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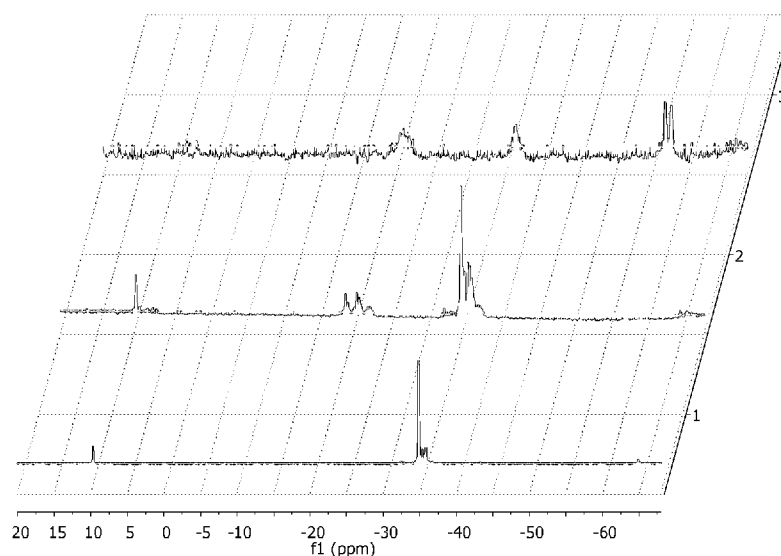
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— as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))

[Continued on next page]

(54) Title: HYDROSILATION OF VINYL-TERMINATED MACROMONOMERS

Figure 1



(57) Abstract: This invention relates to the reaction product(s) of a polyalkylhydrosiloxane and a vinyl terminated macromonomer (VTM).



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HYDROSILATION OF VINYL-TERMINATED MACROMONOMERS

FIELD OF THE INVENTION

[0001] This invention relates to functionalization of vinyl terminated polyolefins by hydrosilation (also known as hydrosilylation).

BACKGROUND OF THE INVENTION

[0002] Methods for the production of polyolefins with end-functionalized groups are typically multi-step processes that often create unwanted by-products and waste of reactants and energy. For reviews of methods to form end-functionalized polyolefins, see: (a) S. B. Amin and T. J. Marks, *Angewandte Chemie, International Edition*, **2008**, 47, pp. 2006-2025; (b) T. C. Chung *Prog. Polym. Sci.* **2002**, 27, pp. 39-85; and (c) R. G. Lopez, F. D'Agosto, C. Boisson *Prog. Polym. Sci.* **2007**, 32, pp. 419-454. A process with a reduced number of steps, even one step, would be desirable.

[0003] U.S. Patent No. 4,110,377 discloses secondary aliphatic amines alkylated with alpha-olefins, such as ethylene, propylene, hexene, and undecene. Likewise, several literature references disclose hydroaminoalkylation of olefins using various catalysts (see J. Am. Chem. Soc. 2008, 130, pp. 14940-14941; J. Am. Chem. Soc. 2007, 129, pp. 6690-6691; *Angewandte Chemie, International Edition*, 2009, 48, pp. 8361-8365; *Angewandte Chemie, International Edition*, 2009, 48, pp. 4892-4894; *Yuki Gosei Kagaku Kyokaiishi* (2009), 67(8), pp. 843-844; *Angewandte Chemie, International Edition* (2009), 48(6), pp. 1153-1156; *Tetrahedron Letters* (2003), 44(8), pp. 1679-1683; and *Synthesis* (1980), (4), pp. 305-306). Corey discloses low molecular weight olefins treated with hydrosilanes in the presence of Cp_2MgCl_2 and $n\text{-BuLi}$ to prepare low molecular weight hydrosilylated products.

[0004] None of the above references, however, disclose functionalization of polyolefins, particularly polyolefins having M_n 's over 500 g/mol having large amounts of vinyl terminal groups.

[0005] U.S. Patent No. 8,399,725 discloses certain vinyl terminated polymers that are functionalized, optionally, for use in lubricant applications.

[0006] U.S. Patent No. 8,372,930 discloses certain vinyl terminated polymers that are functionalized in U.S. Patent No. 8,399,725.

[0007] U.S. Patent No. 8,283,419 discloses a process to functionalize propylene homo- or copolymer comprising contacting an alkene metathesis catalyst with a heteroatom containing alkene and a propylene homo- or copolymer having terminal unsaturation.

[0008] Additional references of interest include: WO9706201(A1), Journal of Applied

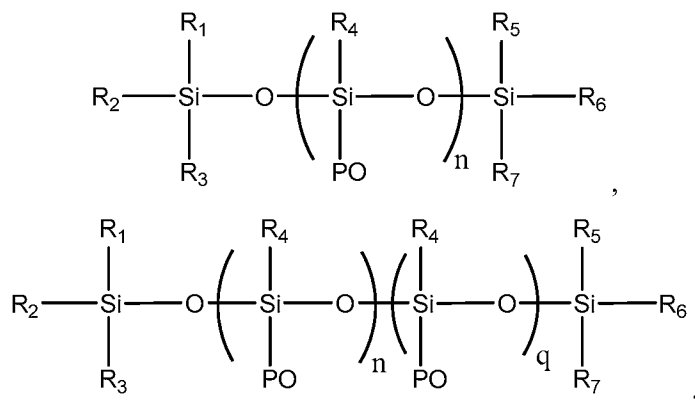
Polymer Science, Vol. 114, pp. 892–900 (2009), G. Out; A. Turetskii; M. Moller; D. Oelfin, Macromolecules, (1994), 27, p. 3310, J. Applied Polymer Science, 104, p. 1176 (2007), Japanese patent number JP 2010070673, U.S. Patent Nos. 6,111,027; 7,183,359; 6,100,224; and 5,616,153.

[0009] Thus, there is a need to develop a means to provide functionalized polyolefins (particularly end-functionalized) by efficient reactions, particularly reactions with good conversion, preferably under mild reaction conditions with a minimal number of steps, preferably one or two steps. The instant invention's use of hydrosilation to introduce silyl groups and/or carbon functionality is both a commercially economical and an "atom-economical" route to end-functionalized polyolefins.

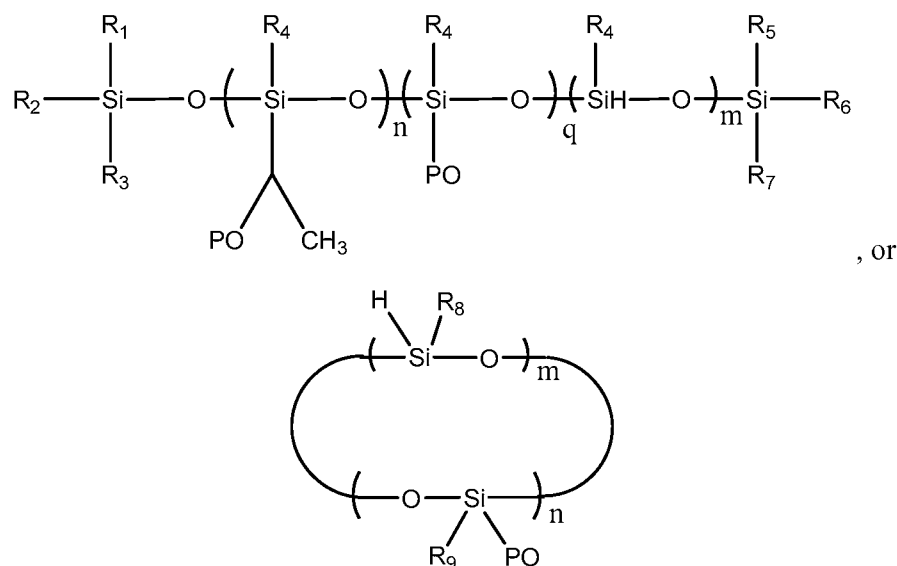
[0010] End-functionalized polyolefins that feature a chemically reactive or polar end group are of interest for use in a broad range of applications as compatibilizers, tie-layer modifiers, surfactants, adhesives, and surface modifiers. Herein is described a novel method for their production by the reaction of vinyl-terminated polyolefins with hydrosilating agents. This method is useful for a range of vinyl terminated polyolefins, including isotactic polypropylene (iPP), atactic polypropylene (aPP), ethylene propylene copolymer (EP), polyethylene (PE), and particularly propylene copolymers with larger alpha-olefin comonomers such as butene, hexene octene, etc. The vinyl terminated polyolefin useful herein can be linear or branched.

SUMMARY OF THE INVENTION

[0011] This invention relates to the reaction product(s) of a polyalkylhydrosiloxane and a vinyl terminated macromonomer (VTM), desirably resulting in a polyolefin composition comprising one or more of the following formulae:







wherein

each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , and R_9 is, independently, an alkyl group;

each PO is, independently, the residual portion of a vinyl terminated macromonomer (VTM) having had a terminal unsaturated carbon of an allylic chain and a vinyl carbon adjacent to the terminal unsaturated carbon;

each m is 0 to 1000;

each n is 1 to 1000;

each q is 1 to 1000; and

m , n , and q can alternate or m , n , and q , can be randomly distributed throughout the polyolefin.

[0012] Alkylated PHMS (polymethylhydrosiloxane) backbones have been synthesized herein using vinyl terminated macromonomers (VTM) and a platinum hydrosilation catalyst. The degree of alkylation is dependent on reaction conditions and VTM composition. Further functionalization is possible by reaction with R-OH molecules including MeOH, H₂O and (NH₂)C_x-OH or self-condensation (dehydrocoupling) to give highly branched products, where R is an alkyl group and x is 2 to 12. All transformations can be done in a one-pot synthesis.

[0013] The latter condensation reactions can be mostly avoided and new materials made by reaction of the VTM alkylated PHMS (such as aPP-alkylated PHMS) with other reactive molecules such as MeOH to yield material with high levels of MeO-side chains. These would be reactive for grafting with inorganic substrates containing -OH moieties such as SiO₂.

BRIEF DESCRIPTION OF THE FIGURES

[0014] Figure 1 is a series of NMR from Example 9: Spectrum 1 is PHMS; Spectrum 2 is VTM + PMHS; and Spectrum 3 is final methanolysis product of 2.

[0015] Figure 2 is a ^1H NMR of PMHS X, C_6D_6 , RT, 500 MHz.

[0016] Figure 3 is a ^1H NMR of Example 3 Product, C_6D_6 , RT, 500 MHz.

[0017] Figure 4 is a ^1H NMR of Example 4 Product, C_6D_6 , 500 MHz.

[0018] Figure 5 provides the complex viscosity as a function of temperature for polymer Example 6 obtained by dynamic melt shear rheology using a frequency of 1 rad/s and a strain of 1%.

[0019] Figure 6 provides dynamic moduli as a function of temperature for polymer Example 6 obtained by dynamic melt shear rheology using a frequency of 1 rad/s and a strain of 1%.

[0020] Figure 7 provides tan delta as a function of temperature for polymer Example 6 obtained by dynamic melt shear rheology using a frequency of 1 rad/s and a strain of 1%.

[0021] Figure 8 provides complex viscosity as a function of frequency for polymer Example 10 obtained by dynamic melt shear rheology using strains of 1% and 10%. Shear thickening observed at $T > 60^\circ\text{C}$.

[0022] Figure 9 provides complex viscosity as a function of frequency for polymer 12 obtained by dynamic melt shear rheology using strains of 1% and 10%. Shear thickening observed at $T > 150^\circ\text{C}$.

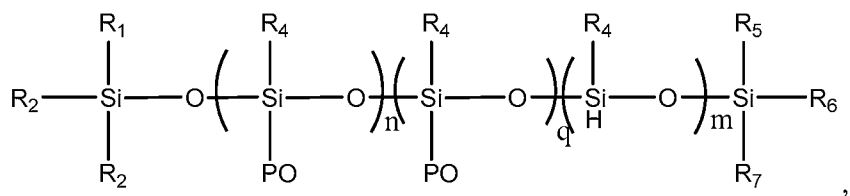
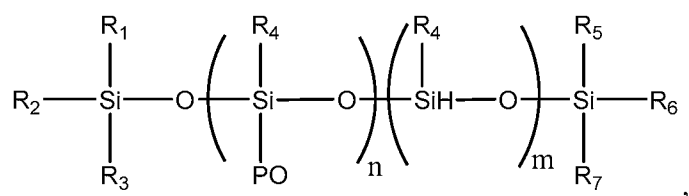
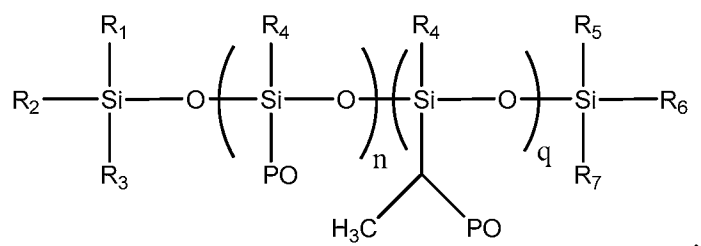
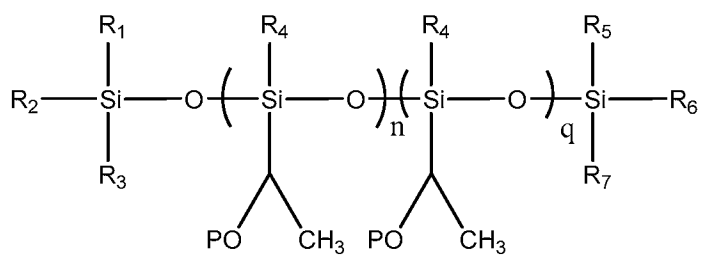
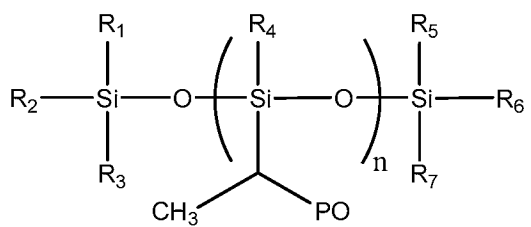
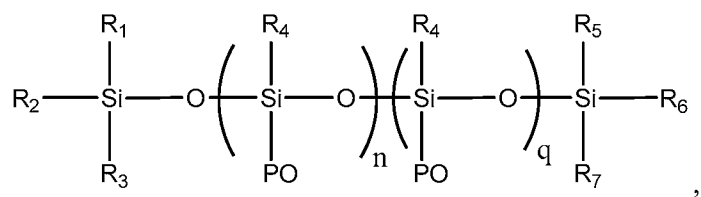
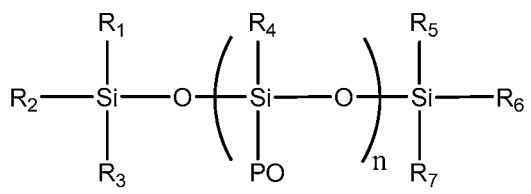
[0023] Figure 10 provides complex viscosity as a function of frequency for polymer 16 obtained by dynamic melt shear rheology using strains of 1% and 10%. Shear thickening observed at $T \geq 25^\circ\text{C}$.

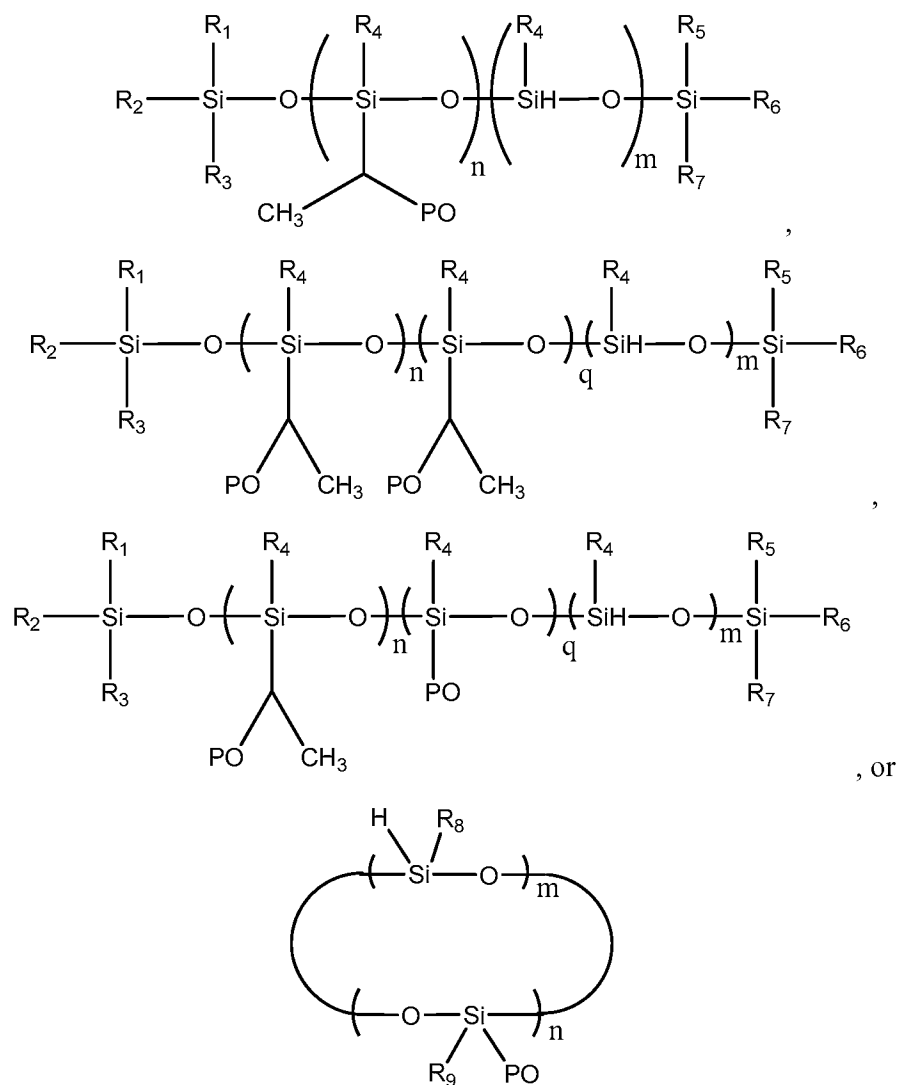
[0024] Figure 11 provides complex viscosity as a function of frequency for polymer 20 obtained by dynamic melt shear rheology using strains of 1% and 10%. Shear thickening observed at $T > 80^\circ\text{C}$.

