



(51) International Patent Classification:

C08F 8/42 (2006.01) *C08L 23/26* (2006.01)
C08F 10/02 (2006.01) *C08J 5/00* (2006.01)

(21) International Application Number:

PCT/US2013/060547

(22) International Filing Date:

19 September 2013 (19.09.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/704,611 24 September 2012 (24.09.2012) 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, 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, SA, 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, KM, ML, MR, NE, SN, TD, TG).

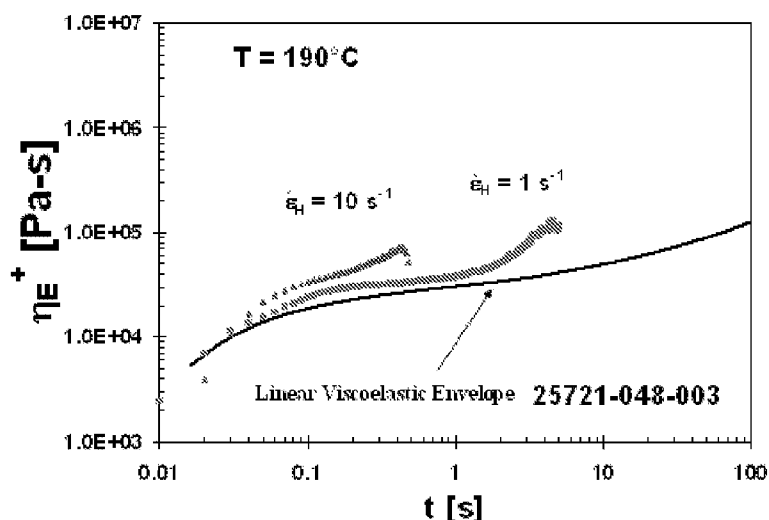
Declarations under Rule 4.17:

- as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))
- as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))

[Continued on next page]

(54) Title: BRANCHED POLYETHYLENES BY HYDROSILATION GRAFTING TO IMPROVE PROCESSABILITY OF POLYETHYLENE

Figure 1. Example 2 Extensional Rheology Plot



(57) Abstract: This invention relates to blends of polyolefins (PAOs) and polyhydrosilane-modified polyolefins, methods to prepare the blends and methods to prepare polyhydrosilane-modified polyolefins.

WO 2014/047248 A1



Published:

— *with international search report (Art. 21(3))*

**BRANCHED POLYETHYLENES BY HYDROSILATION GRAFTING TO
IMPROVE PROCESSABILITY OF POLYETHYLENE**

FIELD OF THE INVENTION

[0001] This invention relates to coupling of vinyl terminated polyolefins with a polysilane or a polysiloxane in the presence of a non-metallocene catalyst.

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: S. B. Amin and T. J. Marks, *Angew. Chem. Int. Ed.* **2008**, 47, pp. 2006-2025; T. C. Chung, *Prog. Polym. Sci.* **2002**, 27, pp. 39-85; and R. G. Lopez, F. D'Agosto, C. Boisson, *Prog. Polym. Sci.* **2007**, 32, pp. 419-454. A process with a reduced number of steps 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; *Angew. Chem. Int. Ed.* 2009, 48, pp. 8361-8365; *Angew. Chem. Int. Ed.* 2009, 48, pp. 4892-4894; Yuki Gosei Kagaku Kyokaishi (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.

[0004] WO 98/33842 discloses the production of branched polyolefins comprising a silicon containing polymeric backbone with branches extending therefrom in which the branches are formed of polyolefins wherein the branched polymers are produced by a hydrosilation reaction between the polyolefin prearms with a hydrosilane containing group.

[0005] U.S. Patent No. 6,084,030 discloses branched polyolefin polymers in the form of a comb, star, nanogel, and structural combinations thereof comprising a plurality of polyolefin arms selected from the group consisting of (1) polymers of ethylene; (2) polymers of propylene; and (3) copolymers of ethylene with one or more 1-alkenes, said arms being linked to the polymeric backbone, wherein the reactive polymeric backbone is formed from a siloxane, and said backbone contains at least 4-300 polyolefin arms, and said branched polyolefin polymer is prepared by coupling the polyolefin prearms with said polymeric backbone.

[0006] U.S. Patent No. 8,399,725 discloses certain vinyl terminated oligomers and

polymers that are functionalized for use in lubricant applications.

[0007] U.S. Patent No. 8,372,930 discloses certain vinyl terminated oligomers and polymers that are functionalized in U.S. Patent No. 8,399,725.

[0008] U.S. Patent No. 8,283,419 discloses a process to functionalize propylene homo- or co-oligomer comprising contacting an alkene metathesis catalyst with a heteroatom containing alkene and a propylene homo- or co-oligomer having terminal unsaturation.

[0009] U.S. Patent No. 8,501,894 discloses a process to functionalize polyolefins comprising contacting a metallocene catalyst with a hydrosilane, and one or more vinyl terminated polyolefins. This invention further relates to the hydrosilane-functionalized polyolefins produced thereby.

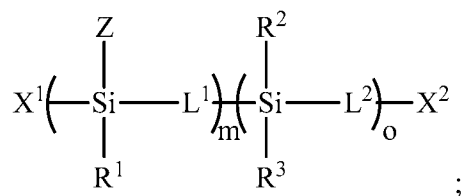
[0010] U.S. Publication No. 2012-0245293 discloses a process to functionalize polyolefins comprising contacting a metallocene catalyst with a difunctional diblock hydrosilane, and one or more vinyl terminated polyolefins. This invention further relates to the diblock hydrosilane-functionalized polyolefins produced thereby.

[0011] 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, and surface modifiers.

[0012] Thus, there is an ongoing need to develop a means to provide functionalized polyolefins with different polymeric architectures by efficient reactions, particularly reactions with good conversion, preferably under mild reaction conditions with a minimal number of steps, preferably one or two steps, preferably without solvent.

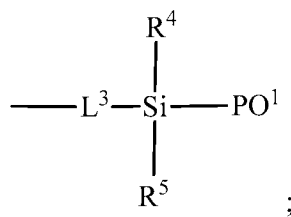
SUMMARY OF THE INVENTION

[0013] This invention relates to a modified polyolefin represented by the formula:



wherein:

Z is a group represented by the formula:



wherein PO¹ is a substituted or unsubstituted hydrocarbyl group having from 20 or 30 or 40 or 50 or 100 or 200 to 10,000 carbon atoms;

R¹ is Z, hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or PO⁴, wherein PO⁴ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms;

each R², R³, R⁴, and R⁵, independently, is hydrogen, a C₁ to a C_j substituted or unsubstituted hydrocarbyl group, wherein R² and R³ and/or R⁴ and R⁵ may form a cyclic structure with Si, or, a PO⁴;

each L¹, L², and L³, independently, is a bond or a linking group;

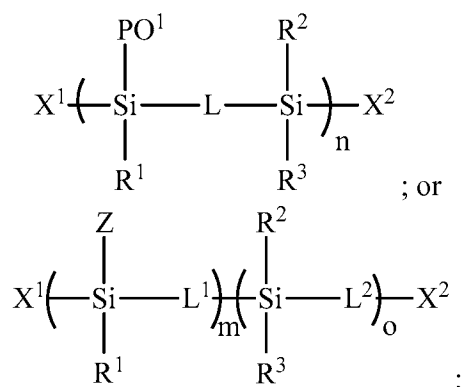
m is an integer from 1 to 1000;

o is an integer from 0 to 1000; and

X¹ and X², each independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or a PO⁴;

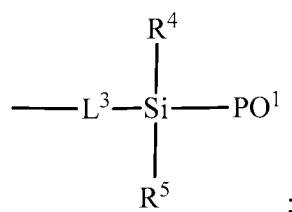
wherein each PO¹ and PO⁴ may be the same or different.

[0014] This invention also relates to modified polyolefin represented by the formula:



wherein:

Z is a group represented by the formula:



wherein PO¹ is a substituted or unsubstituted hydrocarbyl group having from 20 or 30 or 50 or 100 to 10,000 carbon atoms derived from a vinyl terminated macromonomer;

each R¹, R², R³, R⁴, and R⁵, independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, where R² and R³ may form a cyclic structure with Si, or a PO⁴, wherein PO⁴ is a substituted or unsubstituted hydrocarbyl group having

from 20 to 10,000 carbon atoms derived from a vinyl terminated macromonomer;
each L, L¹, L², and L³, is a bond or a linking group;
m is an integer from 1 to 1000 (preferably m is from 100 to 500);
n is an integer 1 to 1000 (preferably n is from 100 to 500);
o is an integer from 0 to 1000 (preferably o is 0; preferably o is from 100 to 500); and
X¹ and X², each independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted
hydrocarbyl group, or a PO⁴;
wherein each PO¹ and PO⁴ may be the same or different.

BRIEF DESCRIPTION OF THE FIGURES

[0015] Figure 1 depicts an extensional rheology plot for Example 2 comparative modified polymers.

[0016] Figure 2 is a VanGurp-Palmen Plot for Example 2 comparative modified copolymers and their comparison with raw materials.

[0017] Figure 3 provides a complex viscosity vs. frequency plot for Example 2 comparative modified copolymers and their comparison with raw materials.

DETAILED DESCRIPTION

[0018] This invention is related to polyolefins modified by hydrosilylation. Methods of producing these modified polyolefins are also disclosed. Articles comprising these modified polyolefins are also within the scope of this invention.

[0019] The present invention relates to ethylene-based hydrosilylated polyolefins and blends thereof, especially for blown film applications. Films made using conventional high density polyethylene typically have low processability and often tend to have gels. The low processability of these HDPE polymers coupled with the undesirable gel formation affects bubble stability in blown film processes. Current attempts to improve this involve adding LDPE at low loadings, typically at around 5 wt%; however, this generally leads to an undesirable decrease in mechanical properties such as dart drop strength, bubble stability, and tear properties.

[0020] The inventors have surprisingly found that blends of the hydrosilylated polyolefins (and/or macromers) disclosed herein with HDPE, even at lower loadings than traditionally used for LDPE, demonstrated improved processability without the same sacrifice of desirable properties such as haze, internal haze, and desired mechanical properties. This provides a cost advantage as less of the modified polyolefin is needed. The inventive processes to produce these modified polyolefins, the modified polyolefins, and

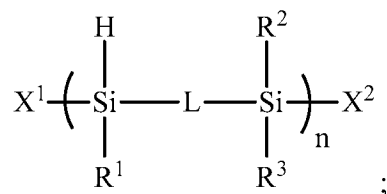
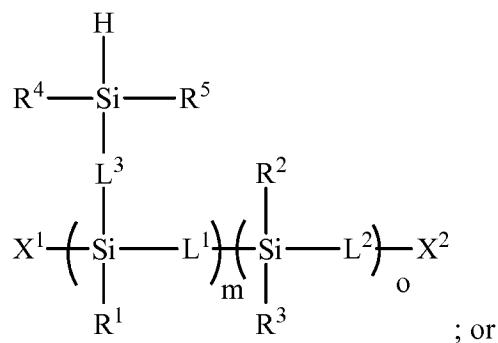
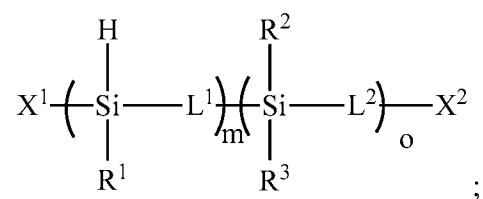
applications for their use are described, in turn, below. Note that any definitions not set forth herein are described in detail in “Branched Polyethylenes by Hydrosilylation Grafting to Improve Processability of Polyethylene”, U.S.S.N. _____, filed concurrently herewith.

Processes to Produce Modified Polyolefins

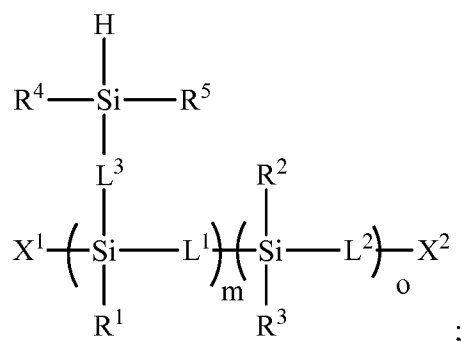
[0021] This invention relate to processes to prepare a modified polyolefin comprising the steps of:

(i) contacting a non-metallocene catalyst, a hydrosilylation modifier, and one or more vinyl terminated polyolefin selected from a vinyl terminated polyolefin and a vinyl terminated macromonomer;

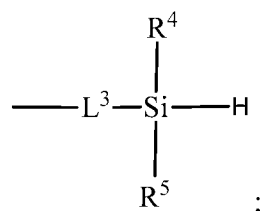
wherein when the vinyl terminated polyolefin is a vinyl terminated macromonomer, the hydrosilylation modifier is represented by one of more of the formulae:



wherein when the vinyl terminated polyolefin is a vinyl terminated polyolefin, the hydrosilylation modifier is represented by the formula:



wherein R^1 is hydrogen, Z' , or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group; and wherein Z' is a group represented by the formula:



each R^2 , R^3 , R^4 , and R^5 , independently, is a H, or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group, where R^2 and R^3 and/or R^4 and R^5 may form a cyclic structure with Si;

each L, L^1 , L^2 , and L^3 , independently, is a bond or a linking group;

m is an integer from 1 to 1000;

n is an integer from 1 to 1000;

o is an integer from 0 to 1000;

each of X^1 and X^2 , independently, is hydrogen or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group;

wherein the vinyl terminated polyolefin is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms and at least 5% allyl chain ends; and

(ii) obtaining a modified polyolefin.

