



- (51) **International Patent Classification:**
C08G 77/44 (2006.01) *H01L 23/29* (2006.01)
C08L 83/10 (2006.01)
- (21) **International Application Number:**
PCT/US2013/027904
- (22) **International Filing Date:**
27 February 2013 (27.02.2013)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/608,732 9 March 2012 (09.03.2012) US
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- (81) **Designated States** (*unless otherwise indicated, for every
kind of national protection available*): AE, AG, AL, AM,
AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY,
BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM,

DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT,
HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP,
KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD,
ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI,
NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU,
RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ,
TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA,
ZM, ZW.

- (84) **Designated States** (*unless otherwise indicated, for every
kind of regional protection available*): ARIPO (BW, GH,
GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ,
UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ,
TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK,
EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV,
MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,
ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*
- *before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments (Rule 48.2(h))*

(54) **Title:** COMPOSITIONS OF RESIN-LINEAR ORGANOSILOXANE BLOCK COPOLYMERS

(57) **Abstract:** Organosiloxane block copolymers containing at least one Rf fluorine-containing group, curable compositions and solid compositions derived from these block copolymers are disclosed.



COMPOSITIONS OF
RESIN-LINEAR ORGANOSILOXANE BLOCK COPOLYMERS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 **[0001]** This application claims the benefit of U.S. Provisional Patent Appl. Ser. No. 61/608,732, filed March 9, 2012, the entire disclosure of which is incorporated by reference as if fully set forth herein.

BACKGROUND

10 **[0002]** Light emitting diodes (LEDs) and solar panels use an encapsulant coating to protect electronic components from environmental factors. Such protective coatings must be optically clear to ensure maximum efficiency of these devices. Furthermore, these protective coatings must be tough, durable, long lasting, and yet easy to apply. Many of the currently available coatings, however, lack toughness; are not durable; are not long-lasting; and/or are not
15 easy to apply. There is therefore a continuing need to identify protective and/or functional coatings in many areas of emerging technologies.

SUMMARY

[0003] Embodiment 1 relates to an organosiloxane block copolymer comprising:

40 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$,

10 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$,

0.5 to 35 mole percent silanol groups $[≡SiOH]$;

wherein:

20 each R^1 , at each occurrence, is independently a C_1 to C_{30} hydrocarbyl or an R^f group,

each R^2 , at each occurrence, is independently a C_1 to C_{20} hydrocarbyl or an R^f group,

wherein R^f represents a fluorine-containing group, with the
25 proviso that there is at least one R^f group in the organosiloxane block copolymer;

wherein:

the disiloxy units $[R^1_2SiO_{2/2}]$ are arranged in linear blocks having an average of from 10 to 400 disiloxy units $[R^1_2SiO_{2/2}]$ per linear block,
the trisiloxy units $[R^2SiO_{3/2}]$ are arranged in non-linear blocks having a molecular weight of at least 500 g/mole, and at least 30% of the non-linear blocks are crosslinked with each other, each linear block is linked to at least one non-linear block; and the organosiloxane block copolymer has a weight average molecular weight (M_w) of at least 20,000 g/mole.

[0004] Embodiment 2 relates to the organosiloxane block copolymer of Embodiment 1, wherein R^1 comprises an R^f group.

[0005] Embodiment 3 relates to the organosiloxane block copolymer of Embodiment 1 or 2, wherein R^2 comprises an R^f group.

5 [0006] Embodiment 4 relates to the organosiloxane block copolymer of Embodiments 1-3, wherein the R^f group comprises $-CH_2CH_2CF_3$.

[0007] Embodiment 5 relates to the organosiloxane block copolymer of Embodiments 1-4, wherein R^2 is phenyl.

[0008] Embodiment 6 relates to the organosiloxane block copolymer of
10 Embodiments 1-5, wherein R^1 is methyl or phenyl.

[0009] Embodiment 7 relates to the organosiloxane block copolymer of Embodiments 1-6, wherein the disiloxy units have the formula $[(CH_3)(CF_3CH_2CH_2)SiO_{2/2}]$.

[0010] Embodiment 8 relates to a curable composition comprising an
15 organosiloxane block copolymer of Embodiment 1-7.

[0011] Embodiment 9 relates to a solid film composition comprising the curable composition of Embodiment 8.

[0012] Embodiment 10 relates to the cured product of the composition of Embodiments 8 or 9.

20 [0013] Embodiment 11 relates to the solid film composition of Embodiment 9, wherein the solid composition has an optical transmittance of at least 95%.

[0014] Embodiment 12 relates to the solid film composition of Embodiment 9, wherein the solid composition has a low refractive index.

[0015] Embodiment 13 relates to an LED encapsulant comprising an organosiloxane block copolymer of Embodiments 1-12.

5 [0016] Embodiment 14 relates to a process for preparing an organosiloxane block copolymer of Embodiment 1, comprising:

I) reacting

a) a linear organosiloxane having the formula:



wherein each R^1 , at each occurrence, is independently a C_1 to

C_{30} hydrocarbyl or an R^f group,

n is 10 to 400, q is 0, 1, or 2,

E is a hydrolyzable group containing at least one carbon atom,

and

b) an organosiloxane resin comprising at least 60 mole % of

$[R^2SiO_{3/2}]$ siloxyunits in its formula, wherein each R^2 , at each

occurrence, is independently a C_1 to C_{20} hydrocarbyl or an R^f group;

in c) an organic solvent;

to form a resin-linear organosiloxane block copolymer;

wherein the amounts of a) and b) used in step I) are selected to provide the resin-linear organosiloxane block copolymer with 40 to 90 mole % of disiloxy units $[R^1_2SiO_{2/2}]$ and 10 to 60 mole % of trisiloxy units $[R^2SiO_{3/2}]$, and

wherein at least 95 weight percent of the linear organosiloxane added in step I) is incorporated into the resin-linear organosiloxane block copolymer;

II) reacting the resin-linear organosiloxane block copolymer from step I) to crosslink the trisiloxy units of the resin-linear organosiloxane block copolymer sufficiently to increase the weight average molecular weight (M_w) of the resin-linear organosiloxane block copolymer by at least 50%;

III) optionally, further processing the resin-linear organosiloxane block copolymer; and

IV) optionally, removing the organic solvent.

[0017] Embodiment 15 relates to the process of Embodiment 14, wherein the further processing enhances storage stability and/or optical clarity

[0018] Embodiment 16 relates to the process of Embodiment 14, wherein R^1 comprises an R^f group.

5 [0019] Embodiment 17 relates to the process of Embodiment 14 or 16, wherein R^2 comprises an R^f group.

[0020] Embodiment 18 relates to the process of Embodiments 14-17, wherein the R^f group comprises $-\text{CH}_2\text{CH}_2\text{CF}_3$.

[0021] Embodiment 19 relates to the process of Embodiments 14-18,
10 wherein R^2 is phenyl.

[0022] Embodiment 20 relates to the process of Embodiments 14-19, wherein R^1 is methyl, phenyl or combinations thereof.

[0023] Embodiment 21 relates to the process of Embodiments 14-20, wherein the linear organosiloxane has the formula
15 $(\text{CH}_3)_q(\text{E})_{(3-q)}\text{SiO}[(\text{CH}_3)(\text{CF}_3\text{CH}_2\text{CH}_2)\text{SiO}_{2/2}]_n\text{Si}(\text{E})_{(3-q)}(\text{CH}_3)_q$.

[0024] Embodiment 22 relates to the process of Embodiments 14-21, wherein E is $\text{H}_3\text{CC}(=\text{O})\text{O}-$ and q is 1.

[0025] Embodiment 23 relates to an organosiloxane block copolymer prepared by the process of Embodiments 14-22.

20 [0026] Embodiment 24 relates to the organopolysiloxane block copolymer of Embodiment 23, wherein the organopolysiloxane block copolymer is the reaction product of step II).

[0027] Embodiment 25 relates to a composition comprising the organopolysiloxane block copolymer of Embodiment 23.

25 [0028] Embodiment 26 relates to the composition of Embodiment 25, which is curable.

[0029] Embodiment 27 relates to the composition of Embodiment 25, which is solid.

[0030] Embodiment 28 relates to the cured product of the composition of
30 Embodiments 25-27.

[0031] Embodiment 29 relates to a solid film composition comprising the composition of Embodiments 24-26.

[0032] Embodiment 30 relates to the solid film composition of Embodiment 29, wherein the solid composition has an optical transmittance of at least 95%.

[0033] Embodiment 31 relates to an LED encapsulant comprising the
5 compositions of Embodiments 25-30.

DESCRIPTION

[0034] The present disclosure relates to “resin linear” fluorinated organosiloxane block copolymers, curable compositions and solid compositions comprising such fluorinated organosiloxane block copolymers. Compositions
10 comprising such fluorinated organosiloxane block copolymers have, in some embodiments, different physical properties relative to non-fluorinated “resin-linear” organosiloxane block copolymers. For example, curable composition of fluorinated “resin-linear” organosiloxane block copolymers of the embodiments described herein may have improved stability, *e.g.*, at higher temperatures. In
15 addition, curable composition of fluorinated “resin-linear” organosiloxane block copolymers of the embodiments described herein may be useful in the preparation of low refractive index coatings, *e.g.*, those having refractive indices from about 1.3 to about 1.45 or from about 1.35 to about 1.42. The fluorinated “resin-linear” organosiloxane block copolymers comprise:

20 40 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$,

10 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$,

0.5 to 35 mole percent silanol groups $[≡SiOH]$;

wherein:

25 R^1 is, at each occurrence, independently a C_1 to C_{30} hydrocarbyl or an R^f group,

R^2 is, at each occurrence, independently a C_1 to C_{20} hydrocarbyl or an R^f group,

where R^f represents a fluorine-containing group, with the proviso that there is at least one R^f group in the organosiloxane block
30 copolymer;

wherein:

- the disiloxy units $[R^1_2SiO_{2/2}]$ are arranged in linear blocks
having an average of from 10 to 400 disiloxy units $[R^1_2SiO_{2/2}]$
per linear block,
the trisiloxy units $[R^2SiO_{3/2}]$ are arranged in non-linear blocks
5 having a molecular weight of at least 500 g/mole, and at least
30% of the non-linear blocks are crosslinked with each other,
each linear block is linked to at least one non-linear block, and
the organosiloxane block copolymer has a weight average
molecular weight (M_w) of at least 20,000 g/mole.
- 10 **[0035]** The organopolysiloxanes of the embodiments described herein as
“resin-linear” organosiloxane block copolymers. Organopolysiloxanes are
polymers containing siloxy units independently selected from $[R_3SiO_{1/2}]$,
 $[R_2SiO_{2/2}]$, $[RSiO_{3/2}]$, or $[SiO_{4/2}]$ siloxy units, where R may be, *e.g.*, an organic
group. These siloxy units are commonly referred to as M, D, T, and Q units
15 respectively. These siloxy units can be combined in various manners to form
cyclic, linear, or branched structures. The chemical and physical properties of the
resulting polymeric structures vary depending on the number and type of siloxy
units in the organopolysiloxane. For example, “linear” organopolysiloxanes may
contain mostly D, or $[R_2SiO_{2/2}]$ siloxy units, which results in
20 polydiorganosiloxanes that are fluids of varying viscosities, depending on the
“degree of polymerization” or “dp” as indicated by the number of D units in the
polydiorganosiloxane. “Linear” organopolysiloxanes may have glass transition
temperatures (T_g) that are lower than 25°C. “Resin” organopolysiloxanes result
when a majority of the siloxy units are selected from T or Q siloxy units. When T
25 siloxy units are predominately used to prepare an organopolysiloxane, the resulting
organosiloxane is often referred to as a “resin” or a “silsesquioxane resin.”
Increasing the amount of T or Q siloxy units in an organopolysiloxane may result
in polymers having increasing hardness and/or glass like properties. “Resin”
organopolysiloxanes thus have higher T_g values, for example siloxane resins often
30 have T_g values greater than 40°C, *e.g.*, greater than 50°C, greater than 60°C,
greater than 70°C, greater than 80°C, greater than 90°C or greater than 100°C. In
some embodiments, T_g for siloxane resins is from about 60°C to about 100°C, *e.g.*,

from about 60°C to about 80°C, from about 50°C to about 100°C, from about 50°C to about 80°C or from about 70°C to about 100°C.

[0036] As used herein “organosiloxane block copolymers” or “resin-linear organosiloxane block copolymers” refer to organopolysiloxanes containing “linear” D siloxy units in combination with “resin” T siloxy units. In some embodiments, the organosiloxane copolymers are “block” copolymers, as opposed to “random” copolymers. As such, the “resin-linear organosiloxane block copolymers” of the disclosed embodiments refer to organopolysiloxanes containing D and T siloxy units, where the D units (*i.e.*, $[R^1_2SiO_{2/2}]$ units) are primarily bonded together to form polymeric chains having, in some embodiments, an average of from 10 to 400 D units (*e.g.*, an average of from about 10 to about 400 D units; about 10 to about 300 D units; about 10 to about 200 D units; about 10 to about 100 D units; about 50 to about 400 D units; about 100 to about 400 D units; about 150 to about 400 D units; about 200 to about 400 D units; about 300 to about 400 D units; about 50 to about 300 D units; about 100 to about 300 D units; about 150 to about 300 D units; about 200 to about 300 D units; about 100 to about 150 D units, about 115 to about 125 D units, about 90 to about 170 D units or about 110 to about 140 D units), which are referred herein as “linear blocks.”

[0037] The T units (*i.e.*, $[R^2SiO_{3/2}]$) are, in some embodiments, primarily bonded to each other to form branched polymeric chains, which are referred to as “non-linear blocks.” In some embodiments, a significant number of these non-linear blocks may further aggregate to form “nano-domains” when solid forms of the block copolymer are provided. In some embodiments, these nano-domains form a phase separate from a phase formed from linear blocks having D units, such that a resin-rich phase forms.