DETAILED DESCRIPTION OF THE INVENTION

[0025] This invention relates to the reaction product(s) of a polyalkylhydrosiloxane and a vinyl terminated macromonomer (VTM), resulting in the inventive polyolefin composition.

[0026] In one aspect, the inventive polyolefin composition comprising one or more of the following formulae:





wherein

each R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, and R₉ is, independently, an alkyl group;

each PO is, independently, the residual portion of a vinyl terminated macromonomer (VTM) having had a terminal unsaturated carbon of an allylic chain and a vinyl carbon adjacent to the terminal unsaturated carbon;

each m is 0 to 1000;

each n is 1 to 1000;

each q is 1 to 1000; and

m, n, and q can alternate or m, n, and q, can be randomly distributed throughout the polyolefin. Definitions not apparent to one of ordinary skill in the art are also set forth in "HYDROSILATION OF VINYL-TERMINATED MACROMONOMERS", U.S.S.N. _____, filed concurrently herewith.

[0027] Preferably, $n+q$ is at least 5, preferably at least 6, preferably at least 8, preferably at least 10, preferably $n+q$ is from 5 to 40, preferably from 6 to 30, preferably from 16 to 20, and PO has an M_n of from 160 to 30,000 g/mol, preferably from 180 to less than the entanglement molecular weight of PO, preferably from 200 to 20,000 g/mol, preferably from 300 to 10,000 g/mol, preferably from 1,000 to 5,000 g/mol.

[0028] Preferably, $n+q$ is 1, 2, 3, or 4, preferably 3 or 4, and PO has an M_n of from 160 to 40,000 g/mol, preferably from 180 to less than the entanglement molecular weight of PO, preferably from 200 to 30,000 g/mol, preferably from 300 to 20,000 g/mol, preferably from 1,000 to 15,000 g/mol, preferably from 2,000 to 10,000 g/mol.

[0029] Most preferably, the composition described herein shows shear thickening. Shear thickening is defined to be an increase in viscosity at increasing shear rates at the same temperature. Examples of shear thickening behavior are provided in Figures 8, 9, 10 and 11 for polymers, respectively. For information on Shear thickening please see Wagner, N. J. and Brady J. F., Physics Today, October 2009, 27, et seq.; Lee Y. S. and Wagner N. J., Rheol. Acta, 42, p. 199 (2003); and Lee Y. S., Wetzel E. D. and Wagner N. J., J. Matt. Sci., 38, p. 2825 (2003). Preferably, shear thickening is represented by a difference in viscosity at 10 rad/s and 100 rad/s at the same temperature. The difference is denoted as "Delta Viscosity" (Delta Viscosity = $\log \text{Viscosity (at Frequency 2)} - \log \text{Viscosity (at Frequency 1)}$), where Frequency 2 > Frequency 1) and represents the shear response of the fluid. Negative Delta Viscosity values represent shear thinning, zero value represents shear independence and positive values represent shear thickening. Preferably, the Delta Viscosity at 190°C is at least 0.5 units, preferably at least 1 unit, preferably at least 1.5 units, where shear is measured according using the procedure described below for dynamic shear melt rheology. Preferably, the Delta Viscosity at 180°C is at least 0.4 units, preferably at least 0.8 units, preferably at least 1.2 units, where shear is measured according using the procedure described below for dynamic shear melt rheology. Preferably, the Delta Viscosity at 170°C is at least 0.3 units, preferably at least 0.6 units, preferably at least 0.9 units, where shear is measured according using the procedure described below for dynamic shear melt rheology. Preferably, the Delta Viscosity at 160°C is at least 0.2 units, preferably at least 0.4 units, preferably at least 0.6 units, where shear is measured according using the procedure described below for dynamic shear melt rheology.

[0030] Dynamic shear melt rheological data is measured with MCR 501 rheometer (Anton-Paar) using serrated parallel plates (diameter=25 mm) at several temperatures ranging

from 25°C to 190°C. The samples are heated at 100°C in a vacuum oven for 10 min to increase their fluidity and facilitate their loading into the rheometer. The measurements are made over the angular frequency (ω) ranged from 0.01-100 rad/s. Depending on the molecular weight and temperature, strains of 1% and 10% were used and linearity of the response was verified. A nitrogen stream was circulated through the sample oven to minimize chain extension or cross-linking during the experiments. No stabilizers were added to the samples. A sinusoidal shear strain is applied to the material if the strain amplitude is sufficiently small and the material behaves linearly. It can be shown that the resulting steady-state stress will also oscillate sinusoidally at the same frequency but will be shifted by a phase angle δ with respect to the strain wave. The stress leads the strain by δ . For purely elastic materials $\delta=0^\circ$ (stress is in phase with strain) and for purely viscous materials, $\delta=90^\circ$ (stress leads the strain by 90° although the stress is in phase with the strain rate). For viscoelastic materials $0^\circ < \delta < 90^\circ$.

[0031] Dynamic shear melt rheological data from the different temperature tests were used to construct master curves of the elastic and viscous moduli (G' and G'' respectively), using the time-temperature superposition (tTs) method. The tTs method relies on the Boltzman superposition principle, which assumes that all relaxation mechanisms and the stress magnitude at all frequencies have the same temperature-dependence. The tTs method consist on subjecting the dynamic moduli data measured at a temperature, T , to a horizontal shift (i.e., in the frequency axis) and to a vertical shift (i.e., in the moduli axis), until the data overlap with the corresponding data measured at a reference temperature, T_r . If such overlapping is achievable, the material is said to be thermo-rheologically simple. Hence, the master curves of the dynamic moduli, are obtained by plotting the reduced moduli, $b_T G'$ and $b_T G''$, versus the reduced frequency, $a_T \omega$. The horizontal and vertical shift factors, a_T and b_T , respectively, are temperature dependent, although b_T dependence is typically weak for entangled polymers. For information on time-temperature superposition please see Dealy J. and Plazek D., Rheol. Bull 78 p. 16 (2009).

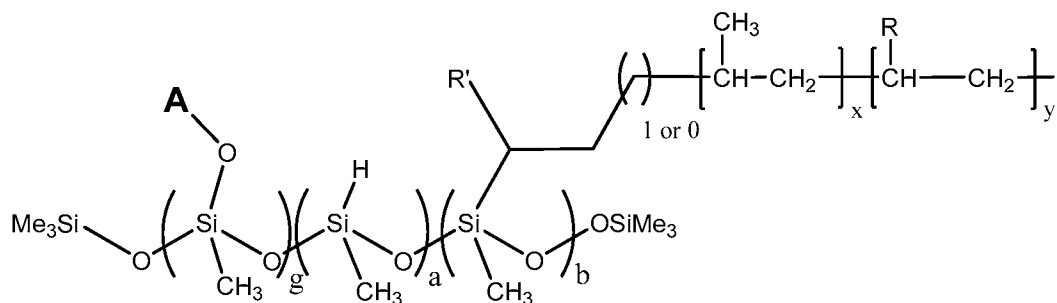
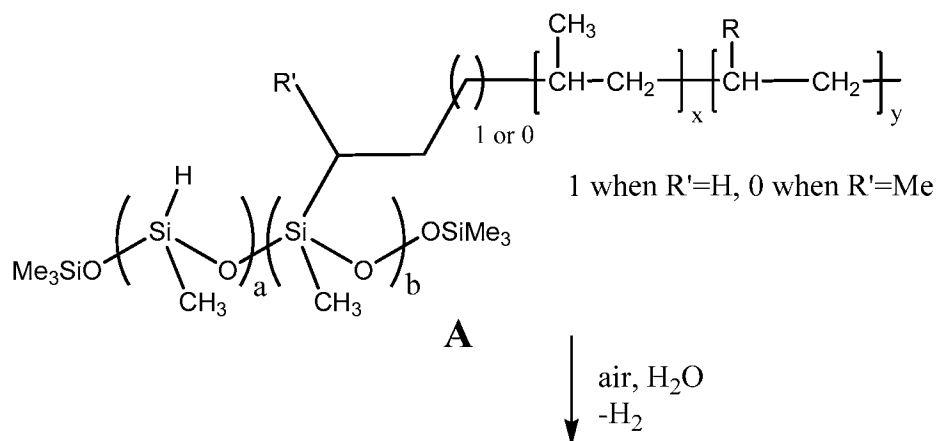
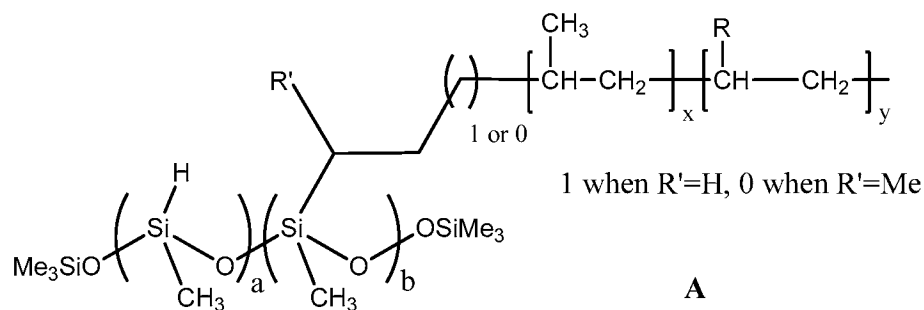
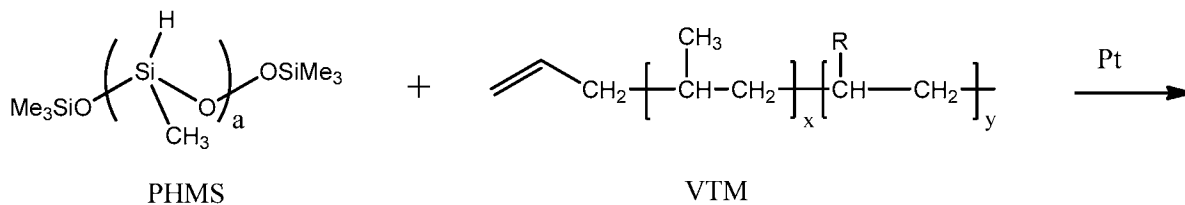
[0032] Preferably, the composition produced herein (particularly where n is 3 and M_n is 3000) shows a tan delta (G''/G') of 1 or less at 50°C and at least 30 or more at 80°C. Tan delta is determined by dynamic shear melt rheology. The frequency and the strain amplitude are maintained at 1 rad/s and 1%, respectively. The temperature is ramped down from 100°C to 33°C with a cooling rate of 1°C/min. A nitrogen stream was circulated through the sample oven to minimize chain extension or cross-linking during the experiments. No stabilizers

were added to the samples.

[0033] Preferably, the composition produced herein (particularly where n is 3 and M_n is 3000) shows a $\tan \delta$ (G''/G') of 1 or less at 50°C below the inflection point and at least 30 or more at 80°C above the inflection point. This transition is identified as an order-disorder transition (ODT), characterized by an order-disorder transition temperature, T_{ODT} . The inflection point is determined by a geometrical method. The method consist on drawing two parallel lines, overlapping the viscosity data at high temperatures (above the T_{ODT}) and at low temperatures (below T_{ODT}). These lines are shown as solid lines in the Figure 5. A third line (dotted line) is drawn perpendicular to the solid lines connecting them. A fourth line parallel to the solid lines and intersecting the dotted line in the center is drawn (dashed line). The intersection between the dashed line and the viscosity curve corresponds to the inflection point. The T_{ODT} (temperature at the inflection point) is read in the abscissa.

[0034] PMHS (polymethylhydrosiloxane) of varying molar masses are commercially available in research grade quantities and are relatively inexpensive sources of Si-H for hydrosilation reactions. PMHS materials have been functionalized by a myriad of organic or inorganic molecules containing reactive groups such as carbonyl, vinyl, alkyne, hydroxy, thiol, or amine. The interest lies in part because of the inorganic Si-O- backbone in addition to the ability to modify through the Si-H moiety. The synthesis of comb-type polyolefin oligomers (or “co-oligomers” or “homo-oligomers”) by hydrosilation of VTM’s could potentially produce a range of materials with interesting properties depending on the alkyl composition, length and number. Such properties include increased thermal and oxidative stability, rheological and tribological. Potential exists for the use of these materials in engine oil applications and the synthesis of organic-inorganic hybrid materials. Alkyl-modified PMHS oligomers have previously been synthesized by hydrosilation of PMHS materials with low molar mass 1-alkenes from hexene to dodecene to give combs with short alkyl side chains. The availability of VTM’s with varying C_2 , C_3 , and higher olefin content and much higher number average masses from 500 to 70,000 g/mol presents the potential synthesis of a variety of novel materials. Amorphous VTM’s are available by solution polymerization of olefins as disclosed in U.S. Patent No. 8,372,930; U.S. Patent No. 8,318,998; and/or U.S. Patent No. 8,455,597. The Si-H bond is found to react with VTMs (aPP VTM, 2K Mn, exemplified) to yield alkylated PHMS under mild reaction conditions. The alkylated PHMS can be further coupled to yield materials with very low g'_{vis} by GPC-3D and indicates these could be viscosity modifiers in polyolefin products such as motor oils or films depending on

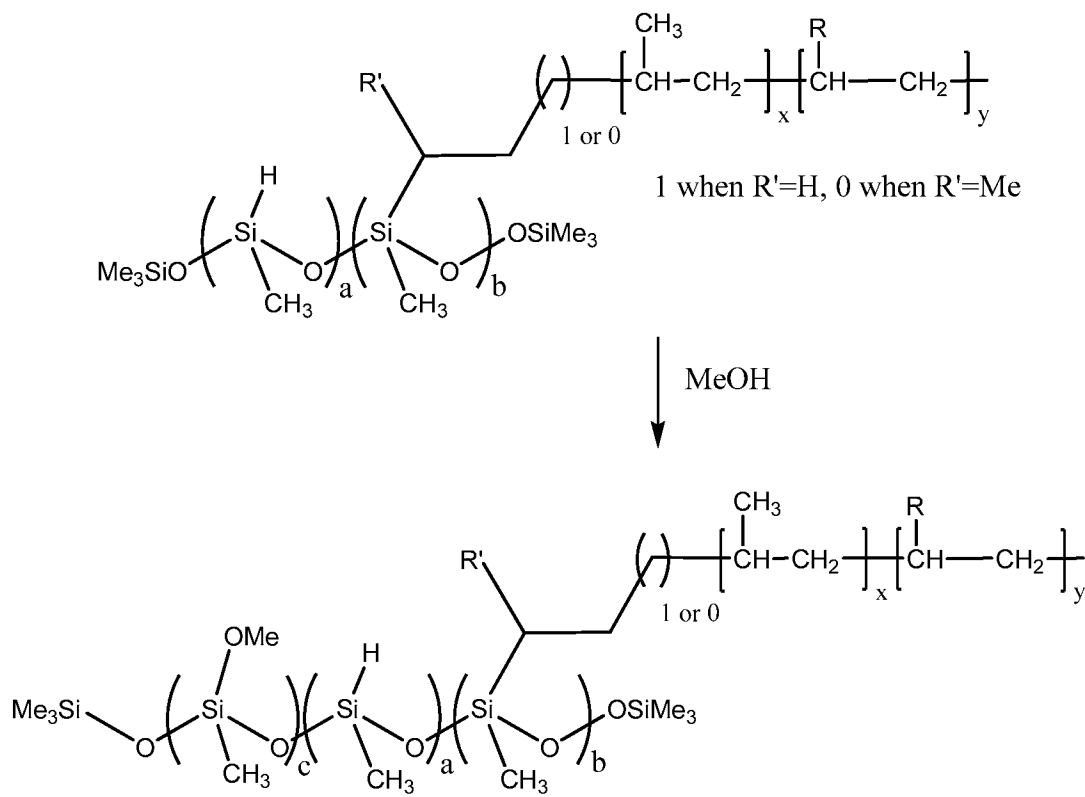
initial VTM composition. For example (where “Me” is methyl),



where R is H or an alkyl group, preferably a C₂ to C₄₀ alkyl group, preferably ethyl, propyl, hexyl, octyl, or decyl; R' is H or methyl; a is 50 to 100 mol% (based upon a+b+g); b is 50 to

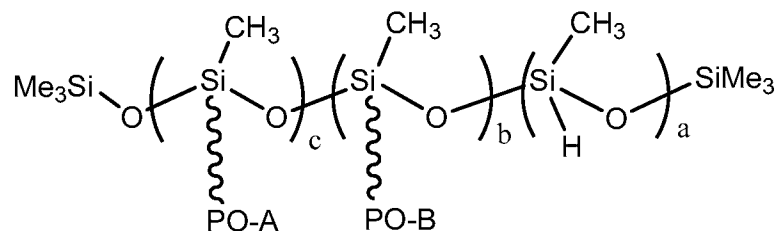
0 mol% (based upon a+b+g); x is 100 to 30 mol% (based upon x+y); y is 0 to 70 mol% (based upon x+y); and g is 0 to 10 mol% (based upon a+b+g).

[0035] Instead of branched materials by dehydrogenative intermolecular coupling, the alkylated PHMS can be further modified with MeOH to yield MeO- bonded to Si. This would provide points of attachment with inorganic (or organic materials) with inorganic-OH groups.



where R, R', a, b, x and y are as defined above.

[0036] Alternatively, a VTM could be reacted to form materials having the formulae:



wherein each PO-A and PO-B, independently, are the residual terminal portions of VTMs which can be same or different (and "Me" is methyl);

c is from 1 to 1000;

b is from 1 to 1000;

a is from 0 to 1000; and

the “” symbol means polymer chain.

[0037] Preferably of the invention, any of the materials described herein may have a ratio of Si-alkylated to Si-H of 1:1000, preferably of 1:100, preferably of 1:10 preferably 1:1, preferably 0.1:10, preferably 0.1:100, as determined by ^{29}Si NMR.