[0022] Accordingly, this invention relates to a process to modify polyolefins, for example, high density polyethylene (HDPE), comprising contacting a non-metallocene catalyst with a hydrosilylation modifier (typically a polyhydrosilane), and one or more vinyl terminated polyolefins. “Modified polyolefin,” “hydrosilylated polyolefin,” and “polyhydrosilane-modified polyolefin” may be used interchangeably throughout this disclosure.

[0023] Each of the non-metallocene catalyst, the hydrosilylation modifier, and the vinyl terminated polyolefins will be discussed in turn, below. The reactants are typically combined

in a reaction zone, such as a BRABENDER™ extruder, mill equipment, a reaction vessel or a stirred tank reactor. Preferably, the process is carried out without the use of a solvent (except the solvent that may be present in the catalyst, if the catalyst used is in a solution formulation). Preferably, the process of this invention occurs in the melt phase. Preferably, the process of this invention occurs in an extruder such as a BRABENDER™ extruder. Preferably, the process occurs at a temperature in the range of from 60°C to 300°C, and more preferably from 100°C to 250°C.

[0024] 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.

[0025] Preferably, the productivity of the process is at least 200 g of a hydrosilane-modified polyolefin per mmol of catalyst per hour, preferably at least 5000 g/mmol/hour, preferably at least 10,000 g/mmol/hr, preferably at least 300,000 g/mmol/hr.

[0026] This invention further relates to a process, preferably an in-line process, preferably a continuous process, to produce a modified polyolefin, comprising introducing polymer and non-metallocene catalyst into a reactor, obtaining a reactor effluent containing vinyl terminated polyolefin, optionally removing (such as flashing off) any solvent, unused monomer, and/or other volatiles, obtaining vinyl terminated polyolefin (such as those described herein), introducing vinyl terminated polyolefin, non-metallocene catalyst, and hydrosilylation modifier, as described herein, into a reaction zone (such as a reactor, an extruder, a pipe, and/or a pump), and obtaining the modified polyolefin described herein.

[0027] Typically, the modified polyolefin is added in small amounts to a base polymer, in order to improve the properties of the blend as compared to the base polymer alone. The base polymer may be comprised of one or more other polymers, including but not limited to, thermoplastic polymer(s) and/or elastomer(s). Accordingly, the process may further comprise: (iii) adding a polymer; and, (iv) obtaining a blend comprising the modified polyolefin. Preferably, the polymer from step (iii) is added during step (i). Alternately, the polymer from step (iii) is added after step (i).

[0028] Preferably, the amount of modified polyolefin in the blend is from 0.5 wt% to 10.0 wt%, based on the total weight of the blend. Preferably, the amount of modified polyolefin is from 0.5 wt% to 5.0 wt%, based on the total weight of the blend. Most preferably, the amount of modified polyolefin is from 0.5 wt% to 3.0 wt%, based on the total

weight of the blend.

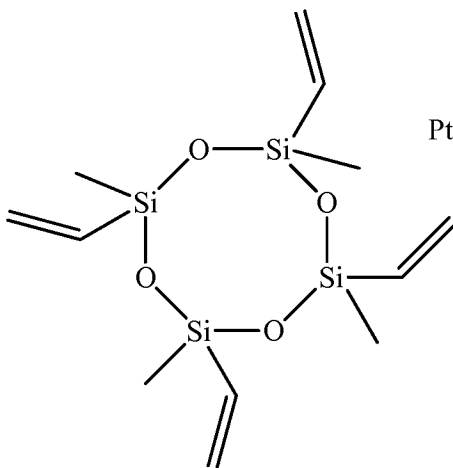
[0029] Typically, the amount of base polymer in the blend is from 90.0 wt% to 99.5 wt%, based on the total weight of the blend. Preferably, the amount of base polymer is from 95.0 wt% to 99.5 wt%, based on the total weight of the blend. Most preferably, the amount of modified polyolefin is from 97.0 wt% to 99.5 wt%, based on the total weight of the blend.

Non-Metallocene Catalyst

[0030] Suitable non-metallocene catalysts include, for example, chloroplatinic acid, platinum complexes such as platinum cyclovinyldimethylsiloxane from Gelest Inc. (Morrisville, PA), rhodium complexes, peroxides, for example TRIGONOX-101 from Akzo Nobel (Baton Rouge, LA) and di-cumyl peroxide, Ziegler Natta catalysts, and iridium, cobalt, ruthenium, osmium, nickel and palladium complexes.

[0031] Preferably, the non-metallocene catalyst is one or more of: platinum-divinyldimethylsiloxane complex (desirably, in a solvent such as xylene); platinum-carbonyl-cyclovinyldimethylsiloxane complex; platinum-cyclovinyldimethylsiloxane complex; platinum-octanal/octanol complex; hexachloroplatinic acid; and dimethylplatinum cyclooctadiene complex; all available from Gelest Inc. (Morrisville, PA).

[0032] Preferably, the non-metallocene catalyst is a platinum-cyclovinyldimethylsiloxane complex, having the following structure:

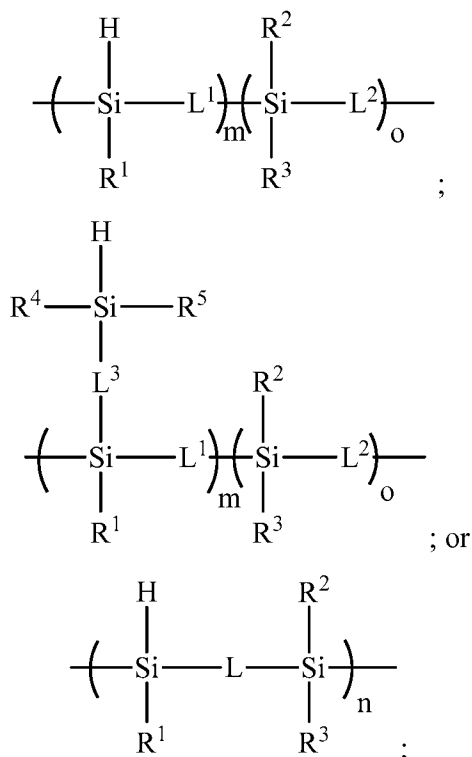


[0033] The amount of non-metallocene catalyst used may range from 5 ppm of metal to 1000 ppm. Preferably, the amount of non-metallocene catalyst used ranges from 5 ppm to 25 ppm of metal. For example, 18 ppm platinum of a platinum catalyst may be used.

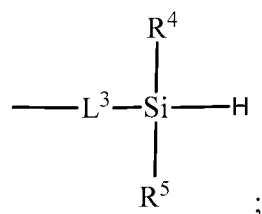
Hydrosilylation Modifier

[0034] The polyolefins are modified in this invention with a hydrosilylation modifier, preferably a polyhydrosilane. Preferably, the hydrosilylation modifier is represented by one

or more of the following formulae:



wherein R¹ is hydrogen, Z', or a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group; and wherein Z' is a group represented by the formula:



each R², R³, R⁴, and R⁵, independently, is hydrogen, or a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, where R² and R³ and/or R⁴ and R⁵ may form a cyclic structure with Si;

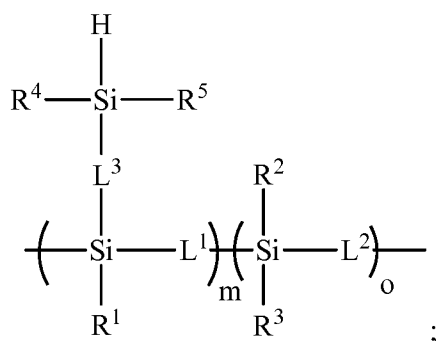
each L, L¹, L², and L³, independently, is a bond or a linking group;

m is an integer from 1 to 1000;

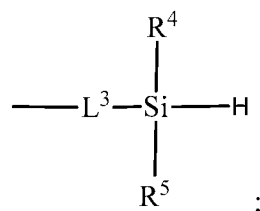
n is an integer from 1 to 1000; and

o is an integer from 0 to 1000.

[0035] Preferably, the hydrosilylation modifier is represented by the following formula:



wherein R^1 is hydrogen, Z' , or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group; and wherein Z' is a group represented by the formula:



each R^2 , R^3 , R^4 , and R^5 , independently, is hydrogen, or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group, where R^2 and R^3 and/or R^4 and R^5 may form a cyclic structure with Si (preferably R^1 is an aromatic group; preferably phenyl);

each L^1 , L^2 , and L^3 , independently, is a bond or a linking group (preferably, L^1 is O);

m is an integer from 1 to 1000 (preferably m is 100 to 500); and

o is zero.

[0036] Preferably of this invention, one or more of the terminal groups of the hydrosilylation modifier is a hydrogen atom, or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group. Each hydrosilylation modifier has at least one hydrogen atom attached to a silicon group. This hydrogen atom reacts during the hydrosilylation reaction with the vinyl group of the polyolefin to be modified. Where one of the terminal groups is hydrogen, this provides an additional site for reaction during the hydrosilation process. Accordingly, more than one mole of vinyl terminated polyolefin may react with such a hydrosilylation agent having more than one hydrogen atoms available for reaction.

[0037] Preferably, the hydrosilylation modifier may be poly-(phenyl dimethylhydrosiloxy)siloxane, hydride terminated or polymethylhydrosiloxane, trimethylsilyl terminated, both of which are commercially available from Gelest Inc. (Morrisville, PA).

[0038] Preferably of this invention, the molar ratio of the hydride groups of the hydrosilylation modifier to the vinyl group of the vinyl terminated polyolefin may be 20:1, preferably 10:1, more preferably 5:1, more preferably 3:1, and more preferably 2:1. One of

skill in the art will appreciate that this ratio may be tailored for desired modified polyolefin structure or for economics.

Vinyl Terminated Polyolefins

[0039] The vinyl terminated polyolefin that is reacted with the hydrosilylation modifier is a substituted or unsubstituted hydrocarbyl group having from 20 or 30 or 40 or 50 or 100 to 10,000 carbon atoms and at least 5% vinyl chain ends (relative to total unsaturations). The vinyl terminated polyolefin may be selected from a vinyl terminated polyolefin and a vinyl terminated macromonomer.

[0040] Preferably, the vinyl terminated polyolefins have greater than 50% allyl chain ends (relative to total unsaturation), preferably greater than 60% allyl chain ends, preferably greater than 70% allyl chain ends, preferably greater than 80% allyl chain ends, preferably greater than 90% allyl chain ends, and most preferably greater than 95% allyl chain ends.

[0041] Preferred vinyl terminated polyolefins include high density polyethylene (HDPE), for example those commercially available from ExxonMobil Chemical Company (Baytown, Texas) under the tradename PAXON™ polyethylene.

[0042] Preferably herein, the vinyl terminated polyolefin comprises vinyl terminated macromonomers (also referred to as “vinyl terminated oligomers” or “macromers”), and most preferably, the vinyl terminated polyolefin is a vinyl terminated macromonomer (VTM). Macromonomers having allyl chain ends (as defined below) are referred to as “vinyl terminated macromonomers”. Preferably, the vinyl terminated polyolefin comprises macromonomers having 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).

[0043] Preferably of the invention, the macromonomers have a Mn in the range of from 300 g/mol to 30,000 g/mol.

[0044] Preferably of the invention, the macromonomers are a recycle stream from another process, such as a polyolefin process, and may comprise a mixture of different macromonomers.

[0045] Preferably of the invention, the vinyl terminated polyolefin comprises a vinyl terminated macromonomer. Preferably, a vinyl terminated macromonomer, includes, one or more of:

- (i) a vinyl terminated polymer having a Mn of at least 200 g/mol (measured by ¹H NMR) comprising of one or more C₄ to C₄₀ 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;

(ii) a copolymer having a Mn of 200 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;

(iii) a copolymer having a Mn of 200 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, and (b) from 0.1 mol% to 20 mol% of propylene; wherein the vinyl terminated macromonomer has at least 40% allyl chain ends relative to total unsaturation;

(iv) a co-oligomer having a Mn of 200 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 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;

(v) a propylene oligomer, comprising more than 90 mol% propylene and less than 10 mol% ethylene wherein the 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, and less than 100 ppm aluminum;

(vi) a propylene oligomer, comprising: at least 50 mol% propylene and from 10 mol% to 50 mol% ethylene, wherein the oligomer has: at least 90% allyl chain ends, a 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 1.2:1.0, wherein monomers having four or more carbon atoms are present at from 0 mol% to 3 mol%;

(vii) a propylene oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% C_4 to C_{12} olefin, wherein the oligomer has: at least 90% allyl chain ends, a 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;

(viii) a propylene oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% diene (preferably such as C_4 to C_{12} alpha-omega dienes (such as butadiene, hexadiene, octadiene), norbornene, ethylidene norbornene,

vinylbornene, norbornadiene, and dicyclopentadiene), wherein the oligomer has: at least 90% allyl chain ends, a 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;

(ix) a homo-oligomer, comprising propylene, wherein the oligomer has: at least 93% allyl chain ends, a Mn of 500 g/mol to 20,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, and less than 1400 ppm aluminum;

(x) a co-oligomer having a Mn (¹H NMR) of 7,500 to 60,000 g/mol comprising one or more alpha olefin derived units comprising ethylene and/or propylene, having 50% or greater allyl chain ends, relative to total number of unsaturated chain ends, and a g'vis of 0.90 or less (g'vis is determined using GPC-DRI, as described below);

(xi) a branched polyolefin having a Mn (GPC) greater than 60,000 g/mol comprising one or more alpha olefins comprising ethylene and/or propylene, having: (i) 50% or greater allyl chain ends, relative to total unsaturated chain ends; (ii) a g'vis of 0.90 or less; and optionally, (iii) a bromine number which, upon complete hydrogenation, decreases by at least 50% (bromine number is determined by ASTM D 1159); and

(xii) a branched polyolefin having a Mn (¹H NMR) of less than 7,500 g/mol comprising one or more alpha olefin derived units comprising ethylene and/or propylene, having: a ratio of percentage of saturated chain ends to percentage of allyl chain ends of 1.2 to 2.0 and 50% or greater allyl chain ends, relative to total unsaturated chain ends.