[0038] In some embodiments, the non-linear blocks have a number average molecular weight of at least 500 g/mole, *e.g.*, at least 1000 g/mole, at least 2000 g/mole, at least 3000 g/mole or at least 4000 g/mole; or have a molecular weight of from about 500 g/mole to about 4000 g/mole, from about 500 g/mole to about 3000 g/mole, from about 500 g/mole to about 2000 g/mole, from about 500 g/mole to about 1000 g/mole, from about 1000 g/mole to 2000 g/mole, from about 1000 g/mole to about 1500 g/mole, from about 1000 g/mole to about 1200 g/mole, from about 1000 g/mole to 3000 g/mole, from about 1000

g/mole to about 2500 g/mole, from about 1000 g/mole to about 4000 g/mole, from about 2000 g/mole to about 3000 g/mole or from about 2000 g/mole to about 4000 g/mole.

[0039] The organosiloxane block copolymers (*e.g.*, those comprising 40 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$ and 10 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$) may be represented by the formula $[R^1_2SiO_{2/2}]_a[R^2SiO_{3/2}]_b$ where the subscripts a and b represent the mole fractions of the siloxy units in the copolymer,

a is about 0.4 to about 0.9,

alternatively about 0.5 to about 0.9,

alternatively about 0.6 to about 0.9,

b is from 0.1 to 0.6,

alternatively about 0.1 to about 0.5,

alternatively about 0.1 to about 0.4,

where R^1 is independently a C_1 to C_{30} hydrocarbyl or an R^f group,

R^2 is independently a C_1 to C_{20} hydrocarbyl or an R^f group,

where R^f represents a fluorine-containing group, with the proviso that there is at least one R^f group in the organosiloxane block copolymer.

[0040] In some embodiments, the organosiloxane block copolymers of the embodiments described herein comprise 40 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$, *e.g.*, 50 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 60 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 65 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 70 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; or 80 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 40 to 80 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 40 to 70 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 40 to 60 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 40 to 50 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$;

50 to 80 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 50 to 70 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 50 to 60 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 60 to 80 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 60 to 70 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; or 70 to 80 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$.

[0041] In some embodiments, the organosiloxane block copolymers of the embodiments described herein comprise 10 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$, *e.g.*, 10 to 20 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 10 to 30 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 10 to 35 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 10 to 40 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 10 to 50 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 20 to 30 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 20 to 35 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 20 to 40 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 20 to 50 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 20 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 30 to 40 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 30 to 50 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 30 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 40 to 50 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; or 40 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$.

[0042] It should be understood that the organosiloxane block copolymers of the embodiments described herein may contain additional siloxy units, such as M siloxy units, Q siloxy units, other unique D or T siloxy units (for example, having organic groups other than R^1 or R^2), provided that the organosiloxane block copolymer contains the mole fractions of the disiloxy and trisiloxy units as described herein. In other words, the sum of the mole fractions as designated by subscripts a and b, do not necessarily have to sum to one. The sum of a + b may

be less than one to account for minor amounts of other siloxy units that may be present in the organosiloxane block copolymer. Alternatively, the sum of $a + b$ is greater than 0.6, alternatively greater than 0.7, alternatively greater than 0.8, or alternatively greater than 0.9. In some embodiments, the sum of $a + b$ is from
 5 about 0.6 to about 0.9, *e.g.*, from about 0.6 to about 0.8, from about 0.6 to about 0.7, from about 0.7 to about 0.9, from about 0.7 to about 0.8, or from about 0.8 to about 0.9.

[0043] In one embodiment, the organosiloxane block copolymer consists essentially of the disiloxy units of the formula $[R^1_2SiO_{2/2}]$ and trisiloxy units of
 10 the formula $[R^2SiO_{3/2}]$, while also containing 0.5 to 25 mole percent silanol groups $[≡SiOH]$ (*e.g.*, 0.5 to 5 mole percent, 0.5 to 10 mole percent, 0.5 to 15 mole percent, 0.5 to 20 mole percent, 5 to 10 mole percent, 5 to 15 mole percent, 5 to 20 mole percent, 5 to 25 mole percent, 10 to 15 mole percent, 10 to 20 mole percent, 10 to 25 mole percent, 15 to 20 mole percent, 15 to 25 mole percent, or
 15 20 to 25 mole percent), where R^1 and R^2 are as defined herein. Thus, in some embodiments, the sum of $a + b$ (when using mole fractions to represent the amount of disiloxy and trisiloxy units in the copolymer) is greater than 0.95, alternatively greater than 0.98.

[0044] In some embodiments, the resin-linear organosiloxane block
 20 copolymers may also contain from 0.5 to 35 mole percent silanol groups $[≡SiOH]$, alternatively from 2 to 32 mole percent silanol groups $[≡SiOH]$, and alternatively from 8 to 22 mole percent silanol groups $[≡SiOH]$.

[0045] The silanol groups may be present on any siloxy units within the organosiloxane block copolymer. The amount described herein represent the
 25 total amount of silanol groups found in the organosiloxane block copolymer. In some embodiments, the majority (*e.g.*, greater than 75%, greater than 80%, greater than 90%; from about 75% to about 90%, from about 80% to about 90%, or from about 75% to about 85%) of the silanol groups will reside on the trisiloxy units, *i.e.*, the resin component of the block copolymer. Although not
 30 wishing to be bound by any theory, the silanol groups present on the resin component of the organosiloxane block copolymer allows for the block copolymer to further react or cure at elevated temperatures.

[0046] At each occurrence, each R^1 in the above disiloxy unit is independently a C_1 to C_{30} hydrocarbyl or an R^f group, where the hydrocarbyl group may independently be an alkyl, aryl, or alkylaryl group. Each R^1 , at each occurrence, may independently be a C_1 to C_{30} alkyl group, alternatively, at each
5 occurrence, each R^1 may be a C_1 to C_{18} alkyl group. Alternatively each R^1 , at each occurrence, may be a C_1 to C_6 alkyl group such as methyl, ethyl, propyl, butyl, pentyl, or hexyl. Alternatively each R^1 , at each occurrence, may be methyl. Each R^1 , at each occurrence, may be an aryl group, such as phenyl, naphthyl, or an anthryl group. Alternatively, each R^1 , at each occurrence, may
10 be any combination of the aforementioned alkyl, aryl or R^f groups such that, in some embodiments, each disiloxy unit may have two alkyl groups (*e.g.*, two methyl groups); two aryl groups (*e.g.*, two phenyl groups); an alkyl (*e.g.*, methyl) and an aryl group (*e.g.*, phenyl), two R^f groups; one R^f group and one alkyl group (*e.g.*, methyl); or one R^f group and one aryl group (*e.g.*, phenyl).
15 Alternatively, each R^1 , at each occurrence, is phenyl, methyl or R^f .

[0047] Each R^2 , at each occurrence, in the above trisiloxy unit is independently a C_1 to C_{20} hydrocarbyl or an R^f group, where the hydrocarbyl group may independently be an alkyl, aryl, or alkylaryl group. Each R^2 , at each occurrence, may be a C_1 to C_{20} alkyl group, alternatively each R^2 , at each
20 occurrence, may be a C_1 to C_{18} alkyl group. Alternatively each R^2 , at each occurrence, may be a C_1 to C_6 alkyl group such as methyl, ethyl, propyl, butyl, pentyl, or hexyl. Alternatively each R^2 , at each occurrence, may be methyl. Each R^2 , at each occurrence, may be an aryl group, such as phenyl, naphthyl, or an anthryl group. Alternatively, each R^2 , at each occurrence, may be any
25 combination of the aforementioned alkyl, aryl or R^f groups such that, in some embodiments, each disiloxy unit may have two alkyl groups (*e.g.*, two methyl groups); two aryl groups (*e.g.*, two phenyl groups); an alkyl (*e.g.*, methyl) and an aryl group (*e.g.*, phenyl), two R^f groups; one R^f group and one alkyl group (*e.g.*, methyl); or one R^f group and one aryl group (*e.g.*, phenyl). Alternatively, each
30 R^2 , at each occurrence, is phenyl, methyl or R^f .

[0048] As used throughout the specification, hydrocarbyl also includes substituted hydrocarbyls. "Substituted" as used throughout the specification refers broadly to replacement of one or more of the hydrogen atoms of the group with substituents known to those skilled in the art and resulting in a stable compound as described herein. Examples of suitable substituents include, but are not limited to, alkyl, alkenyl, alkynyl, cycloalkyl, aryl, alkaryl, hydroxy, alkoxy, aryloxy, carboxy (*i.e.*, CO₂H), carboxyalkyl, carboxyaryl, cyano, nitro and the like. Substituted hydrocarbyl also includes halogen substituted hydrocarbyls, where the halogen may be chlorine, bromine or combinations thereof.

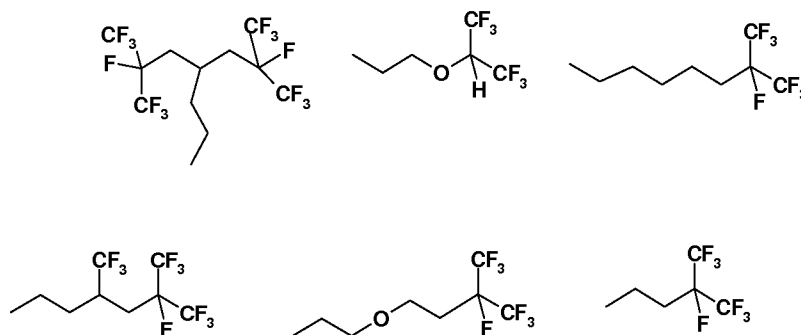
10 [0049] The organosiloxane block copolymers of the embodiments described herein comprise at least one R^f group. The R^f group may be present on any siloxy unit within the organosiloxane block copolymer. For example, the R^f group may be present on the linear block disiloxy units; on the non-linear block trisiloxy unit; or on both the linear block disiloxy units and the non-linear block trisiloxy units. In some embodiments, if R^f groups are contained on both the linear block disiloxy units and on the non-linear block trisiloxy units, the mole percent of R^f groups on the linear block disiloxy units versus the mole percent of R^f groups on the non-linear block trisiloxy units should be such that the linear and non-linear blocks are substantially incompatible (*e.g.*, where a solid organosiloxane block copolymer, as described herein, contains a first phase and an incompatible second phase, the first phase containing predominately the disiloxy units [R¹₂SiO_{2/2}] as defined herein, the second phase containing predominately the trisiloxy units [R²SiO_{3/2}] as defined herein, the non-linear blocks being sufficiently aggregated into nano-domains which are incompatible with the first phase).

[0050] As used herein, R^f represents a fluorine-containing group. Thus, R^f may be selected from various fluorocarbyls, perfluorocarbyls, or hydrocarbyls containing at least one CF₃ group, any of which may be linear or branched. For example, the fluorine-containing group may be selected from various perfluorocarbyls, including, but not limited to CF₃-, CF₃CF₂-, CF₃(CF₂)₂-, CF₃(CF₂)₃-, C₃F₇-, (CF₃)₂CF-, C₄F₉-, C₅F₁₁-C₆F₁₃- groups or the like. The fluorine-containing group may also be hydrocarbyls containing at least one CF₃

group including, but not limited to $-\text{CH}_2\text{CH}_2\text{CF}_3$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}_3$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}_3$, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CF}_3$, similar hydrocarbyls in the series or the like. Fluorocarbyls include hydrocarbyls where at least one hydrogen atom has been replaced with a fluorine. Fluorocarbyls include, but are not limited to $-\text{CHFCH}_3$, $-\text{CF}_2\text{CH}_3$, $-\text{CF}_2\text{CHFCH}_3$, $-\text{CHFCH}_2\text{CF}_2\text{CH}_3$, $-\text{CF}_2\text{CF}_2\text{CH}_3$, similar hydrocarbyls in the series or the like. It should be appreciated that the term “fluorocarbyl” encompasses “perfluorocarbyls and “hydrocarbyls containing at least one CF_3 group.”

[0051] The fluorine-containing group may also be selected from those represented by the formula $-\text{CH}_2\text{CH}_2\text{CH}_2(\text{G})_a[\text{CR}^3(\text{CF}_3)_2]_b$ where G is a linking group comprising at least one atom selected from C, O or combinations thereof; each R^3 is independently selected from F or H; the subscript a has a value of 0 or 1; and the subscript b has a value of 1 or 2. In some embodiments, the linking group, G, is $-\text{O}-$. In other embodiments, the linking group, G, is an ether group having 2 to 4 carbon atoms, such as $\text{O}-\text{CH}_2\text{CH}_2\text{CH}_2-$; an alkylene group having 2 to 4 carbon atoms, such as $-\text{CH}_2\text{CH}_2\text{CH}_2-$; a branched alkylene group having 3 to 5 carbon atoms, such as $-\text{CH}(\text{CH}_2-)_2$; or a fluorinated alkylene group having 2 to 4 carbon atoms, such as $(-\text{CH}(\text{CF}_3)\text{CH}_2-)_c$ where c is an integer from 1 to 8.

[0052] Other fluorine-containing groups useful herein may include, but are not limited to:



[0053] In one embodiment, the fluorine-containing group is $-\text{CH}_2\text{CH}_2\text{CF}_3$.

[0054] The number or amount of R^f groups present on the organosiloxane block copolymer may vary, providing there is at least one siloxy unit containing an R^f group. In some embodiments, the organosiloxane block copolymer contains from about 20 to about 80 mole%, from about 20 to about 50 mole%, or from about 25 to about 45 mole % siloxy units comprising an R^f group.

[0055] In certain embodiments, the disiloxy units of the organosiloxane block copolymer have the formula $[(CH_3)(CF_3CH_2CH_2)SiO_{2/2}]$. In some embodiments, the organosiloxane block copolymer contains from about 20 to about 80 mole %, from about 20 to about 50 mole %, or from about 25 to about 45 mole % siloxy units dilsiloxy units the formula $[(CH_3)(CF_3CH_2CH_2)SiO_{2/2}]$.