[0038] Preferably of the invention, any of the materials described herein may have a ratio of Si-H to Si-alkylated of 1:1000, preferably of 1:100, preferably of 1:10 preferably 1:1, preferably 0.1:10, preferably 0.1:100, as determined by ^{29}Si NMR.

Vinyl Terminated Macromonomers

[0039] A "vinyl terminated macromonomer," as used herein, refers to one or more of compounds as first described in US 2009/0318644, and also in US 8,399,724, which may have the following characteristics:

- (i) a vinyl terminated polymer having at least 5% allyl chain ends (preferably 15%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 98%, or 99%);
- (ii) a vinyl terminated polymer having an Mn of at least 160 g/mol, preferably at least 200 g/mol (measured by ^1H NMR) comprising of one or more C_4 to C_{40} higher olefin derived units, where the higher olefin polymer comprises substantially no propylene derived units; and wherein the higher olefin polymer has at least 5% allyl chain ends;
- (iii) a copolymer having an Mn of 300 g/mol or more (measured by ^1H NMR) comprising (a) from 20 mol% to 99.9 mol% of at least one C_5 to C_{40} higher olefin, and (b) from 0.1 mol% to 80 mol% of propylene, wherein the higher olefin copolymer has at least 40% allyl chain ends;
- (iv) a copolymer having an Mn of 300 g/mol or more (measured by ^1H NMR), and comprises (a) from 80 mol% to 99.9 mol% of at least one C_4 olefin, (b) from 0.1 mol% to 20 mol% of propylene; and wherein the vinyl terminated macromonomer has at least 40% allyl chain ends relative to total unsaturation;
- (v) a co-oligomer having an Mn of 300 g/mol to 30,000 g/mol (measured by ^1H NMR) comprising 10 mol% to 90 mol% propylene and 10 mol% to 90 mol% of ethylene, wherein the co-oligomer has at least X% allyl chain ends (relative to total unsaturations), where: 1) $X = (-0.94 * (\text{mol\% ethylene incorporated}) + 100)$, when 10 mol% to 60 mol% ethylene is present in the co-oligomer, 2) $X = 45$, when greater than 60 mol% and less than 70 mol% ethylene is present in the co-oligomer, and 3) $X = (1.83 * (\text{mol\% ethylene incorporated}) - 83)$, when 70 mol% to 90 mol% ethylene is present in the co-oligomer;

- (vi) a propylene co-oligomer, comprising more than 90 mol% propylene and less than 10 mol% ethylene wherein the co-oligomer has: at least 93% allyl chain ends, a number average molecular weight (Mn) of 500 g/mol to 20,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0, less than 100 ppm aluminum, and/or less than 250 regio defects per 10,000 monomer units;
- (vii) a propylene co-oligomer, comprising: at least 50 mol% propylene and from 10 mol% to 50 mol% ethylene, wherein the co-oligomer has: at least 90% allyl chain ends, an Mn of 150 g/mol to 20,000 g/mol, preferably 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, wherein monomers having four or more carbon atoms are present at from 0 mol% to 3 mol%;
- (viii) a propylene co-oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% C₄ to C₁₂ olefin, wherein the co-oligomer has: at least 90% allyl chain ends, an Mn of 150 g/mol to 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0;
- (ix) a propylene co-oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% diene, wherein the co-oligomer has: at least 90% allyl chain ends, an Mn of 150 g/mol to 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.7:1 to 1.35:1.0;
- (x) a homo-oligomer, comprising propylene, wherein the co-oligomer has: at least 93% allyl chain ends, an Mn of 500 g/mol to 70,000 g/mol, alternately to 20,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, and less than 1400 ppm aluminum;
- (xi) vinyl terminated polyethylene having: (a) at least 60% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.0; (c) a $g'_{(vis)}$ of greater than 0.95; and (d) an Mn (¹H NMR) of at least 20,000 g/mol; and
- (xii) vinyl terminated polyethylene having: (a) at least 50% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.0; (c) a $g'_{(vis)}$ of 0.95 or less; (d) an Mn (¹H NMR) of at least 7,000 g/mol; and (e) a Mn (GPC)/Mn (¹H NMR) in the range of from 0.8 to 1.2.

[0040] It is understood by those of ordinary skill in the art that when the VTM's, as described here, are reacted with another material the "vinyl" (e.g. the allyl chain end) is involved in the reaction and has been transformed. Thus, the language used herein describing that a fragment of the final product (typically referred to as PO in the formulae herein) is the

residual portion of a vinyl terminated macromonomer (VTM) having had a terminal unsaturated carbon of an allylic chain and a vinyl carbon adjacent to the terminal unsaturated carbon, is meant to refer to the fact that the VTM has been incorporated in the product. Similarly stating that a product or material comprises a VTM means that the reacted form of the VTM is present, unless the context clearly indicates otherwise (such as a mixture of ingredients that do not have a catalytic agent present.)

[0041] Preferably, the vinyl terminated macromonomer has an M_n of at least 200 g/mol, (e.g., 200 g/mol to 100,000 g/mol, e.g., 200 g/mol to 75,000 g/mol, e.g., 200 g/mol to 60,000 g/mol, e.g., 300 g/mol to 60,000 g/mol, or e.g., 750 g/mol to 30,000 g/mol) (measured by ^1H NMR) and comprises one or more (e.g., two or more, three or more, four or more, and the like) C_4 to C_{40} (e.g., C_4 to C_{30} , C_4 to C_{20} , or C_4 to C_{12} , e.g., butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted derivatives thereof, and isomers thereof) olefin derived units, where the vinyl terminated macromonomer comprises substantially no propylene derived units (e.g., less than 0.1 wt% propylene, e.g., 0 wt%); and wherein the vinyl terminated macromonomer has at least 5% (at least 10%, at least 15%, at least 20%, at least 30%, at least 40%, at least 50%, at least 60%, at least 70%; at least 80%, at least 90%, or at least 95%) allyl chain ends (relative to total unsaturation); and optionally, an allyl chain end to vinylidene chain end ratio of 1:1 or greater (e.g., greater than 2:1, greater than 2.5:1, greater than 3:1, greater than 5:1, or greater than 10:1); and even further optionally, e.g., substantially no isobutyl chain ends (e.g., less than 0.1 wt% isobutyl chain ends). Preferably, the vinyl terminated macromonomers may also comprise ethylene derived units, e.g., at least 5 mol% ethylene (e.g., at least 15 mol% ethylene, e.g., at least 25 mol% ethylene, e.g., at least 35 mol% ethylene, e.g., at least 45 mol% ethylene, e.g., at least 60 mol% ethylene, e.g., at least 75 mol% ethylene, or e.g., at least 90 mol% ethylene). Such vinyl terminated macromonomers are further described in U.S. Patent No. 8,426,659.

Process to Functionalize Polyolefins

[0042] This invention relates to a process to functionalize polyolefins comprising contacting, optionally, a catalyst, and one or more vinyl terminated macromonomers in the presence of a hydrosilation reagent.

[0043] The reactants are typically combined in a reaction vessel at a temperature of -50°C to 300°C (preferably 25°C, preferably 150°C). Likewise the reactants are typically

combined at a pressure of 0 to 1000 MPa (preferably 0.5 to 500 MPa, preferably 1 to 250 MPa) for a residence time of 0.5 seconds to 10 hours (preferably 1 second to 5 hours, preferably 1 minute to 2 hours).

[0044] Typically, from 5 to 1 (e.g., 3 to 1), preferably from 1.5 to 1, and most preferably from 1 to 1 per equivalent of the sum of VTM and other reactive molecules (e.g., MeOH) to each available Si-H group.

[0045] Typically, from 1×10^{-2} to 1×10^{-7} , preferably from 5×10^{-2} to 1×10^{-6} , and most preferably from 1×10^{-3} to 1×10^{-5} moles of catalyst reagent are charged to the reactor per mole of VTM charged.

[0046] The process is typically a solution process, although it may be a bulk or high pressure process. Homogeneous processes are preferred. (A homogeneous process is defined to be a process where at least 90 wt% of the product is soluble in the reaction media.) A bulk homogeneous process is particularly preferred. (A bulk process is defined to be a process where reactant concentration in all feeds to the reactor is 70 vol% or more.) Alternately no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the carrier for the catalyst or other additives, or amounts typically found with the reactants; e.g., propane in propylene).

[0047] Suitable diluents/solvents for the process include non-coordinating, inert liquids. Examples include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof such as can be found commercially (IsoparTM); perhalogenated hydrocarbons such as perfluorinated C₄₋₁₀ alkanes, chlorobenzene, and aromatic and alkylsubstituted aromatic compounds such as benzene, toluene, mesitylene, and xylene. Preferably, the feed concentration for the process is 60 vol% solvent or less, preferably 40 vol% or less, preferably 20 vol% or less.

[0048] The process may be batch, semi-batch or continuous. As used herein, the term continuous means a system that operates without interruption or cessation. For example, a continuous process to produce a polymer would be one where the reactants are continually introduced into one or more reactors and polymer product is continually withdrawn.

[0049] Useful reaction vessels include reactors, including continuous stirred tank reactors, batch reactors, reactive extruders, tubular reactors, pipes or pumps.

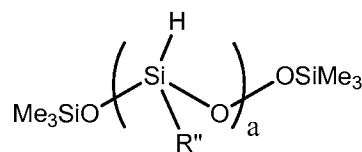
[0050] This invention further relates to a process, preferably an in-line process,

preferably a continuous process, to produce functionalized polyolefins, comprising introducing macromonomer, hydrosilation reagent and a catalyst into a reactor, obtaining a reactor effluent containing hydrosilated terminated polyolefin, optionally removing (such as flashing off) solvent, unused monomer and/or other volatiles, obtaining hydrosilated terminated polyolefin (such as those described herein), preferably an in-line process, preferably a continuous process, to produce functionalized polyolefins, comprising introducing vinyl terminated polyolefin, catalyst (as described herein) and a hydrosilating compound (as described herein) into a reaction zone (such as a reactor, an extruder, a pipe and/or a pump) and obtaining functionalized polyolefin (such as those described herein).

[0051] For further information on hydrosilylation processes, catalysts, etc., please see Comprehensive Handbook on Hydrosilylation, B. Marciniec, ed. Pergamon, New York, 1992.

Hydrosilation Agents

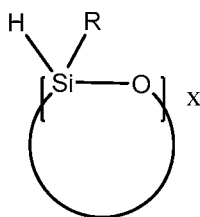
[0052] Useful hydrosilation agents include those represented by the formula:



PHMS

that have one or more reactive hydrogen atoms that can react with a terminal vinyl group, where "a" is an integer from 1 to 1000, and R" is an alkyl or an aryl group such as methyl, hexyl, phenyl, fluoroalkanes, etc. or other copolymers containing PHMS units substituted through the polymeric backbone, preferably R" is CH₃.

[0053] Cyclic versions of hydrosilation agents are also included and can be represented by the formula:



wherein x is from 2 to 40 SiO-groups/moities, e.g. a siloxane chain; and

R is an alkyl or an aryl group, e.g., methyl, ethyl, propyl, pentyl, phenyl, anthracenyl, and the like.

Catalysts

[0054] Useful catalysts include Pt based materials having 0.1 to 10 wt% Pt-containing complexes in a suitable solvent. Actual amount in the reaction mixture is ppm (1-100 or more) chloroplatinic acid, H_2PtCl_6 and derivatives such as with tetramethyldisiloxane or other versions of Speirs catalyst, $\text{RhCl}(\text{PPh}_3)_3$, heterocarbene containing Pt complexes such as those found in Journal of Organometallic Chemistry 696 (2011) p. 2918, or supported/reclaimable catalysts such as Pt-nanoclusters (Macromolecules 2006, 39, pp. 2010-2012). Karstedt catalyst (typically a compound of platinum(0) and divinyltetramethyldisiloxane) is one example of a suitable platinum catalyst. It was found that similar zirconium based catalysts were not as effective as their platinum counterparts. Organic peroxides can be used to further crosslink functionalized PMHS with other vinyl ended compounds.

Blends of Functionalized Polyolefins

[0055] Preferably, the functionalized (and optionally derivatized) polyolefins produced by this invention may be blended with from 0.5 wt% to 99 wt% (typically 1.0 wt% wt% to 98 wt%, and ideally 50 wt% to 98 wt%) of one or more other polymers, including but not limited to, thermoplastic polymer(s) and/or elastomer(s).

[0056] By thermoplastic polymer(s) is meant a polymer that can be melted by heat and then cooled without appreciable change in properties. Thermoplastic polymers typically include, but are not limited to, polyolefins, polyamides, polyesters, polycarbonates, polysulfones, polyacetals, polylactones, acrylonitrile-butadiene-styrene resins, polyphenylene oxide, polyphenylene sulfide, styrene-acrylonitrile resins, styrene maleic anhydride, polyimides, aromatic polyketones, or mixtures of two or more of the above. Preferred polyolefins include, but are not limited to, polymers comprising one or more linear, branched or cyclic C_2 to C_{40} olefins, preferably polymers comprising propylene copolymerized with one or more C_3 to C_{40} olefins, preferably a C_3 to C_{20} alpha-olefin, more preferably C_3 to C_{10} alpha-olefins. More preferred polyolefins include, but are not limited to, polymers comprising ethylene including but not limited to ethylene copolymerized with a C_3 to C_{40} olefin, preferably a C_3 to C_{20} alpha-olefin, more preferably propylene and/or butene.

[0057] By elastomers is meant all natural and synthetic rubbers, including those defined in ASTM D1566. Examples of preferred elastomers include, but are not limited to, ethylene propylene rubber, ethylene propylene diene monomer rubber, styrenic block copolymer rubbers (including SI, SIS, SB, SBS, SIBS, and the like, where S=styrene, I=isobutylene, and

B=butadiene), butyl rubber, halobutyl rubber, copolymers of isobutylene and para-alkylstyrene, halogenated copolymers of isobutylene and para-alkylstyrene, natural rubber, polyisoprene, copolymers of butadiene with acrylonitrile, polychloroprene, alkyl acrylate rubber, chlorinated isoprene rubber, acrylonitrile chlorinated isoprene rubber, polybutadiene rubber (both cis and trans).

[0058] Preferably, the functionalized (and optionally derivitized) polyolefins produced herein may further be combined with one or more of polybutene, ethylene vinyl acetate, low density polyethylene (density 0.915 to less than 0.935 g/cm³) linear low density polyethylene, ultra low density polyethylene (density 0.86 to less than 0.90 g/cm³), very low density polyethylene (density 0.90 to less than 0.915 g/cm³), medium density polyethylene (density 0.935 to less than 0.945 g/cm³), high density polyethylene (density 0.945 to 0.98 g/cm³), ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, EPDM, block copolymer, styrenic block copolymers, polyamides, polycarbonates, PET resins, crosslinked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, polyacetal, polyvinylidene fluoride, polyethylene glycols and/or polyisobutylene. Preferred polymers include those available from ExxonMobil Chemical Company in Baytown, Texas under the tradenames EXCEEDTM and EXACTTM.

[0059] Tackifiers may be blended with the functionalized (and optionally derivitized) polyolefins produced herein and/or with blends of the functionalized (and optionally derivitized) polyolefins produced by this inventions (as described above). Examples of useful tackifiers include, but are not limited to, aliphatic hydrocarbon resins, aromatic modified aliphatic hydrocarbon resins, hydrogenated polycyclopentadiene resins, polycyclopentadiene resins, gum rosins, gum rosin esters, wood rosins, wood rosin esters, tall oil rosins, tall oil rosin esters, polyterpenes, aromatic modified polyterpenes, terpene phenolics, aromatic modified hydrogenated polycyclopentadiene resins, hydrogenated aliphatic resin, hydrogenated aliphatic aromatic resins, hydrogenated terpenes and modified terpenes, and hydrogenated rosin esters. Preferably the tackifier is hydrogenated. Preferably the tackifier has a softening point (Ring and Ball, as measured by ASTM E-28) of 80°C to 140°C, preferably 100°C to 130°C. The tackifier, if present, is typically present at 1 wt% to 50 wt%, based upon the weight of the blend, more preferably 10 wt% to 40 wt%, even more

preferably 20 wt% to 40 wt%.

[0060] Preferably, the functionalized (and optionally derivitized) polyolefins of this invention, and/or blends thereof, further comprise typical additives known in the art such as fillers, cavitating agents, antioxidants, surfactants, adjuvants, plasticizers, block, antiblock, color masterbatches, pigments, dyes, processing aids, UV stabilizers, neutralizers, lubricants, waxes, and/or nucleating agents. The additives may be present in the typically effective amounts well known in the art, such as 0.001 wt% to 10 wt%. Preferred fillers, cavitating agents and/or nucleating agents include titanium dioxide, calcium carbonate, barium sulfate, silica, silicon dioxide, carbon black, sand, glass beads, mineral aggregates, talc, clay and the like. Preferred antioxidants include phenolic antioxidants, such as Irganox 1010, Irganox, 1076 both available from Ciba-Geigy. Preferred oils include paraffinic or naphthenic oils such as Primol 352, or Primol 876 available from ExxonMobil Chemical France, S.A. in Paris, France. More preferred oils include aliphatic naphthenic oils, white oils or the like.

[0061] Most preferably, the functionalized (and optionally derivitized) polyolefins produced herein are combined with polymers (elastomeric and/or thermoplastic) having functional groups such as unsaturated molecules-vinyl bonds, ketones or aldehydes under conditions such that they react. Reaction may be confirmed by an at least 20% (preferably at least 50%, preferably at least 100%) increase in Mw as compared to the Mw of the functionalized polyolefin prior to reaction. Such reaction conditions may be increased heat (for example, above the Tm of the functionalized polyolefin), increased shear (such as from a reactive extruder), presence or absence of solvent. Conditions useful for reaction include temperatures from 150°C to 240°C and where the components can be added to a stream comprising polymer and other species via a side arm extruder, gravimetric feeder, or liquids pump. Useful polymers having functional groups that can be reacted with the functionalized polyolefins produced herein include polyesters, polyvinyl acetates, nylons (polyamides), polybutadiene, nitrile rubber, hydroxylated nitrile rubber. Preferably, the functionalized (and optionally derivitized) polyolefin of this invention may be blended with up to 99 wt% (preferably up to 25 wt%, preferably up to 20 wt%, preferably up to 15 wt%, preferably up to 10 wt%, preferably up to 5 wt%), based upon the weight of the composition, of one or more additional polymers. Suitable polymers include those described as PM 1) to PM 7) in US 8,003,725.