[0046] Any of the vinyl terminated macromonomers described herein may be homopolymers, copolymers, terpolymers, and so on.

[0047] Preferably, the vinyl terminated macromonomers may have a Tg of less than 0°C or less (as determined by differential scanning calorimetry as described below), preferably -10°C or less, more preferably -20°C or less, more preferably -30°C or less, more preferably -50°C or less.

[0048] Preferably, the vinyl terminated macromonomers described herein may have a melting point (DSC first melt, as described below) of from 60°C to 130°C, alternately 50°C to 100°C. More preferably, the vinyl terminated macromonomers described herein have no detectable melting point by DSC following storage at ambient temperature (23°C) for at least 48 hours.

[0049] Preferably, the vinyl terminated macromonomers may be a liquid at 25°C. Also preferably, the vinyl terminated macromonomers may have an isobutyl chain end to allylic vinyl group ratio of 0.7:1 to 1.35:1.0, preferably 0.8:1 to 1.35:1.0, and more preferably 0.8:1

to 1.2:1.0.

[0050] Preferably, the vinyl terminated macromonomers may have less than 3 wt% of functional groups selected from hydroxide, aryls and substituted aryls, halogens, alkoxys, carboxylates, esters, acrylates, oxygen, nitrogen, and carboxyl, preferably less than 2 wt%, more preferably less than 1 wt%, more preferably less than 0.5 wt%, more preferably less than 0.1 wt%, more preferably 0 wt%, based upon the weight of the oligomer.

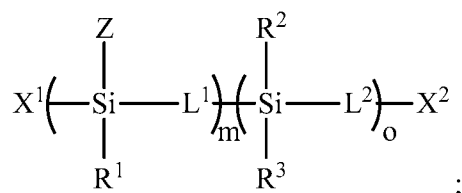
[0051] Vinyl terminated macromonomers generally have a saturated chain end (or terminus) and/or an unsaturated chain end or terminus. The unsaturated chain end of the vinyl terminated macromonomer comprises an “allyl chain end” or a “3-alkyl” chain end. An allyl chain end is represented by $\text{CH}_2\text{CH}=\text{CH}_2$, as shown in the formula:



where M represents the polymer chain. “Allylic vinyl group,” “allyl chain end,” “vinyl chain end,” “vinyl termination,” “allylic vinyl group,” and “vinyl terminated” are used interchangeably in the following description. The number of allyl chain ends, vinylidene chain ends, vinylene chain ends, and other unsaturated chain ends is determined using ^1H NMR at 120°C using deuterated tetrachloroethane as the solvent on an at least 250 MHz NMR spectrometer, and in selected cases, confirmed by ^{13}C NMR. Resconi has reported proton and carbon assignments (neat perdeuterated tetrachloroethane used for proton spectra, while a 50:50 mixture of normal and perdeuterated tetrachloroethane was used for carbon spectra; all spectra were recorded at 100°C on a BRUKER spectrometer operating at 500 MHz for proton and 125 MHz for carbon) for vinyl terminated oligomers in *J. American Chemical Soc.*, 114, 1992, pp. 1025-1032 that are useful herein. Allyl chain ends are reported as a molar percentage of the total number of moles of unsaturated groups (that is, the sum of allyl chain ends, vinylidene chain ends, vinylene chain ends, and the like). Note that any description of the VTM not set forth herein are described in detail in “Branched Polyethylenes by Hydrosilation Grafting to Improve Processability of Polyethylene”, U.S.S.N. _____, filed concurrently herewith

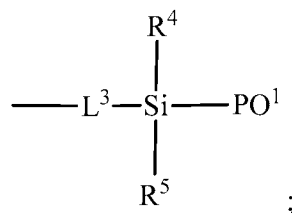
Modified Polyolefins

[0052] This invention also relates to a modified polyolefin represented by the formula:



wherein:

Z is a group represented by the formula:



wherein PO¹ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms;

R¹ is Z, hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or PO⁴,

wherein PO⁴ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms;

each R², R³, R⁴, and R⁵, independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, wherein R² and R³ and/or R⁴ and R⁵ may form a cyclic structure with Si, or, a PO⁴;

each L¹, L², and L³, independently, is a bond or a linking group;

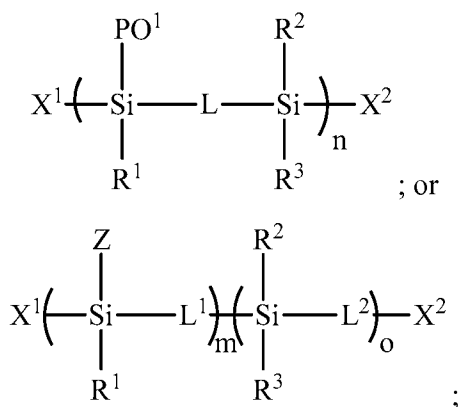
m is an integer from 1 to 1000;

o is an integer from 0 to 1000; and

X¹ and X², each independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or a PO⁴;

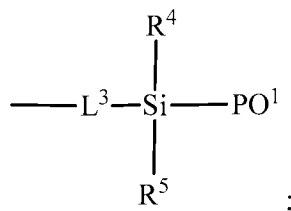
wherein each PO¹ and PO⁴ may be the same or different.

[0053] This invention also relates to a modified polyolefin represented by the formula:



wherein:

Z is a group represented by the formula:



wherein PO¹ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms derived from a vinyl terminated macromonomer;

each R¹, R², R³, R⁴, and R⁵, independently, is a H, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, where R² and R³ may form a cyclic structure with Si, or a PO⁴, wherein PO⁴ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms derived from a vinyl terminated macromonomer;

each L, L¹, L², and L³, if present, is a bond or a linking group;

m is an integer from 1 to 1000;

n is an integer from 1 to 1000;

o is an integer from 0 to 1000; and

X¹ and X², each independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or a PO⁴;

wherein each PO¹ and PO⁴ may be the same or different.

[0054] Each PO¹ and PO⁴, independently, is derived from a vinyl terminated polyolefin or a vinyl terminated macromonomer. Preferably, the PO¹ and/or PO⁴ in the formulae above is a hydrocarbyl or substituted hydrocarbyl having 100 to 10,000 carbon atoms, preferably 500 to 10,000, preferably 1000 to 10,000, preferably 5000 to 10,000 carbon atoms, preferably PO¹ and/or PO⁴ is derived from substituted or unsubstituted eicosene, polyethylene or polypropylene.

[0055] Preferably of the invention, R¹ is an aromatic group; L¹ is an oxygen atom; L³ is an oxygen atom; each R⁴ and R⁵, independently, is a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group; m is 100 to 500; and o is 0.

[0056] Preferably, the modified polyolefin has a Mn of from 500 to 50,000 g/mol, preferably from 1000 to 30,000 g/mol, preferably from 1500 to 10,000 g/mol. Preferably the “polyolefin” portion of the hydrosilane-modified polyolefin is derived from a homopolymer, homo-oligomer, copolymer or co-oligomer comprising one or more C₂ to C₄₀ olefins, preferably C₂ to C₄₀ alpha-olefins, preferably ethylene, propylene, butene, pentene, hexene, octene, nonene, decene, undecene, and dodecene.

[0057] Preferably, the hydrosilane-modified polyolefin is an oligomer having a Mn of

from 500 to 21,000 g/mol (preferably 700 to 21,000, preferably 800 to 20,000 g/mol) comprising one or more alpha-olefins selected from the group consisting of C₂ to C₄₀ alpha-olefins, preferably ethylene, propylene, butene, pentene, hexene, octene, nonene, decene, undecene, and dodecene. Preferably, the oligomer portion of the polyhydrosilane-modified polyolefin is an ethylene oligomer, e.g., a homo-oligomer of ethylene or co-oligomer of ethylene and up to 50 mol% (preferably from 0.5 mol% to 25 mol%, preferably from 1 mol% to 20 mol%) of one or more C₂ to C₄₀ alpha-olefin comonomers, preferably selected from the group consisting of propylene, butene, pentene, hexene, octene, nonene, decene, undecene, and dodecene. Alternately, the oligomer portion of the polyhydrosilane-modified polyolefin is a propylene oligomer, e.g., a homo-oligomer of propylene or co-oligomer of propylene and up to 50 mol% (preferably from 0.5 mol% to 25 mol%, preferably from 1 mol% to 20 mol%) of one or more C₂ to C₄₀ alpha-olefin comonomers, preferably selected from the group consisting of ethylene, butene, pentene, hexene, octene, nonene, decene, undecene, and dodecene.

[0058] Preferably, the polyhydrosilane-modified polyolefin is a polymer having a Mn of greater than 21,000 g/mol (preferably from 25,000 to 100,000, preferably 25,000 to 50,000 g/mol) comprising one or more alpha-olefins selected from the group consisting of C₂ to C₄₀ alpha-olefins, preferably ethylene, propylene, butene, pentene, hexene, octene, nonene, decene, undecene, and dodecene. Preferably, the polymer portion of the polyhydrosilane-modified polyolefin is an ethylene polymer, e.g., a homopolymer of ethylene or co-polymer of ethylene and up to 50 mol% (preferably from 0.5 mol% to 25 mol%, preferably from 1 mol% to 20 mol%) of one or more C₃ to C₄₀ alpha-olefin comonomers, preferably selected from the group consisting of propylene, butene, pentene, hexene, octene, nonene, decene, undecene, and dodecene. Alternately, the polymer portion of the polyhydrosilane-modified polyolefin is propylene polymer, e.g., a homopolymer of propylene or a co-polymer of propylene and up to 50 mol% (preferably from 0.5 mol% to 25 mol%, preferably from 1 mol% to 20 mol%) of one or more C₂ to C₄₀ alpha-olefins comonomers, preferably selected from the group consisting of ethylene, butene, pentene, hexene, octene, nonene, decene, undecene, and dodecene.

[0059] More preferably, the polyhydrosilane-modified polyolefins consist essentially of propylene, functional group and, optionally, ethylene. Alternately, C₄ olefins (such as isobutylene, butadiene, n-butene) are substantially absent from the polyhydrosilane-modified polyolefins. Alternately, C₄₋₂₀ olefins are substantially absent from the polyhydrosilane-

modified polyolefins. Alternately, isobutylene is substantially absent from the polyhydrosilane-modified polyolefins. By substantially absent is meant that the monomer is present in the polyolefin at 1 wt% or less, preferably at 0.5 wt% or less, preferably at 0 wt%.

[0060] Preferably, the polyhydrosilane-modified polyolefins produced herein have a melting point (DSC, second melt) of 100°C or more, preferably 120°C or more, preferably 130°C or more. More preferably, the polyhydrosilane-modified polyolefin produced herein is a polyhydrosilane-modified propylene polymer having a melting point (DSC, second melt) of 145°C or more, preferably 150°C or more, preferably 155°C or more. Preferably, the polyhydrosilane-modified polyolefin produced herein is a polyhydrosilane-modified ethylene polymer having a melting point (DSC, second melt) of 100°C or more, preferably 110°C or more, preferably 125°C or more.

[0061] The polyhydrosilane-modified polyolefins may be characterized by any degree of tacticity, including isotacticity or syndiotacticity, and/or may be atactic. Preferably, the polyhydrosilane-modified polyolefin has more than 50% meso dyads as measured by ¹³C NMR, preferably more than 60%. Alternatively, the polyhydro-silane modified polyolefin has more than 50% racemic dyads as measured by ¹³C NMR, preferably more than 60%.

[0062] Particularly useful polyhydrosilane-modified polyolefins may be isotactic, highly isotactic, syndiotactic, or highly syndiotactic propylene polymer, particularly isotactic polypropylene. As used herein, “isotactic” is defined as having at least 10% isotactic pentads, preferably having at least 40% isotactic pentads of methyl groups derived from propylene according to analysis by ¹³C NMR. As used herein, “highly isotactic” is defined as having at least 60% isotactic pentads according to analysis by ¹³C NMR. Most preferably, the polyhydrosilane-modified polyolefin (preferably polypropylene) has at least 85% isotacticity. As used herein, “syndiotactic” is defined as having at least 10% syndiotactic pentads, preferably at least 40%, according to analysis by ¹³C NMR. As used herein, “highly syndiotactic” is defined as having at least 60% syndiotactic pentads according to analysis by ¹³C NMR. More preferably, the polyhydrosilane modified polyolefin (preferably polypropylene) has at least 85% syndiotacticity.

[0063] Preferably, the polyhydrosilane-modified polyolefins described herein have less than 10% allyl chain ends, preferably less than 8%, preferably less than 6%, preferably less than 5%, preferably less than 4%, preferably less than 3%, preferably less than 2%, preferably less than 1% (relative to total unsaturations as measured by ¹H NMR, using the protocol described in USSN 12/143,663, filed on June 20, 2008). No hydrogen or chain

transfer/termination agent should be used during functionalization, derivatization, or stripping (of unreacted monomer) for measurement of unsaturations.

[0064] More preferably, the modified polyolefin may have a branching index, g'_{vis} (as determined by GPC) greater than that of the unmodified polyolefin. The modified polyolefin produced herein has a branching index, g'_{vis} (as determined by GPC), of 0.98 or less, alternately 0.96 or less, alternately 0.95 or less, alternately 0.93 or less, alternately 0.90 or less, alternately 0.85 or less, alternately 0.80 or less, alternately 0.75 or less, alternately 0.70 or less, alternately 0.65 or less, alternately 0.60 or less, alternately 0.55 or less.