[0056] The formula $[R^1_2SiO_{2/2}]_a[R^2SiO_{3/2}]_b$, and related formulae using mole fractions, as used herein to describe the organosiloxane block copolymers, does not indicate structural ordering of the disiloxy $[R^1_2SiO_{2/2}]$ and trisiloxy $[R^2SiO_{3/2}]$ units in the copolymer. Rather, this formula is meant to provide a convenient notation to describe the relative amounts of the two units in the copolymer, as per the mole fractions described herein via the subscripts a and b. The mole fractions of the various siloxy units in the present organosiloxane block copolymers, as well as the silanol content, may be readily determined by ^{29}Si NMR techniques.

[0057] The organosiloxane block copolymers of the embodiments described herein have a weight average molecular weight (M_w) of at least 20,000 g/mole, alternatively a weight average molecular weight of at least 40,000 g/mole, alternatively a weight average molecular weight of at least 50,000 g/mole, alternatively a weight average molecular weight of at least 60,000 g/mole, alternatively a weight average molecular weight of at least 70,000 g/mole, or alternatively a weight average molecular weight of at least 80,000 g/mole. In some embodiments, the organosiloxane block copolymers of the embodiments described herein have a weight average molecular weight (M_w) of from about 20,000 g/mole to about 250,000 g/mole or from about 100,000 g/mole to about 250,000 g/mole, alternatively a weight average

molecular weight of from about 40,000 g/mole to about 100,000 g/mole, alternatively a weight average molecular weight of from about 50,000 g/mole to about 100,000 g/mole, alternatively a weight average molecular weight of from about 50,000 g/mole to about 80,000 g/mole, alternatively a weight average molecular weight of from about 50,000 g/mole to about 70,000 g/mole, alternatively a weight average molecular weight of from about 50,000 g/mole to about 60,000 g/mole. In some embodiments, the organosiloxane block copolymers of the embodiments described herein have a number average molecular weight (M_n) of from about 15,000 to about 50,000 g/mole; from about 15,000 to about 30,000 g/mole; from about 20,000 to about 30,000 g/mole; or from about 20,000 to about 25,000 g/mole. The average molecular weight may be readily determined using Gel Permeation Chromatography (GPC) techniques.

[0058] In some embodiments, the structural ordering of the disiloxy and trisiloxy units may be further described as follows: the disiloxy units $[R^1_2SiO_{2/2}]$ are arranged in linear blocks having an average of from 10 to 400 disiloxy units $[R^1_2SiO_{2/2}]$ per linear block, and the trisiloxy units $[R^2SiO_{3/2}]$ are arranged in non-linear blocks having a molecular weight of at least 500 g/mole. Each linear block is linked to at least one non-linear block in the block copolymer. Furthermore, at least 30% of the non-linear blocks are crosslinked with each other,

alternatively at least at 40% of the non-linear blocks are crosslinked with each other,

alternatively at least at 50% of the non-linear blocks are crosslinked with each other, wherein all of the percentages given herein to indicate percent non-linear blocks that are crosslinked are in weight percent.

[0059] In other embodiments, from about 30% to about 80% of the non-linear blocks are crosslinked with each other; from about 30% to about 70% of the non-linear blocks are crosslinked with each other; from about 30% to about 60% of the non-linear blocks are crosslinked with each other; from about 30% to about 50% of the non-linear blocks are crosslinked with each other; from about 30% to about 40% of the non-linear blocks are crosslinked with each other; from about 40% to about 80% of the non-linear blocks are crosslinked with each other; from about 40% to about 70% of the non-linear blocks are crosslinked

with each other; from about 40% to about 60% of the non-linear blocks are crosslinked with each other; from about 40% to about 50% of the non-linear blocks are crosslinked with each other; from about 50% to about 80% of the non-linear blocks are crosslinked with each other; from about 50% to about 70% of the non-linear blocks are crosslinked with each other; from about 50% to about 60% of the non-linear blocks are crosslinked with each other; from about 60% to about 80% of the non-linear blocks are crosslinked with each other; or from about 60% to about 70% of the non-linear blocks are crosslinked with each other.

5 of the non-linear blocks are crosslinked with each other; from about 50% to about 60% of the non-linear blocks are crosslinked with each other; from about 60% to about 80% of the non-linear blocks are crosslinked with each other; or from about 60% to about 70% of the non-linear blocks are crosslinked with each other.

10 **[0060]** The crosslinking of the non-linear blocks may be accomplished via a variety of chemical mechanisms and/or moieties. For example, crosslinking of non-linear blocks within the block copolymer may result from the condensation of residual silanol groups present in the non-linear blocks of the copolymer. Crosslinking of the non-linear blocks within the block copolymer may also occur between “free resin” components and the non-linear blocks. “Free resin” components may be present in the block copolymer compositions as a result of using an excess amount of an organosiloxane resin during the preparation of the block copolymer. The free resin component may crosslink with the non-linear blocks by condensation of the residual silanol groups present on the non-blocks and on the free resin. The free resin may provide crosslinking by reacting with lower molecular weight compounds added as crosslinkers, as described herein. The free resin, when present, may be present in an amount of from about 10% to about 20% by weight of the organosiloxane block copolymers of the embodiments described herein, *e.g.*, from about 15% to about 20% by weight organosiloxane block copolymers of the embodiments described herein.

15 **[0061]** In some embodiments, certain compounds may be added during the preparation of the block copolymer to, *e.g.*, crosslink the non-resin blocks. These crosslinking compounds may include an organosilane having the formula

20 $R^5_qSiX_{4-q}$, which is added during the formation of the block copolymer (step II) as discussed herein), where R^5 is a C_1 to C_8 hydrocarbyl or a C_1 to C_8 halogen-substituted hydrocarbyl; X is a hydrolyzable group; and q is 0, 1, or 2. R^5 is a C_1 to C_8 hydrocarbyl or a C_1 to C_8 halogen-substituted hydrocarbyl, or

alternatively R^5 is a C_1 to C_8 alkyl group, or alternatively a phenyl group, or alternatively R^5 is methyl, ethyl, or a combination of methyl and ethyl. X is any hydrolyzable group, E or, alternatively, X may be an oximo, acetoxy, halogen atom, hydroxyl (OH), or an alkoxy group.

- 5 **[0062]** In one embodiment, the organosilane having the formula $R^5_qSiX_{4-q}$ is an alkyltriacetoxysilane, such as methyltriacetoxysilane, ethyltriacetoxysilane, or a combination of both. Commercially available representative alkyltriacetoxysilanes include ETS-900 (Dow Corning Corp., Midland, MI).
- 10 **[0063]** Other suitable, non-limiting organosilanes useful as crosslinkers include; methyl tris(methylethylketoxime)silane (MTO), methyl triacetoxysilane, ethyl triacetoxysilane, tetraacetoxysilane, tetraoximesilane, dimethyl diacetoxysilane, dimethyl dioximesilane, and methyl tris(methylmethylketoxime)silane.
- 15 **[0064]** The amount of organosilane having the formula $R^5_qSiX_{4-q}$ when added during step II) may vary, but, in some embodiments, is based on the amount of organosiloxane resin used in the process. For example, the amount of silane used may provide a molar stoichiometry of 2 to 15 mole % of organosilane/moles of Si in the organosiloxane resin, *e.g.*, 2 to 10 mole % of organosilane/moles of Si in the organosiloxane resin; 5 to 15 mole % of organosilane/moles of Si in the organosiloxane resin; 2 to 5 mole % of organosilane/moles of Si in the organosiloxane resin; 10 to 15 mole % of organosilane/moles of Si in the organosiloxane resin; 5 to 10 mole % of organosilane/moles of Si in the organosiloxane resin; or 2 to 12 mole % of organosilane/moles of Si in the organosiloxane resin. Furthermore, the amount of the organosilane having the formula $R^5_qSiX_{4-q}$ added during step II) is, in some embodiments, controlled to ensure a stoichiometry that does not consume all the silanol groups on the organosiloxane block copolymer. In one embodiment, the amount of the organosilane used in step II is selected to provide an organosiloxane block copolymer containing 0.5 to 35 mole percent of silanol groups [$\equiv SiOH$].
- 20
- 25
- 30

[0065] The crosslinks within the block copolymer may primarily be siloxane bonds, $\equiv\text{Si-O-Si}\equiv$, resulting from the condensation of silanol groups, as discussed herein.

[0066] The amount of crosslinking in the block copolymer may be estimated by determining the average molecular weight of the block copolymer, such as with GPC techniques. In some embodiments, crosslinking the block copolymer increases its average molecular weight. Thus, an estimation of the extent of crosslinking may be made, given the average molecular weight of the block copolymer, the selection of the linear siloxy component (that is the chain length as indicated by its degree of polymerization), and the molecular weight of the non-linear block (which is primarily controlled by the selection of the organosiloxane resin used to prepare the block copolymer).

[0067] The organosiloxane block copolymer of the embodiments described herein may be prepared by the methods known in the art, including the methods disclosed in Published PCT Application Nos. WO2012/040302 and WO2012/040305, which are incorporated herein by reference in their entirety.

[0068] In some embodiments, solid compositions, which include a resin-linear organosiloxane block copolymer, also contain a superbase catalyst. *See, e.g.*, PCT Appl. No. PCT/US2012/069701, filed December 14, 2012; and U.S. Provisional Appl. No. 61/570,477, filed December 14, 2012, the entireties of which are incorporated by reference as if fully set forth herein.

[0069] In some embodiments, solid compositions, which include a resin-linear organosiloxane block copolymer, also contain a stabilizer. *See, e.g.*, PCT Appl. No. PCT/US2012/067334, filed November 30, 2012; and U.S. Provisional Appl. No. 61/566,031, filed December 2, 2011, the entireties of which are incorporated by reference as if fully set forth herein.

[0070] The present disclosure further provides curable compositions comprising:

- a) the organosiloxane block copolymers as described herein, in some embodiments in combination with a stabilizer or a superbase as described herein, and
- b) an organic solvent.

[0071] In some embodiments, the organic solvent is an aromatic solvent, such as benzene, toluene, or xylene.

[0072] In one embodiment, the curable compositions may further contain an organosiloxane resin (*e.g.*, free resin that is not part of the block copolymer). The organosiloxane resin present in these compositions is, in some embodiments, the same organosiloxane resin used to prepare the organosiloxane block copolymer. Thus, the organosiloxane resin may comprise at least 60 mole % of $[R^2SiO_{3/2}]$ siloxy units in its formula (*e.g.*, at least 70 mole % of $[R^2SiO_{3/2}]$ siloxy units or at least 80 mole % of $[R^2SiO_{3/2}]$ siloxy units; or 60-70 mole % $[R^2SiO_{3/2}]$ siloxy units, 60-80 mole % $[R^2SiO_{3/2}]$ siloxy units or 70-80 mole % $[R^2SiO_{3/2}]$ siloxy units), wherein each R^2 , at each occurrence, is independently a C_1 to C_{20} hydrocarbyl. Alternatively, the organosiloxane resin is a silsesquioxane resin, or alternatively a phenyl silsesquioxane resin.

[0073] The amount of the organosiloxane block copolymers, organic solvent, and optional organosiloxane resin in a curable composition may vary. A curable composition may contain:

40 to 80 weight % of the organosiloxane block copolymer as described herein (*e.g.*, 40 to 70 weight %, 40 to 60 weight %, 40 to 50 weight %);
 10 to 80 weight % of the organic solvent (*e.g.*, 10 to 70 weight %, 10 to 60 weight %, 10 to 50 weight %, 10 to 40 weight %, 10 to 30 weight %, 10 to 20 weight %, 20 to 80 weight %, 30 to 80 weight %, 40 to 80 weight %, 50 to 80 weight %, 60 to 80 weight %, or 70 to 80 weight %);
 and
 5 to 40 weight % of the organosiloxane resin (*e.g.*, 5 to 30 weight %, 5 to 20 weight %, 5 to 10 weight %, 10 to 40 weight %, 10 to 30 weight %, 10 to 20 weight %, 20 to 40 weight % or 30 to 40 weight %);

such that the sum of the weight % of these components does not exceed 100%. In one embodiment, curable compositions consist essentially of the organosiloxane block copolymer as described herein, the organic solvent, and the organosiloxane resin. In some embodiments, the weight % of these components sum to 100%, or nearly 100%.

[0074] In yet another embodiment, the curable compositions contain a cure catalyst. The cure catalyst may be selected from any catalyst known in the art to effect condensation cure of organosiloxanes, such as various tin or titanium catalysts. Condensation catalyst can be any condensation catalyst that may be

used to promote condensation of silicon bonded hydroxy (=silanol) groups to form Si-O-Si linkages. Examples include, but are not limited to, amines and complexes of lead, tin, titanium, zinc, and iron. Other examples include, but are not limited to basic compounds, such as trimethylbenzylammonium hydroxide, tetramethylammonium hydroxide, n-hexylamine, tributylamine, diazabicycloundecene (DBU) and dicyandiamide; and metal-containing compounds such as tetraisopropyl titanate, tetrabutyl titanate, titanium acetylacetonate, aluminum triisobutoxide, aluminum triisopropoxide, zirconium tetra(acetylacetonato), zirconium tetrabutylate, cobalt octylate, cobalt acetylacetonato, iron acetylacetonato, tin acetylacetonato, dibutyltin octylate, dibutyltin laurate, zinc octylate, zinc bezoate, zinc p-tert-butylbenzoate, zinc laurate, zinc stearate, aluminium phosphate, and aluminium triisopropoxide; organic titanium chelates such as aluminium trisacetylacetonate, aluminium bisethylacetoacetate monoacetylacetonate, diisopropoxybis(ethylacetoacetate)titanium, and diisopropoxybis(ethylacetoacetate)titanium. In some embodiments, the condensation catalysts include zinc octylate, zinc bezoate, zinc p-tert-butylbenzoate, zinc laurate, zinc stearate, aluminium phosphate, and aluminum triisopropoxide. *See, e.g.*, U.S. Patent No. 8,193,269, the entire disclosure of which is incorporated by reference as if fully set forth herein. Other examples of condensation catalysts include, but are not limited to aluminum alkoxides, antimony alkoxides, barium alkoxides, boron alkoxides, calcium alkoxides, cerium alkoxides, erbium alkoxides, gallium alkoxides, silicon alkoxides, germanium alkoxides, hafnium alkoxides, indium alkoxides, iron alkoxides, lanthanum alkoxides, magnesium alkoxides, neodymium alkoxides, samarium alkoxides, strontium alkoxides, tantalum alkoxides, titanium alkoxides, tin alkoxides, vanadium alkoxide oxides, yttrium alkoxides, zinc alkoxides, zirconium alkoxides, titanium or zirconium compounds, especially titanium and zirconium alkoxides, and chelates and oligo- and polycondensates of the above alkoxides, dialkyltin diacetate, tin(II) octoate, dialkyltin diacylate, dialkyltin oxide and double metal alkoxides. Double metal alkoxides are alkoxides containing two different metals in a particular ratio. In some embodiments, the condensation catalysts include titanium tetraethylate, titanium tetrapropylate, titanium tetraisopropylate, titanium tetrabutylate, titanium tetraisooctylate,

titanium isopropylate tristearoylate, titanium trisopropylate stearylolate, titanium diisopropylate distearoylate, zirconium tetrapropylate, zirconium tetraisopropylate, zirconium tetrabutylate. *See, e.g.*, U.S. Patent No. 7,005,460, the entire disclosure of which is incorporated by reference as if fully set forth
5 herein. In addition, the condensation catalysts include titanates, zirconates and hafnates as described in DE 4427528 C2 and EP 0 639 622 B1, both of which are incorporated by reference as if fully set forth herein.