Applications

[0062] The functionalized VTMs of this invention (and blends thereof as described

above) may be used in any known thermoplastic or elastomer application. Examples include uses in molded parts, films, tapes, sheets, tubing, hose, sheeting, wire and cable coating, adhesives, shoe soles, bumpers, gaskets, bellows, films, fibers, elastic fibers, nonwovens, spun bonds, corrosion protection coatings and sealants. Preferred uses include additives for lubricants and/or fuels.

[0063] Preferably, the functionalized vinyl terminated macromonomers produced herein are further functionalized (derivitized), such as described in U.S. Patent No. 6,022,929; A. Toyota, T. Tsutsui, and N. Kashiwa, Polymer Bulletin 48, pp. 213-219, 2002; J. Am. Chem. Soc., 1990, 112, pp. 7433-7434; and U.S. Patent No. 8,399,725.

[0064] The functionalized vinyl terminated materials prepared herein may be used in oil additivation, lubricants, fuels and many other applications. Preferred uses include additives for lubricants and or fuels.

[0065] Preferably, the vinyl terminated macromonomers disclosed herein, or functionalized/derivitized analogs thereof, are useful as additives, preferably in a lubricant.

[0066] The functionalized VTM's and/or derivitized VTM's produced herein have uses as lubricating additives which can act as dispersants, viscosity index improvers, or multifunctional viscosity index improvers. Additionally they may be used as disinfectants (functionalized amines) and or wetting agents.

[0067] Functionalized VTMs and/or derivitized VTMs having uses as dispersants typically have Mn's (g/mol) of less than 20,000, preferably less than 10,000 and most preferably less than 8,000 and typically can range from 500 to 10,000 (e.g. 500 to 5,000), preferably from 1,000 to 8,000 (e. g. 1,000 to 5,000) and most preferably from 1,500 to 6,000 (e.g. 1,500 to 3,000).

[0068] The functionalized VTMs and/or derivitized VTMs described herein having Mn's (g/mol) of greater than 10,000 g/mol, preferably greater than 10,000 to 100,000 g/mol (preferably 20,000 to 60,000 g/mol) are useful for viscosity index improvers for lubricating oil compositions, adhesive additives, antifogging and wetting agents, ink and paint adhesion promoters, coatings, tackifiers and sealants, and the like. In addition, such VTMs may be functionalized and derivitized to make multifunctional viscosity index improvers which also possess dispersant properties. (For more information please see U.S. Patent No. 6,022,929.)

[0069] The functionalized VTMs and/or derivitized VTMs described herein may be combined with other additives (such as viscosity index improvers, corrosion inhibitor, oxidation inhibitor, dispersant, lube oil flow improver, detergents, demulsifiers, rust

inhibitors, pour point depressant, anti-foaming agents, antiwear agents, seal swellant, friction modifiers, and the like (described for example in U.S. Patent No. 6,022,929 at columns 60, line 42 to column 78, line 54 and the references cited therein) to form compositions for many applications, including but not limited to lube oil additive packages, lube oils, and the like.

[0070] Compositions containing these additives are typically blended into a base oil in amounts which are effective to provide their normal attendant function. Representative effective amounts of such additives are illustrated as follows:

Compositions	(Typical)	(Preferred)
	wt %*	wt %*
V.I. Improver	1-12	1-4
Corrosion Inhibitor	0.01-3	0.01-1.5
Oxidation Inhibitor	0.01-5	0.01-1.5
Dispersant	0.1-10	0.1-5
Lube Oil Flow Improver	0.01-2	0.01-1.5
Detergents and Rust inhibitors	0.01-6	0.01-3
Pour Point Depressant	0.01-1.5	0.01-1.5
Anti-Foaming Agents	0.001-0.1	0.001-0.01
Antiwear Agents	0.001-5	0.001-1.5
Seal Swellant	0.1-8	0.1-4
Friction Modifiers	0.01-3	0.01-1.5
Lubricating Base Oil	Balance	Balance

[0071] In the table above, wt%'s are based on active ingredient content of the additive, and/or upon the total weight of any additive-package, or formulation which will be the sum of the A.I. weight of each additive plus the weight of total oil or diluent.

[0072] When other additives are employed, it may be desirable, although not necessary, to prepare additive concentrates comprising concentrated solutions or dispersions of the subject additives of this invention (in concentrate amounts hereinabove described), together with one or more of said other additives (said concentrate when constituting an additive mixture being referred to herein as an additive-package) whereby several additives can be added simultaneously to the base oil to form the lubricating oil composition. Dissolution of the additive concentrate into the lubricating oil may be facilitated by solvents and by mixing

accompanied with mild heating, but this is not essential. The subject functionalized or derivitized VTMs of the present invention can be added to small amounts of base oil or other compatible solvents along with other desirable additives to form additive-packages containing active ingredients in collective amounts of typically from 2.5% to 90%, and preferably from 15% to 75%, and most preferably from 25% to 60% by weight additives in the appropriate proportions with the remainder being base oil.

[0073] The final formulations may employ typically 10 wt% of the additive-package with the remainder being base oil.

[0074] Preferably, the vinyl terminated polyolefins described herein can be used in any process, blend or product disclosed in WO 2009/155472 or U.S. Patent No. 6,022,929.

[0075] Preferably, this invention relates to a fuel comprising any VTM produced herein. Preferably, this invention relates to a lubricant comprising any VTM produced herein.

[0076] Depending on functionalization, the polymers described herein are useful as plasticisers, surface-modifiers, surfactants, wetting agents, in ink formulations, lubricants, oil well defoamers, water-proofing agents, sealants. Highly alkylated PMHS materials could also be useful as viscosity modifiers. PMHS materials alkylated with different PO-VTMs could be useful as compatibilizers. If reactive Si-H groups remain these materials would be useful as cross-linking reagents with other vinyl-containing materials such as vinyl silanes, 1,2-butadiene polymers and copolymers, OH-containing materials and polymers.

EXPERIMENTAL

Product Characterization

[0077] Products were characterized by ^1H NMR and ^{13}C NMR as follows:

^1H NMR

[0078] Unless otherwise stated, ^1H NMR data was collected at either 25°C or 120°C (for purposes of the claims, 120°C shall be used) in a 5 mm probe using a spectrometer with a ^1H frequency of at least 400 MHz. Data was recorded using a maximum pulse width of 45° and either a 1 or 2 second delay between pulses. Typical NMR solvents such as CDCl_3 , CD_2Cl_2 , or C_6D_6 were purchased from Cambridge Isotope Laboratories and were used at ambient temperatures in collection of the NMR data.

^{13}C NMR

[0079] Unless otherwise stated, ^{13}C NMR data was collected at 120°C using a spectrometer with a ^{13}C frequency of at least 100 MHz. A 90 degree pulse, an acquisition time adjusted to give a digital resolution between 0.1 and 0.12 Hz, at least a 2 second pulse

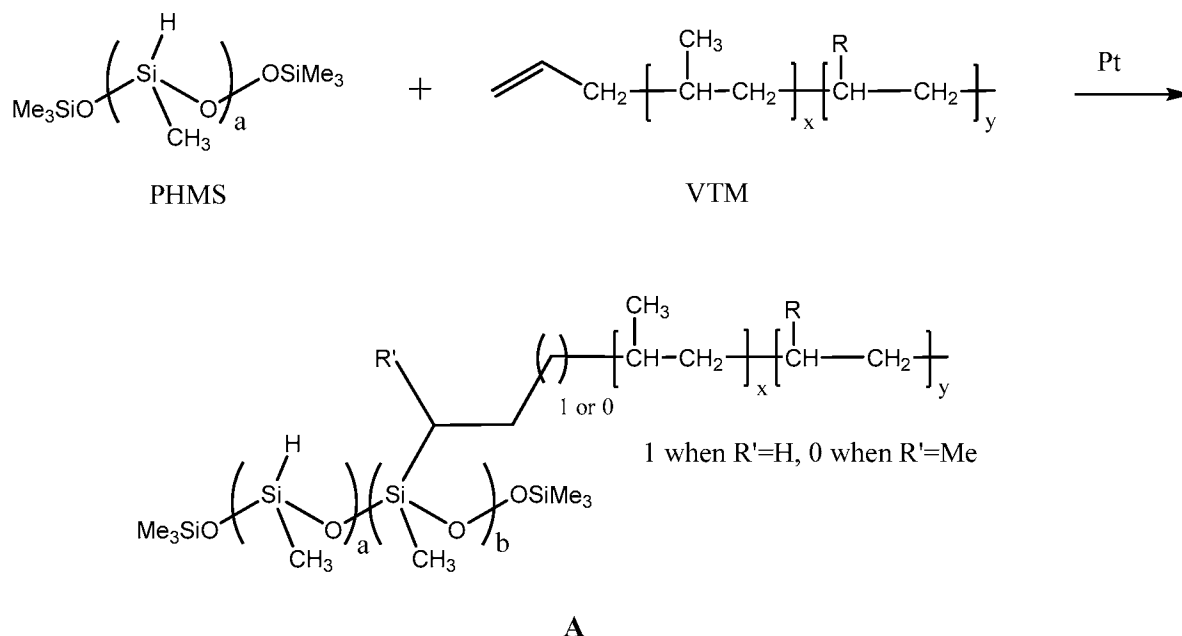
acquisition delay time with continuous broadband proton decoupling using swept square wave modulation without gating was employed during the entire acquisition period. The spectra were acquired with time averaging to provide a signal to noise level adequate to measure the signals of interest. Samples were dissolved in tetrachloroethane- d_2 (TCE) for high temperature measurements. Other solvents such as $CDCl_3$, CD_2Cl_2 , or C_6D_6 were used at ambient temperatures.

^{29}Si NMR

[0080] ^{29}Si spectra were taken at 99.4 MHz using the standard Bruker ^{29}Si program and a delay time of 60 seconds between pulses. ^{29}Si NMR spectra were referenced to tetramethylsilane at 0 ppm. Molecular weights of products were determined by GPC-MALLS/3D analysis or by GPC-DRI analysis with polystyrene standards. MH coefficients used were based on the polyolefin macromere or that employed in the hydrosilation reaction. Molecular weights of VTM's were determined by both ^1H NMR and by GPC-DRI analysis. The mass recovered was always greater than 95% unless stated otherwise. TGAs were measured on a Universal V4.7A TA Instrument with heating rate at $10^\circ C/min$, balance of 10 mL/min N_2 , purge 25 mL/min N_2 , and a range from $30^\circ C$ to $500^\circ C$. DSCs were also measured on a Universal V4.7A TA Instrument from $-170^\circ C$ to $30^\circ C$. The sample was equilibrated at $-170^\circ C$ for 5 minutes then heated at a rate of $10^\circ C$ per minute to $30^\circ C$ and held for 2 minutes.

[0081] Hydrosilation Reactions of VTM's (vinyl terminated macromonomers) with PMHS (Polymethylhydrosiloxane)

Scheme 1.



[0082] Vinyl Terminated Monomacromers (Table 1) were made according to the processes described in U.S. Patent No. 8,318,998 and/or U.S. Patent No. 8,455,597. Macromer D was similarly synthesized using the catalyst system composed of a 1 to 1 molar amount of (CpHMe₄)(CpH₄n-propyl)ZrMe₂ and dimethylanilinium tetrakis(perfluoronaphthyl)borate. Octene and eicosene were purchased from Aldrich Chemical and dried with 3A sieves prior to use.

[0083] PMHS materials of 390 g/mol and 1700 to 2300 g/mol were purchased from Aldrich and dried over 3 A sieves. Methylhydrocyclosiloxane with Mn of 180 to 360 g/mol was purchased from Gelest and dried over 3 A sieves. Kardstedt catalyst was purchased from Gelest as a 2 wt% solution of Platinum-divinyltetramethyldisiloxane complex in xylenes and used without further purification. Anhydrous solvents such as toluene were purchased from Aldrich and dried over 3 A sieves. Dimethylanilinium tetrakis(perfluoronaphthyl)borate was purchased from Grace-Davison. (CpHMe₄)(CpH₄n-propyl)ZrMe₂ was purchased from Boulder.

Table 1. Vinyl Terminated Monomacromers

VTM Macromer	Composition	% Vinyl Chain ends	% Vinylidene Chain Ends	Mn, ¹ H NMR, g/mol	Mn, GPC-DRI, g/mol	Mw/Mn GPC/GPC
A	C ₃	95	5	1700		
B	C ₃	98	2	2789	2558	2.5
C	C ₃	97	3	2100		
D	C ₃	5	95	2000		
E	C ₃ C ₄ , 45% C ₄	95	5	2200	1941	2.6
F	C ₃ C ₄ , 46% C ₄	85	9	15,400	14,400	2.3
G	octene	100	0	112		
H	C ₂ C ₃ , 17% C ₂	76	23	7876	7274	2.7
I	C ₃	98	2	416 ⁱ		1.02
J	C ₂ C ₃ , 53 % C ₂	99	1	1004		
K	C ₃	97	3	4844	4906	2.6

ⁱ Mn determined by GPC-DRI at 40°C in THF

Table 2. PMHS Materials

Source	PMHS	Mn (g/mol)
Aldrich	X	1700 to 2300
Aldrich	Y	390

Examples 1-16. Standard Hydrosilation Reaction

[0084] Reactions were performed in a vacuum atmospheres drybox with continuous N₂ purge. The VTM was dissolved in toluene (generally 60 to 150 mls) and 3A sieves (2-5 g) were added for removal of water. After at least 48 hrs, the mixture was decanted from the sieves, with the aid of additional toluene, into another glass vessel with a teflon stir bar. PMHS was added with vigorous stirring and a t=0 aliquot pulled for reference. The reaction mixture if heated was brought to desired reaction temperature at this point. Karstedt catalyst was added and the reaction stirred for 3 hrs unless stated otherwise. An aliquot was taken before the reaction mixture was transferred from the drybox to the atmosphere into a hood. The reaction was generally reacted with MeOH for 2 hrs or exposed to air for 2 hrs before product work-up. The volatiles were removed and the product dried in a vacuum oven at 100°C to remove all toluene. The products were generally light to medium yellow clear viscous materials that were soluble in hydrocarbons.

Temperature and Oxygen Effects on Hydrosilation Reactions

Example	VTM, g	PMHS, g	Karstedt , mg	Temp, °C	Rxn. Time in Drybox, hrs	Conversion under N ₂	Rxn. Time in Air, minutes	Conversion after air
1	C, 18.3	X, 0.55	60	110	2	0	na	na
2	C, 7.8	X, 0.9	50 at t=0 hrs, additional 50 at t=2 hrs	60	4	44% at 2 hrs, 44% at 4 hrs	na	na
3	C, 8.9	X, 1.0	50 at t=0 hrs, additional 40 at t=50 hrs	30	52	77% at 2 hrs, 78% at 48 hrs, 83% at 51 hrs	10	100
4	C, 8.4	X, 0.4	40	30	0.1	na	30	100

Product Characterization

Example	Mn ^a	Mw	Mz	g' _{vis}	g'(z avg)	% Isomerized vinylene	% Unreacted vinyls
3	159.2	1693	8011	0.045	0.018	0	0
4	48.4	185.2	522.6	0.166	0.091	17.8	0

^aGPC values are from MALLS/3D analysis and are in Kg/mol

[0085] Figure 1 provides the following: 1 is Aldrich PMHS X, 2 is Alkylated PMHS before methanolysis, 3 is final product. All from Example 9, ²⁹Si NMR, C₆D₆, RT, 99.4 MHz.

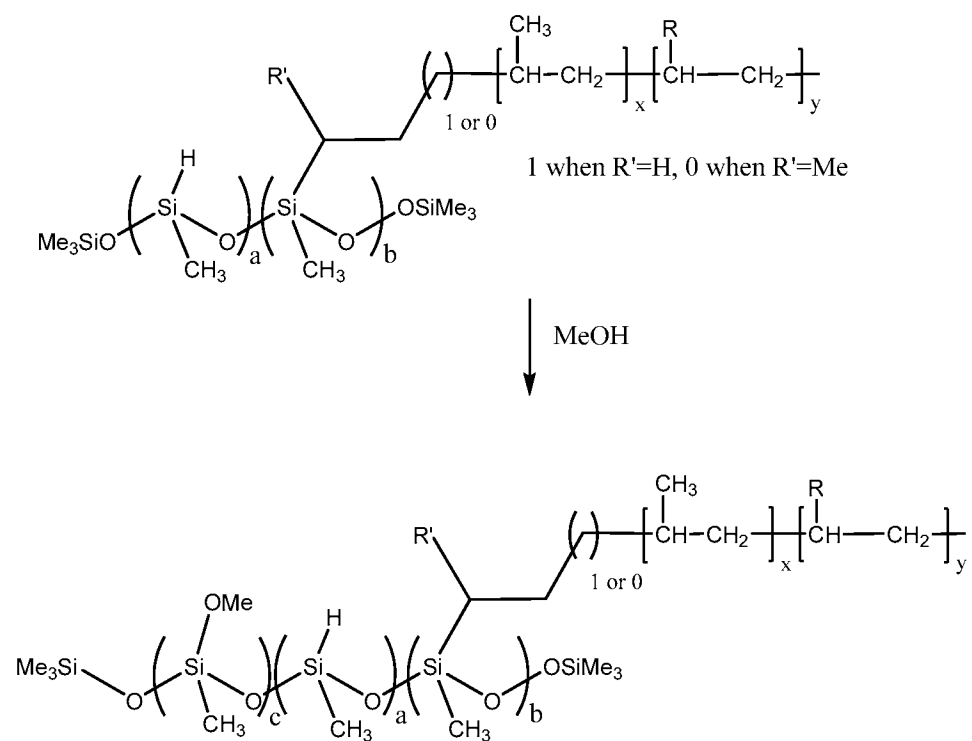
[0086] Figure 2 provides an ¹H NMR spectra of PHMS X.

[0087] Figure 3 provides an ¹H NMR spectra of Example 3.

