11, wherein each of R⁴ and R⁵ is a straight chain alkyne group independently selected from a (C₄)alkylene group, a (C₆)alkylene group, and a (C₉)alkylene group.

Embodiment 13 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 9-12, wherein DP3 is about 0-10.

Embodiment 14 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-13, wherein the copolymer has a molecular weight of about 5,000 Daltons to about 500,000 Daltons.

Embodiment 15 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-14, wherein the copolymer has a molecular weight of about 10,000 Daltons to about 100,000 Daltons.

Embodiment 16 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-15, wherein the copolymer has a polydispersity relative to polystyrene strands in THF of about 1 to about 20.

Embodiment 17 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-16, wherein the copolymer has a polydispersity relative to polystyrene strands in THF of about 2 to about 10.

Embodiment 18 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-17, wherein the copolymer has a melt viscosity at about 190 °C of about 1,000 cP to about 50,000 cP.

Embodiment 19 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-18, wherein the copolymer has a melt viscosity at about 190 °C of about 5,000 cP to about 20,000 cP.

Embodiment 20 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-19, wherein the copolymer has a melting point of about 100 °C to about 300 °C.

Embodiment 21 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-20, wherein the copolymer has a melting point of about 130 °C to about 220 °C.
[00137] Embodiment 22 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-21, wherein the copolymer comprises the following repeat unit:

\[-[\text{SiR}^1\text{R}^2\text{Si}]_\text{DP2}-\text{R}^3\text{C(O)}\text{[NH-R}^4\text{-NHC(O)-R}^5\text{C(O)]]}_\text{DP3NH-R}^4\text{-NHC(O)-R}^3\text{]}_\text{DP1}-,\]

wherein each of R3, R4, and R5 is independently at least one of straight-chain, branched, and cyclic, divalent (C1-C30)alkylene group, DP2 is about 1-500, and DP3 is about 0-50.

[00138] Embodiment 23 provides the polysiloxane-polyamide block copolymer of any one of Embodiments 1-22, wherein the copolymer has the following structure:

\[E^1\text{-SiR}^1\text{R}^2\text{Si}]_\text{DP2}-\text{R}^3\text{C(O)}\text{[NH-R}^4\text{-NHC(O)-R}^5\text{C(O)]]}_\text{DP3NH-R}^4\text{-NHC(O)-R}^3\text{]}_\text{DP1}-E^2,\]

wherein E1 is HR3\text{C(O)}\text{[NH-R}^4\text{-NHC(O)-R}^5\text{C(O)]]}_\text{DP3NH-R}^4\text{-NHC(O)-R}^3\text{]}_\text{DP1}-E^2,\text{ or }\text{HSiR}^1\text{R}^2\text{Si}\]

[00139] Embodiment 24 provides a method of making the copolymer of any one of Embodiments 1-23, the method comprising: obtaining or providing a mixture comprising an Si-H-terminated polydiorganosiloxane having the formula HSiR^1R^2\text{Si}]_\text{DP2}H, wherein each of R1 and R2 at each occurrence is an organic functional group, and DP2 is about 1 to about 500; an alkenyl-terminated polyamide having the formula R^6\text{C(O)}\text{[NH-R}^4\text{-NHC(O)-R}^5\text{C(O)]]}_\text{DP3NH-R}^4\text{-NHC(O)-R}^6\text{]}, wherein R6 at each occurrence is independently a monovalent (C1-C30)hydrocarbyl group having at least one nonaromatic unsaturated carbon-carbon bond, each of R4 and R5 is independently a divalent (C1-C30)alkylene group, and DP3 is about 0-50; and a hydrosilylation catalyst; and subjecting the mixture to reaction conditions to give the copolymer of any one of Embodiments 1-23.

[00140] Embodiment 25 provides a personal care composition comprising the copolymer of any one of Embodiments 1-23.

[00141] Embodiment 26 provides the personal care composition of Embodiment 25, comprising at least one of a cosmetic or a deodorant.

[00142] Embodiment 27 provides a thermoplastic composition comprising: the copolymer of any one of any one of Embodiments 1-23; at least one organic polymer.

[00143] Embodiment 28 provides a substrate comprising a coating comprising a composition comprising the copolymer of Embodiment 1.
[00144] Embodiment 29 provides the coated substrate of Embodiment 28, wherein the substrate comprises a fiber, a film, a spun yarn, or a combination thereof.