[0075] Solid compositions containing the resin-linear organosiloxane block copolymers may be prepared by removing the solvent from curable
10 organosiloxane block copolymer compositions as described herein. The solvent may be removed by any known processing techniques. In one embodiment, a film of a curable composition containing the organosiloxane block copolymers is formed, and the solvent is allowed to evaporate from the film. Subjecting the films to elevated temperatures, and/or reduced pressures, will accelerate solvent
15 removal and subsequent formation of the solid curable composition. Alternatively, the curable compositions may be passed through an extruder to remove solvent and provide the solid composition in the form of a ribbon or pellets. Coating operations against a release film could also be used as in slot die coating, knife over roll, rod, or gravure coating. Also, roll-to-roll coating
20 operations could be used to prepare a solid film. In coating operations, a conveyor oven or other means of heating and evacuating the solution can be used to drive off the solvent and obtain the final solid film.

[0076] Although not wishing to be bound by any theory, it is possible that the structural ordering of the disiloxy and trisiloxy units in the
25 organosiloxane block copolymer, as described herein, may provide the copolymer with certain unique physical property characteristics when solid compositions of the block copolymer are formed. For example, the structural ordering of the disiloxy and trisiloxy units in the copolymer may provide solid coatings that allow for a high optical transmittance of visible light (*e.g.*, at least
30 an 85% transmittance; at least a 90% transmittance; at least a 95% transmittance; at least a 99% transmittance; or 100% transmittance at wavelengths above 350 nm). The structural ordering may also allow the organosiloxane block copolymer to flow and cure upon heating, yet remain stable at room temperature. They may also be processed using lamination techniques. These properties are

useful to provide coatings for various electronic articles to improve weather resistance and durability, while providing low cost and easy procedures that are energy efficient.

[0077] The present disclosure further relates to solid forms of the
5 aforementioned organosiloxane block copolymers and solid compositions
derived from the curable compositions described herein comprising the
organosiloxane block copolymers. Thus, the present disclosure provides
organosiloxane block copolymers comprising:

40 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$,

10 10 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$,

0.5 to 25 mole percent silanol groups $[≡SiOH]$;

wherein:

each R^1 , at each occurrence, is independently a C_1 to C_{30}

hydrocarbyl or an R^f group,

15 each R^2 , at each occurrence, is independently a C_1 to C_{20}

hydrocarbyl or an R^f group,

where R^f represents a fluorine-containing group, with the proviso

that there is at least one R^f group in the organosiloxane block
copolymer;

20 wherein:

the disiloxy units $[R^1_2SiO_{2/2}]$ are arranged in linear blocks

having an average of from 10 to 400 disiloxy units $[R^1_2SiO_{2/2}]$ per
linear block,

the trisiloxy units $[R^2SiO_{3/2}]$ are arranged in non-linear blocks

25 having a molecular weight of at least 500 g/mole, at least 30% of
the non-linear blocks are crosslinked with each other and are
predominately aggregated together in nano-domains,

each linear block is linked to at least one non-linear block; and

the organosiloxane block copolymer has a weight average molecular

30 weight of at least 20,000 g/mole, and is a solid at 25°C.

[0078] In some embodiments, the organosiloxane block copolymers contained in the solid forms and solid compositions comprise 40 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$, *e.g.*, 50 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 60 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 65 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 70 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; or 80 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 40 to 80 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 40 to 70 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 40 to 60 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 40 to 50 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 50 to 80 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 50 to 70 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 50 to 60 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 60 to 80 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; 60 to 70 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$; or 70 to 80 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$.

[0079] In some embodiments, the organosiloxane block copolymers contained in the solid forms and solid compositions comprise 10 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$, *e.g.*, 10 to 20 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 10 to 30 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 10 to 35 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 10 to 40 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 10 to 50 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 20 to 30 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 20 to 35 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 20 to 40 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 20 to 50 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 20 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 30

to 40 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 30 to 50 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 30 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; 40 to 50 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$; or 40 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$.

[0080] In some embodiments, the organosiloxane block copolymers contained in the solid forms and solid compositions comprise 0.5 to 25 mole percent silanol groups $[≡SiOH]$ (*e.g.*, 0.5 to 5 mole percent, 0.5 to 10 mole percent, 0.5 to 15 mole percent, 0.5 to 20 mole percent, 5 to 10 mole percent, 5 to 15 mole percent, 5 to 20 mole percent, 5 to 25 mole percent, 10 to 15 mole percent, 10 to 20 mole percent, 10 to 25 mole percent, 15 to 20 mole percent, 15 to 25 mole percent, or 20 to 25 mole percent).

[0081] In some embodiments, the disiloxy units $[R^1_2SiO_{2/2}]$ in the organosiloxane block copolymers contained in the solid forms and solid compositions are arranged in linear blocks having an average of 10 to 400 disiloxy units, *e.g.*, an average of from about 10 to about 400 disiloxy units; about 10 to about 300 disiloxy units; about 10 to about 200 disiloxy units; about 10 to about 100 disiloxy units; about 50 to about 400 disiloxy units; about 100 to about 400 disiloxy units; about 150 to about 400 disiloxy units; about 200 to about 400 disiloxy units; about 300 to about 400 disiloxy units; about 50 to about 300 disiloxy units; about 100 to about 300 disiloxy units; about 150 to about 300 disiloxy units; about 200 to about 300 disiloxy units; about 100 to about 150 disiloxy units, about 115 to about 125 disiloxy units, about 90 to about 170 disiloxy units or about 110 to about 140 disiloxy units).

[0082] In some embodiments, the non-linear blocks in the organosiloxane block copolymers contained in the solid forms and solid compositions have a number average molecular weight of at least 500 g/mole, *e.g.*, at least 1000 g/mole, at least 2000 g/mole, at least 3000 g/mole or at least 4000 g/mole; or have a molecular weight of from about 500 g/mole to about 4000 g/mole, from about 500 g/mole to about 3000 g/mole, from about 500 g/mole to about 2000 g/mole, from about 500 g/mole to about 1000 g/mole, from about 1000 g/mole to 2000 g/mole, from about 1000 g/mole to about 1500

g/mole, from about 1000 g/mole to about 1200 g/mole, from about 1000 g/mole to 3000 g/mole, from about 1000 g/mole to about 2500 g/mole, from about 1000 g/mole to about 4000 g/mole, from about 2000 g/mole to about 3000 g/mole or from about 2000 g/mole to about 4000 g/mole.

5 **[0083]** In some embodiments, at least 30% of the non-linear blocks in the organosiloxane block copolymers contained in the solid forms and solid compositions are crosslinked with each other, *e.g.*, at least 40% of the non-linear blocks are crosslinked with each other; at least 50% of the non-linear blocks are crosslinked with each other; at least 60% of the non-linear blocks are crosslinked with each other; at least 70% of the non-linear blocks are crosslinked with each other; or at least 80% of the non-linear blocks are crosslinked with each other. In other embodiments, from about 30% to about 80% of the non-linear blocks are crosslinked with each other; from about 30% to about 70% of the non-linear blocks are crosslinked with each other; from about 30% to about 60% of the non-linear blocks are crosslinked with each other; from about 30% to about 50% of the non-linear blocks are crosslinked with each other; from about 30% to about 40% of the non-linear blocks are crosslinked with each other; from about 40% to about 80% of the non-linear blocks are crosslinked with each other; from about 40% to about 70% of the non-linear blocks are crosslinked with each other; from about 40% to about 60% of the non-linear blocks are crosslinked with each other; from about 40% to about 50% of the non-linear blocks are crosslinked with each other; from about 50% to about 80% of the non-linear blocks are crosslinked with each other; from about 50% to about 70% of the non-linear blocks are crosslinked with each other; from about 55% to about 70% of the non-linear blocks are crosslinked with each other; from about 50% to about 60% of the non-linear blocks are crosslinked with each other; from about 60% to about 80% of the non-linear blocks are crosslinked with each other; or from about 60% to about 70% of the non-linear blocks are crosslinked with each other.

30 **[0084]** In some embodiments, the organosiloxane block copolymers contained in the solid forms and solid compositions have a weight average molecular weight (M_w) of at least 20,000 g/mole, alternatively a weight average molecular weight of at least 40,000 g/mole, alternatively a weight average molecular weight of at least 50,000 g/mole, alternatively a weight average

molecular weight of at least 60,000 g/mole, alternatively a weight average molecular weight of at least 70,000 g/mole, or alternatively a weight average molecular weight of at least 80,000 g/mole. In some embodiments, the organosiloxane block copolymers contained in the solid forms and solid compositions have a weight average molecular weight (M_w) of from about 20,000 g/mole to about 250,000 g/mole or from about 100,000 g/mole to about 250,000 g/mole, alternatively a weight average molecular weight of from about 40,000 g/mole to about 100,000 g/mole, alternatively a weight average molecular weight of from about 50,000 g/mole to about 100,000 g/mole, alternatively a weight average molecular weight of from about 50,000 g/mole to about 80,000 g/mole, alternatively a weight average molecular weight of from about 50,000 g/mole to about 70,000 g/mole, alternatively a weight average molecular weight of from about 50,000 g/mole to about 60,000 g/mole. In some embodiments, the organosiloxane block copolymers of the embodiments described herein have a number average molecular weight (M_n) of from about 15,000 to about 50,000 g/mole; from about 15,000 to about 30,000 g/mole; from about 20,000 to about 30,000 g/mole; or from about 20,000 to about 25,000 g/mole.

[0085] In some embodiments, the aforementioned organosiloxane block copolymers are isolated in a solid form, for example by casting films of a solution of the block copolymer in an organic solvent (*e.g.*, benzene, toluene, xylene or combinations thereof) and allowing the solvent to evaporate. Under these conditions, the aforementioned organosiloxane block copolymers can be provided as solutions in an organic solvent containing from about 50 wt % to about 80 wt % solids, *e.g.*, from about 60 wt % to about 80 wt %, from about 70 wt % to about 80 wt % or from about 75 wt % to about 80 wt % solids. In some embodiments, the solvent is toluene. In some embodiments, such solutions will have a viscosity of from about 1500 cSt to about 4000 cSt at 25°C, *e.g.*, from about 1500 cSt to about 3000 cSt, from about 2000 cSt to about 4000 cSt or from about 2000 cSt to about 3000 cSt at 25°C.

[0086] Upon drying or forming a solid, the non-linear blocks of the block copolymer further aggregate together to form “nano-domains.” As used herein, “predominately aggregated” means the majority (*e.g.*, greater than 50%; greater than 60%; greater than 75%, greater than 80%, greater than 90%; from about

75% to about 90%, from about 80% to about 90%, or from about 75% to about 85%) of the non-linear blocks of the organosiloxane block copolymer are found in certain regions of the solid composition, described herein as “nano-domains.”

As used herein, “nano-domains” refers to those phase regions within the solid block copolymer compositions that are phase separated within the solid block copolymer compositions and possess at least one dimension sized from 1 to 100 nanometers. The nano-domains may vary in shape, providing at least one dimension of the nano-domain is sized from 1 to 100 nanometers. Thus, the nano-domains may be regular or irregularly shaped. The nano-domains may be spherically shaped, tubular shaped, and, in some instances, lamellar shaped.

[0087] In a further embodiment, the solid organosiloxane block copolymers as described herein contain a first phase and an incompatible second phase, the first phase containing predominately the disiloxo units $[R^1_2SiO_{2/2}]$ as defined herein, the second phase containing predominately the trisiloxo units $[R^2SiO_{3/2}]$ as defined herein, the non-linear blocks being sufficiently aggregated into nano-domains which are incompatible with the first phase.

[0088] When solid compositions are formed from the curable compositions of the organosiloxane block copolymer, which may also contain an organosiloxane resin, as described herein, the organosiloxane resin also predominately aggregates within the nano-domains.

[0089] The structural ordering of the disiloxo and trisiloxo units in the solid block copolymers of the present disclosure, and characterization of the nano-domains, may be determined explicitly using certain analytical techniques such as Transmission Electron Microscopic (TEM) techniques, Atomic Force Microscopy (AFM), Small Angle Neutron Scattering, Small Angle X-Ray Scattering, and Scanning Electron Microscopy.