[0088] Figure 3 provides an ¹H NMR spectra of Example 4.

Alkylation Followed by Methanolysis; 1 Pot Reaction

[0089] Any unreacted Si-H groups remaining after alkylation can be potentially transformed into other functionalities. Not only would this introduce a second or third functionality but also help preserve the linearity of the original PMHS backbone. Methanolysis of the intermediate A by reaction with methanol is easily carried out in a one pot reaction. First hydrosilation of aPP-VTM with PHMS is performed in the drybox followed by addition of MeOH immediately after the reaction is brought outside the drybox. The reaction is indicated by Scheme 3.



Scheme 3. Methanolysis Alkylation Followed by Methanolysis Examples

Example	VTM, g	PMHS, g	Toluene, ml	Karstedt, mg	MeOH, ml	VTM/PMHS mol/mol	Mn ^a	Mw	Mz	g' vis	g'(z avg)
5	C, 8.5	Y, .55	60	60	3	2.8	6.7	11.3	17	0.731	0.668
6	B, 75	Y, 3.2	150	90	0	3.3	7.6	13.8	21.3	0.691	0.639
7	E, 76	Y, 4.5	120	70	0	3	3.3	6.4	12.4	0.631	0.595
8	F, 86	Y, 0.8	200	70	0	2.7	35	77.4	135.3	0.698	0.601
9	C, 7.7	X, 0.8	60	105	3	9.2	41.7	126.5	701.8	0.209	0.081
Comp. Ex 1	D, 7.8	X, 0.7	70	105	0	11.1	19	95.6	209.7	0.218	0.132
10	B, 74	X, 2.5	100	80	20	21.2	41.8	172.5	445.5	0.189	0.111
11	E, 81	X, 3.7	150	80	30	19.9	5.3	37.3	225.5	0.302	0.129
12	F, 69	X, 2.1	200	100	30	4.3	85.3	228.7	602.4	.41	0.262
13	A, 63	X, 3.7	100	80	40	20	24.9	91.7	229.1	.261	0.166
14	G, 5.3	X, 3.0	40	60	0	31.5					
15	H, 63	X, 0.8	80	60	10	20	29.0	194.8	596.3	.382	0.227
16	I, 5.3	X, 1.2	30	30	2	21	11.8	52.1	205.5	0.138	0.087

^a GPC values are from MALLS/3D analysis and are in Kg/mol

¹H NMR Characterization of Alkylation Followed by Methanolysis Examples

¹ H NMR: Integration values of proton regions						
Example	5.3 to 5.0, ppm	3.9 to 3.3, ppm	2.0 to 0.7, ppm	0.6 to 0.0, ppm	Vinylene	Vinyl
5	0.92	0	829	30	.05	0
6	.94	0	1330.9	30	0.33	0
7	0	0	911.3	30	.66	1.2
8	1.98	0	2158.9	30	0.65	0
9	2.3	33.2	2383.1	108	0	0
Comp. Ex 1	13.1	0.6	2881.2	108	0	0
10	2.7	5.0	7560	108	0	.4
11	5.5	0	5057.3	108	9.1	0
12	0.6	39.0	12,016	108	0	0
13	5.1	15.2	3838.5	108	0	0
14	.1	0	454.9	108	0	0
15	2.2	22.9	24,578.8	108	3.3	1.5
16	4.0	0.6	1293.4	108	0	0

Thermal Analysis and DSC

Example	T _g , °C	1% Mass Loss, °C	50% Mass Loss, °C	Total Mass Loss, %
6	-18.1	327.6	446.5	98.9
7	-41.5	202.3	431.7	98.6
9	-16.1	363.3	451.4	99.6
10	-15.8	326.3	443.7	96.6
11	-37.7	244.4	440.2	96.6

Viscometer instrumentation

[0090] Dynamic viscosity and density of a blend of functionalized polysiloxane and poly(alpha)olefin (PAO) base oil were measured on a Stabinger Viscometer (Model SVM 3000 manufactured by Anton Paar) at both 40°C and 100°C. The kinematic viscosity and viscosity index (VI) were calculated from the dynamic viscosity and density determined at these two temperatures.

Preparation of blend for viscosity measurement

[0091] A 1 wt% of functionalized polysiloxane in 4 cSt poly(alpha)olefin (PAO4) base oil available from ExxonMobil Chemical Company in Houston Texas under the Tradename SpectraSyn™ 4 was prepared dissolving 1 part by weight of functionalized polysiloxane in 99 parts by weight of PAO4. The blend was warmed to 50°C to 60°C for 15 to 30 minutes until a clear solution was obtained.

Viscosity and viscosity index (VI)

Example	Wt% in PAO4	Kv 40 °C (mm ² /s)	Kv 100 °C (mm ² /s)	Viscosity Index
7	1	19.5	4.31	130.9
10	1	21.1	4.62	140.3
9	1	24.1	5.22	154.7
6	1	20.6	4.50	135.6
11	1	19.7	4.36	133.3
12	1	24.9	5.40	159.5
PAO4	neat	18.4	4.11	126.3

[0092] Figure 1 is the overlay of three ²⁹Si NMR spectra from Example 9. Spectrum 1 is

Aldrich PMHS X, 2 is Alkylated PMHS before methanolysis, and 3 is final product.

[0093] The amount of O-SiR(Me)-O (alkylated PMHS) to O-SiH(Me)-O (unreacted PMHS) where R is from the VTM is determined by the integration of the ^{29}Si NMR spectrum. The region from -30 to -35 ppm is due to the O-SiH(Me)-O. The region from -17 to -23 ppm is due to O-SiR(Me)-O. Where there was further reaction with MeOH, then the region from -52 to -60 ppm is due to O-Si(OMe)(Me)-O. Usually apparent in the linear PMHS materials are the smaller resonances from 10 to 13 ppm are due to the Me₃Si-O termini which can be normalized to 2. The resonances around -67 ppm are unidentified but may be due to dehydrogenative coupling of PMHS chains to form -OSiO(Me)O- units.

Additional Hydrosilation Reactions

[0094] Use of dry air sparge to react all (or most) of vinyl chain ends-improved the alkylation.

Example 17. Reaction of EP-VTM H with Methylhydrocyclosiloxane

[0095] EP-VTM H (9.0 g,) was dissolved in toluene (125 ml) and dried over 3 A sieves for 48 hrs. The reaction mixture was decanted away from the mole sieves and methylhydrocyclosiloxane (100 mg) was added with vigorous stirring under an N₂ atmosphere. Kardstedt catalyst (40 mg of 2 wt% solution) was next added to the reaction mixture. An aliquot at 2 hrs indicated that only 25% of the vinyl chain ends had been consumed. The reaction was taken out of the drybox and the reaction was sparged with dry air for 2 hrs. An analysis of an aliquot by ^1H NMR indicated all vinyl chain ends had been consumed. The volatiles were removed and the product dried in a vacuum oven at 80°C for 14 hrs (8.9 g). ^1H NMR (500 MHz, C₆D₆) δ ppm; 2.0 to 0.6 (m, 3890.5 H), 0.6 to 0 (m, 12 H). GPC-3D; Mn = 40.4 Kg/mol, Mw = 162.2 Kg/mol, Mz = 514.1 Kg/mol, $g'_{\text{vis}} = 0.517$, $g'(\text{Z av}) = 0.33$. ^{29}Si NMR (C₆D₆, 79.5 MHz) δ ppm; -17 to -26 (m, O-SiR(Me)-O, 1.0 Si), -27 to -35 (m, O-SiH(Me)-O, .03 Si).

Example 18. Reaction of iPP-VTM with PMHS at Ambient Temperature

[0096] iPP-VTM monomacromer L synthesis: A 2 L autoclave was filled with 0.5 ml triisobutylaluminum (1 M in hexanes), 200 ml propylene and 800 ml isohexanes. The reactor contents were heated to 85°C and stirring speed set to 750 rpms. A catalyst solution of rac-dimethylsilyl(2-methylindenyl)₂ZrMe₂ (3 mg) and dimethylaniliniumperfluoronaphthylborate (6.3 mg) in toluene (5 ml) was added by catalyst bomb with the aid of N₂. After 17 minutes, the reactor contents were cooled, depressurized and the solid polymer collected. The product

was dried in a vacuum oven for 12 hrs at 70°C (68 g). GPC-DRI; Mn = 12.8 Kg/mol, Mw = 27.0 Kg/mol, PD = 2.12, g'_{vis} = 0.930. Mn by ^1H NMR = 10.3 Kg/mol. Vinyls = 95%.

[0097] iPP-VTM L (21.2 g) was slurried in toluene (200 ml). PMHS X (0.65 g) was added to the reaction mixture. Dry air was continuously bubbled through the reaction mixture. Karsted catalyst (90 mg) was added and an aliquot was withdrawn at 1.5 hrs and analysis by ^1H NMR indicated all vinyl chain ends had been consumed. After 3 hrs, EP-VTM J (19.5 g) was added and the reaction mixture stirred overnight with the dry air sparge. The reaction mixture was filtered and washed with hexane (3 X 200 ml) and dried in a vacuum oven at 80°C (30.5 g). The ^1H NMR (380 K, $\text{C}_2\text{D}_2\text{Cl}_4$) spectrum of the reaction product indicated vinyl groups were present from excess EP macromer not separated by hexane washings. The Si-H region was unchanged in comparison to the 1.5 hr aliquot and remained at 55% compared to PMHS starting material. GPC-DRI; Mn = 11.4 Kg/mol; Mw = 34.5 Kg/mol; Mw/Mn = 3.0; g'_{vis} = 0.874. This shows that very little iPP or EP macromer was hydrosilated.

Example 19. Improved Synthesis of Crystalline VTM with PMHS: Reaction of iPP-VTM with PMHS at 100°C)/Blocky Composition

[0098] iPP-VTM macromonomer M synthesis: A 2 L autoclave was filled with 0.5 ml Triisobutylaluminum (1 M in hexanes), 400 ml propylene and 600 ml isohexanes. The reactor contents were heated to 100°C and stirring speed set to 750 rpms. A catalyst solution of $\text{rac-C}_2\text{H}_4(4\text{-methylindenyl})_2\text{HfMe}_2$ (3.5 mg) and dimethylanilinium-perfluoronaphthylborate (7 mg) in toluene (5 ml) was added by catalyst bomb with the aid of N_2 . After 20 minutes, the reactor contents were cooled, depressurized and the solid polymer collected. The product was dried in a vacuum oven for 12 hrs at 70°C (84 g). GPC-DRI; Mn = 6.3 Kg/mol; Mw = 13.9 Kg/mol; Mw/Mn = 2.2; g'_{vis} = 0.979. Mn = 7.0 Kg/mol by ^1H NMR. Vinyls = 87.7%, Vinylidenes = 7.5%. DSC; 2nd melt = 114.3 (d H = 37.7 J/g), sh at 117°C, cryst = 81.1, 92.1°C.

[0099] iPP-VTM M (12.5 g) was slurried in toluene (125 ml). PMHS X (2.1 g) was added to the reaction mixture. The reaction mixture was sparged with dry air and heated to 100°C. Kardsted catalyst (50 mg) was added and an aliquot withdrawn at 10 minutes. After 15 minutes, EP-VTM (6.5 g, 26826-81-6, J) was added and an aliquot withdrawn at 1 hr total reaction time. After 1 hr, octene (20 ml) was added and the reaction cooled after 1.5 hrs. Analysis of each aliquot at 10 minutes, 1 hr, and 1.5 hrs indicated no vinyl chain ends

remained and the Si-H region decreasing concomitantly. The final Si-H content was 8.9% compared to the original PMHS starting material. GPC-3D; Mn = 22.1 Kg/mol; Mw = 89.7 Kg/mol; Mz = 780.2 Kg/mol; $g'_{vis} = 0.414$. DSC; 2nd melt = 124.7°C (d H = 47.1 J/g); cryst. = 95.9°C.

Example 20. Reaction of aPP-VTM K with PMHS Y

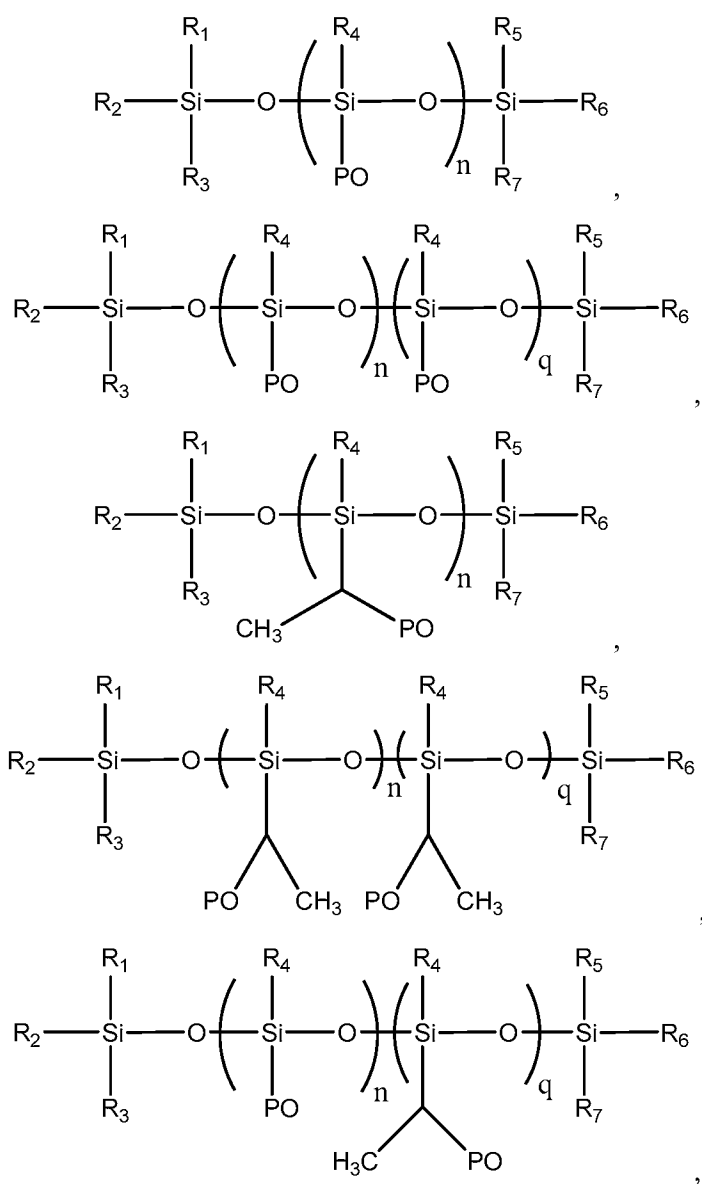
[00100] aPP-VTM H (32.5 g.) was dissolved in toluene (125 ml) and dried over 3 Å sieves. After decanting the solution, PMHS y (0.75 g.) was added and the reaction mixture was sparged with dry air. Kardstedt catalyst (60 mg) was added and the reaction mixture was stirred and sparged for 12 hrs. The volatiles were removed and the product dried in a vacuum oven at 80°C for 4 days (32.8 g). ²⁹Si NMR (C₆D₆, 79.5 MHz) δ ppm; 13 to 10 (m, -OSiMe₃, 2 Si), -17 to -26 (m, O-SiR(Me)-O, 3.7 Si), -27 to -35 (m, O-SiH(Me)-O, 0.4 Si).

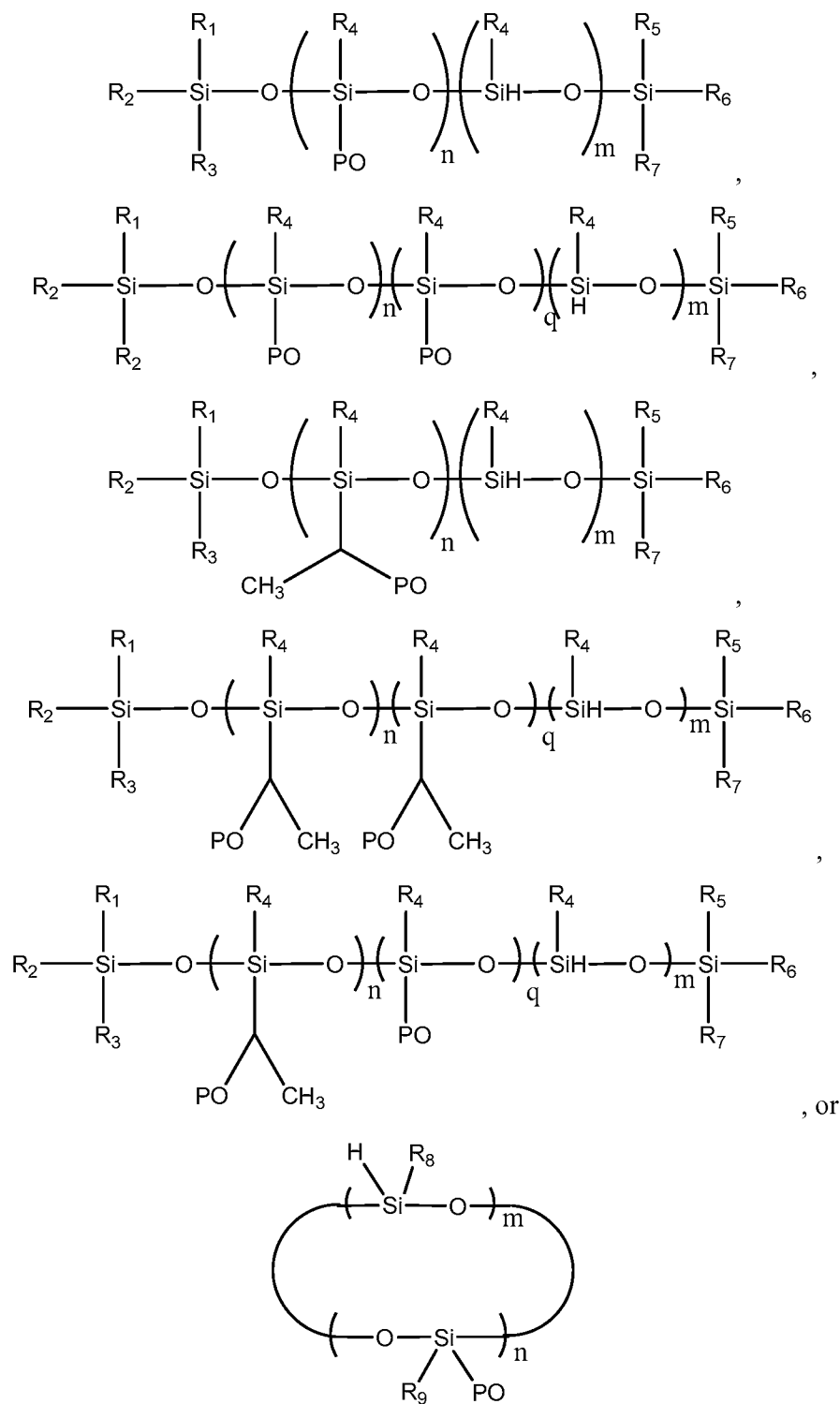
Comparative Example 2. Attempted Hydrosilation of Eicosene with PMHS Catalyzed by Cp₂ZrCl₂/nBuLi

[00101] Cp₂ZrCl₂ (62 mg, 0.21 mmol) in 10 mls of toluene was cooled to -30°C. nBuLi (0.3 mls, 0.42 mmol, 1.6M in hexanes) was added to the reaction mixture and the mixture warmed to 0°C. In a separate glass vessel, PMHS Y (1.00g, 2.5 mmol,) was dissolved in 10 mls toluene and was mixed with 1- eicosene (3.5 g, 12.5 mmol), dissolved in toluene (30 ml). Catalyst solution (2 ml) was added to the eicosene/PMHS reaction mixture. The reaction mixture was heated to 90°C and an aliquot taken at 1.5 hr. Analysis by ¹H NMR indicated > 95% vinyl chain ends remained. The reaction was continued at 90°C and monitored periodically at 3.5, 19, and 56 hrs. Analysis by ¹H NMR indicated that in all samples > 95% vinyl chain ends remained.