Blends with Ethylene Polymers

[0065] The materials described herein may be combined with at least one ethylene polymer to prepare modified polyethylene blends.

[0066] In one aspect of the invention, the ethylene polymer is selected from ethylene homopolymer, ethylene copolymers, and blends thereof. Useful copolymers may comprise one or more comonomers in addition to ethylene and can be a random copolymer, a statistical copolymer, a block copolymer, and/or blends thereof. In particular, the ethylene polymer blends described herein may be physical blends or *in situ* blends of more than one type of ethylene polymer or blends of ethylene polymers with polymers other than ethylene polymers where the ethylene polymer component is the majority component (e.g., greater than 50 wt%). The method of making the polyethylene is not critical, as it can be made by slurry, solution, gas phase, high pressure, or other suitable processes, and by using catalyst systems appropriate for the polymerization of polyethylenes, such as Ziegler-Natta-type catalysts, chromium catalysts, metallocene-type catalysts, other appropriate catalyst systems, or combinations thereof, or by free-radical polymerization. Preferably, the ethylene polymers are made by the catalysts, activators and processes described in U.S. Patent Nos. 6,342,566; 6,384,142; 5,741,563; PCT publications WO 03/040201; and WO 97/19991. Such catalysts are well known in the art, and are described in, for example, ZIEGLER CATALYSTS (Gerhard Fink, Rolf Mülhaupt and Hans H. Brintzinger, eds., Springer-Verlag 1995); Resconi et al.; and I, II METALLOCENE-BASED POLYOLEFINS (Wiley & Sons 2000).

[0067] Preferred ethylene polymers and copolymers that are useful in this invention include those sold by ExxonMobil Chemical Company in Houston Texas, including those sold as ExxonMobil HDPE, ExxonMobil LLDPE, and ExxonMobil LDPE; and those sold under the ENABLE™, EXACT™, EXCEED™, ESCORENE™, EXXCO™, ESCOR™, PAXON™, and OPTEMA™ tradenames.

[0068] Preferably of the invention, the ethylene copolymers preferably have a composition distribution breadth index (CDBI) of 60% or more, preferably 60% to 80%, preferably 65% to 80%. Preferably, the ethylene copolymer has a density of 0.910 to 0.950 g/cm³ (preferably 0.915 to 0.940 g/cm³, preferably 0.918 to 0.925 g/cm³) and a CDBI of 60% to 80%, preferably between 65% and 80%. Preferably these polymers are metallocene polyethylenes (mPEs).

[0069] More preferably, the ethylene copolymer comprises one or more mPEs described in US 2007/0260016 and U.S. Patent No. 6,476,171, e.g., copolymers of an ethylene and at least one alpha olefin having at least 5 carbon atoms obtainable by a continuous gas phase polymerization using supported catalyst of an activated molecularly discrete catalyst in the substantial absence of an aluminum alkyl based scavenger (e.g., triethylaluminum, trimethylaluminum, tri-isobutyl aluminum, tri-n-hexylaluminum, and the like), which polymer has a Melt Index of from 0.1 to 15 (ASTM D 1238, condition E); a CDBI of at least 70%, a density of from 0.910 to 0.930 g/cc; a Haze (ASTM D1003) value of less than 20; a Melt Index ratio (I_{21}/I_2 , ASTMD 1238) of from 35 to 80; an averaged Modulus (M) (as defined in U.S. Patent No. 6,255,426) of from 20,000 to 60,000 psi (13790 to 41369 N/cm²); and a relation between M and the Dart Impact Strength (26 inch, ASTM D 1709) in g/mil (DIS) complying with the formula:

$$DIS \geq 0.8 \times [100 + e^{(11.71 - 0.000268 \times M + 2.183 \times 10^{-9} \times M^2)}],$$

where "e" represents 2.1783, the base Napierian logarithm, M is the averaged Modulus in psi and DIS is the 26 inch (66cm) dart impact strength. (See U.S. Patent No. 6,255,426 for further description of such ethylene polymers.)

[0070] More preferably, the ethylene polymer comprises a Ziegler-Natta polyethylene, e.g., CDBI less than 50, preferably having a density of 0.910 to 0.950 g/cm³ (preferably 0.915 to 0.940 g/cm³, preferably 0.918 to 0.925 g/cm³).

[0071] More preferably, the ethylene polymer comprises olefin block copolymers as described in EP 1 716 190.

[0072] More preferably, the ethylene polymer is produced using chrome based catalysts, such as, for example, in U.S. Patent No. 7,491,776 including that fluorocarbon does not have to be used in the production. Commercial examples of polymers produced by chromium include the Paxon™ grades of polyethylene produced by ExxonMobil Chemical Company, Houston Texas.

[0073] More preferably, the ethylene polymer comprises ethylene and an optional comonomer of propylene, butene, pentene, hexene, octene nonene or decene, and said polymer has a density of more than 0.86 to less than 0.910 g/cm³, an Mw of 20,000 g/mol or more (preferably 50,000 g/mol or more) and a CDBI of 90% or more.

[0074] More preferably, the ethylene polymer comprises a substantially linear and linear ethylene polymers (SLEPs). Substantially linear ethylene polymers and linear ethylene polymers and their method of preparation are fully described in U.S. Patent Nos. 5,272,236; 5,278,272; 3,645,992; 4,937,299; 4,701,432; 4,937,301; 4,935,397; 5,055,438; EP 129,368; EP 260,999; and WO 90/07526. As used herein, "a linear or substantially linear ethylene polymer" means a homopolymer of ethylene or a copolymer of ethylene and one or more alpha-olefin comonomers having a linear backbone (i.e., no cross linking), a specific and limited amount of long-chain branching or no long-chain branching, a narrow molecular weight distribution, a narrow composition distribution (e.g., for alpha-olefin copolymers), or a combination thereof. More explanation of such polymers is discussed in U.S. Patent No. 6,403,692.

[0075] Ethylene homopolymers and copolymers useful in this invention typically have:

1. an M_w of 20,000 g/mol or more, 20,000 to 2,000,000 g/mol preferably 30,000 to 1,000,000, preferably 40,000 to 200,000, preferably 50,000 to 750,000, as measured by size exclusion chromatography according to the procedure described in the Test Methods section of USSN 13/584,137, filed August 13, 2012; and/or
2. an M_w/M_n of 1 to 40, preferably 1.6 to 20, more preferably 1.8 to 10, more preferably 1.8 to 4, preferably 8 to 25 as measured by size exclusion chromatography as described in the Test Methods section of USSN 13/584,137, filed August 13, 2012; and/or
3. a T_m of 30°C to 150°C, preferably 30°C to 140°C, preferably 50°C to 140°C, more preferably 60°C to 135°C as determined by the DSC method described in the Test Methods section of USSN 13/584,137, filed August 13, 2012; and/or
4. a crystallinity of 5% to 80%, preferably 10% to 70%, more preferably 20% to 60% (alternatively, the polyethylene may have a crystallinity of at least 30%, preferably at least 40%, alternatively at least 50%), where crystallinity is determined by the DSC method described in the Test Methods section of USSN 13/584,137, filed August 13, 2012; and/or
5. a heat of fusion of 300 J/g or less, preferably 1 to 260 J/g, preferably 5 to 240 J/g, preferably 10 to 200 J/g as measured by the DSC method described in the Test Methods section of USSN 13/584,137, filed August 13, 2012; and/or

6. a crystallization temperature (T_c) of 15°C to 130°C, preferably 20°C to 120°C, preferably 25°C to 110°C, preferably 60°C to 125°C, as measured by the method described in the Test Methods section of USSN 13/584,137, filed August 13, 2012; and/or
7. a heat deflection temperature of 30°C to 120°C, preferably 40°C to 100°C, more preferably 50°C to 80°C as measured according to ASTM D648 on injection molded flexure bars, at 66 psi load (455kPa); and/or
8. a Shore hardness (D scale) of 10 or more, preferably 20 or more, preferably 30 or more, preferably 40 or more, preferably 100 or less, preferably from 25 to 75 (as measured by ASTM D 2240); and/or
9. a percent amorphous content of at least 50%, alternatively at least 60%, alternatively at least 70%, even alternatively between 50% and 95%, or 70% or less, preferably 60% or less, preferably 50% or less, as determined by subtracting the percent crystallinity from 100 as described in the Test Methods section of U.S. Publication No. 2013-0211008; and/or
10. a branching index (g'_{vis}) of 0.97 or more, preferably 0.98 or more, preferably 0.99 or more, preferably 1, as measured using the method described in the Test Methods section of USSN 13/584,137, filed August 13, 2012; and/or
11. a density of 0.860 to 0.980 g/cm³ (preferably from 0.880 to 0.940 g/cm³, preferably from 0.900 to 0.935 g/cm³, preferably from 0.910 to 0.930 g/cm³) (alternately from 0.85 to 0.97 g/cm³, preferably 0.86 to 0.965 g/cm³, preferably 0.88 to 0.96 g/cm³, alternatively between 0.860 and 0.910 g/cm³, alternatively between 0.910 and 0.940 g/cm³, or alternatively between 0.94 to 0.965 g/cm³) (determined according to ASTM D 1505 using a density-gradient column on a compression-molded specimen that has been slowly cooled to 25°C (i.e., over a period of 10 minutes or more) and allowed to age for a sufficient time that the density is constant within ± 0.001 g/cm³).

[0076] Preferably, the polyethylene comprises less than 20 mol% propylene units (preferably less than 15 mol%, preferably less than 10 mol%, preferably less than 5 mol%, preferably 0 mol% propylene units).

[0077] More preferably of the invention, the ethylene polymer is an ethylene copolymer, either random, or block, of ethylene and one or more comonomers selected from C₃ to C₂₀ α -olefins, typically from C₃ to C₁₀ α -olefins. More preferably, the comonomers are present from 0.1 wt% to 50 wt% of the copolymer, from 0.5 wt% to 30 wt% more preferably, from 1 wt% to 15 wt% even more preferably, and from 0.1 wt% to 5 wt% even more preferably, wherein a desirable copolymer comprises ethylene and C₃ to C₂₀ α -olefin derived

units in any combination of any upper wt% limit with any lower wt% limit described herein. Preferably, the ethylene copolymer will have a weight average molecular weight of from greater than 8,000 g/mol, greater than 10,000 g/mol more preferably, greater than 12,000 g/mol even more preferably, greater than 20,000 g/mol even more preferably, less than 1,000,000 g/mol even more preferably, and less than 800,000 g/mol even more preferably, wherein a desirable copolymer may comprise any upper molecular weight limit with any lower molecular weight limit described herein.

[0078] More preferably, the ethylene copolymer comprises ethylene and one or more other monomers selected from the group consisting of C_3 to C_{20} linear, branched or cyclic monomers, and Preferably is a C_3 to C_{12} linear or branched alpha-olefin, preferably butene, pentene, hexene, heptene, octene, nonene, decene, dodecene, 4-methyl-pentene-1, 3-methyl-pentene-1, 3,5,5-trimethyl-hexene-1, and the like. The monomers may be present at up to 50 wt%, preferably from 0 wt% to 40 wt%, more preferably from 0.5 wt% to 30 wt%, more preferably from 2 wt% to 30 wt%, more preferably from 5 wt% to 20 wt%.

[0079] Preferred linear alpha-olefins useful as comonomers for the ethylene copolymers useful in this invention include C_3 to C_8 alpha-olefins, more preferably 1-butene, 1-hexene, and 1-octene, even more preferably 1-hexene. Preferred branched alpha-olefins include 4-methyl-1-pentene, 3-methyl-1-pentene, and 3,5,5-trimethyl-1-hexene, 5-ethyl-1-nonene. Preferred aromatic-group-containing monomers contain up to 30 carbon atoms. Suitable aromatic-group-containing monomers comprise at least one aromatic structure, preferably from one to three, more preferably a phenyl, indenyl, fluorenyl, or naphthyl moiety. The aromatic-group-containing monomer further comprises at least one polymerizable double bond such that after polymerization, the aromatic structure will be pendant from the polymer backbone. The aromatic-group containing monomer may further be substituted with one or more hydrocarbyl groups including but not limited to C_1 to C_{10} alkyl groups. Additionally, two adjacent substitutions may be joined to form a ring structure. Preferred aromatic-group-containing monomers contain at least one aromatic structure appended to a polymerizable olefinic moiety. Particularly preferred aromatic monomers include styrene, alpha-methylstyrene, para-alkylstyrenes, vinyltoluenes, vinylnaphthalene, allyl benzene, and indene, especially styrene, paramethyl styrene, 4-phenyl-1-butene, and allyl benzene.

[0080] Preferred diolefin monomers useful in the ethylene polymer or copolymer include any hydrocarbon structure, preferably C_4 to C_{30} , having at least two unsaturated bonds, wherein at least two of the unsaturated bonds are readily incorporated into a polymer by

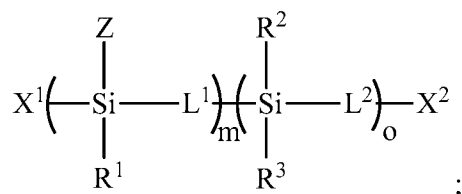
either a stereospecific or a non-stereospecific catalyst(s). It is further preferred that the diolefin monomers be selected from alpha, omega-diene monomers (i.e., di-vinyl monomers). More preferably, the diolefin monomers are linear di-vinyl monomers, most preferably those containing from 4 to 30 carbon atoms. Examples of preferred dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene, tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene, triacontadiene, particularly preferred dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, and low molecular weight polybutadienes (M_w less than 1000 g/mol). Preferred cyclic dienes include cyclopentadiene, vinyl norbornene, norbornadiene, ethylidene norbornene, divinylbenzene, dicyclopentadiene, or higher ring containing diolefins with or without substituents at various ring positions.