[0090] Alternatively, the structural ordering of the disiloxo and trisiloxo units in the block copolymer, and formation of nano-domains, may be implied by characterizing certain physical properties of coatings resulting from the present organosiloxane block copolymers. For example, the present organosiloxane copolymers may provide coatings that have an optical transmittance of visible light greater than 95%. One skilled in the art recognizes that such optical clarity is possible (other than refractive index matching of the

two phases) only when visible light is able to pass through such a medium and not be diffracted by particles (or domains as used herein) having a size greater than 150 nanometers. As the particle size, or domains further decreases, the optical clarity may be further improved. Thus, coatings derived from the present
5 organosiloxane copolymers may have an optical transmittance of visible light of at least 95%, *e.g.*, at least 96%; at least 97%; at least 98%; at least 99%; or 100% transmittance of visible light. As used herein, the term “visible light” includes light with wavelengths above 350 nm.

[0091] One advantage of the present resin-linear organopolysiloxanes
10 block copolymers is that they can be processed several times, because the processing temperature ($T_{\text{processing}}$) is less than the temperature required to finally cure (T_{cure}) the organosiloxane block copolymer, *i.e.*, $T_{\text{processing}} < T_{\text{cure}}$. However the organosiloxane copolymer will cure and achieve high temperature stability when $T_{\text{processing}}$ is taken above T_{cure} . Thus, the present resin-linear
15 organopolysiloxanes block copolymers offer a significant advantage of being “re-processable” in conjunction with the benefits that may be associated with silicones, such as; hydrophobicity, high temperature stability, moisture/UV resistance.

[0092] In one embodiment, the solid compositions of the organosiloxane
20 block copolymers may be considered as “melt processable.” In some embodiments, the solid compositions, such as a coating formed from a film of a solution containing the organosiloxane block copolymers, exhibit fluid behavior at elevated temperatures, that is upon “melting.” The “melt processable” features of the solid compositions of the organosiloxane block copolymers may be monitored by measuring the “melt flow temperature” of the solid
25 compositions, that is when the solid composition demonstrates liquid behavior. The melt flow temperature may specifically be determined by measuring the storage modulus (G'), loss modulus (G'') and tan delta ($\tan \delta$) as a function of temperature storage using commercially available instruments. For example, a commercial rheometer (such as TA Instruments’ ARES-RDA with 2KSTD
30 standard flexural pivot spring transducer, with forced convection oven) may be used to measure the storage modulus (G'), loss modulus (G'') and tan delta as a function of temperature. Test specimens (*e.g.*, 8 mm wide, 1 mm thick) may be loaded in between parallel plates and measured using small strain oscillatory

rheology while ramping the temperature in a range from 25°C to 300°C at 2°C/min (frequency 1Hz). The flow onset may be calculated as the inflection temperature in the G' drop (labeled FLOW), the viscosity at 120°C is reported as a measure for melt processability and the cure onset is calculated as the onset
5 temperature in the G' rise (labeled CURE). Typically, the FLOW of the solid compositions will also correlate to the glass transition temperature of the non-linear segments (*i.e.*, the resin component) in the organosiloxane block copolymer.

[0093] In some embodiments, the $\tan \delta = 1$ is from about 3 to about 5
10 hours at 150°C, *e.g.*, from about 3 to about 5 minutes at 150°C, from about 10 to about 15 minutes at 150°C, from about 10 to about 12 minutes at 150°C, from about 8 to about 10 minutes at 150°C, from about 30 minutes to about 2.5 hours at 150°C, from about 1 hour to about 4 hours at 150°C or from about 2.5 hours to about 5 hours at 150°C.

15 [0094] In a further embodiment, the solid compositions may be characterized as having a melt flow temperature ranging from 25°C to 200°C, alternatively from 25°C to 160°C, or alternatively from 50°C to 160°C.

[0095] It is believed that the melt processability benefits enables the reflow of solid compositions of the organosiloxane block copolymers around
20 device architectures at temperatures below T_{cure} , after an initial coating or solid is formed on the device. This feature is very beneficial to encapsulated various electronic devices.

[0096] In one embodiment, the solid compositions of the organosiloxane block copolymers may be considered as "curable." In some embodiments, the
25 solid compositions, such as a coating formed from a film of a solution containing the organosiloxane block copolymers, may undergo further physical property changes by further curing the block copolymer. As discussed herein, the present organosiloxane block copolymers contain a certain amount of silanol groups. It is possible that the presence of these silanol groups on the block copolymer
30 permit further reactivity, *e.g.*, a cure mechanism. Upon curing, the physical properties of solid compositions may be further altered.

[0097] Alternatively, the "melt processability," the extent of cure and/or the rate of cure of the solid compositions of the organosiloxane block

copolymers may be determined by rheological measurements at various temperatures.

[0098] The solid compositions containing the organosiloxane block copolymers may have a storage modulus (G') at 25°C ranging from 0.01 MPa to 500 MPa and a loss modulus (G'') ranging from 0.001 MPa to 250 MPa, alternatively a storage modulus (G') at 25°C ranging from 0.1 MPa to 250 MPa and a loss modulus (G'') ranging from 0.01 MPa to 125 MPa, alternatively a storage modulus (G') at 25°C ranging from 0.1 MPa to 200 MPa and a loss modulus (G'') ranging from 0.01 MPa to 100 MPa.

[0099] The solid compositions containing the organosiloxane block copolymers may have a storage modulus (G') at 120°C ranging from 10 Pa to 500,000 Pa and a loss modulus (G'') ranging from 10 Pa to 500,000 Pa, alternatively a storage modulus (G') at 120°C ranging from 20 Pa to 250,000 Pa and a loss modulus (G'') ranging from 20 Pa to 250,000 Pa, alternatively a storage modulus (G') at 120°C ranging from 30 Pa to 200,000 Pa and a loss modulus (G'') ranging from 30 Pa to 200,000 Pa.

[0100] The solid compositions containing the organosiloxane block copolymers may have a storage modulus (G') at 200°C ranging from 10 Pa to 100,000 Pa and a loss modulus (G'') ranging from 5 Pa to 80,000 Pa, alternatively a storage modulus (G') at 200°C ranging from 20 Pa to 75,000 Pa and a loss modulus (G'') ranging from 10 Pa to 65,000 Pa, alternatively a storage modulus (G') at 200°C ranging from 30 Pa to 50,000 Pa and a loss modulus (G'') ranging from 15 Pa to 40,000 Pa.

[0101] The solid compositions may be further characterized by certain physical properties such as tensile strength and % elongation at break. The present solid compositions derived from the aforementioned organosiloxane block copolymers may have an initial tensile strength greater than 0.1 MPa, alternatively greater than 0.5 MPa, alternatively greater than 1.5 MPa, or alternatively greater than 2 MPa. In some embodiments, the solid compositions may have an initial tensile strength from about 0.1 MPa to about 10 MPa, *e.g.*, from about 0.5 to about 10 MPa, from about 1.5 MPa to about 10 MPa, from about 2 MPa to about 10 MPa, from about 5 MPa to about 10 MPa or from about 7 MPa to about 10 MPa. The present solid compositions derived from the aforementioned organosiloxane block copolymers may have an initial %

elongation at break (or rupture) greater than 40%, alternatively greater than 50%, or alternatively greater than 75%. In some embodiments, the solid compositions may have a % elongation at break (or rupture) of from about 20% to about 90%, *e.g.*, from about 25% to about 50%, from about 20% to about 60%, from about 40% to about 60%, from about 40% to about 50%, or from about 75% to about 90%. As used herein, tensile strength and % elongation at break are measured according to ASTM D412.

[0102] The aforementioned resin-linear organosiloxane block copolymers may be prepared by a process comprising:

10 I) reacting

a) a linear organosiloxane having the formula



wherein each R^1 , at each occurrence, is independently a C_1 to

C_{30} hydrocarbyl or an R^f group,

15 n is 10 to 400, q is 0, 1, or 2,

E is a hydrolyzable group containing at least one carbon atom, and

b) an organosiloxane resin comprising at least 60 mole % of $[R^2SiO_{3/2}]$ siloxy units in its formula, wherein each R^2 , at each

20 occurrence, is independently a C_1 to C_{20} hydrocarbyl or an R^f group,

in c) an organic solvent;

to form a resin-linear organosiloxane block copolymer;

wherein the amounts of a) and b) used in step I) are selected to provide the resin-linear organosiloxane block copolymer with 40

25 to 90 mole % of disiloxy units $[R^1_2SiO_{2/2}]$ and 10 to 60 mole %

of trisiloxy units $[R^2SiO_{3/2}]$, and

wherein at least 95 weight percent of the linear organosiloxane used in step I) is incorporated into the resin-linear organosiloxane block copolymer;

30 II) reacting the resin-linear organosiloxane block copolymer from step I) to

crosslink the trisiloxy units of the resin-linear organosiloxane block copolymer sufficiently to increase the weight average molecular weight (M_w) of the resin-linear organosiloxane block copolymer by at least 50%;

III) optionally further processing the resin-linear organosiloxane block copolymer from step II) to enhance storage stability and/or optical clarity and/or optionally adding to the resin-linear organosiloxane block copolymer from step II) a stabilizer or a superbase; and

IV) optionally, removing the organic solvent.

[0103] Step I) in the process comprises reacting:

10 a) a linear organosiloxane having the formula



wherein each R^1 , at each occurrence, is independently a C_1 to

C_{30} hydrocarbyl or an R^f group,

n is 10 to 400, q is 0, 1, or 2,

15 E is a hydrolyzable group containing at least one carbon atom, and

b) an organosiloxane resin comprising at least 60 mole % of $[R^2SiO_{3/2}]$ siloxy units in its formula, wherein each R^2 , at each occurrence, is independently a C_1 to C_{20} hydrocarbyl or an R^f group,

20 in c) an organic solvent;

to form a resin-linear organosiloxane block copolymer;

wherein the amounts of a) and b) used in step I) are selected to provide the resin-linear organosiloxane block copolymer with 40

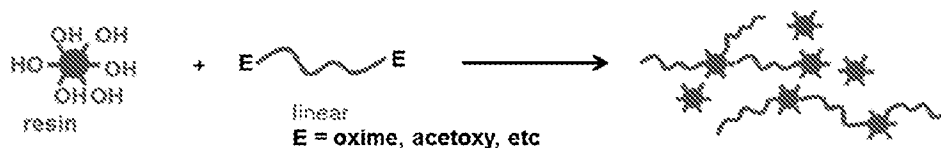
to 90 mole % of disiloxy units $[R^1_2SiO_{2/2}]$ and 10 to 60 mole %

25 of trisiloxy units $[R^2SiO_{3/2}]$, and

wherein at least 95 weight percent of the linear organosiloxane added in step I) is incorporated into the resin-linear organosiloxane block copolymer.

[00100] The reaction of step I) of the process may be represented

30 generally according to the following schematic:



where various OH groups on the organosiloxane resin are reacted with the hydrolyzable groups (E) on the linear organosiloxane, to form a resin-linear organosiloxane block copolymer and a H-(E) compound. The reaction in step I) may be considered as a condensation reaction between the organosiloxane resin and the linear organosiloxane.

The Linear Organosiloxane

[0104] Component a) in step I) of the process is a linear organosiloxane having the formula $R^1_q(E)_{(3-q)}SiO(R^1_2SiO_{2/2})_nSi(E)_{(3-q)}R^1_q$, where each R^1

- is independently a C_1 to C_{30} hydrocarbyl, an R^f group, or combinations thereof; the subscript “n” may be considered as the degree of polymerization (dp) of the linear organosiloxane and may vary from 10 to 400 (*e.g.*, an average of from about 10 to about 400 D units; about 10 to about 300 D units; about 10 to about 200 D units; about 10 to about 100 D units; about 50 to about 400 D units; about 100 to about 400 D units; about 150 to about 400 D units; about 200 to about 400 D units; about 300 to about 400 D units; about 50 to about 300 D units; about 100 to about 300 D units; about 150 to about 300 D units; about 200 to about 300 D units; about 100 to about 150 D units, about 115 to about 125 D units, about 90 to about 170 D units or about 110 to about 140 D units); the subscript “q” may be 0, 1, or 2; and E is a hydrolyzable group containing at least one carbon atom. While component a) is described as a linear organosiloxane having the formula $R^1_q(E)_{(3-q)}SiO(R^1_2SiO_{2/2})_nSi(E)_{(3-q)}R^1_q$, one skilled in the art recognizes small amount of alternative siloxy units, such as a T ($R^1SiO_{3/2}$) siloxy units, may be incorporated into the linear organosiloxane of component a). As such, the organosiloxane may be considered as being “predominately” linear by having a majority of D ($R^1_2SiO_{2/2}$) siloxy units. Furthermore, the linear organosiloxane used as component a) may be a combination of several linear organosiloxanes. Still further, the linear organosiloxane used as component a) may comprise silanol groups. In some embodiments, the linear organosiloxane used as component a) comprises from about 0.5 to about 5 mole % silanol groups, *e.g.*,

from about 1 mole % to about 3 mole %; from about 1 mole % to about 2 mole % or from about 1 mole % to about 1.5 mole % silanol groups.

[00101] At each occurrence, each R^1 in the above linear organosiloxane formula is independently a C_1 to C_{30} hydrocarbyl or an R^f group, where the hydrocarbyl group may independently be an alkyl, aryl, or alkylaryl group. Each R^1 , at each occurrence, may independently be a C_1 to C_{30} alkyl group, alternatively, at each occurrence, each R^1 may be a C_1 to C_{18} alkyl group. Alternatively each R^1 , at each occurrence, may be a C_1 to C_6 alkyl group such as methyl, ethyl, propyl, butyl, pentyl, or hexyl. Alternatively each R^1 , at each occurrence, may be methyl. Each R^1 , at each occurrence, may be an aryl group, such as phenyl, naphthyl, or an anthryl group. Alternatively, each R^1 , at each occurrence, may be any combination of the aforementioned alkyl, aryl or R^f groups such that, in some embodiments, each disiloxy unit may have two alkyl groups (*e.g.*, two methyl groups); two aryl groups (*e.g.*, two phenyl groups); an alkyl (*e.g.*, methyl) and an aryl group (*e.g.*, phenyl), two R^f groups; one R^f group and one alkyl group (*e.g.*, methyl); or one R^f group and one aryl group (*e.g.*, phenyl). Alternatively, each R^1 , at each occurrence, is phenyl, methyl or R^f .