CLAIMS

1. The reaction product of a polyalkylhydrosiloxane and one or more vinyl terminated macromonomers (VTMs).
2. The reaction product of claim 1, wherein the alkyl group of the polyalkylhydrosiloxane is one of methyl, ethyl, propyl, butyl, pentyl, hexyl or combinations thereof.
3. A polyolefin composition comprising one or more of the following formulae:





wherein

each R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, and R₉ is, independently, an alkyl group;

each PO is, independently, the residual portion of a vinyl terminated macromonomer

(VTM) having had a terminal unsaturated carbon of an allylic chain and a vinyl carbon adjacent to the terminal unsaturated carbon;

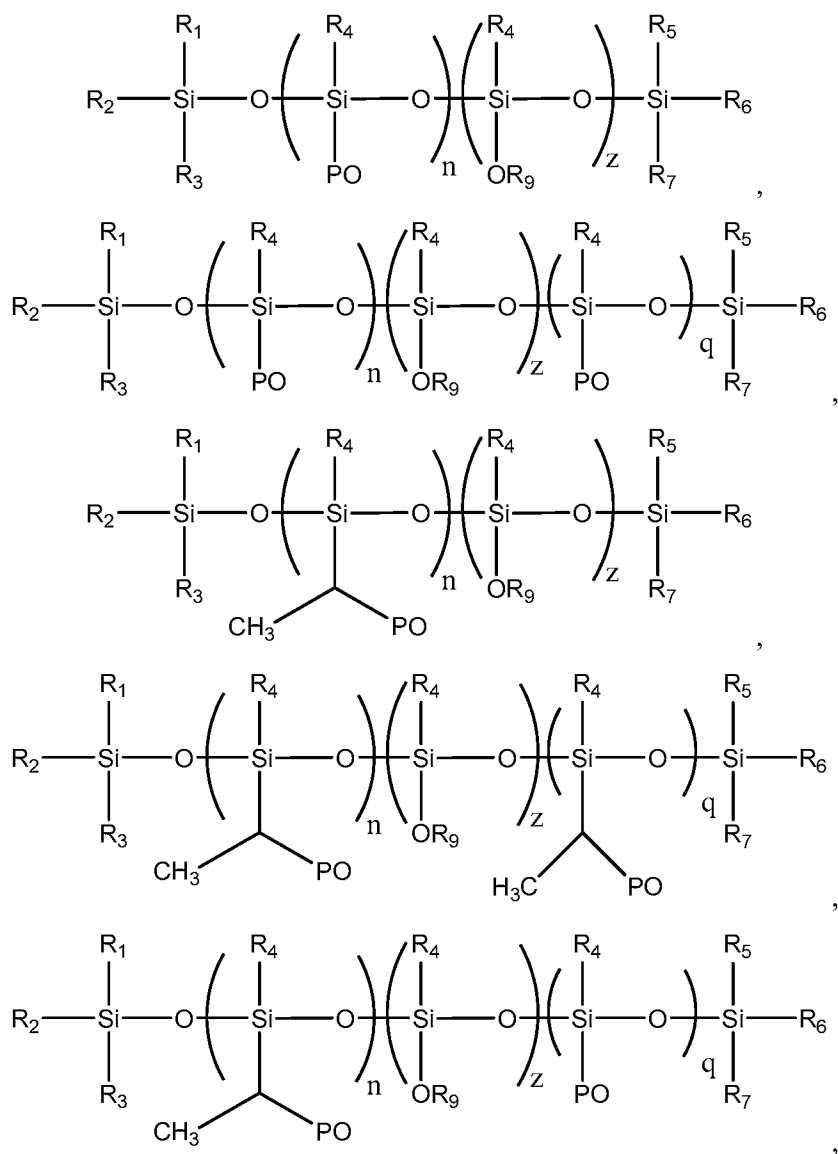
each m is 0 to 1000;

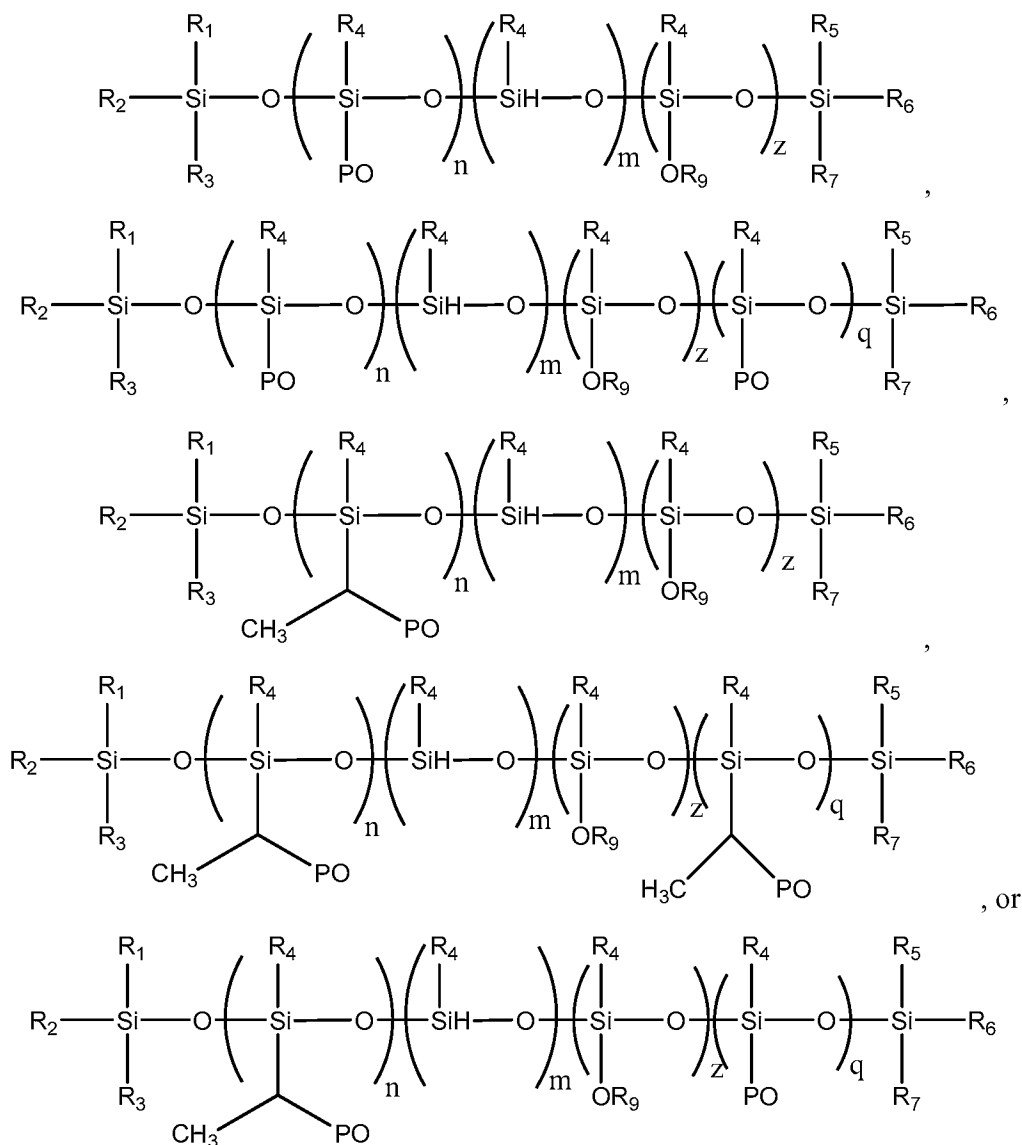
each n is 1 to 1000;

each q is 1 to 1000; and

m, n, and q can alternate or m, n, and q, can be randomly distributed throughout the polyolefin.

4. The polyolefin composition of claim 3, wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are each methyl groups.
5. A polyolefin composition comprising one or more of the following formulae:





wherein

each R₁, R₂, R₃, R₄, R₅, R₆, R₇, and R₉ is, independently, an alkyl group;

each PO is, independently, the residual portion of a vinyl terminated macromonomer (VTM) having had a terminal unsaturated carbon of an allylic chain and a vinyl carbon adjacent to the terminal unsaturated carbon;

each m is 0 to 1000;

each n is 1 to 1000;

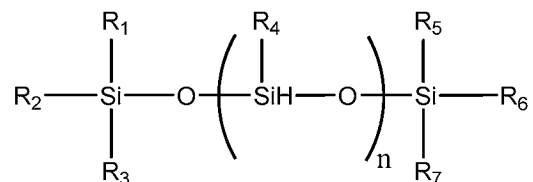
each q is 1 to 1000;

each z is 1 to 100; and

m, n, q, and z can alternate or m, n, q, and z can be randomly distributed throughout

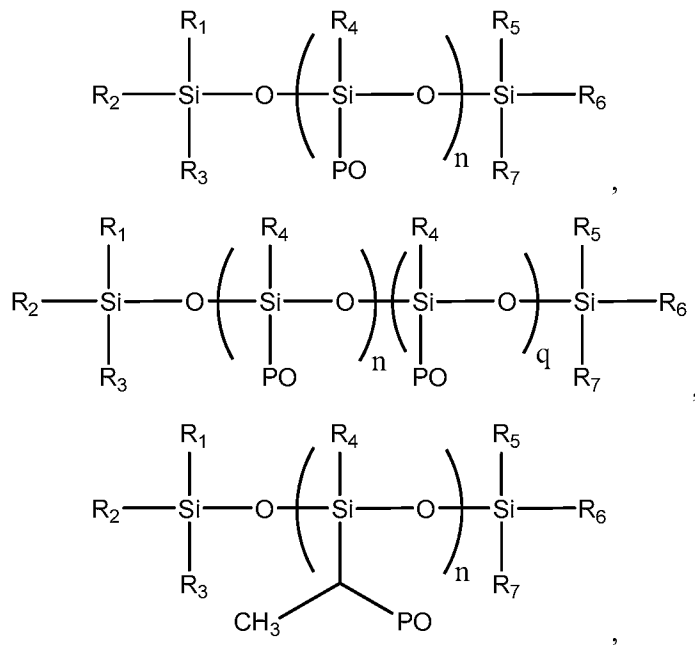
the polyolefin.

6. The polyolefin composition of claim 5, wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_9 are each methyl groups.
7. A method to functionalize a vinyl terminated macromonomer (VTM) comprising the step: contacting one or more VTMs with a compound having the formula

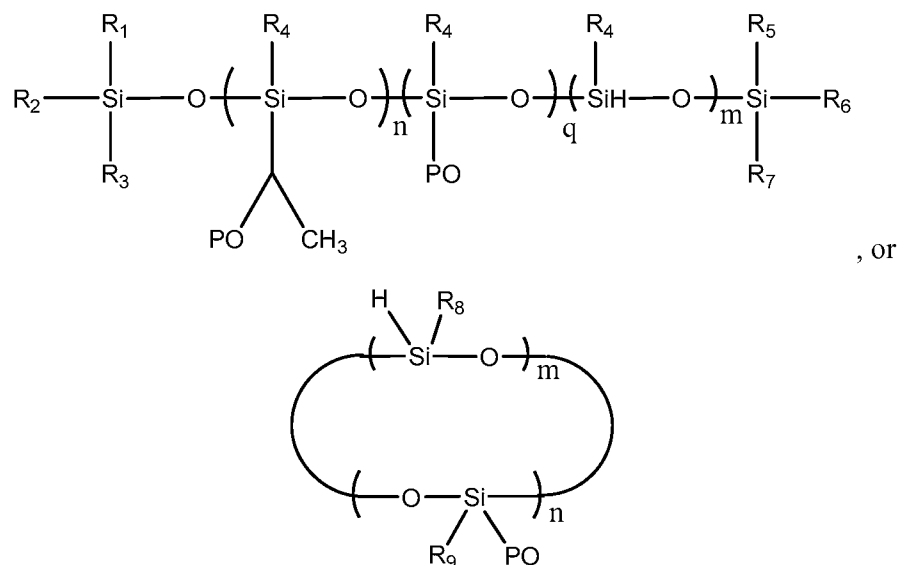


in the presence of a non Group IV metal catalyst to provide a hydrosilated functionalized VTM in the presence of a non Group IV metal catalyst to provide a hydrosilated functionalized VTM, wherein each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 is, independently, an alkyl group; each m is 0 to 1000.

8. The method of claim 7, wherein the catalyst is a platinum catalyst.
9. The method of claims 7 or 8, wherein the hydrosilated functionalized VTM comprises one or more of the following formulae:







wherein

each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , R_8 , and R_9 is, independently, an alkyl group;

each PO is, independently, the residual portion of a vinyl terminated macromonomer (VTM) having had a terminal unsaturated carbon of an allylic chain and a vinyl carbon adjacent to the terminal unsaturated carbon;

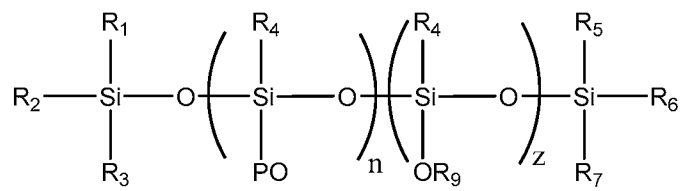
each m is 0 to 1000;

each n is 1 to 1000;

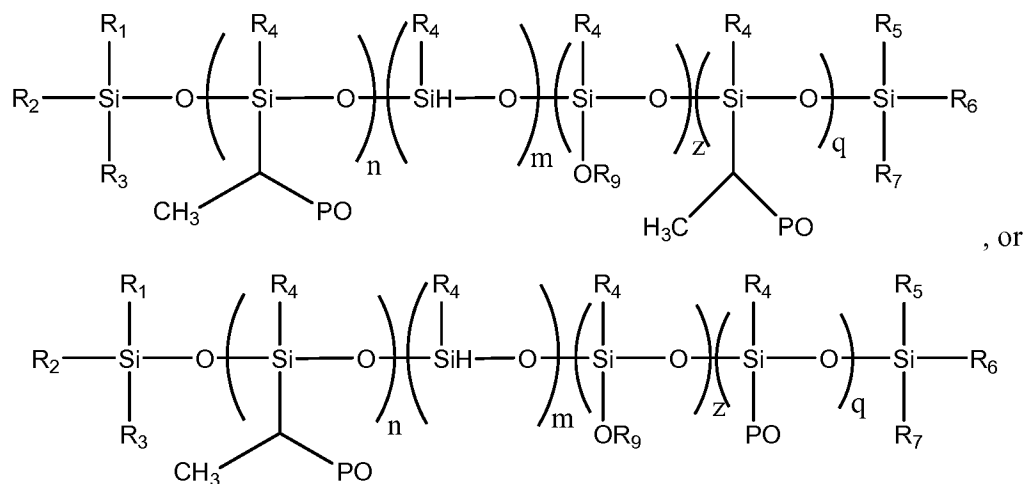
each q is 1 to 1000; and

m , n , and q can alternate or m , n , and q , can be randomly distributed throughout the polyolefin.

10. The method of claim 9, wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are each methyl groups.
11. The method of claims 7 through 10, further comprising the step:
treating the hydrosilated polyolefin with an alcohol to provide a composition comprising one or more of the following formulae:







wherein

each R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_9 is, independently, an alkyl group;

each PO is, independently, the residual portion of a vinyl terminated macromonomer (VTM) having had a terminal unsaturated carbon of an allylic chain and a vinyl carbon adjacent to the terminal unsaturated carbon;

each m is 0 to 1000;

each n is 1 to 1000;

each q is 1 to 1000;

each z is 1 to 100; and

m , n , q , and z can alternate or m , n , q , and z can be randomly distributed throughout the polyolefin.