Applications

[0081] The modified polyolefins 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 and in blown film applications.

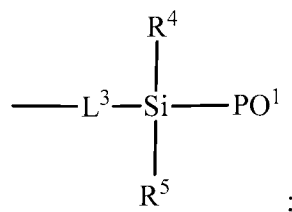
[0082] This invention further relates to:

1. A modified polyolefin represented by the formula:



wherein:

Z is a group represented by the formula:



wherein PO¹ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms;

R¹ is Z, hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or PO⁴, wherein PO⁴ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms (preferably R¹ is a methyl group or PO⁴; alternately R¹ is an aromatic group, preferably phenyl; preferably R¹ is a phenyl group and R⁴ and R⁵ are methyl groups);

each R², R³, R⁴, and R⁵, independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, wherein R² and R³ and/or R⁴ and R⁵ may form a cyclic structure with Si, or, a PO⁴;

each L¹, L², and L³, independently, is a bond or a linking group (preferably each L¹, L², and L³, independently, is O, S, NRA, PR^B, SiR^C₂, or a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group; wherein each R^A, R^B, and R^C, independently, is hydrogen, or a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group; preferably each L¹, L², and L³, independently, is O);

m is an integer from 1 to 1000 (preferably m is from 100 to 500);

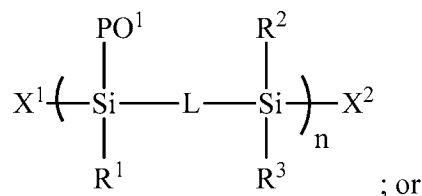
o is an integer from 0 to 1000 (preferably o is 0; preferably o is from 100 to 500); and

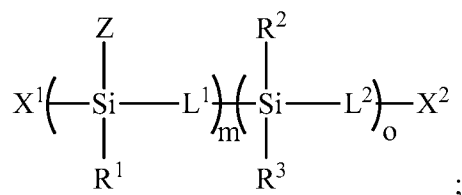
X¹ and X², each independently, is hydrogen; a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or PO⁴;

wherein PO¹ and PO⁴ can be the same or different (preferably each of PO¹ and PO⁴, independently, is derived from a vinyl terminated polyolefin selected from a vinyl terminated polyalphaolefin or a vinyl terminated macromonomer; preferably the vinyl terminated polyolefin is ethylene-based; preferably the polyalphaolefin is polyethylene).

2. The modified polyolefin of paragraph 1, wherein R¹ is an aromatic group (group preferably phenyl); L¹ is an oxygen atom; L³ is an oxygen atom; each R⁴ and R⁵, independently, is a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group; m is 100 to 500; and o is 0.

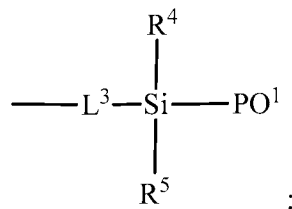
3. A modified polyolefin represented by the formula:





wherein:

Z is a group represented by the formula:



wherein PO¹ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms derived from a vinyl terminated macromonomer;

each R¹, R², R³, R⁴, and R⁵, independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, where R² and R³ may form a cyclic structure with Si, or a PO⁴;

wherein PO⁴ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms derived from a vinyl terminated macromonomer (preferably the vinyl terminated macromonomer is ethylene-based);

each L, L¹, L², and L³, is a bond or a linking group (preferably each L, L¹, L², and L³, independently, is O, S, N^{R^A}, P^{R^B}, SiR^C₂, or a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group; wherein each R^A, R^B, and R^C, independently, is hydrogen, or a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group; preferably each L, L¹, L², and L³, independently, is O;

m is an integer from 1 to 1000 (preferably m is from 100 to 500);

n is an integer 1 to 1000 (preferably n is from 100 to 500);

o is an integer from 0 to 1000 (preferably o is 0; preferably o is from 100 to 500); and

X¹ and X², each independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or a PO⁴.

4. The modified polyolefin of paragraphs 1 to 3, wherein the vinyl terminated macromonomer is one or more of:

(i) a vinyl terminated polymer having a Mn of at least 200 g/mol (measured by ¹H NMR) comprising of one or more C₄ to C₄₀ 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;

(ii) a copolymer having a Mn of 200 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;

(iii) a copolymer having a Mn of 200 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, and (b) from 0.1 mol% to 20 mol% of propylene; wherein the vinyl terminated macromonomer has at least 40% allyl chain ends relative to total unsaturation;

(iv) a co-oligomer having a Mn of 200 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 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;

(v) a propylene oligomer, comprising more than 90 mol% propylene and less than 10 mol% ethylene wherein the 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, and less than 100 ppm aluminum;

(vi) a propylene oligomer, comprising: at least 50 mol% propylene and from 10 mol% to 50 mol% ethylene, wherein the oligomer has: at least 90% allyl chain ends, a 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 1.2:1.0, wherein monomers having four or more carbon atoms are present at from 0 mol% to 3 mol%;

(vii) a propylene oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% C_4 to C_{12} olefin, wherein the oligomer has: at least 90% allyl chain ends, a 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;

(viii) a propylene oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% diene (preferably such as C_4 to C_{12} alpha-omega dienes (such as butadiene, hexadiene, octadiene), norbornene, ethylidene norbornene, vinylnorbornene, norbornadiene, and dicyclopentadiene), wherein the oligomer has: at least

90% allyl chain ends, a 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;

(ix) a homo-oligomer, comprising propylene, wherein the oligomer has: at least 93% allyl chain ends, a Mn of 500 g/mol to 20,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, and less than 1400 ppm aluminum;

(x) a co-oligomer having a Mn (^1H NMR) of 7,500 to 60,000 g/mol comprising one or more alpha olefin derived units comprising ethylene and/or propylene, and having 50% or greater allyl chain ends, relative to total number of unsaturated chain ends and a g'vis of 0.90 or less (g'vis is determined using GPC-DRI, as described below);

(xi) a branched polyolefin having a Mn (GPC) greater than 60,000 g/mol comprising one or more alpha olefins comprising ethylene and/or propylene, and having: (i) 50% or greater allyl chain ends, relative to total unsaturated chain ends; (ii) a g'vis of 0.90 or less; and optionally; (iii) a bromine number which, upon complete hydrogenation, decreases by at least 50% (bromine number is determined by ASTM D 1159); and

(xii) a branched polyolefin having a Mn (^1H NMR) of less than 7,500 g/mol comprising one or more alpha olefin derived units comprising ethylene and/or propylene, and having: a ratio of percentage of saturated chain ends to percentage of allyl chain ends of 1.2 to 2.0; and 50% or greater allyl chain ends, relative to total unsaturated chain ends.

5. The modified polyolefin of claim 12, wherein R^1 is a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group; L^1 is an oxygen atom, m is from 100 to 500; each R^2 and R^3 , independently, are a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group; L^2 is an oxygen atom; and o is from 100 to 500.

6. A blend comprising the modified polyolefin of paragraphs 1 or 3.

7. The blend of paragraph 6, further comprising polyethylene.

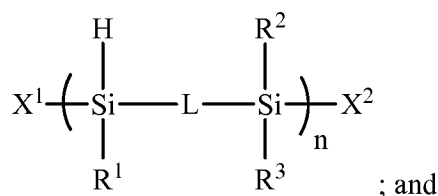
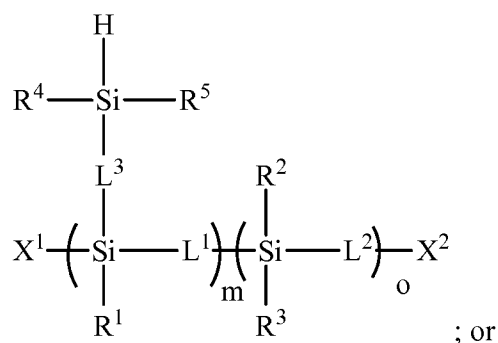
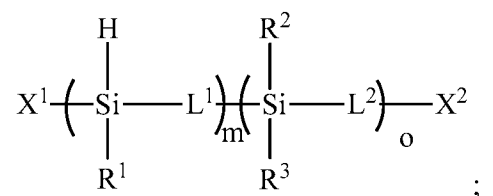
8. An article comprising the modified polyolefin of paragraphs 1 to 7 (preferably, the article is a blown film).

9. A process to prepare the modified polyolefin of paragraphs 1 to 5 (carried out in the melt phase), comprising the steps of:

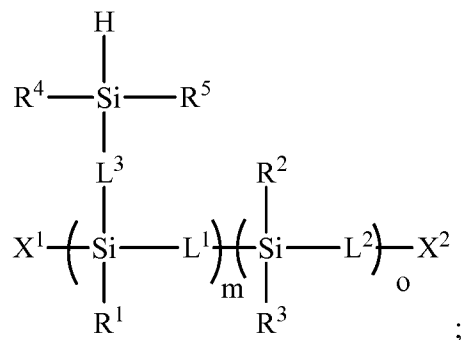
(i) contacting a non-metallocene catalyst (non-metallocene catalyst is one or more of: chloroplatinic acid, platinum complexes such as platinum cyclovinylmethyldisiloxane, rhodium complexes, peroxides, such as di-cumyl peroxide, Ziegler Natta catalysts, and iridium, cobalt, ruthenium, osmium, nickel and palladium complexes; more preferably platinum-divinyltetramethyldisiloxane complex (desirably, in a solvent such as xylene); platinum-

carbonyl-cyclovinyldimethylsiloxane complex; platinum-cyclovinyldimethylsiloxane complex; platinum-octanal/octanol complex; hexachloroplatinic acid; and dimethylplatinum cyclooctadiene complex), a hydrosilylation modifier, and one or more vinyl terminated polyolefin selected from a vinyl terminated polyalphaolefin and a vinyl terminated macromonomer;

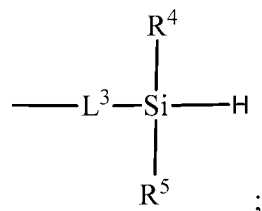
wherein when the vinyl terminated polyolefin is a vinyl terminated macromonomer, the hydrosilylation modifier is represented by one of more of the formulae:



wherein the vinyl terminated polyolefin is a polyalphaolefin, the hydrosilylation modifier is represented by the formula:



wherein R^1 is hydrogen, Z' , or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group; and wherein Z' is a group represented by the formula:



each R^2 , R^3 , R^4 , and R^5 , independently, is a H, or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group, where R^2 and R^3 and/or R^4 and R^5 may form a cyclic structure with Si; each L, L^1 , L^2 , and L^3 , independently, is a bond or a linking group (each L^1 , L^2 , and L^3 , independently, is O, S, NR^A , PR^B , SiRC_2 , or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group; wherein each R^A , R^B , and R^C , independently, is hydrogen, or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group);

m is an integer from 1 to 1000;

n is an integer from 1 to 1000;

o is an integer from 0 to 1000;

each of X^1 and X^2 , independently, is hydrogen or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group;

the vinyl terminated polyolefin is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms (preferably the vinyl terminated polyolefin is one or more of a polyalphaolefin and a vinyl terminated macromonomer; preferably, the vinyl terminated polyolefin of step (i) is ethylene-based) and at least 5% allyl chain ends;

(ii) obtaining a modified polyolefin;

(iii) optionally, adding a polyalphaolefin (preferably, the polyalphaolefin from step (iii) is added during step (i), alternately, the polyalphaolefin from step (iii) is added after step (i); preferably, the polyalphaolefin of step (iii) is polyethylene); and

(iv) obtaining a blend comprising the modified polyolefin.

EXAMPLES

Tests and Materials

[0083] Products were characterized by ^1H NMR as follows:

^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 Varian spectrometer with a proton frequency of at least 400 MHz or a Bruker 500 MHz. Data was recorded using a maximum pulse width of 45° , 8 seconds between pulses and signal averaging 120 transients. Spectral signals were integrated and the number of unsaturation types per 1000 carbons was calculated by multiplying the different groups by 1000 and dividing the result by the total number of carbons. M_n of the

macromer is determined by ^1H NMR spectroscopy by comparison of integrals of the aliphatic region to the olefin region as determined using the protocol described in the Experimental section of USSN 12/143,663, filed on June 20, 2008.

[0084] GPC conditions are those described above.

[0085] 1% Secant Modulus (M), reported in pounds per square inch (psi), was measured as specified by ASTM D-882.

[0086] Yield strength and tensile strength, report as pounds per square inch (psi), were measured as specified by ASTM D-882 except that the gauge thickness, reported in mils, was measured using a HEIDENHAIN micrometer. For each film sample, twenty random film thickness data points were measured around the circumference of the bubble. From these measurements, an average gauge measurement was determined and reported.

[0087] Elongation at Yield and Elongation at Break, reported as a percentage (%), were measured as specified by ASTM D-882.

[0088] Elmendorf Tear, reported in grams (g) or grams per mil (g/mil), was measured as specified by ASTM D-1922. Verification of scale was done using the check weight method.

[0089] Haze, reported as a percentage (%), was measured as specified by ASTM D-1003, using procedure A. Internal haze refers to the inherent haze level of the film or molded article, excluding any surface-related contribution. The surface(s) is coated with an ASTM-approved inert liquid (Immersion Oil Type B, typically used for microscopy) to eliminate any contribution to haze from surface topology effects. The resulting haze value is termed internal haze, and is reported as a percentage (%). Haze measurements that include surface topology effects are referred to as total haze. Unless particularly specified, the haze levels reported here are total haze values.