[0105] E may be selected from any hydrolyzable group containing at least one carbon atom (*e.g.*, from one to ten carbon atoms; from one to five carbon atoms; from one to four carbon atoms; or from one to three carbon atoms). In some embodiments, E is selected from an oximo, epoxy, carboxy, amino, amido group or combinations thereof. Alternatively, E may have the formula $R^1C(=O)O-$, $R^1_2C=N-O-$, or $R^4C=N-O-$, where R^1 is as defined herein, and R^4 is hydrocarbyl. In one embodiment, E is $H_3CC(=O)O-$ (acetoxy) and q is 1. In one embodiment, E is $(CH_3)(CH_3CH_2)C=N-O-$ (methylethylketoximyl) and q is 1.

[0106] In one embodiment, the linear organosiloxane has the formula $(CH_3)_q(E)_{(3-q)}SiO[(CF_3CH_2CH_2)SiO_{2/2}]_nSi(E)_{(3-q)}(CH_3)_q$, where E, n, and q are as defined herein.

[0107] In one embodiment, the linear organosiloxane has the formula

$(\text{CH}_3)_q(\text{E})_{(3-q)}\text{SiO}[(\text{CF}_3\text{CH}_2\text{CH}_2)(\text{C}_6\text{H}_5)\text{SiO}_{2/2}]_n\text{Si}(\text{E})_{(3-q)}(\text{CH}_3)_q$, where E, n, and q are as defined herein.

[0108] Processes for preparing linear organosiloxanes suitable as component a) are known. In some embodiments, a silanol terminated
 5 polydiorganosiloxane is reacted with an “endblocking” compound such as an alkyltriacetoxysilane or a dialkylketoxime. The stoichiometry of the endblocking reaction is typically adjusted such that a sufficient amount of the endblocking compound is added to react with all the silanol groups on the
 10 compound may be used per mole of silanol on the polydiorganosiloxane. Alternatively, a slight molar excess such as 1 to 10% of the endblocking compound may be used. The reaction is, in some embodiments, conducted under anhydrous conditions to minimize condensation reactions of the silanol polydiorganosiloxane. In some embodiments, the silanol ended
 15 polydiorganosiloxane and the endblocking compound may be dissolved in an organic solvent under anhydrous conditions, and allowed to react at room temperature, or at elevated temperatures (up to the boiling point of the solvent).

The Organosiloxane Resin

[0109] Component b) in the present process is an organosiloxane resin
 20 comprising at least 60 mole % of $[\text{R}^2\text{SiO}_{3/2}]$ siloxy units in its formula, where each R^2 , at each occurrence, is independently a C_1 to C_{20} hydrocarbyl, an R^f group or combinations thereof. The organosiloxane resin may contain any amount and combination of other M, D, and Q siloxy units, provided the organosiloxane resin contains at least 70 mole % of $[\text{R}^2\text{SiO}_{3/2}]$ siloxy units,
 25 alternatively the organosiloxane resin contains at least 80 mole % of $[\text{R}^2\text{SiO}_{3/2}]$ siloxy units, alternatively the organosiloxane resin contains at least 90 mole % of $[\text{R}^2\text{SiO}_{3/2}]$ siloxy units, or alternatively the organosiloxane resin contains at least 95 mole % of $[\text{R}^2\text{SiO}_{3/2}]$ siloxy units. In some embodiments, the organosiloxane resin contains from about 70 to about 100 mole % of $[\text{R}^2\text{SiO}_{3/2}]$
 30 siloxy units, e.g., from about 70 to about 95 mole % of $[\text{R}^2\text{SiO}_{3/2}]$ siloxy units, from about 80 to about 95 mole % of $[\text{R}^2\text{SiO}_{3/2}]$ siloxy units or from about 90

to about 95 mole % of $[R^2SiO_{3/2}]$ siloxy units. Organosiloxane resins useful as component b) include those known as “silsesquioxane” resins.

[0110] Each R^2 , at each occurrence, in the above trisiloxy unit is independently a C_1 to C_{20} hydrocarbyl or an R^f group, where the hydrocarbyl group may independently be an alkyl, aryl, or alkylaryl group. Each R^2 , at each occurrence, may be a C_1 to C_{20} alkyl group, alternatively each R^2 , at each occurrence, may be a C_1 to C_{18} alkyl group. Alternatively each R^2 , at each occurrence, may be a C_1 to C_6 alkyl group such as methyl, ethyl, propyl, butyl, pentyl, or hexyl. Alternatively each R^2 , at each occurrence, may be methyl. Each R^2 , at each occurrence, may be an aryl group, such as phenyl, naphthyl, or an anthryl group. Alternatively, each R^2 , at each occurrence, may be any combination of the aforementioned alkyl, aryl or R^f groups such that, in some embodiments, each disiloxy unit may have two alkyl groups (*e.g.*, two methyl groups); two aryl groups (*e.g.*, two phenyl groups); an alkyl (*e.g.*, methyl) and an aryl group (*e.g.*, phenyl), two R^f groups; one R^f group and one alkyl group (*e.g.*, methyl); or one R^f group and one aryl group (*e.g.*, phenyl). Alternatively, each R^2 , at each occurrence, is phenyl, methyl or R^f .

[0111] The weight average molecular weight (M_w) of the organosiloxane resin is not limiting, but, in some embodiments, ranges from 1000 to 10000, or alternatively 1500 to 5000 g/mole.

[0112] Organosiloxane resins containing at least 60 mole % of $[R^2SiO_{3/2}]$ siloxy units, and methods for preparing them, are known in the art. They are typically prepared by hydrolyzing an organosilane having three hydrolyzable groups on the silicon atom, such as a halogen or alkoxy group in an organic solvent. A representative example for the preparation of a silsesquioxane resin may be found in U.S. Patent No. 5,075,103. Furthermore, many organosiloxane resins are available commercially and sold either as a solid (flake or powder), or dissolved in an organic solvent. Suitable, non-limiting, commercially available organosiloxane resins useful as component b) include; Dow Corning® 217 Flake Resin, 233 Flake, 220 Flake, 249 Flake, 255 Flake, Z-6018 Flake (Dow Corning Corporation, Midland MI).

[0113] One skilled in the art recognizes that organosiloxane resins containing such high amounts of $[R^2SiO_{3/2}]$ siloxy units may have a certain concentration of Si-OZ where Z may be hydrogen (*i.e.*, silanol), an alkyl group (so that OZ is an alkoxy group), or alternatively OZ may also be any of the “E” hydrolyzable groups as described herein. The Si-OZ content as a mole percentage of all siloxy groups present on the organosiloxane resin may be readily determined by ^{29}Si NMR. The concentration of the OZ groups present on the organosiloxane resin will vary, as dependent on the mode of preparation, and subsequent treatment of the resin. In some embodiments, the silanol (Si-OH) content of organosiloxane resins suitable for use in the present process will have a silanol content of at least 5 mole %, alternatively of at least 10 mole %, alternatively 25 mole %, alternatively 40 mole %, or alternatively 50 mole %. In other embodiments, the silanol content is from about 5 mole % to about 60 mole %, *e.g.*, from about 10 mole % to about 60 mole %, from about 25 mole % to about 60 mole %, from about 40 mole % to about 60 mole %, from about 25 mole % to about 40 mole % or from about 25 mole % to about 50 mole %.

[0114] One skilled in the art further recognizes that organosiloxane resins containing such high amounts of $[R^2SiO_{3/2}]$ siloxy units and silanol contents may also retain water molecules, especially in high humidity conditions. Thus, it is often beneficial to remove excess water present on the resin by “drying” the organosiloxane resin prior to reacting in step I). This may be achieved by dissolving the organosiloxane resin in an organic solvent, heating to reflux, and removing water by separation techniques (for example Dean Stark trap or equivalent process).

[0115] The amounts of a) and b) used in the reaction of step I) are selected to provide the resin-linear organosiloxane block copolymer with 40 to 90 mole % of disiloxo units $[R^1_2SiO_{2/2}]$ and 10 to 60 mole % of trisiloxo units $[R^2SiO_{3/2}]$. The mole % of disiloxo and trisiloxo units present in components a) and b) may be readily determined using ^{29}Si NMR techniques. The starting mole % then determines the mass amounts of components a) and b) used in step I).

[0116] In some embodiments, the amount of components a) and b) may be selected to ensure there is a molar excess of the silanol groups on the organosiloxane resin versus the amount of linear organosiloxane added. Thus, a sufficient amount of the organosiloxane resin may, in some embodiments, be added to potentially react with all the linear organosiloxane used in step I). As such, a molar excess of the organosiloxane resin may be used. The amounts used may be determined by accounting for the moles of the organosiloxane resin used per mole of the linear organosiloxane.

[0117] As discussed herein, the reaction effected in step I) is a condensation reaction between the hydrolyzable groups of linear organosiloxane with the silanol groups on the organosiloxane resin. In some embodiments, a sufficient amount of silanol groups remains on the resin component of the formed resin-linear organosiloxane copolymer to further react in step II) of the present process. In some embodiments, at least 10 mole %, alternatively at least 20 mole %, or alternatively at least 30 mole % silanol remains on the trisiloxy units of the resin-linear organosiloxane copolymer as produced in step I) of the present process. In some embodiments, from about 10 mole % to about 60 mole %, *e.g.*, from about 20 mole % to about 60 mole %, or from about 30 mole % to about 60 mole %, remains on the trisiloxy units of the resin-linear organosiloxane copolymer as produced in step I) of the present process.

[0118] The reaction conditions for reacting the aforementioned (a) linear organosiloxane with the (b) organosiloxane resin are not limited. In some embodiments, reaction conditions are selected to effect a condensation type reaction between the a) linear organosiloxane and b) organosiloxane resin. Various non-limiting embodiments, and reaction conditions, are described in the Examples herein. In some embodiments, the (a) linear organosiloxane and the (b) organosiloxane resin are reacted at room temperature. In other embodiments, (a) and (b) are reacted at temperatures that exceed room temperature and that range up to about 50, 75, 100, or even up to 150°C. Alternatively, (a) and (b) can be reacted together at reflux of the solvent. In still other embodiments, (a) and (b) are reacted at temperatures that are below room temperature by 5, 10, or even more than 10°C. In still other embodiments (a) and (b) react for times of 1, 5, 10, 30, 60, 120, or 180 minutes, or even longer. In some embodiments, (a) and (b) are reacted under an inert atmosphere, such as nitrogen or a noble gas.

Alternatively, (a) and (b) may be reacted under an atmosphere that includes some water vapor and/or oxygen. Moreover, (a) and (b) may be reacted in any size vessel and using any equipment including mixers, vortexers, stirrers, heaters, etc. In other embodiments, (a) and (b) are reacted in one or more organic solvents which may be polar or non-polar. In some embodiments, aromatic solvents such as toluene, xylene, benzene, and the like are utilized. The amount of the organosiloxane resin dissolved in the organic solvent may vary, but may be an amount that minimizes the chain extension of the linear organosiloxane or premature condensation of the organosiloxane resin.

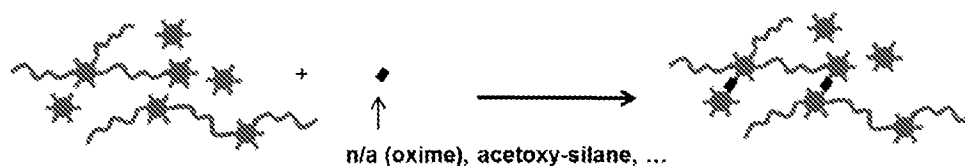
5 [0119] The order of addition of components a) and b) may vary. In some embodiments, the linear organosiloxane is added to a solution of the organosiloxane resin dissolved in the organic solvent. This order of addition may enhance the condensation of the hydrolyzable groups on the linear organosiloxane with the silanol groups on organosiloxane resin, while
15 minimizing chain extension of the linear organosiloxane or premature condensation of the organosiloxane resin. In other embodiments, the organosiloxane resin is added to a solution of the linear organosiloxane dissolved in the organic solvent.

[0120] The progress of the reaction in step I), and the formation of the resin-linear organosiloxane block copolymer, may be monitored by various analytical techniques, such as GPC, IR, or ^{29}Si NMR. In some embodiments, the reaction in step I) is allowed to continue until at least 95 weight percent (*e.g.*, at least 96%, at least 97%, at least 98%, at least 99% or 100%) of the linear organosiloxane used in step I) is incorporated into the resin-linear
25 organosiloxane block copolymer.

[0121] Step II) of the present process involves further reacting the resin-linear organosiloxane block copolymer from step I) to crosslink the trisiloxy units of the resin-linear organosiloxane block copolymer to increase the molecular weight of the resin-linear organosiloxane block copolymer by at least
30 50%, alternatively by at least 60%, alternatively by 70%, alternatively by at least 80%, alternatively by at least 90%, or alternatively by at least 100%. In some embodiments, step II) of the present process involves further reacting the resin-linear organosiloxane block copolymer from step I) to crosslink the trisiloxy units of the resin-linear organosiloxane block copolymer to increase the

molecular weight of the resin-linear organosiloxane block copolymer from about 50% to about 100%, *e.g.*, from about 60% to about 100%, from about 70% to about 100%, from about 80% to about 100 % or from about 90% to about 100%.