12. The method of claim 11, wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R_7 , and R_9 are each methyl groups.
13. The reaction product of claim 1, or the composition or method of any of claims 3 through 11, wherein the VTM is one or more of:
 - (i) a vinyl terminated oligomer or co-oligomer having at least 5% allyl chain ends;
 - (ii) a vinyl terminated oligomer or co-oligomer having an M_n of at least 160 g/mol (measured by ^1H NMR) comprising of one or more C_4 to C_{40} higher olefin derived units, where the higher olefin polymer comprises substantially no propylene derived units; and wherein the higher olefin polymer has at least 5% allyl chain ends;
 - (iii) a co-oligomer having an M_n of 300 g/mol or more (measured by ^1H NMR)

comprising (a) from 20 mol% to 99.9 mol% of at least one C₅ to C₄₀ higher olefin derived units, and (b) from 0.1 mol% to 80 mol% of propylene derived units, wherein the higher olefin copolymer has at least 40% allyl chain ends;

(iv) a co-oligomer having an Mn of 300 g/mol or more (measured by ¹H NMR), and comprises (a) from 80 mol% to 99.9 mol% of at least one C₄ olefin derived unit, (b) from 0.1 mol% to 20 mol% of propylene derived units; and wherein the vinyl terminated macromonomer has at least 40% allyl chain ends relative to total unsaturation;

(v) a co-oligomer having an Mn of 300 g/mol to 30,000 g/mol (measured by ¹H NMR) comprising 10 mol% to 90 mol% propylene derived units and 10 mol% to 90 mol% of ethylene derived units, wherein the co-oligomer has at least X% allyl chain ends (relative to total unsaturations), where: 1) $X = (-0.94 * (\text{mol\% ethylene incorporated}) + 100)$, when 10 mol% to 60 mol% ethylene derived units are present in the co-oligomer, 2) $X = 45$, when greater than 60 mol% and less than 70 mol% ethylene derived units are present in the co-oligomer, and 3) $X = (1.83 * (\text{mol\% ethylene incorporated}) - 83)$, when 70 mol% to 90 mol% ethylene derived units are present in the co-oligomer;

(vi) a propylene co-oligomer, comprising more than 90 mol% propylene derived units and less than 10 mol% ethylene derived units; wherein the co-oligomer has: at least 93% allyl chain ends, a number average molecular weight (Mn) of 500 g/mol to 20,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.35:1.0, less than 100 ppm aluminum, and/or less than 250 regio defects per 10,000 monomer units;

(vii) a propylene co-oligomer, comprising: at least 50 mol% propylene derived units and from 10 mol% to 50 mol% ethylene derived units, wherein the co-oligomer has: at least 90% allyl chain ends, an Mn of 150 g/mol to 20,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, wherein monomers having four or more carbon atoms are present at from 0 mol% to 3 mol%;

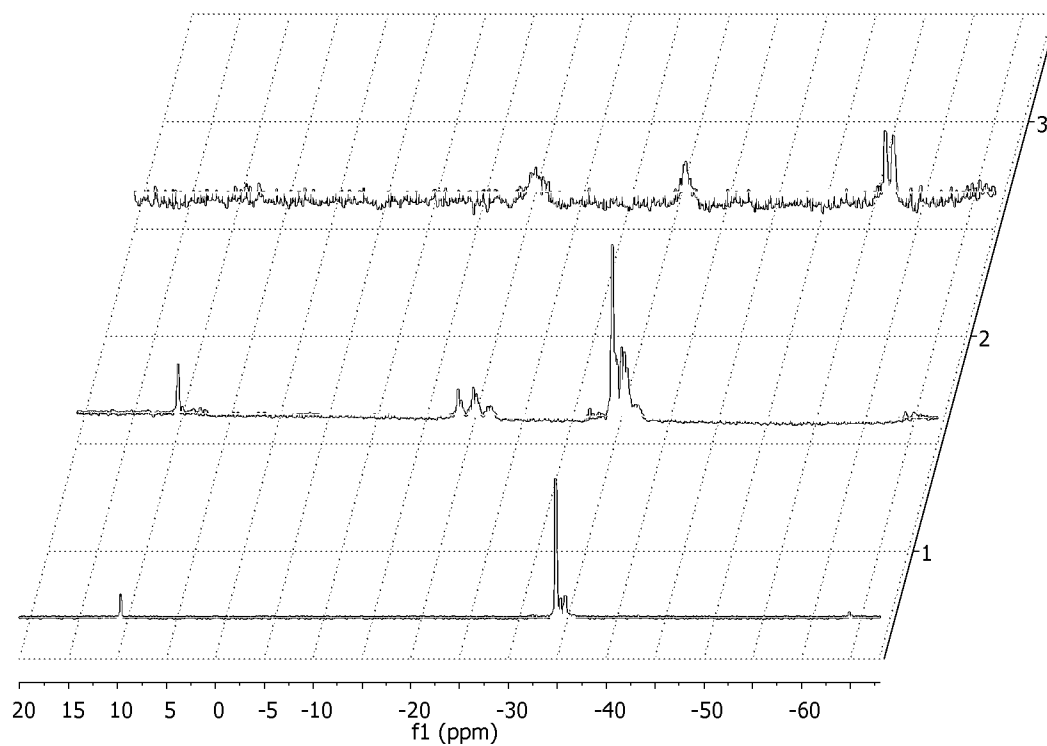
(viii) a propylene co-oligomer, comprising: at least 50 mol% propylene derived units, from 0.1 mol% to 45 mol% ethylene derived units, and from 0.1 mol% to 5 mol% C₄ to C₁₂ olefin derived units, wherein the co-oligomer has: at least 90% allyl chain ends, an Mn of 150 g/mol to 10,000 g/mol, and an isobutyl chain end to allylic

- vinyl group ratio of 0.8:1 to 1.35:1.0;
- (ix) a propylene co-oligomer, comprising: at least 50 mol% propylene derived units, from 0.1 mol% to 45 mol% ethylene derived units, and from 0.1 mol% to 5 mol% diene derived units, wherein the co-oligomer has: at least 90% allyl chain ends, an Mn of 150 g/mol to 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.7:1 to 1.35:1.0;
 - (x) a homo-oligomer, comprising propylene, wherein the homo-oligomer has: at least 93% allyl chain ends, an Mn of 500 g/mol to 70,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, and less than 1400 ppm aluminum;
 - (xi) vinyl terminated polyethylene having: (a) at least 60% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.0; (c) a $g'(\text{vis})$ of greater than 0.95; and (d) an Mn (^1H NMR) of at least 20,000 g/mol; and
 - (xii) vinyl terminated polyethylene having: (a) at least 50% allyl chain ends; (b) a molecular weight distribution of less than or equal to 4.0; (c) a $g'(\text{vis})$ of 0.95 or less; (d) an Mn (^1H NMR) of at least 7,000 g/mol; and (e) a Mn (GPC)/Mn (^1H NMR) in the range of from 0.8 to 1.2.
14. The polyolefin composition of any of claims 1 through 6 or 13, wherein $n+q$ is at least 5 and PO has an Mn of from 160 to 30,000 g/mol.
 15. The polyolefin composition of any of claims 1 through 6 or 13, wherein $n+q$ is 1, 2, 3, 4, or 5; PO has an Mn of from 160 to 40,000 g/mol, and the composition shows a $\tan \delta (G''/G')$ of 1 or less at 50°C and at least 30 or more at 80°C.
 16. The polyolefin compositions of any of claims 1 through 6 or 13, wherein the ratio of Si-alkylated to Si-H is 1000:1.
 17. The method of any of claims 7 through 12, further comprising the step of passing dry air through the polyolefin product.

Attorney Docket No. 2012EM282 PCT; Inventor(s): Donna CROWTHER et al.
Title: Hydrosilation of Vinyl-Terminated Macromonomers with Polalkylhydrosiloxane to Yield
Highly Branched Materials or Linear Materials by Further Modification

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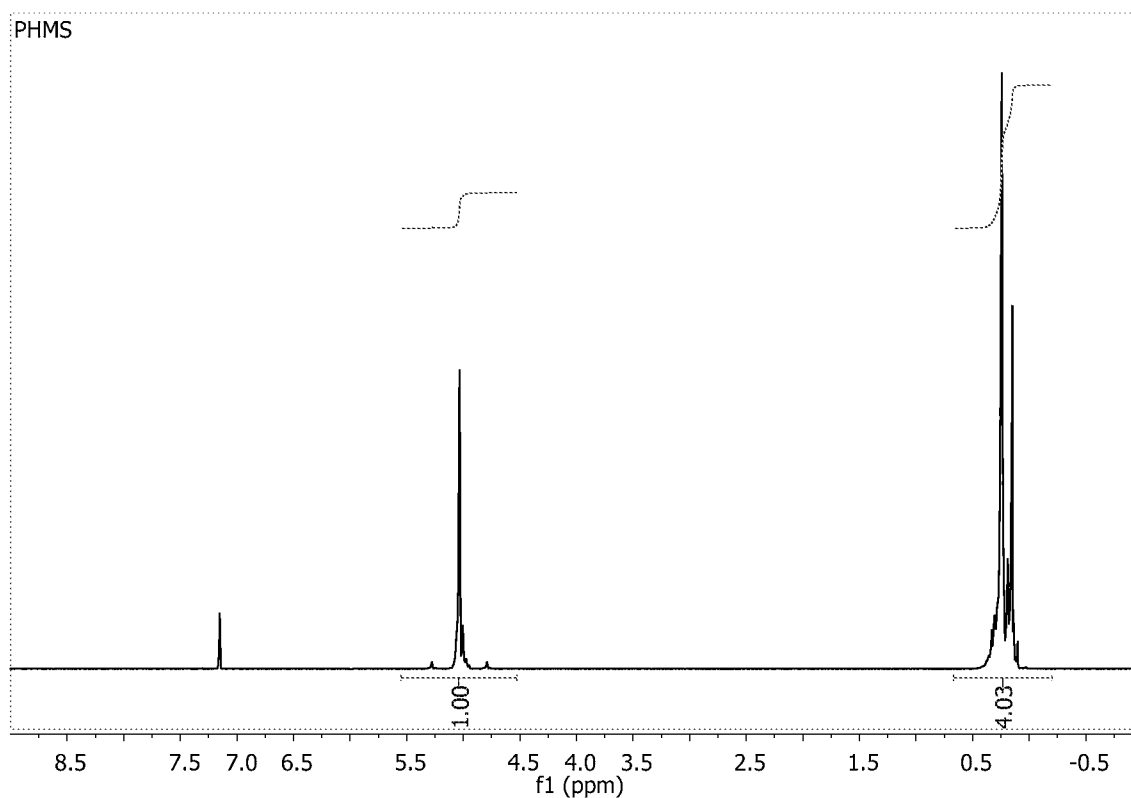
Figure 1



Attorney Docket No. 2012EM282 PCT; Inventor(s): Donna CROWTHER et al.
Title: Hydrosilation of Vinyl-Terminated Macromonomers with Polalkylhydrosiloxane to Yield
Highly Branched Materials or Linear Materials by Further Modification

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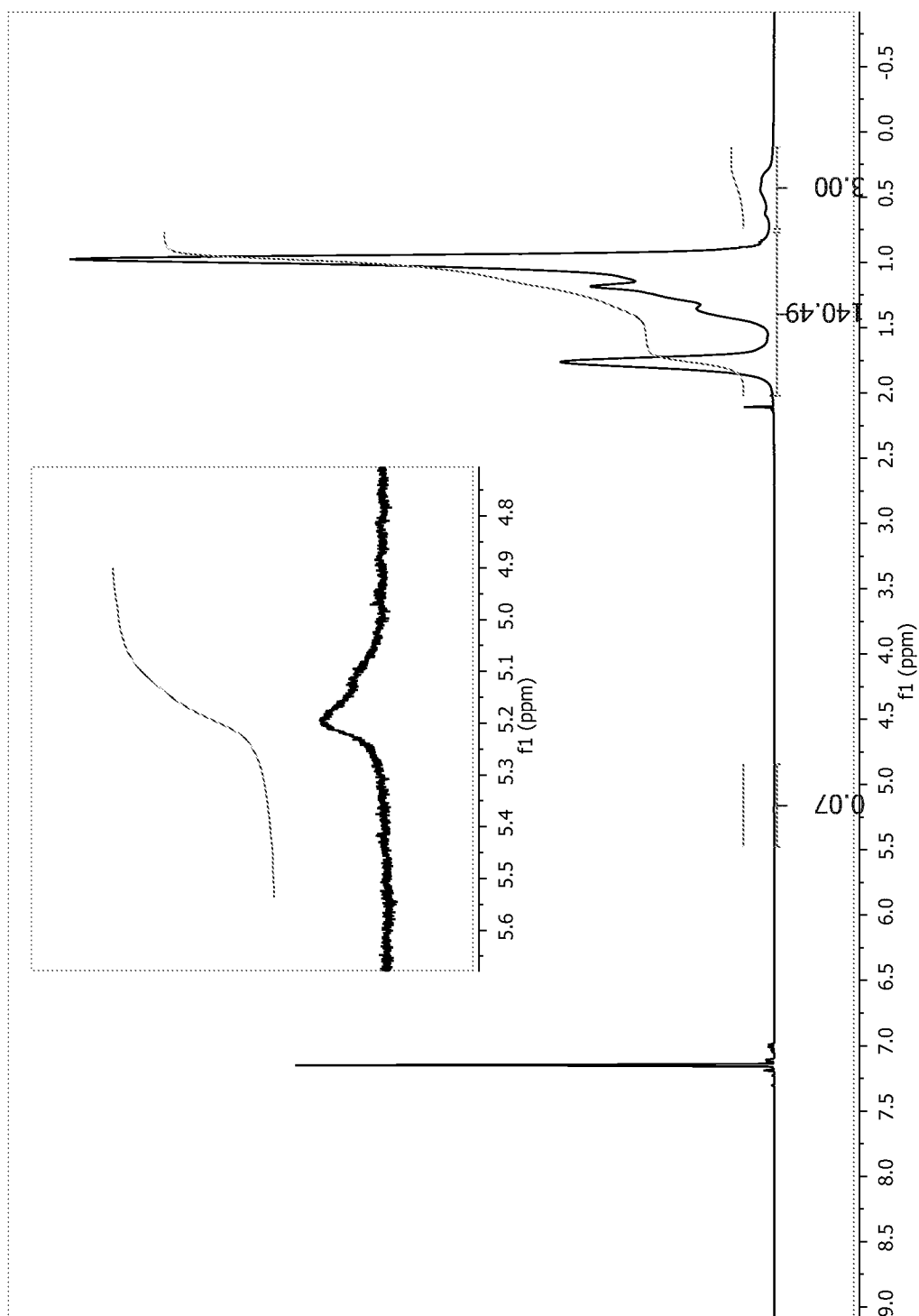
Figure 2



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Title: Hydrosilation of Vinyl-Terminated Macromonomers with Polyalkylhydrosiloxane to Yield
Highly Branched Materials or Linear Materials by Further Modification

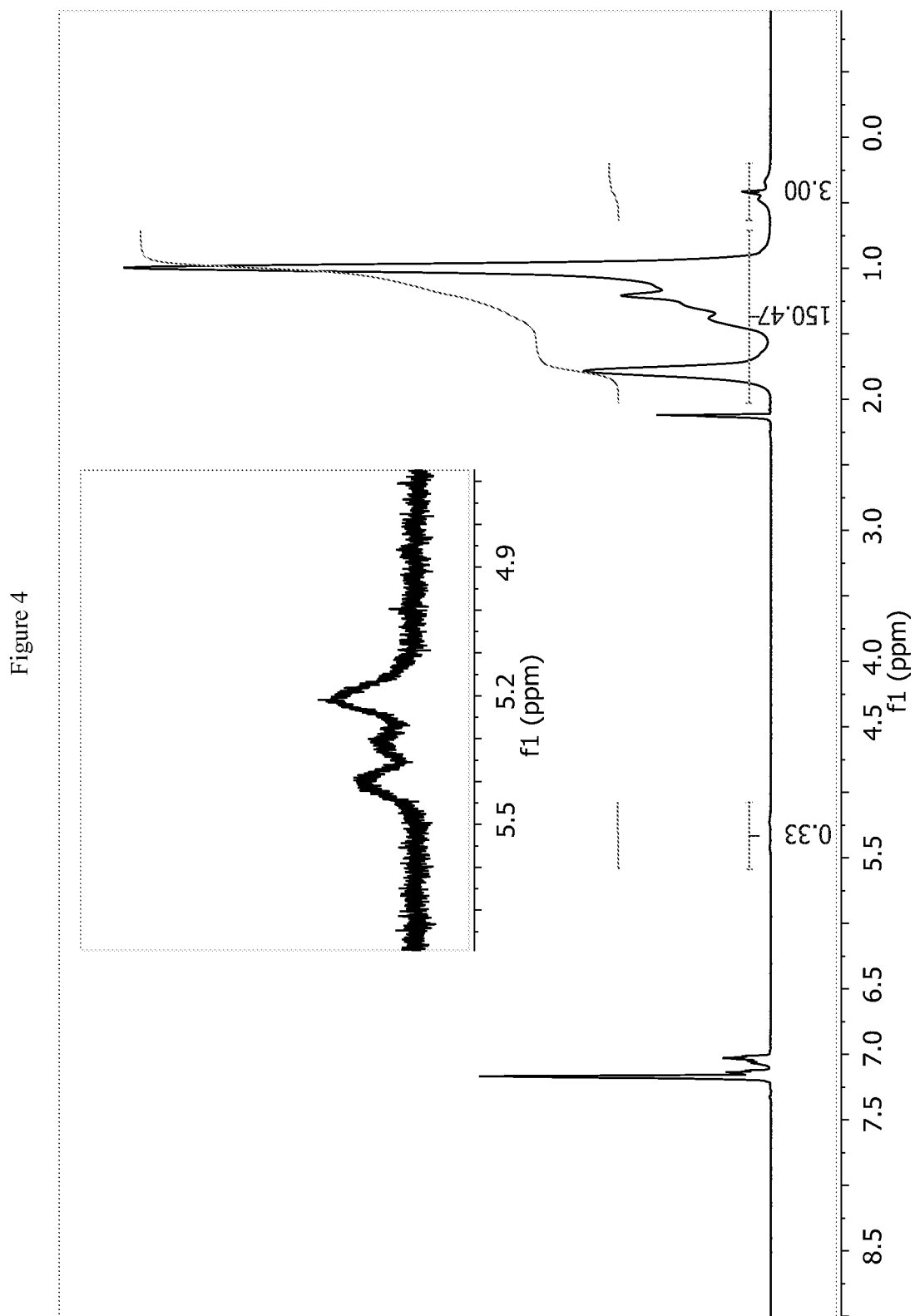
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Figure 3