[00145] Embodiment 30 provides a thermoplastic film comprising a composition comprising the copolymer of any one of any one of Embodiments 1-23.

[00146] Embodiment 31 provides a method of coating a substrate, comprising: obtaining or providing a substrate; and coating the substrate with a composition comprising the copolymer of any one of Embodiments 1-23.

[00147] Embodiment 32 provides the coated substrate of Embodiment 31, wherein the substrate comprises a fiber, a film, or a spun yarn, or a combination thereof.

[00148] Embodiment 33 provides a method of forming a film, comprising: obtaining or providing a thermoplastic composition comprising the copolymer of any one of any one of Embodiments 1-23; and forming the thermoplastic composition into a film.

[00149] Embodiment 34 provides an article of manufacture, comprising the copolymer of any one of Embodiments 1-23.

[00150] Embodiment 35 provides the article of manufacture of Embodiment 34, wherein the article is at least one of sheet product, a molded article, a fiber, a spun yarn, a textile, and a nonwoven fabric.

[00151] Embodiment 35 provides the apparatus or method of any one or any combination of Embodiments 1-34 optionally configured such that all elements or options recited are available to use or select from.
CLAIMS

What is claimed is:

1. A polysiloxane-polyamide block copolymer comprising the following repeating unit:
   
   \[-[M^1\cdot M^2]_{DP^1}\cdot\]
   
   wherein \(M^1\) is a divalent polydiorganosiloxane,
   \(M^2\) is a divalent polyamide, and
   \(DP^1\) is about 1-200.

2. The polysiloxane-polyamide block copolymer of claim 1, wherein the block copolymer has the following structure:
   
   \(E^1\cdot[M^1\cdot M^2]_{DP^1}\cdot E^2\)
   
   wherein \(E^1\) is \(Y\)- or \(X\)-\(M^2\)-,
   \(E^2\) is \(-X\) or \(-M^1\cdot Y\),
   \(X\) is a monovalent polydiorganosiloxane corresponding to \(M^1\), and
   \(Y\) is a monovalent polyamide corresponding to \(M^2\).

3. The polysiloxane-polyamide block copolymer of claim 2, wherein the block copolymer has the following structure:
   
   \(Y\cdot[M^1\cdot M^2]_{DP^1}\cdot X\),
   \(Y\cdot[M^1\cdot M^2]_{DP^1}\cdot M^1\cdot Y\),
   \(X\cdot M^2\cdot [M^1\cdot M^2]_{DP^1}\cdot X\), or
   \(X\cdot M^2\cdot [M^1\cdot M^2]_{DP^1}\cdot M^2\cdot Y\).

4. The polysiloxane-polyamide block copolymer of any one of claims 1-3, wherein \(M^1\) is
   
   \(-SiR^1R^2\cdot [OSiR^1R^2]_{DP^2}\),
   
   wherein each of \(R^1\) and \(R^2\) at each occurrence is an organic functional group, and
   \(DP^2\) is about 1 to about 500.
5. The polysiloxane-polyamide block copolymer of claim 4, wherein each of R¹ and R² are at each occurrence independently at least one of straight chain, branched, and cyclic, substituted or unsubstituted (C₁-C₂₀)hydrocarbyl, with the proviso that R¹ and R² do not include an aliphatic unsaturated carbon-carbon bond.

6. The polysiloxane-polyamide block copolymer of any one of claims 1-5, wherein M² is

$$-R³.C(O)[NH-R⁴.NHC(O)-R⁵.C(O)]_{DP3}NH-R⁴.NHC(O)-R³,$$

wherein each of R³, R⁴, and R⁵ at each occurrence is independently at least one of straight-chain, branched, and cyclic, divalent (C₁-C₃₀)alkylene group, and DP3 is about 0-50.

7. The polysiloxane-polyamide block copolymer of any one of claims 1-6, wherein the copolymer comprises the following repeat unit:

$$-[SiR¹R²-[OSiR¹R²]_{DP2}R³.C(O)[NH-R⁴.NHC(O)-R⁵.C(O)]_{DP3}NH-R⁴.NHC(O)-R³.]_{DP1}-,$$

wherein each of R³, R⁴, and R⁵ at each occurrence is independently at least one of straight-chain, branched, and cyclic, divalent (C₁-C₃₀)alkylene group,

DP2 is about 1-500, and

DP3 is about 0-50.