[0090] Dart Drop Impact or Dart Drop Impact Strength (DIS), reported in grams (g) and/or grams per mil (g/mil), was measured as specified by ASTM D-1709, method A, unless otherwise specified.

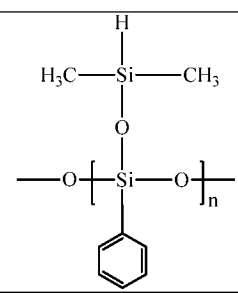
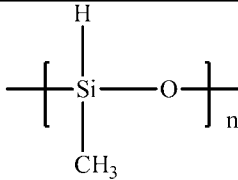
Polyolefins

[0091] The commercially available polyolefins used in the Examples are as described below in Table 1.

TABLE 1: COMMERCIAL POLYOLEFINS		
Polyolefins	Source	Description
PAXON™ AL55-003	ExxonMobil Chemicals (Houston, Texas)	High density polyethylene; MI = 0.3 g/10 min; density = 0.954 g/cm ³ M _n = 17,000

TABLE 1: COMMERCIAL POLYOLEFINS		
Polyolefins	Source	Description
		> 95% vinyl chain ends
EXCEED™ 1018CA	ExxonMobil Chemicals (Houston, Texas)	Ethylene-based polymer; hexene comonomer; MI = 1.0 g/10 min; density = 0.918 g/cm ³
EXCEED™ 2018CA	ExxonMobil Chemicals (Houston, Texas)	Ethylene-hexene copolymer; metallocene-produced; MI = 2.0 g/10min; density = 0.918 g/cm ³

[0092] The commercially available polysiloxanes used in the Examples are as described below in Table 2.

TABLE 2: COMMERCIAL POLYSILOXANES		
Polysiloxane	Source	Description
Polyphenyl(dimethylhydrosiloxy)siloxane, hydride terminated (PPDMHS) 50-80 cSt	Gelest Inc. (Morrisville, PA)	
Polymethylhydrosiloxane, trimethyl silyl terminated (PHMS) 30-45 cSt	Gelest Inc. (Morrisville, PA)	

General Procedure for Hydrosilylation

[0093] Vinyl terminated polymers, inclusive of polyolefins and vinyl terminated macromonomers, were modified with various polysiloxane backbones. Reactions were carried out in the melt in a BRABENDER™ extruder. The BRABENDER™ extruder was connected to a nitrogen gas inlet through which a continuous stream of nitrogen gas flowed. The catalyst was added by syringe once the torque stabilized. The silane was added, 1 minute later. The torque dropped initially and then rose to a point where it leveled, generally after 1 to 30 minutes. The modified polyolefin was then removed from the BRABENDER™ extruder and used without further modification.

General Procedure for Modified Polyolefins Blends

[0094] Viscosity matching when blending these hydrosilylated polymers with lower density LLDPE materials was of interest. Blends were prepared (between 10% to 50% vinyl

terminated HDPE was blended with a base resin). Additives were used in all samples, except where the base resin already comprises an additive package. Where additional additives were used, the additive package was composed of 500 ppm IRGANOX™ 1076 and 1000 ppm IRGAFOS™ 168.

Films

[0095] The modified polyolefin may be blended with base resin materials, and the blend made into films (both compression molded and blown films).

[0096] The modified polyolefin material was formed into sheets via conventional compression molding techniques. 100mm x 100mm x 2mm pads were formed using the following conditions: 5 minutes preheat at ambient pressure at 190°C, followed by a 20 minute press cycle at 5 tons (4,535 kg) pressure and finally a 180 second press cycle at 10 tons (9,072 kg) pressure. The pressure was removed and the sample was cooled to 25°C over 5 minutes.

[0097] Blown films were prepared using a laboratory Haake blown film line. The line contained a 1" single screw extruder and a 1" mono-layer blown film die. The films produced had a 1.5 mil gauge and a 2.8 bubble blow-up ratio (BUR). "MD" refers to machine direction and "TD" refers to transverse direction.

[0098] Chromium catalyzed high density polyethylene (PAXON™ AL55-003), which has over 95% vinyl terminated chains, was modified with various polysiloxane modifiers.

Example 1 (Inventive): Hydrosilylation of PAXON™ AL55-003 Polyethylene with PPDMHS

[0099] PAXON™ AL55-003 polyethylene (50g) was fed into the BRABENDER™ extruder set at 150°C. After 9 minutes, once the torque stabilized, a platinum cyclovinyldimethylsiloxane complex catalyst (Gelest Inc., Morrisville, PA, 2.0 - 2.3% platinum concentration in cyclic methylvinylsiloxanes, 0.04 mL) was added by syringe. Hydride terminated polyphenyl-(dimethylhydrosiloxy)siloxane (PPDMHS, 0.9 mL) was then added 1 minute later. The resulting mixture was melt mixed at 40 rpm for an additional 10 minutes. The modified polyolefin was blended for 5 minutes further before removal to produce Example 1 modified polyolefin. FTIR showed suppression of the Si-H peak at 2170 cm⁻¹ once the reaction was completed as this Si-H bond is converted to Si-C bonds during reaction. Example 1 modified polyolefin was made into a compression molded film.

[00100] Upon inspection, the compression molded films made from Example 1 modified polyolefin showed no gel particles. A polyolefin film having gels present can have reduced

physical properties and be visually unacceptable for the product application. Therefore, it is highly desirable to reduce or eliminate gel formation during processing. The hydrosilylated (PPDMHS) PAXON™ polyethylene (Example 1) advantageously did not exhibit any gels.

Example 2 (Comparative): Modified (PHMS) Polyethylene Blends

[00101] PAXON™ AL55-003 polyethylene (5g) was dry blended with EXCEED™ 1018 CA polyethylene pellets (45g). The blend was fed into a BRABENDER™ extruder set to a temperature of 150°C. After 9 minutes, once the torque stabilized, the platinum cyclovinyldimethylsiloxane complex catalyst was added by syringe (0.04 mL). Polyhydromethylsiloxane (PHMS, 0.06 mL) was then added 1 minute later. The resulting mixture was melt mixed at 40 rpm for 15 minutes further to provide a 10% blend in EXCEED™ 1018 CA polyethylene.

[00102] The Example 2 10% blend in EXCEED™ 1018 CA polyethylene demonstrated extensional strain hardening (Figure 1) which provided improved bubble stability during blown film operations.

[00103] The rheological data were analyzed using the Van Gorp-Palmen treatment (reference: M. Van Gorp and J. Palmen, Rheology Bulletin, 67, 5, 1998), whereby the phase angle δ ($=\tan^{-1}(G''/G')$) is plotted against the absolute value of the complex modulus $|G^*| = (G'^2 + G''^2)^{0.5}$. This representation of linear viscoelastic data is a powerful means of characterizing molecular and structural features of polymers. For example, low levels of long chain branching in polyolefins can be detected and quantified on a relative basis, using this methodology. For Example 2, rheological changes were observed in the Van Gorp-Palmen plot (Figure 2) and there was an increase in zero-shear viscosity on addition of the reactive PHMS with catalyst (Figure 3).

Examples 3-6 (Inventive): Modified Polyethylene Blends

[00104] The modified polyolefin blends for Examples 3 through 6 were prepared as follows. PAXON™ AL55-003 polyethylene was treated with PPDMHS as described above in Example 1 to produce the modified PAXON™ polyethylene. The amount of PPDMHS was varied from a mole to mole ratio of 8:1, 4:1, 2:1, and 1:1 for Examples 3, 4, 5, and 6, respectively, based on the calculated moles of reactive end groups of the PAXON™ AL55-003. The modified PAXON™ AL55-003 polyethylene (3 wt%) was then dry blended with EXCEED™ 2018 polyethylene to provide Example 3 through 6 blends. Blown films were prepared, as described above, using a laboratory HAAKE blown film line.

Example C (Comparative): No Modified Polyethylene

[00105] Control Example C was EXCEED™ 2018 without the addition of the modified PAXON™ AL55-003 polyethylene. A blown film was prepared, as described above, for comparison to the inventive films.

TABLE 3: BLOWN FILMS MADE FROM EXAMPLES 3-6					
	Sample C (CONTROL)	Example 3	Example 4	Example 5	Example 6
Ratio of PPDMHS:PAXON™ in Modified PAXON™ PE	-	8:1	4:1	2:1	1:1
Film Properties					
1% Secant					
MD (psi)	23,332	26,558	29,061	28,915	29,186
MD (MPa)	160.8	183.1	200.3	199.3	201.2
Tensile					
Yield Strength					
MD (psi)	1,293	1,401	1,294	1,355	1,395
TD (psi)	1,349	1,325	1,414	1,334	1,412
MD (MPa)	8.9	9.7	8.9	9.3	9.6
TD (MPa)	9.3	9.1	9.7	9.2	9.7
Elongation @ Yield (%)					
MD	7.5	6.8	5.9	5.8	6.4
TD	6.1	6.4	5.7	5.5	6.5
Tensile Strength					
MD (psi)	7,070	7,436	6,876	6,929	7,306
TD (psi)	7,339	6,667	7,433	6,210	7,113
MD (kPa)	48.7	51.2	47.4	47.7	50.4
TD (kPa)	50.6	45.9	51.2	42.8	49.0
Elongation @ Break (%)					
MD	632	651	655	642	
TD	624	652	668	593	651
Elmendorf Tear					
MD (g)	350	344	318	316	344
TD (g)	432	481	561	519	322
MD (g/mil)	343	331	307	326	489
TD (g/mil)	415	428	449	453	450
MD (g/μm)	13.5	13.0	12.0	12.8	19.2
TD (g/μm)	16.3	16.8	17.6	17.8	17.6
Haze (%)	61.7*	13.1	13.7	12.9	10.7
Internal Haze (%)	4.3	2.1	2.2	2.1	1.5
Dart Drop, Method A					
(g)	371	236	227	212	222
(g/mil)	294	207	185	178	183
Gauge Mic					
Average (mils)	1.26	1.14	1.23	1.19	1.21
Low (mils)	0.87	0.86	1.00	0.92	0.91

TABLE 3: BLOWN FILMS MADE FROM EXAMPLES 3-6					
	Sample C (CONTROL)	Example 3	Example 4	Example 5	Example 6
Ratio of PPDMHS:PAXON™ in Modified PAXON™ PE	-	8:1	4:1	2:1	1:1
High (mils)	1.60	1.37	1.41	1.55	1.53
Average (mils)	32.0	29.0	31.2	30.2	30.7
Low (μm)	22.0	21.8	25.4	23.4	24.6
High (μm)	40.6	34.7	35.8	39.4	38.9
Die Melt Temperature (°C)	165	164	164	164	165
Torque (m.g)	45.6	38.9	41.9	38.6	43.9
Extruder Speed (rpm)	33.0	33.0	33.0	34.0	34.0
Head Pressure (psi)	2963.8	2946.4	2920.3	2937.7	2982.6
Head Pressure (kPa)	20,435	20,315	20,135	20,255	20,564
Frost Line Height (inches)	2.5	2.5	2.5	2.5	2.5
Frost Line Height (m)	0.064	0.064	0.064	0.064	0.064
Output (g/min)	15.5	15.2	15.2	15.5	15.5

*Due in part to gels.

[00106] It was noted that blended Examples 3 through 6 exhibited a decrease in torque as compared to control Sample C. The decrease in torque reduces motor load and allows for the material to be processed using lower energy, or can also give higher throughputs for the same motor loads.

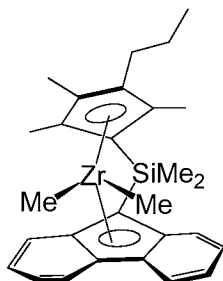
[00107] An increase in tensile strength was observed for Examples 3 through 6, compared with the control Sample C. The increase in tensile strength advantageously increases stiffness and load carrying ability for the polymers.

[00108] Also, dart drop was reduced in Examples 3 through 6 when compared to control sample C. The decrease in dart drop may be due to the increased orientation in the film. This generally is the consequence of adding high density material to LLDPE. Not to be limited by theory, it is believed that this can be mitigated by adding in a lower density PE.

Example 7 (Inventive): Vinyl Terminated Macromonomers

[00109] The vinyl-terminated macromonomers were prepared according to procedures described in U.S. Application Serial No. 61/704,606, filed on September 24, 2012; and U.S. Application Serial No. 61/704,604, filed on September 24, 2012.

[00110] Metallocene A, represented by the following structure was used herein:



Dimethylaniliniumtetrakis(perfluoronaphthyl)borate was used as the activator.

[00111] To a clean and dry standard 2 liter autoclave, hexene and TIBAL (triisobutylalumoxane) in toluene was added using a cannula. Hexanes were added from a storage tank. The autoclave was then sealed. The reactor was then heated to the set temperature and the agitator started. Once the temperature and pressure were stable, the metallocene A/ dimethylaniliniumtetrakis(perfluoronaphthyl)borate (previously prepared in a dry box) was flushed into the system using 200 ml hexanes.

[00112] At this point, ethylene gas was introduced and the inlet was left open so that a constant pressure of ethylene was maintained. The approximate polymer yield was followed by monitoring the flow rate of ethylene to the reactor (to replenish the used ethylene). After 20 minutes, the reactor was cooled to 25°C, depressurized, and the reactor opened to retrieve the polymer. The polymer was dried in a hood for 12 hours to remove residual hexanes and weighed to determine the overall yield. By this procedure, 4 different batches were prepared. The run conditions are shown below, in Table 4.