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Title: Hydrosilation of Vinyl-Terminated Macromonomers with Polyalkylhydrosiloxane to Yield
Highly Branched Materials or Linear Materials by Further Modification

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Figure 5

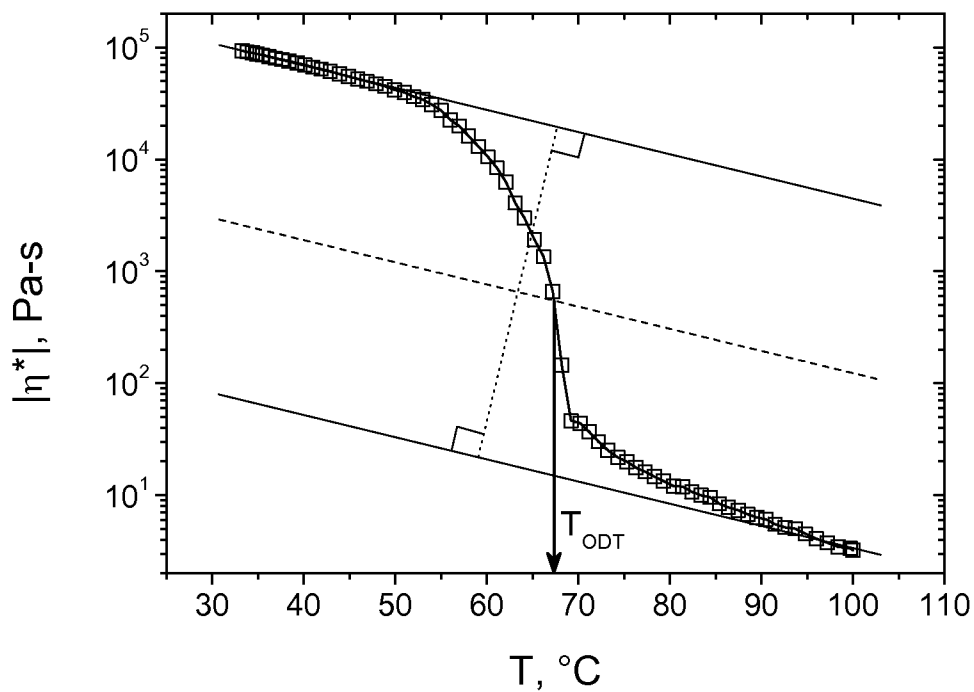
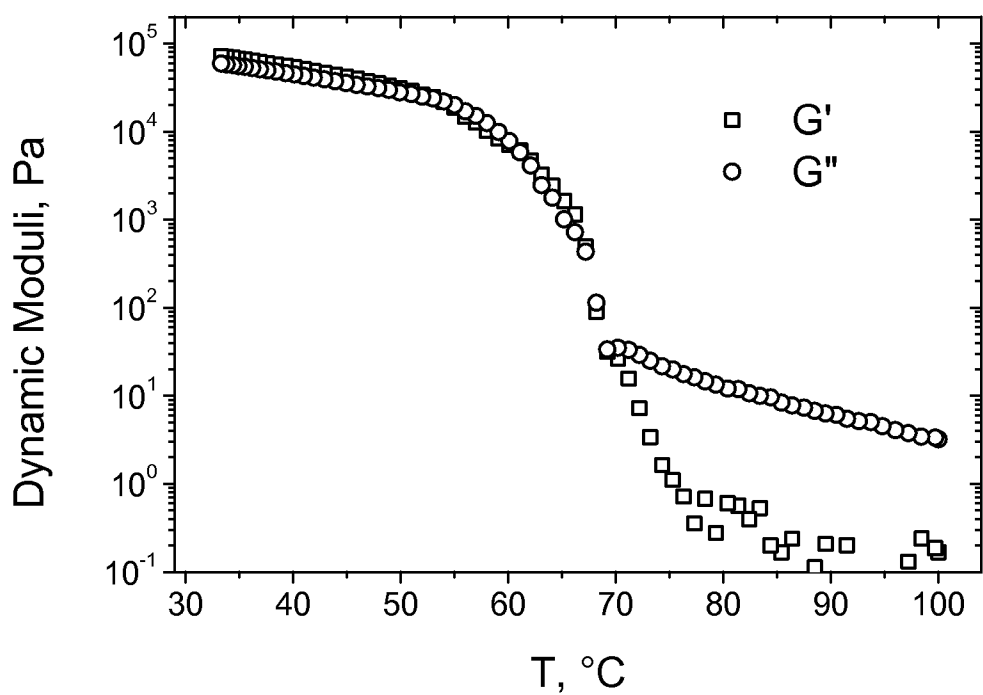


Figure 6



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Highly Branched Materials or Linear Materials by Further Modification

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Figure 7

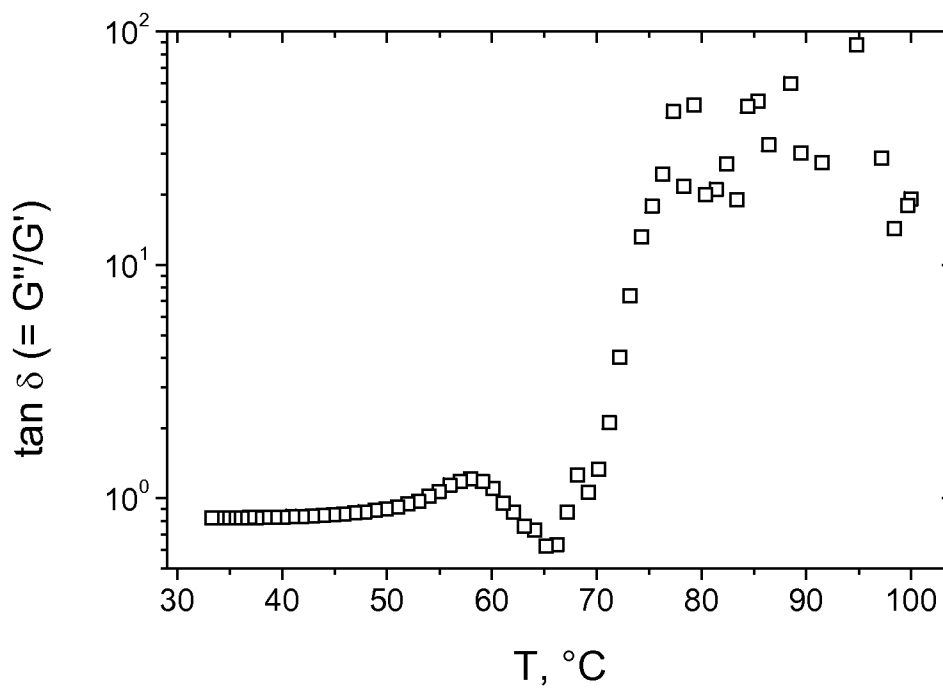
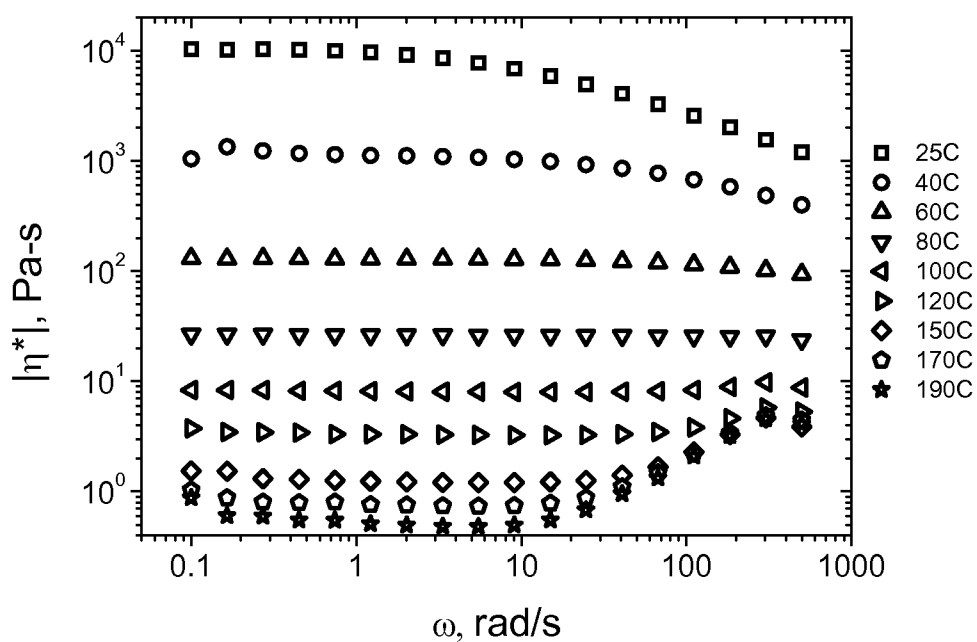


Figure 8



Attorney Docket No. 2012EM282 PCT; Inventor(s): Donna CROWTHER et al.
 Title: Hydrosilation of Vinyl-Terminated Macromonomers with Polyalkylhydrosiloxane to Yield
 Highly Branched Materials or Linear Materials by Further Modification

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Figure 9

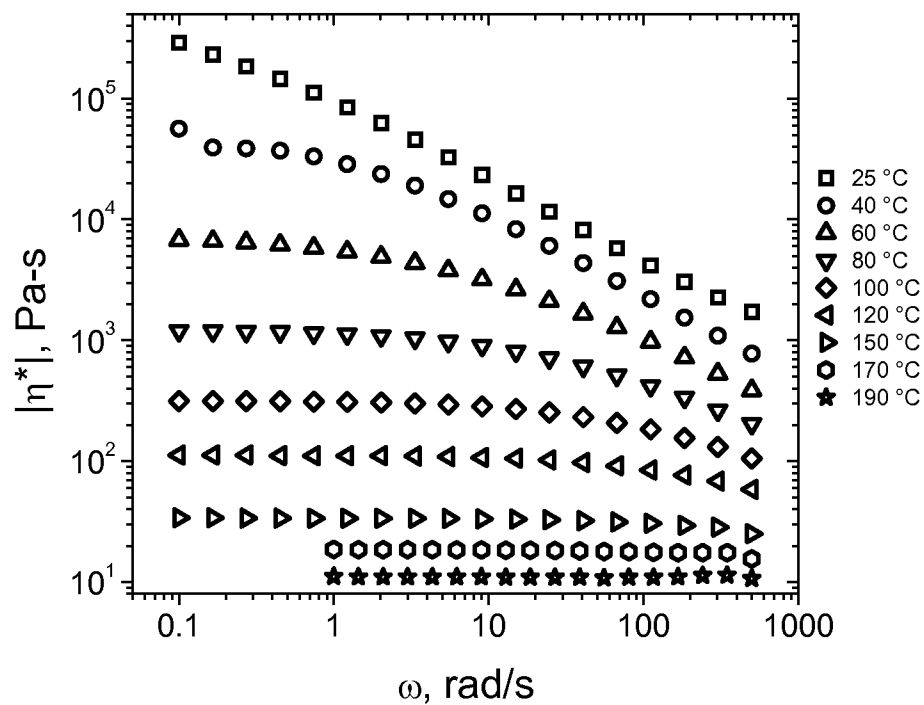
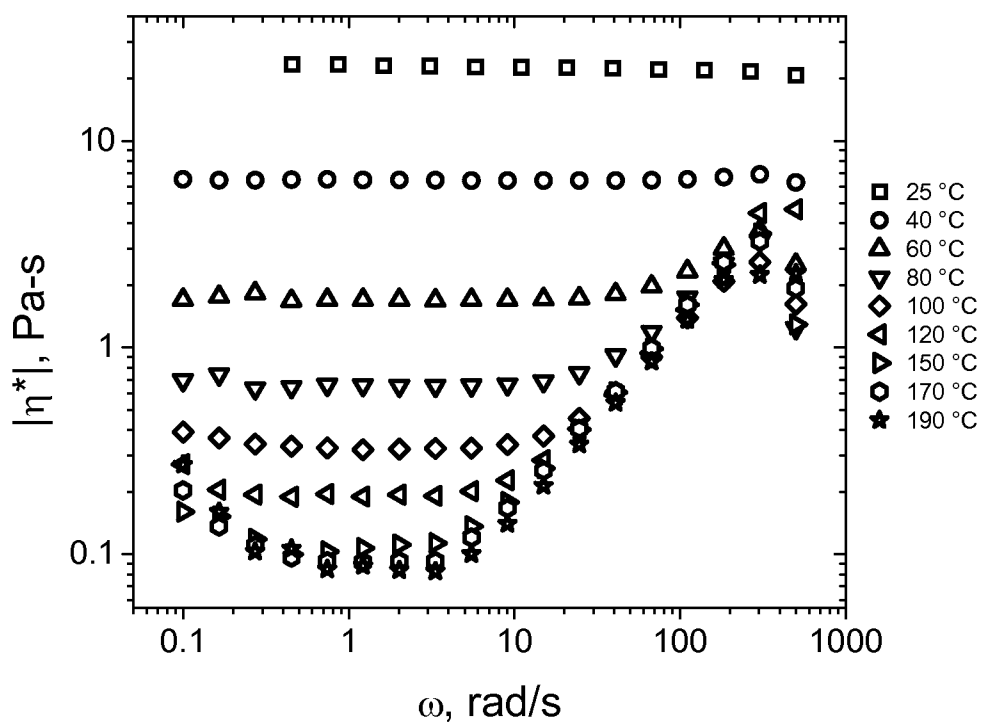


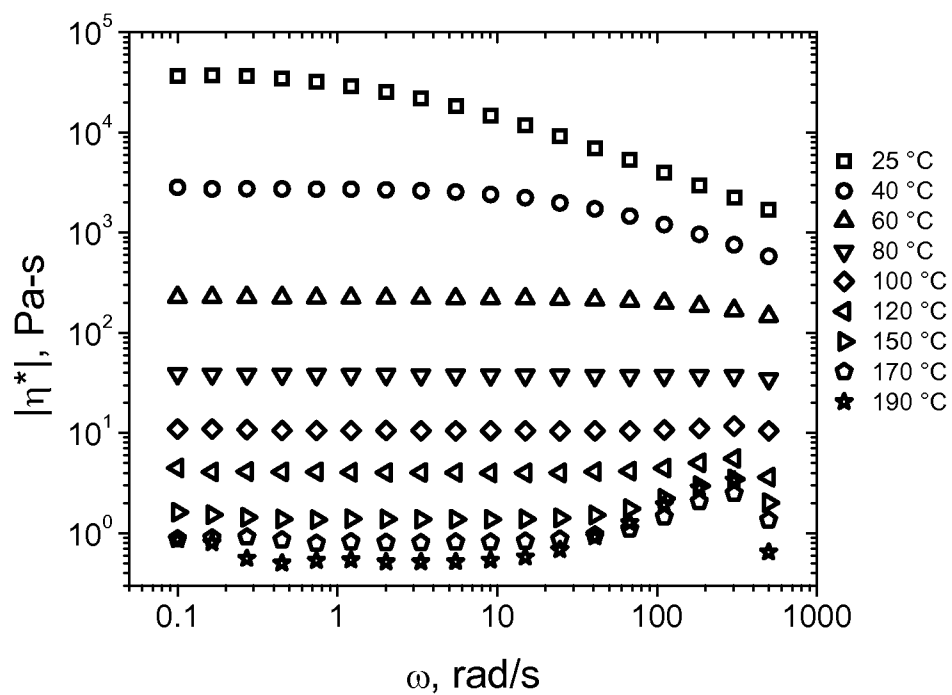
Figure 10



Attorney Docket No. 2012EM282 PCT; Inventor(s): Donna CROWTHER et al.
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Figure 11



A. CLASSIFICATION OF SUBJECT MATTER**C08F 299/08(2006.01)i, C08G 77/442(2006.01)i, C08L 53/00(2006.01)i, C08L 83/10(2006.01)i**

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)

C08F 299/08; G01N 31/22; C08F 4/80; B32B 27/28; C08F 118/02; G01N 21/64; C08G 77/38; C08G 81/02; C08F 4/44; C08G 77/442; C08L 53/00; C08L 83/10

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) & Keywords: polyalkylhydrosiloxane, vinyl terminated macromonomer, VTM, polyolefin, hydrosilation, platinum catalyst.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009-146340 A1 (SEEO, INC.) 03 December 2009 See abstract; claim 1; paragraphs [0001], [0011], [0030].	1-4, 7-10
A		5, 6
A	US 2005-0054793 A1 (REINKING, M. K. et al.) 10 March 2005 See abstract; claims 1, 10; paragraphs [0001], [0011], [0043]-[0045].	1-10
A	US 7247385 B1 (TZOGANAKIS, C. et al.) 24 July 2007 See abstract; claims 1, 7; column 1, lines 14-17; column 1, line 58 - column 2, line 61.	1-10
A	US 2009-0318647 A1 (HAGADORN, J. R. et al.) 24 December 2009 See abstract; claims 1, 24; paragraphs [0003], [0015]-[0021], [0030].	1-10
A	EP 0413114 A2 (PURITAN-BENNETT CORPORATION) 20 February 1991 See abstract; claims 1, 3; page 2, line 54 - page 3, line 19; page 5, lines 18-51.	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

09 December 2013 (09.12.2013)

Date of mailing of the international search report

09 December 2013 (09.12.2013)

Name and mailing address of the ISA/KR


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INTERNATIONAL SEARCH REPORTInternational application No.
PCT/US2013/060993**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 12
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
The above claim refers to a claim which is not drafted in accordance with the third sentence of Rule 6.4(a). Thus, no meaningful search could be carried out.
3. ☒ Claims Nos.: 11, 13-17
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/060993

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009-146340 A1	03/12/2009	None	
US 2005-0054793 A1	10/03/2005	CA 2535025 A1 CN 1849346 A CN 1849346 C EP 1664131 A1 US 6939930 B2 WO 2005-026221 A1	24/03/2005 18/10/2006 18/10/2006 07/06/2006 06/09/2005 24/03/2005
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2013/060993

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		CA 2019726 A1	16/02/1991
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		EP 0468777 B1	01/03/1995
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		US 05182353 A	26/01/1993