[0122] The reaction of step II) of the process may be represented
5 generally according to the following schematic:



[0123] It is believed that reaction of step II) crosslinks the trisiloxy blocks of the resin-linear organosiloxane block copolymer formed in step I), which will increase the average molecular weight of the block copolymer. It is
10 also possible that the crosslinking of the trisiloxy blocks provides the block copolymer with an aggregated concentration of trisiloxy blocks, which ultimately may help to form “nano-domains” in solid compositions of the block copolymer. In other words, this aggregated concentration of trisiloxy blocks may phase separate when the block copolymer is isolated in a solid form such as
15 a film or cured coating. The aggregated concentration of trisiloxy block within the block copolymer and subsequent formation of “nano-domains” in the solid compositions containing the block copolymer, may provide for enhanced optical clarity of these compositions as well as the other physical property benefits associated with these materials.

[0124] The crosslinking reaction in step II) may be accomplished via a variety of chemical mechanisms and/or moieties. For example, crosslinking of non-linear blocks within the block copolymer may result from the condensation of residual silanol groups present in the non-linear blocks of the copolymer. Crosslinking of the non-linear blocks within the block copolymer may also occur
25 between “free resin” components and the non-linear blocks. “Free resin” components may be present in the block copolymer compositions as a result of using an excess amount of an organosiloxane resin in step I) of the preparation of the block copolymer. The free resin component may crosslink with the non-linear blocks by condensation of the residual silanol groups present on the non-
30 linear blocks and on the free resin. The free resin may provide crosslinking by

reacting with lower molecular weight compounds added as crosslinkers, as described herein.

[0125] Step II) of the process may occur simultaneous upon formation of the resin-linear organosiloxane of step I), or involve a separate reaction in which conditions have been modified to effect the step II) reaction. The step II) reaction may occur in the same conditions as step I. In this situation, the step II) reaction proceeds as the resin-linear organosiloxane copolymer is formed. Alternatively, the reaction conditions used for step I) are extended to further the step II) reaction. Alternatively, the reaction conditions may be changed, or additional ingredients added to effect the step II) reaction.

[0126] In some embodiments, the step II) reaction conditions may depend on the selection of the hydrolyzable group (E) used in the starting linear organosiloxane. When (E) in the linear organosiloxane is an oxime group, it is possible for the step II) reaction to occur under the same reaction conditions as step I). That is, as the resin-linear organosiloxane copolymer is formed in step I), it will continue to react via condensation of the silanol groups present on the resin component to further increase the molecular weight of the resin-linear organosiloxane copolymer. Not wishing to be bound by any theory, it is possible that when (E) is an oximo group, the hydrolyzed oximo group (for example, methyl ethylketoxime) resulting from the reaction in step I) may act as a condensation catalyst for the step II) reaction. As such, the step II) reaction may proceed simultaneously under the same conditions for step I). In other words, as the resin-linear organosiloxane copolymer is formed in step I), it may further react under the same reaction conditions to further increase its molecular weight via a condensation reaction of the silanol groups present on the resin component of the copolymer. However, when (E) on the linear organosiloxane is an acetoxy group, the resulting hydrolyzed group (acetic acid), does not sufficiently catalyze the step II) reaction. Thus, in this situation the step II) reaction may be enhanced with a further component to effect condensation of the resin components of the resin-linear organosiloxane copolymer, as described herein.

[0127] In one embodiment of the present process, an organosilane having the formula $R^5_q SiX_{4-q}$ is added during step II), where R^5 is a C_1 to C_8

hydrocarbyl or a C₁ to C₈ halogen-substituted hydrocarbyl, X is a hydrolyzable group, and q is 0, 1, or 2. R⁵ is a C₁ to C₈ hydrocarbyl or a C₁ to C₈ halogen-substituted hydrocarbyl, or alternatively R⁵ is a C₁ to C₈ alkyl group, or alternatively a phenyl group, or alternatively R⁵ is methyl, ethyl, or a combination of methyl and ethyl. X is any hydrolyzable group, alternatively X may be E, as defined herein, a halogen atom, hydroxyl (OH), or an alkoxy group. In one embodiment, the organosilane is an alkyltriacetoxysilane, such as methyltriacetoxysilane, ethyltriacetoxysilane, or a combination of both. Commercially available representative alkyltriacetoxysilanes include ETS-900 (Dow Corning Corp., Midland, MI). Other suitable, non-limiting organosilanes useful in some embodiments include; methyl tris(methylethylketoxime)silane (MTO), methyl triacetoxysilane, ethyl triacetoxysilane, tetraacetoxysilane, tetraoximesilane, dimethyl diacetoxysilane, dimethyl dioximesilane, methyl tris(methylmethylketoxime)silane.

[0128] The amount of organosilane having the formula R⁵_qSiX_{4-q} when added during step II) varies and may be based on the amount of organosiloxane resin used in the process. The amount of silane used should provide a molar stoichiometry of 2 to 15 mole % of organosilane per moles of Si on the organosiloxane resin, *e.g.*, 2 to 10 mole % of organosilane/moles of Si on the organosiloxane resin; 5 to 15 mole % of organosilane/moles of Si on the organosiloxane resin; 2 to 5 mole % of organosilane/moles of Si on the organosiloxane resin; 10 to 15 mole % of organosilane/moles of Si on the organosiloxane resin; 5 to 10 mole % of organosilane/moles of Si on the organosiloxane resin; or 2 to 12 mole % of organosilane/moles of Si on the organosiloxane resin. Furthermore, the amount of the organosilane having the formula R⁵_qSiX_{4-q} added during step II) may be controlled, in some embodiments, to ensure a stoichiometry that does not consume all the silanol groups on the organosiloxane block copolymer. In one embodiment, the amount of the organosilane used in step II) may be selected to provide an organosiloxane block copolymer containing 0.5 to 35 mole percent of silanol groups [≡SiOH].

[0129] Step III) in the process is optional, and involves further processing the resin-linear organosiloxane block copolymer. Further processing

includes, but is not limited to further processing the resin-linear organosiloxane block copolymer to enhance its storage stability and/or optical clarity. Thus, as used herein, the phrase “further processing” refers broadly to any further reaction or treatment of the formed resin-linear organosiloxane copolymer to, among other things, enhance its storage stability, and/or optical clarity. The resin-linear organosiloxane copolymer as produced in step II) may, for example, still contain a significant amount of reactive “OZ” groups (that is $\equiv\text{SiOZ}$ groups, where Z is as defined herein), and/or X groups (where X is introduced into the block copolymer when the organosilane having the formula $\text{R}^5_q\text{SiX}_{4-q}$ is used in step II). The OZ groups present on the resin-linear organosiloxane copolymer at this stage may be silanol groups that were originally present on the resin component, or alternatively may result from the reaction of the organosilane having the formula $\text{R}^5_q\text{SiX}_{4-q}$ with silanol groups, when the organosilane is used in step II). It is possible that such “OZ” or X groups may further react during storage, limiting shelf stability, or diminishing reactivity of the resin-linear organosiloxane copolymer during end-use applications. Alternatively, further reaction of residual silanol groups may further enhance the formation of the resin domains and improve the optical clarity of the resin-linear organosiloxane copolymer. Thus, optional step III) may be performed to further react OZ or X present on the organosiloxane block copolymer produced in step II) to improve storage stability and/or optical clarity. The conditions for step III) may vary, depending on the selection of the linear and resin components, their amounts, and the endcapping compounds used.

[0130] In one embodiment of the process, step III) is performed by reacting the resin-linear organosiloxane from step II) with water and removing any small molecular compounds formed in the process, such as acetic acid. In some embodiments, the resin-linear organosiloxane copolymer may be produced from a linear organosiloxane where E is an acetoxymethyl group, and/or an acetoxymethyl silane is used in step II). Although not wishing to be bound by any theory, it is possible that in some embodiments, the resin-linear organosiloxane formed in step II) contains a significant quantity of hydrolyzable Si-O-C(O)CH_3 groups, which may limit the storage stability of the resin-linear organosiloxane copolymer. Thus, water may be added to the resin-linear organosiloxane

copolymer formed from step II), which may hydrolyze a substantial amount of Si-O-C(O)CH₃ groups to further crosslink the trisiloxy units, and eliminate acetic acid. The formed acetic acid, and any excess water, may be removed by known separation techniques. The amount of water added in some embodiments
5 may vary. In some embodiments, the amount of water added may be 10 weight %, or alternatively 5 weight % is added per total solids (as based on resin-linear organosiloxane copolymer in the reaction medium).

[0131] In one embodiment of the process, step III) is performed by reacting the resin-linear organosiloxane from step II) with an endcapping
10 compound, including endcapping compounds selected from an alcohol, oxime, or trialkylsiloxy compound. In some embodiments, the resin-linear organosiloxane copolymer may be produced from a linear organosiloxane where E is an oxime group. The endcapping compound may be a C₁-C₂₀ alcohol (*e.g.*, C₁-C₂₀ alcohol, C₁-C₁₂ alcohol, C₁-C₁₀ alcohol, C₁-C₆ alcohol or C₁-C₄
15 alcohol) such as methanol, ethanol, propanol, butanol, or others in the series. Alternatively, the alcohol is n-butanol. The endcapping compound may also be a trialkylsiloxy compound, such as trimethylmethoxysilane or trimethylethoxysilane. The amount of endcapping compound may vary. In some
20 embodiments, it is between 3 and 15 wt % (*e.g.*, 3 to 10 wt %, 5 to 15 wt %, 3 to 5 wt %, 10 to 15 wt %, 5 to 10 wt %, or 3 to 12 wt %) with respect to the resin linear organosiloxane block copolymer solids in the reaction medium.

[0132] Optional step III) in the process may, in addition to, or in place of “further processing,” involve contacting the resin-linear organosiloxane block copolymer from step II) with a stabilizer or a superbase.

25 [0133] Step IV) of the present process is optional, and involves removing the organic solvent used in the reactions of steps I) and II). The organic solvent may be removed by any known techniques. In some embodiments, the organic solvent may be removed by heating the resin-linear organosiloxane copolymer compositions at elevated temperature, either at atmospheric conditions or under
30 reduced pressures. In some embodiments, not all of the solvent is removed. In some embodiments, at least 20%, at least 30%, at least 40%, or at least 50% of the solvent is removed, *e.g.*, at least 60%, at least 70%, at least 75%, at least 80% or at least 90% of the solvent is removed. In some embodiments, less than 20%

of the solvent is removed, *e.g.*, less than 15%, less than 10%, less than 5% or 0% of the solvent is removed. In other embodiments, from about 20% to about 100% of the solvent is removed, *e.g.*, from about 30% to about 90%, from about 20% to about 80%, from about 30 to about 60%, from about 50 to about 60%, from
5 about 70 to about 80% or from about 50% to about 90% of the solvent is removed.

[0134] Some of the embodiments of the present invention relate to optical assemblies and articles comprising the compositions described herein such as those described in PCT/US2012/071011, filed December 20, 2012;
10 PCT/US2013/021707, filed January 16, 2013; and PCT/US2013/025126, filed February 7, 2013, all of which are incorporated by reference as if fully set forth herein. Accordingly, some embodiments of the present invention relate to an LED encapsulant comprising an organosiloxane block copolymer described herein.

15 [0135] 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.

[0136] Values expressed in a range format should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the
20 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 were 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-
25 ranges (*e.g.*, 0.1% to 0.5%, 1.1% to 2.2%, 3.3% to 4.4%) within the indicated range.

[0137] Embodiments of the invention described and claimed herein are not to be limited in scope by the specific embodiments herein disclosed, since these embodiments are intended as illustration of several aspects of the
30 disclosure. Any equivalent embodiments are intended to be within the scope of this disclosure. Indeed, various modifications of the embodiments in addition to those shown and described herein will become apparent to those skilled in the art from the foregoing description. Such modifications are also intended to fall within the scope of the appended claims.

[0138] The Abstract is provided to allow the reader to quickly ascertain the nature of the technical disclosure. It is submitted with the understanding that it will not be used to interpret or limit the scope or meaning of the claims.

5

EXAMPLES

[0139] The following examples are included to demonstrate specific embodiments of the invention. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention. All percentages are in wt %. All measurements were conducted at 23°C unless indicated otherwise.

Characterization Techniques

²⁹Si and ¹³C NMR spectrometry

[0140] NMR samples of resin linear products were prepared, *e.g.*, by weighing ~3 grams of solvent free resin linear (prepared by drying sample overnight at room temperature), 1 g of CDCl₃, and 4 grams of 0.04 M Cr(acac)₃ solution in CDCl₃ into a vial and mixing thoroughly. Samples were then transferred into a silicon-free NMR tube. Spectra were acquired using a Varian Mercury 400 MHz NMR. NMR samples of other materials such as 217 Flake and silanol terminated PDMS were prepared by diluting 4 g of sample into 4 grams of 0.04 M Cr(acac)₃ solution in CDCl₃.

[0141] ¹³C NMR experiments were performed, *e.g.*, by placing samples into 16 mm glass NMR tubes. A 5 mm NMR tube was placed inside the 16 mm tube and filled with lock solvent. ¹³C DEPT NMR was acquired in 12 or 20 minute signal averaging blocks. Data was acquired on a Varian Inova NMR spectrometer with a 1 H operational frequency of 400 MHz.

[0142] Silanol content of resin linear products was calculated from the integration values of the T(Ph,OZ) and T(Ph,OZ₂) regions in the ²⁹Si NMR spectrum. T(Alkyl) groups were considered fully condensed (assumption) and subtracted from the T(Ph,OZ) region. The T(Alkyl) content was calculated by multiplying the integration value of D(Me₂) from ²⁹Si NMR by the fraction (moles Si of coupling agent/moles Si of PDMS used in the synthesis formulation). Isopropoxy from 217 Flake was not subtracted out of the OZ

values due to its low concentration. Therefore it was assumed that total OZ = total OH.

GPC analysis

[0143] Samples were prepared, *e.g.*, in certified THF at 0.5% w/v
5 concentration, filtered with a 0.45 μ m PTFE syringe filter, and analyzed against polystyrene standards. The relative calibration (3rd order fit) used for molecular weight determination was based on 16 polystyrene standards ranging in molecular weights from 580 to 2,320,000 Daltons. The chromatographic equipment consisted of a Waters 2695 Separations Module equipped with a
10 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. The separation was performed using certified grade THF programmed to flow at 1.0 mL/min., injection volume was set at 100 μ L and columns and detector were heated to
15 35°C. Data collection was 25 minutes and processing was performed using Atlas/Cirrus software.