8. A polysiloxane-polyamide block copolymer comprising the following repeating unit:

$$-[M¹-M²]_{DP1}-,$$

wherein M¹ is a divalent polydiorganosiloxane, and

M² is a divalent polyamide,

wherein the copolymer has the following structure:

$$E¹-[SiR¹R²-[OSiR¹R²]_{DP2}R³.C(O)[NH-R⁴.NHC(O)-R⁵.C(O)]_{DP3}NH-R⁴.NHC(O)-R³.]_{DP1}-E²,$$

wherein E¹ is

$$HR³.C(O)[NH-R⁴.NHC(O)-R⁵.C(O)]_{DP3}NH-R⁴.NHC(O)-R³.$$

or

$$HSiR¹R²-[OSiR¹R²]_{DP2}R³.C(O)[NH-R⁴.NHC(O)-R⁵.$$

C(O)]_{DP3}NH-R⁴.NHC(O)-R³.$$

E² is
-SiR₁R²-[OSiR₁R²]DP₂H, or
-SiR₁R²-[OSiR₁R²]DP₂-R³-C(O)[NH-R⁴-NHC(O)-R⁵-C(O)]DP₃NH-R⁴-NHC(O)-R³H,

R³ is an n-undecylenyl group,
each of R⁴ and R⁵ is independently a straight chain (C₄-1₅) alkylene group,
DP₁ is about 2-20,
DP₂ is about 10 to about 200, and
DP₃ is about 0-10.

9. A method of making a copolymer, the method comprising:
   obtaining or providing a mixture comprising
   an Si-H-terminated polydiorganosiloxane having the formula HSiR₁R²-[OSiR₁R²]DP₂H,
   wherein each of R¹ and R² at each occurrence is an organic functional group, and
   DP₂ is about 1 to about 500;
   an alkenyl-terminated polyamide having the formula R⁶-C(O)[NH-R⁴-NHC(O)-R⁵-C(O)]DP₃NH-R⁴-NHC(O)-R⁶,
   wherein R⁶ at each occurrence is independently a monovalent (C₁-C₃₀) hydrocarbyl group having at least one nonaromatic unsaturated carbon-carbon bond,
each of R⁴ and R⁵ is independently a divalent (C₁-C₃₀) alkylene group, and
   DP₃ is about 0-50; and
   a hydrosilylation catalyst; and
   subjecting the mixture to reaction conditions to give a polysiloxane-polyamide block copolymer comprising the following repeating unit:
   -[M¹-M²]DP₁⁻,
   wherein M¹ is a divalent polydiorganosiloxane, M² is a divalent polyamide,
   and DP₁ is about 1-200.

10. A personal care composition comprising the copolymer of any one of claims 1-8.
11. A thermoplastic composition comprising:
   the copolymer of any one of claims 1-8;
   at least one organic polymer.

12. A substrate comprising a coating comprising a composition comprising the copolymer of any one of claims 1-8.

13. A method of coating a substrate, comprising:
    obtaining or providing a substrate; and
    coating the substrate with a composition comprising the copolymer of any one of claims 1-8.

14. A method of forming a film, comprising:
    obtaining or providing a thermoplastic composition comprising the copolymer of any one of claims 1-8; and
    forming the thermoplastic composition into a film.

15. An article of manufacture, comprising the copolymer of any one of claims 1-8.
**INTERNATIONAL SEARCH REPORT**

**International Application No:**
PCT/US2014/014082

**A. CLASSIFICATION OF SUBJECT MATTER**

**INV.** C09D183/10  A61K8/898  A61K8/90  C08G77/455  C08L83/10

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)

C09D  A61K  C08G  C08L

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

**Electronics 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**

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<th>Category</th>
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<th>Relevant to claim No.</th>
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☐ Further documents are listed in the continuation of Box C.  
☒ See patent family annex.

**) Special categories of cited documents:**

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "Z" document member of the same patent family

**Date of the actual completion of the international search:**
2 April 2014

**Date of mailing of the international search report:**
09/04/2014

**Name and mailing address of the ISA/ European Patent Office, P.O. 5618 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 540-2040, Fax. (+31-70) 540-3016**

**Authorized officer:**
Dalet, Pierre
## INTERNATIONAL SEARCH REPORT

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