TABLE 4: RUN CONDITIONS TO PREPARE VINYL TERMINATED MACROMONOMER					
Run	Catalyst (mg)	Activator (mg)	25% TIBAL in toluene (mL)	Hexene (mL)	Initial Hexanes (mL)
1	5	12.2	2	40	400
2	5	12.2	2	40	400
3	5	12.2	2	40	400
4	5	12.2	2	40	400

[00113] Because the molecular weights and thermal characteristics of polymer obtained from Runs 1 to 4 were similar, the polymer from these four runs were dry blended together to obtain a single polymer batch (VTM polymer), which was blended in at 3% by weight in EXCEED™ 2018 polyethylene to produce Example 7 polymer.

[00114] VTM polymer (50 g, 60% vinyl chain ends, 1.67 mmol) was fed into a BRABENDER™ extruder set to a temperature of 190°C. After 9 minutes, once the torque stabilized, PPDMS (0.50 mL, 3.37 mmol, 2.02:1 Si-H:vinyl ratio) was added by syringe. The platinum cyclovinyldimethylsiloxane complex catalyst (40 mg) was then added 5 minutes

later. The resulting mixture was melt mixed at 40 rpm for 10 minutes further and then the additive package was added and mixed for an additional 5 minutes. This PPDMHS-modified VTM polymer was blended at 3% by weight in EXCEED™ 2018 polyethylene to produce Example 8.

[00115] Blown films were prepared, as described above, for Examples 7 and 8 polymers using a laboratory HAAKE blown film line. Control Example C2 was EXCEED™ 2018 without the addition of the VTM polymer (either modified or unmodified). A blown film was prepared, as described above, for comparison to the inventive films.

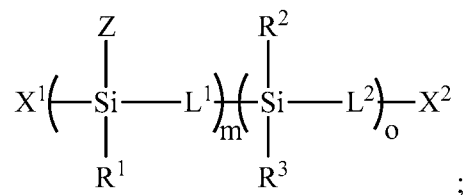
[00116] The film properties are shown in Table 5, below.

TABLE 5: BLOWN FILMS MADE FROM EXAMPLES 7-8			
	Sample C2 (CONTROL)	Example 7	Example 8
Ratio of PPDMHS:PAXON™ in Modified PAXON™ PE	-	2:1	2:1
Elmendorf Tear			
MD (g)	461.1	467.8	418.6
TD (g)	586.2	616.3	625.9
MD (g/mil)	327.3	343.4	278.1
TD (g/mil)	413.0	440.4	409.5
MD (g/μm)	12.9	13.5	10.9
TD (g/μm)	16.3	17.3	16.1
Gauge Mic (MD) (mils)	1.41	1.36	1.55
Gauge Mic (TD) (mils)	1.42	1.40	1.53
Dart Drop, Method A			
(g)	304	267.0	300.5
(g/mil)	201.3	177.4	176.8
Gauge Mic (Avg) (mils)	1.51	1.51	1.7

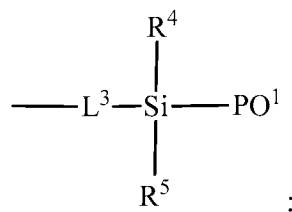
[00117] Example 7 and 8 films had greater bubble stability than the control (C2) film. They also had no gels, in contrast to the control. Advantageously, the film properties remained the same, and the rheology of the blends showed greater zero-shear viscosity than the control (C2) resin.

CLAIMS:

1. A modified polyolefin represented by the formula:



wherein Z is a group represented by the formula:



wherein PO¹ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms;

R¹ is Z, hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or PO⁴,

wherein PO⁴ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms;

each R², R³, R⁴, and R⁵, independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, wherein R² and R³ and/or R⁴ and R⁵ may form a cyclic structure with Si, or, a PO⁴;

each L¹, L², and L³, independently, is a bond or a linking group;

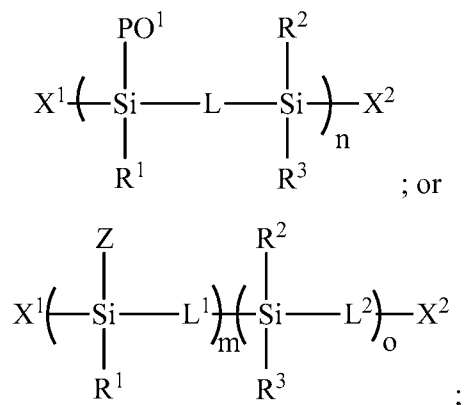
m is an integer from 1 to 1000;

o is an integer from 0 to 1000; and

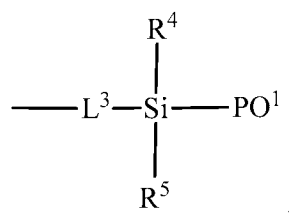
X¹ and X², each independently, is hydrogen; a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or PO⁴;

wherein PO¹ and PO⁴ can be the same or different.

2. The modified polyolefin of claim 1, wherein R¹ is an aromatic group; L¹ is an oxygen atom; L³ is an oxygen atom; each R⁴ and R⁵, independently, is a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group; m is 100 to 500; and o is 0.
3. A modified polyolefin represented by the formula:



wherein Z is a group represented by the formula:



wherein PO¹ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms derived from a vinyl terminated macromonomer;

each R¹, R², R³, R⁴, and R⁵, independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, where R² and R³ may form a cyclic structure with Si, or a PO⁴;

wherein PO⁴ is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms derived from a vinyl terminated macromonomer;

each L, L¹, L², and L³, is a bond or a linking group;

m is an integer from 1 to 1000;

n is an integer 1 to 1000;

o is an integer from 0 to 1000; and

X¹ and X², each independently, is hydrogen, a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group, or a PO⁴.

4. The modified polyolefin of any one of claims 1 to 3, wherein the vinyl terminated macromonomer is one or more of:

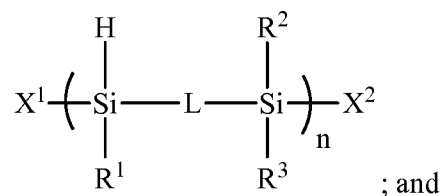
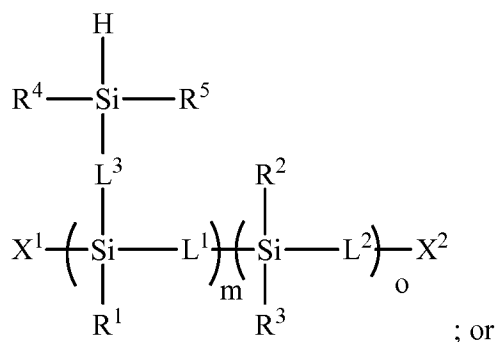
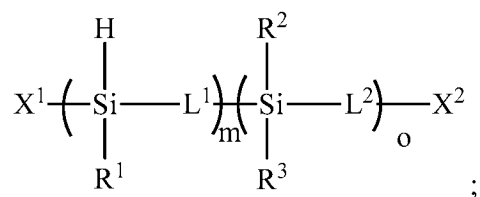
- (i) a vinyl terminated polymer having a Mn of at least 200 g/mol (measured by ¹H NMR) comprising of one or more C₄ to C₄₀ higher olefin derived units, where the higher olefin polymer comprises substantially no propylene derived units; and wherein the higher olefin polymer has at least 5% allyl chain ends;
- (ii) a copolymer having a Mn of 200 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, and (b) from 0.1 mol% to 80 mol% of propylene, wherein the higher olefin copolymer has at least 40% allyl chain ends;
- (iii) a copolymer having a Mn of 200 g/mol or more (measured by ¹H NMR), and comprises (a) from 80 mol% to 99.9 mol% of at least one C₄ olefin, and (b) from 0.1 mol% to 20 mol% of propylene; wherein the vinyl terminated macromonomer has at least 40% allyl chain ends relative to total unsaturation;
 - (iv) a co-oligomer having a Mn of 200 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 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;
 - (v) a propylene oligomer, comprising more than 90 mol% propylene and less than 10 mol% ethylene wherein the 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, and less than 100 ppm aluminum;
 - (vi) a propylene oligomer, comprising: at least 50 mol% propylene and from 10 mol% to 50 mol% ethylene, wherein the oligomer has: at least 90% allyl chain ends, a 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 1.2:1.0, wherein monomers having four or more carbon atoms are present at from 0 mol% to 3 mol%;
 - (vii) a propylene 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 oligomer has: at least 90% allyl chain ends, a 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;
 - (viii) a propylene oligomer, comprising: at least 50 mol% propylene, from 0.1 mol% to 45 mol% ethylene, and from 0.1 mol% to 5 mol% diene, norbornene, ethylidene norbornene, vinylnorbornene, norbornadiene, and

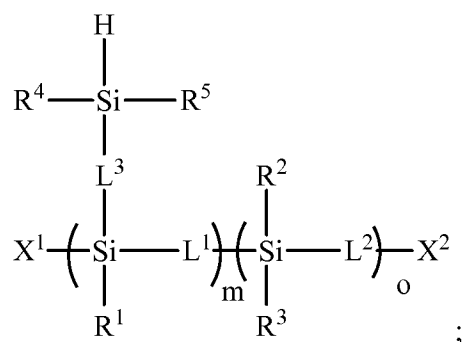
- dicyclopentadiene), wherein the oligomer has: at least 90% allyl chain ends, a Mn of 150 g/mol to 10,000 g/mol, and an isobutyl chain end to allylic vinyl group ratio of 0.7:1 to 1.35:1.0;
- (ix) a homo-oligomer, comprising propylene, wherein the oligomer has: at least 93% allyl chain ends, a Mn of 500 g/mol to 20,000 g/mol, an isobutyl chain end to allylic vinyl group ratio of 0.8:1 to 1.2:1.0, and less than 1400 ppm aluminum;
 - (x) a co-oligomer having a Mn (¹H NMR) of 7,500 to 60,000 g/mol comprising one or more alpha olefin derived units comprising ethylene and/or propylene, and having 50% or greater allyl chain ends, relative to total number of unsaturated chain ends and a g'vis of 0.90 or less (g'vis is determined using GPC-DRI, as described below);
 - (xi) a branched polyolefin having a Mn (GPC) greater than 60,000 g/mol comprising one or more alpha olefins comprising ethylene and/or propylene, and having: (i) 50% or greater allyl chain ends, relative to total unsaturated chain ends; (ii) a g'vis of 0.90 or less; and optionally; (iii) a bromine number which, upon complete hydrogenation, decreases by at least 50% (bromine number is determined by ASTM D 1159); and
 - (xii) a branched polyolefin having a Mn (¹H NMR) of less than 7,500 g/mol comprising one or more alpha olefin derived units comprising ethylene and/or propylene, and having: a ratio of percentage of saturated chain ends to percentage of allyl chain ends of 1.2 to 2.0; and 50% or greater allyl chain ends, relative to total unsaturated chain ends.
5. The modified polyolefin of claim 4, wherein R¹ is a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group; L¹ is an oxygen atom, m is from 100 to 500; each R² and R³, independently, are a C₁ to a C₂₀ substituted or unsubstituted hydrocarbyl group; L² is an oxygen atom; and o is from 100 to 500.
 6. A blend comprising the modified polyolefin of any one of claims 1 to 5.
 7. The blend of claim 6, further comprising polyethylene.
 8. An article comprising the modified polyolefin of any one of claims 1 to 8.
 9. A process to prepare the modified polyolefin of any one of claims 1 to 5 (carried out in the melt phase), comprising the steps of:
 - (i) contacting a non-metallocene catalyst and one or more vinyl terminated

polyolefin selected from a vinyl terminated polyolefin and a vinyl terminated macromonomer;

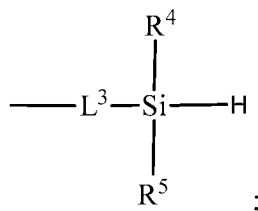
wherein when the vinyl terminated polyolefin is a vinyl terminated macromonomer, the hydrosilylation modifier is represented by one of more of the formulae:



wherein the vinyl terminated polyolefin is a polyolefin, the hydrosilylation modifier is represented by the formula:



wherein R^1 is hydrogen, Z' , or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group; and wherein Z' is a group represented by the formula:



each R^2 , R^3 , R^4 , and R^5 , independently, is a H, or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group, where R^2 and R^3 and/or R^4 and R^5 may form a cyclic structure with Si;

each L, L^1 , L^2 , and L^3 , independently, is a bond or a linking group (each L^1 , L^2 , and L^3 , independently, is O, S, NR^{A} , PR^{B} , SiR^{C}_2 , or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group; wherein each R^{A} , R^{B} , and R^{C} , independently, is hydrogen, or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group);

m is an integer from 1 to 1000;

n is an integer from 1 to 1000;

o is an integer from 0 to 1000;

each of X^1 and X^2 , independently, is hydrogen or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group;

the vinyl terminated polyolefin is a substituted or unsubstituted hydrocarbyl group having from 20 to 10,000 carbon atoms and at least 5% allyl chain ends;

(ii) obtaining a modified polyolefin;

(iii) optionally, adding a polyolefin; and

(iv) obtaining a blend comprising the modified polyolefin.

10. The process of claim 9, wherein the polyolefin from step (iii) is added during step (i), alternately, the polyolefin from step (iii) is added after step (i).

11. The process of claim 9, wherein the non-metallocene catalyst is one or more of: chloroplatinic acid, platinum complexes such as platinum cyclovinyldimethylsiloxane, rhodium complexes, peroxides, such as di-cumyl peroxide, Ziegler Natta catalysts, and iridium, cobalt, ruthenium, osmium, nickel and palladium complexes; platinum-carbonyl-cyclovinyldimethylsiloxane complex; platinum-cyclovinyldimethylsiloxane complex; platinum-octanal/octanol complex; hexachloroplatinic acid; and dimethylplatinum cyclooctadiene complex), a hydrosilylation modifier.