[0144] To determine free resin content, the free resin peak at lower molecular weight was integrated to get the area percent.

Rheology analysis

20 [0145] A commercially available rheometer from TA Instruments (ARES-RDA with 2KSTD standard flexural pivot spring transducer, TA Instruments, New Castle, DE 19720) with forced convection oven was used to measure the storage modulus (G'), loss modulus (G'') and tan delta as a function of temperature. Test specimens (typically 8 mm wide, 1 mm thick) were loaded
25 in between parallel plates and measured using small strain oscillatory rheology while ramping the temperature in a range from 25°C to 300°C at 2°C/min (frequency 1 Hz).

[0146] To characterize the copolymers, the flow onset was calculated as the inflection temperature in the G' drop (labeled FLOW), the viscosity at 120°C
30 will be reported as a measure for melt processability and the cure onset was calculated as the inflection temperature in the G' rise (labeled CURE).

Optical Clarity

[0147] Optical clarity was evaluated as the % transmission of light at wavelengths from about 350-1000 nanometers, measured through 1 mm thick

samples of cast sheets of the present compositions. Samples having a % transmittance of at least 95% were considered to be optically clear.

Example 1 (reference): Preparation of an OH-terminated trifluoropropylmethyl siloxane with a dp of 99

5 [0148] A 500 L 4-neck round bottom flask was loaded with PI fluid (Dow Corning 4-2830; trifluoropropylmethyl siloxane, hydroxy-terminated having a viscosity of 100 cSt at 23°C) (200.0 g). The flask was equipped with a thermometer, Teflon stir paddle, and a Dean Stark apparatus attached to a water-cooled condenser. A nitrogen blanket was applied. The PI fluid was heated to
10 80°C, at which point 0.3 g of a 10% KOH solution in water was added (approx.. 150 ppm KOH). The reaction mixture was heated at 80°C for 2 hours, 20 minutes. Heating was stopped and the reaction mixture was then treated with 10% acetic acid in toluene solution (0.64 g; 1 mole KOH: 3 moles acetic acid). The reaction mixture was heated at room temperature for several hours. During
15 this time the reaction mixture was clear. To the reaction mixture were added 43.7 g of 4-chlorobenzyltrifluoride. The reaction mixture remained clear. The reaction mixture was stirred overnight at room temperature. The next day some precipitate was noticeable. The reaction mixture was treated with Darco G-60 carbon black and stirred overnight. The reaction mixture was pressure filtered
20 through a 0.45 µm filter. The filtrate was clear and colorless. The polymer was stripped on a thin film evaporator at 235°C, stir speed setting of 40, ~0.3 mm Hg, for 1 hour 40 min. Isolated yield: 131.1 g. The polymer was dissolved in 4-chlorobenzotrifluoride at 65 wt % polymer. The solution had a light haze, so it was filtered through a 0.22 µm filter. The resulting product had a dp of 99 with
25 an OH content of 2.02 mole %.

Example 2 (reference): Preparation of $\text{DMe}_{2.0}\text{TMe}_{0.10}\text{TPh}_{0.80}\text{TMe}_{0.10}$ resin for use in the synthesis of low RI resin linear compositions

[0149] A 2 L 3neck round bottom flask was loaded with deionized water (643.7 g) and 4-methyl pentanone (MIBK; 346.8 g). The flask was equipped
30 with a teflon stir paddle, thermometer, and a water-cooled condenser. Cooled water/MIBK down to 10°C using an ice-water bath and then added a premixed solution of phenyltrichlorosilane (30.71 g, 0.145 moles); methyltrichlorosilane (173.64 g, 1.162 moles); dimethyldichlorosilane (18.74 g, 0.145 moles); and MIBK (127.8 g), slowly over about 13 minutes. An exotherm was observed from

10°C up to 48°C. The reaction mixture was allowed to stir for 5 minutes with ice-water bath removed. The temperature dropped to 44°C during this time. The aqueous layer was removed in a 2 L separatory funnel. The organic layer was washed three times at room temperature using the 2 L separatory funnel with
5 58.5 g of DI water for each wash. The following process was repeated several times until the final wash water had a pH of 4.0. The organic phase was transferred to a 1 L 3-neck flask and DI water (58.5 g; 58.5g is 10% of [theoretical yield (110.8 g) + MIBK (474.6 g)]) was added. The reaction mixture was heated at 60°C for 15 minutes. The aqueous phase was then removed.
10 Residual water was removed by heating to reflux via azeotropic distillation. Pressure filtered through a 1.2 µm filter the following day.

[0150] The resin was stripped to dryness using a rotavapor using an oil bath temperature of 120°C for 30 minutes and then poured out resin in a 150°C oven in 15 minutes. Resin was a low viscosity liquid at 120°C and was clear.
15 When the material was removed from the oven it was smoking; a possible indication of volatile oligomers. The product was a clear, “crunchy” solid at room temperature. The isolated yield was 108.5 g.

Example 3: Preparation of a resin-linear having 45 wt % methyl-T resin and 55 wt % 99 dp TFP siloxane

20 [0151] A 500 mL 4-neck round bottom flask was loaded with 4-chlorobenzotrifluoride (CBTF; 120.38 g) and the methyl-T resin from Example 2 (45.0 g, 0.582 moles Si). The flask was equipped with a thermometer, teflon stir paddle, and a Dean Stark apparatus attached to a water-cooled condenser. A nitrogen blanket was applied; the Dean Stark apparatus was prefilled with
25 CBTF; and a heating mantle was used for heating. The reaction mixture was heated at reflux (141°C) for 30 minutes. The reaction mixture was cooled to 138°C (pot temperature). A solution of silanol terminated TFP siloxane (Example 1; 84.62 g solution = 55.00 g siloxane, 0.352 moles Si) was capped with 50/50 by weight methyl triacetoxy silane (MTA)/ethyl triacetoxy silane
30 (ETA) (1.70 g, 0.00746 moles Si). The capped silanol terminated TFP siloxane was prepared in a glove box (the day before) under nitrogen by adding 50/50 MTA/ETA to the siloxane and mixing at room temperature for 2 hours. Reaction was verified complete by IR analysis.

[0152] A solution of the capped silanol terminated TFP siloxane was added to the resin solution quickly at 138°C. The reaction mixture turned very hazy. To this reaction mixture were added 83.3 g of CBTF to reduce the solids content to approximately 30% solids. The reaction mixture was still hazy.

- 5 Another 66.7 g of CBTF were added to further reduce the solids content to about 25% solids. Reaction mixture now only had a light haze.

- [0153] The reaction mixture was heated at reflux for a total of 5 hours. After 2 hours no water was observed on the bottom of the Dean Stark. The solvent had a higher density than water and it was observed that there was some
10 water on the top. The water was removed. After a total of 4 hours, more water was removed from on top, but the amount was less than before. The solids content was increased by distilling off about 150 g of solvent. The reaction mixture was cooled to room temperature. The solution was highly viscous and hazy. CBTF (36.0 g) was added to reduce the viscosity of the solution.

Claims

1. An organosiloxane block copolymer comprising:
 40 to 90 mole percent disiloxy units of the formula $[R^1_2SiO_{2/2}]$,
 10 to 60 mole percent trisiloxy units of the formula $[R^2SiO_{3/2}]$,
 0.5 to 35 mole percent silanol groups $[≡SiOH]$;
 wherein:
 each R^1 , at each occurrence, is independently a C_1 to C_{30}
 hydrocarbyl or an R^f group,
 each R^2 , at each occurrence, is independently a C_1 to C_{20}
 hydrocarbyl or an R^f group,
 5 wherein R^f represents a fluorine-containing group, with the
 proviso that there is at least one R^f group in the organosiloxane
 block copolymer;
 wherein:
 the disiloxy units $[R^1_2SiO_{2/2}]$ are arranged in linear blocks
 having an average of from 10 to 400 disiloxy units $[R^1_2SiO_{2/2}]$
 per linear block,
 the trisiloxy units $[R^2SiO_{3/2}]$ are arranged in non-linear blocks
 having a molecular weight of at least 500 g/mole, and at least
 30% of the non-linear blocks are crosslinked with each other,
 each linear block is linked to at least one non-linear block; and
 the organosiloxane block copolymer has a weight average
 molecular weight (M_w) of at least 20,000 g/mole.
 .
2. The organosiloxane block copolymer of claim 1, wherein R^1 comprises
 an R^f group.
3. The organosiloxane block copolymer of claim 1 or 2, wherein R^2
 comprises an R^f group.

4. The organosiloxane block copolymer of any preceding claim, wherein the R^f group comprises –CH₂CH₂CF₃.
5. The organosiloxane block copolymer of any preceding claim, wherein R² is phenyl.
6. The organosiloxane block copolymer of any preceding claim, wherein R¹ is methyl or phenyl.
7. The organosiloxane block copolymer of any preceding claim, wherein the disiloxy units have the formula [(CH₃)(CF₃CH₂CH₂)SiO_{2/2}].
8. A curable composition comprising an organosiloxane block copolymer of any preceding claim.
9. A solid film composition comprising the curable composition of claim 8.
10. The cured product of the composition of claim 8 or 9.
11. The solid film composition of claim 9, wherein the solid composition has an optical transmittance of at least 95%.
12. The solid film composition of claim 9, wherein the solid composition has a low refractive index.
13. An LED encapsulant comprising an organosiloxane block copolymer of any preceding claim.
14. A process for preparing an organosiloxane block copolymer of claim 1, comprising:
 - I) reacting
 - a) a linear organosiloxane having the formula:



- wherein each R^1 , at each occurrence, is independently a C_1 to C_{30} hydrocarbyl or an R^f group,
 n is 10 to 400, q is 0, 1, or 2,
 E is a hydrolyzable group containing at least one carbon atom,
 and
 b) an organosiloxane resin comprising at least 60 mol % of $[R^2SiO_{3/2}]$ siloxyunits in its formula, wherein each R^2 , at each occurrence, is independently a C_1 to C_{20} hydrocarbyl or an R^f group;
 in c) an organic solvent;
 to form a resin-linear organosiloxane block copolymer;
 wherein the amounts of a) and b) used in step I) are selected to provide the resin-linear organosiloxane block copolymer with 40 to 90 mole % of disiloxy units $[R^1_2SiO_{2/2}]$ and 10 to 60 mole % of trisiloxy units $[R^2SiO_{3/2}]$, and
 wherein at least 95 weight percent of the linear organosiloxane added in step I) is incorporated into the resin-linear organosiloxane block copolymer;
 II) reacting the resin-linear organosiloxane block copolymer from step I) to crosslink the trisiloxy units of the resin-linear organosiloxane block copolymer sufficiently to increase the weight average molecular weight (M_w) of the resin-linear organosiloxane block copolymer by at least 50%;
 III) optionally, further processing the resin-linear organosiloxane block copolymer; and
 IV) optionally, removing the organic solvent.
15. The process of claim 14, wherein the further processing enhances storage stability and/or optical clarity
16. The process of claim 14, wherein R^1 comprises an R^f group.
17. The process of claim 14 or 16, wherein R^2 comprises an R^f group.

18. The process of claims 14-17, wherein the R^f group comprises $-\text{CH}_2\text{CH}_2\text{CF}_3$.
19. The process of claims 14-18, wherein R^2 is phenyl.
20. The process of claims 14-19, wherein R^1 is methyl, phenyl or combinations thereof.
21. The process of claims 14-20, wherein the linear organosiloxane has the formula $(\text{CH}_3)_q(\text{E})_{(3-q)}\text{SiO}[(\text{CH}_3)(\text{CF}_3\text{CH}_2\text{CH}_2)\text{SiO}_{2/2}]_n\text{Si}(\text{E})_{(3-q)}(\text{CH}_3)_q$.
22. The process of claims 14-21, wherein E is $\text{H}_3\text{CC}(=\text{O})\text{O}-$ and q is 1.
23. An organosiloxane block copolymer prepared by the process of claims 14-22.
24. The organopolysiloxane block copolymer of claim 23, wherein the organopolysiloxane block copolymer is the reaction product of step II).
- 5 25. A composition comprising the organopolysiloxane block copolymer of claim 23.
26. The composition of claim 25, which is curable.
- 10 27. The composition of claim 25, which is solid.
28. The cured product of the composition of claim 25-27.
29. A solid film composition comprising the composition of claims 24-26.
30. The solid film composition of claim 29, wherein the solid composition has an optical transmittance of at least 95%.
31. An LED encapsulant comprising the compositions of claims 25-30.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2013/027904

A. CLASSIFICATION OF SUBJECT MATTER INV. C08G77/44 C08L83/10 H01L23/29 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) C08G C08L H01L		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/050852 A1 (KANAMORI TAROU [JP] ET AL) 26 February 2009 (2009-02-26) paragraphs [0047] - [0053]; claims 1,8,10; example 1 -----	1-31
X	JP 2007 277505 A (JSR CORP) 25 October 2007 (2007-10-25) abstract -----	1-31
X	JP 2007 277072 A (JSR CORP) 25 October 2007 (2007-10-25) abstract -----	1-31
X	JP 2006 348284 A (JSR CORP) 28 December 2006 (2006-12-28) abstract -----	1-31
<div style="display: flex; justify-content: space-between; align-items: center;"> <div style="display: flex; align-items: center;"> <input style="width: 20px; height: 20px; margin-right: 5px;" type="checkbox"/> Further documents are listed in the continuation of Box C. </div> <div style="display: flex; align-items: center;"> <input checked="" style="width: 20px; height: 20px; margin-right: 5px;" type="checkbox"/> See patent family annex. </div> </div>		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p> </div> </div>		
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">4 July 2013</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">16/07/2013</div>
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">Buestrich, Ralf</div>

INTERNATIONAL SEARCH REPORT

Information on patent family members

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