12. The polymer or process of any one of the previous claims, wherein each L^1 , L^2 , and L^3 , independently, is O, S, NR^{A} , PR^{B} , SiR^{C}_2 , or a C_1 to a C_{20} substituted or

unsubstituted hydrocarbyl group; wherein each R^A , R^B , and R^C , independently, is hydrogen, or a C_1 to a C_{20} substituted or unsubstituted hydrocarbyl group; preferably each L^1 , L^2 , and L^3 , independently, is O.

13. The polymer or process of any one of the previous claims, wherein each of PO^1 and PO^4 , independently, is derived from a vinyl terminated polyolefin selected from a vinyl terminated polyolefin or a vinyl terminated macromonomer; preferably the vinyl terminated polyolefin is ethylene-based; preferably the polyolefin is polyethylene.

1/3

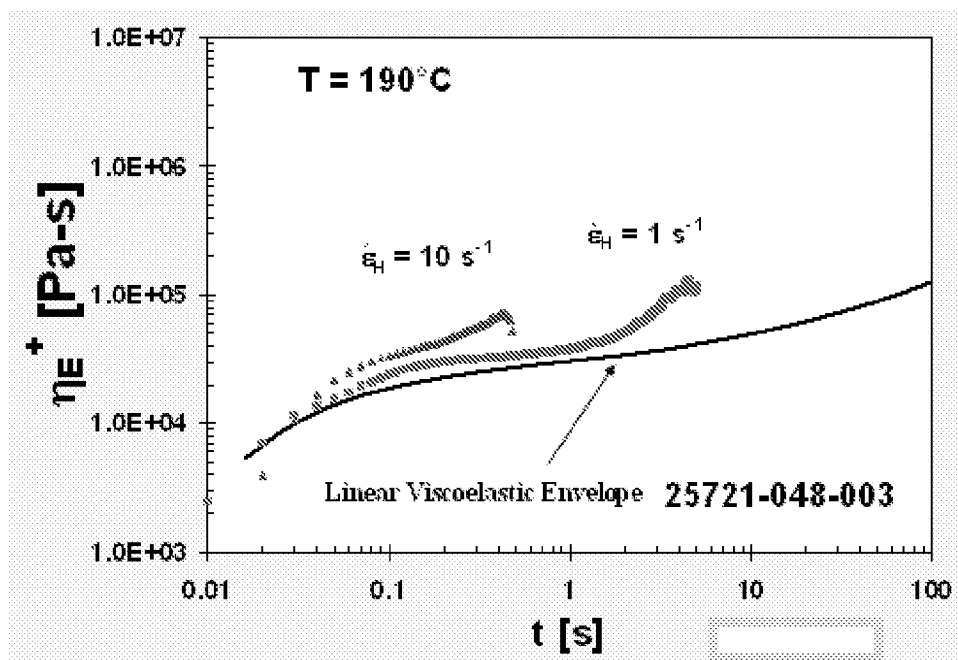
Figure 1. Example 2 Extensional Rheology Plot

Figure 2. VanGurp-Palmen Plot for Example modified polyolefins and their comparison with raw materials.

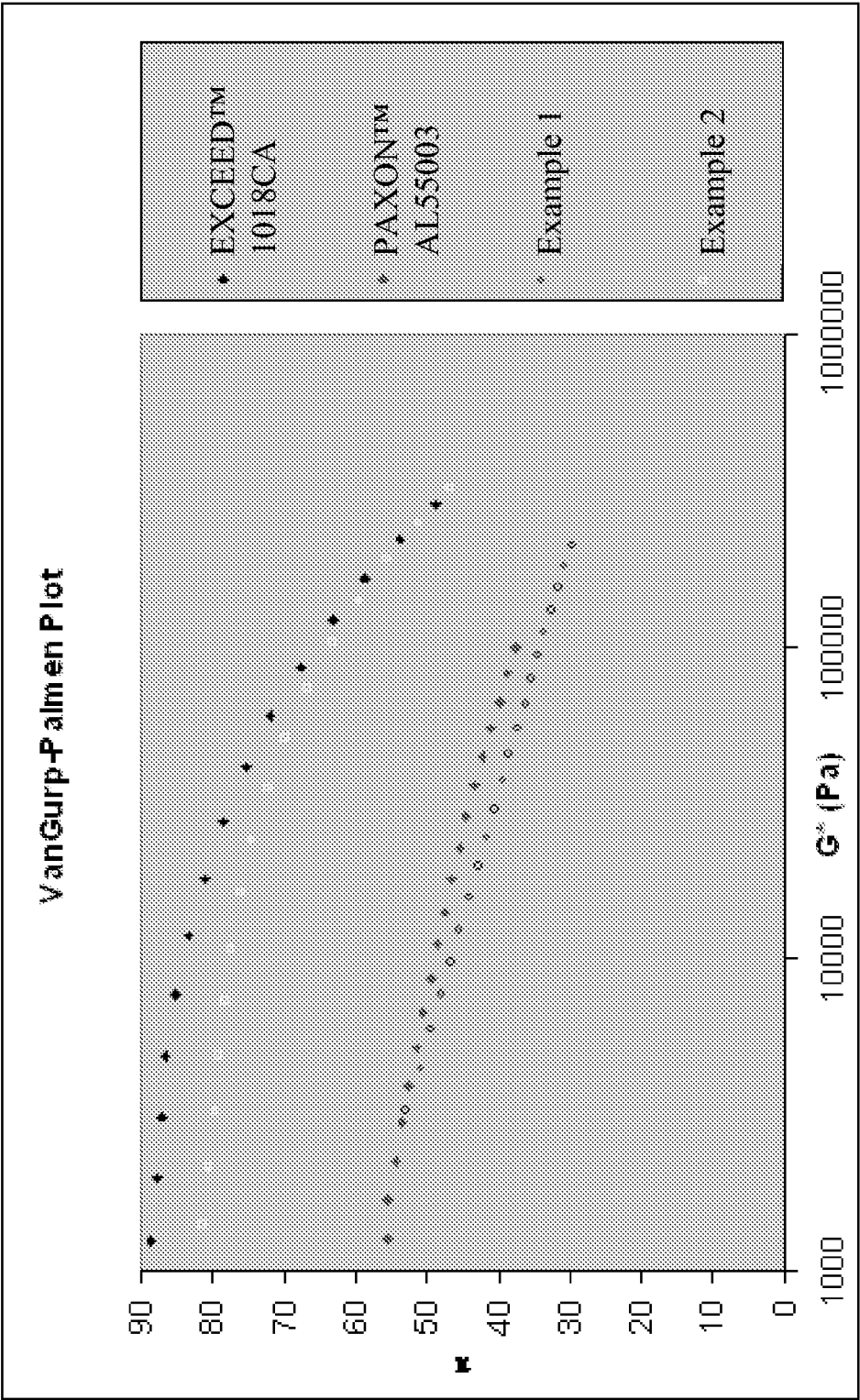
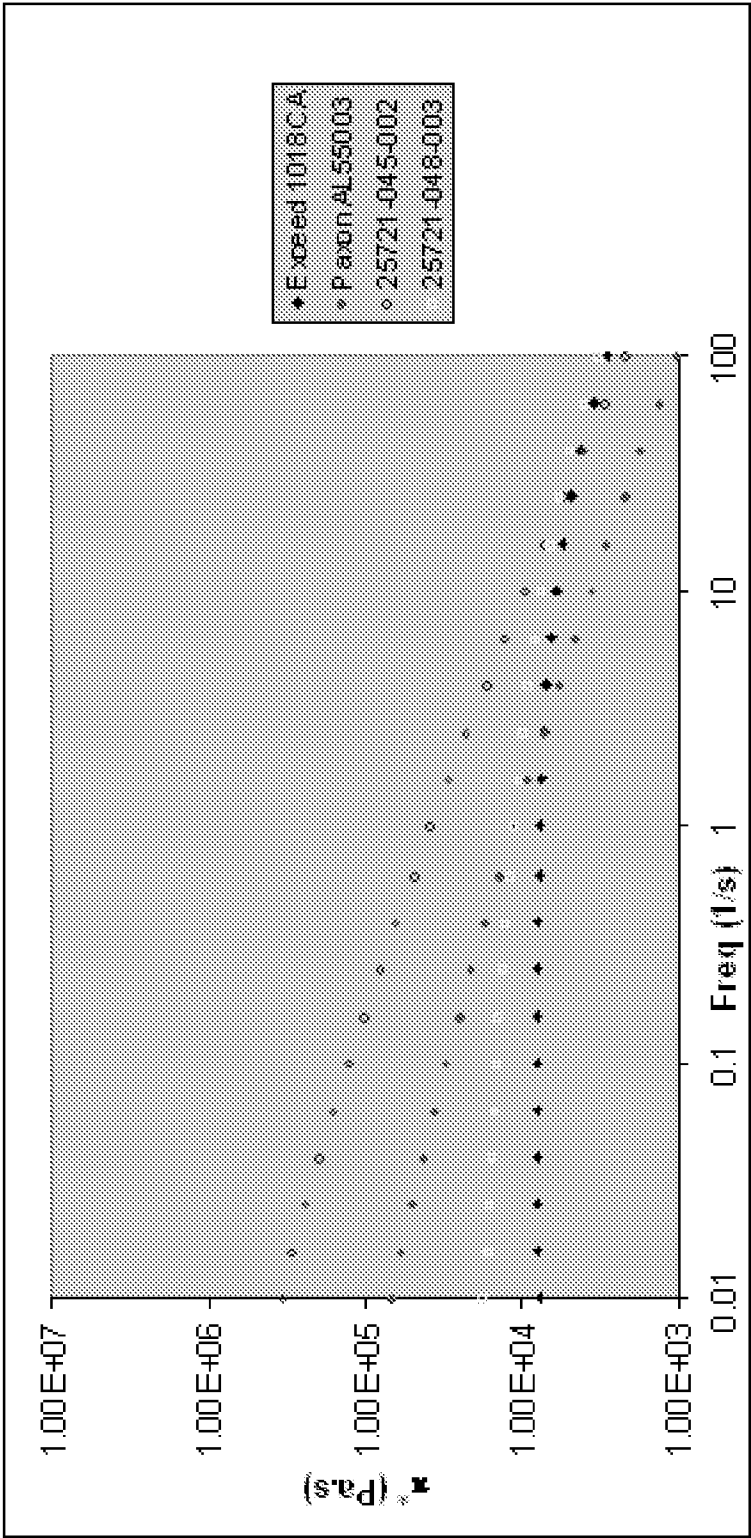


Figure 3. Complex Viscosity vs. Frequency plot for example graft copolymers and their comparison with raw materials.



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2013/060547**A. CLASSIFICATION OF SUBJECT MATTER****C08F 8/42(2006.01)i, C08F 10/02(2006.01)i, C08L 23/26(2006.01)i, C08J 5/00(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 8/42; C08F 257/02; C08G 77/12; C08F 299/00; C08K 3/30; B32B 27/28; C08F 8/00; C08L 83/04; C08G 81/02; C08G 77/455; C08F 10/02; C08L 23/26; C08J 5/00

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: vinyl terminated macromonomer, polypropylene, polyethylene, hydrosilylation, end-functional polymer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6114445 A (TZOGANAKIS, COSTAS et al.) 05 September 2000 See abstract; claims 1-16; column 2; Examples 1 & 6; Table 5; Figures 1-3.	1,3-4
A		2,5
X	US 7247385 B1 (TZOGANAKIS, COSTAS et al.) 24 July 2007 See abstract; claims 1-22; column 1; Examples 1-7.	1,3-4
A	US 2012-0029099 A1 (HSIEH, BING et al.) 02 February 2012 See abstract; claims 1-31; paragraphs [0022] & [0035].	1-5
A	US 2010-0168309 A1 (MACKINNON, IAIN A. et al.) 01 July 2010 See abstract; claims 1-22; page 3, Scheme; page 5, second Formula.	1-5
A	US 7943719 B2 (HAWKER, CRAIG J. et al.) 17 May 2011 See abstract; claims 1-10; Example 1; Figures 1-2.	1-5
PX	US 2012-0245293 A1 (CROWTHER, DONNA J. et al.) 27 September 2012 See abstract; claims 1-28, paragraphs [0054]-[0123].	1,3-4



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 another 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

10 December 2013 (10.12.2013)

Name and mailing address of the ISA/KR

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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.: 7-8, 10-13
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:
 Claims 7 and 10-11 refer to claim(s) which is/are not drafted in accordance with PCT Rule 6.4(a).
 Claim 8 refers to itself, which makes it impossible to clearly define the subject matter for which protection is sought (PCT Article 6).
 Claims 12-13 contain two different categories in a single claim, which is contrary to the requirement of PCT Rule 6.1(a).
3. ☒ Claims Nos.: 6, 8-9, 12-13
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 fees, this Authority did not invite payment of any additional fees.
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/US2013/060547

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6114445 A	05/09/2000	WO 97-47665 A1	18/12/1997
US 7247385 B1	24/07/2007	CA 2340430 A1	24/02/2000
		EP 1115757 A1	18/07/2001
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US 2010-0168309 A1	01/07/2010	AT 484550 T	15/10/2010
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		CN 101679753 A	24/03/2010
		DE 602008003024 D1	25/11/2010
		DK 2142601 T3	07/02/2011
		EP 2142587 A2	13/01/2010
		EP 2142587 B1	19/12/2012
		EP 2142601 A2	13/01/2010
		EP 2142601 B1	13/10/2010
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		JP 5269883 B2	21/08/2013
		KR 10-2010-0017524 A	16/02/2010
		KR 10-2010-0017527 A	16/02/2010
		PT 2142601 E	04/02/2011
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