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(54) **Title:** ALCOHOL-POLYALPHAOLEFINS AND METHODS THEREOF

(57) **Abstract:** The present disclosure provides polyalpha olefins, compositions including poly alpha olefins, and methods thereof, that include a terminal alcohol group and can provide increased viscosity as compared to conventional poly alpha olefins. The viscosity increase can provide alcohol-polyalpha olefins which can be used in a variety of end use applications, such as for viscosity modification of compositions, such as oils.

ALCOHOL-POLYALPHAOLEFINS AND METHODS THEREOF

INVENTORS: Alex E. Carpenter, Patrick C. Chen

PRIORITY CLAIM

[0001] This application claims priority to and the benefit of USSN 62/680,919, filed June 5, 2018 and European Patent Application No. 18177936.4, filed June 15, 2018, which are incorporated by reference in their entirety.

FIELD OF THE INVENTION

[0002] The present disclosure provides alcohol-polyalpha olefins, compositions comprising alcohol-polyalpha olefins, and methods for forming alcohol-polyalpha olefins.

BACKGROUND OF THE INVENTION

[0003] Branched aliphatic primary alcohols, such as those having carbon chains, have found use in many applications such as surfactants, solvents, wetting agents, solubilizing agents, emulsifiers, or as intermediates for making derivatives such as esters and ethers that can be used as surfactants, solvents, wetting agents, solubilizing agents, emulsifiers, and lubricant base stocks or additives.

[0004] For example, there has been interest in long-chain aliphatic alcohols $>C_{10}$. There is also interest in "ultra" long chain aliphatic alcohols containing very high carbon numbers, e.g. $C_{300}>Cx>C_{22}$. Driving this interest is the possible suitability of alcohol-containing polyalpha olefins (PAOs) to be used as friction modifiers, anti-corrosion coatings, wetting agents, viscosity modifiers or synthetic base stock. A terminal alcohol-containing PAO has a gamma-branched alcohol moiety on the polyalpha olefin structure and is unique relative to beta branched ("internal") alcohols, of comparable size. For example, in the case of an internal alcohol PAO (e.g., beta branched alcohol), the polar alcohol moiety is buried within a network of sterically encumbering alkyl chains limiting the ability of the hydroxyl functionality to influence material properties (such as viscosity) and interact with surfaces or substrates. However, it would be expected that PAOs having alcohol moieties that are not sterically encumbered by alkyl chains would increase the polarity such that the PAO would become immiscible with non-polar materials, such as if the PAO were used as a surfactant or viscosity modifier.

[0005] Additionally, metathetical methods (methods that use metathesis) or Guerbet-type chemistry may be utilized to obtain beta branched alcohol compounds, but these methods do not provide terminal alcohol-containing PAOs.

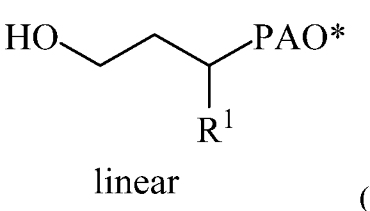
[0006] There is a need for polyalpha olefins having a terminal, gamma-branched alcohol moiety and having a suitable viscosity and polarity for a wide range of applications. There is further a need for methods of forming polyalpha olefins having a terminal, gamma-branched alcohol moiety.

[0007] Additional references of interest include: USSN 15/988,604, filed May 24, 2018; US 6,355,603; JP H082813; R. Barbey, et al. (2009) "Polymer Brushes via Surface-Initiated Controlled Radical Polymerization: Synthesis, Characterization, Properties and Applications" *Chem. Rev.*, v.109, pp. 5437-5527; P. Raffa, et al. (2015) "Polymeric Surfactants, Synthesis, Properties and Links to Applications" *Chem. Rev.*, v.115, pp. 8504-8563; F. Stempfle, et al. (2015) "Long-chain Aliphatic Polymers to Bridge the Gap between Semicrystalline Polyolefins and Traditional Polycondensates" *Chem. Rev.*, v.116, pp. 4597-4641; V. Grumel, et al. (2001) *Macromol. Materi. Eng.*, v.286, pp. 480-487; G. Babu, et al. (1994) *Macromolecules.*, v.27, pp. 3383−3388; X. Zhao, et al. (2000) *J. Polym. Sci., Part A: Polym. Chem.*, v.38, pp. 3802−3811; N. M. G. Franssen, et al. (2013) "Synthesis of functional 'polyolefins': state of the art and remaining challenges" *Chem. Soc. Rev.*, v.42, p. 5809; P. Brant, et al. (2016) "Termination Events in Sterically Hindered Metallocene-Catalyzed Olefin Oligomerizations: Vinyl Chain Ends in Oligooctenes" *Organometallics*, v.35, pp. 2836-2839; US 2018/0037521; X. Li, et al. (2012) "Surface Properties of Bottlebrush Polymer Thin Films" *Macromolecules*, v.45, pp. 7118-7127; O. Azzaroni, (2012) "Polymer Brushes Here, There, and Everywhere: Recent Advances in Their Practical Applications and Emmerging Opportunities in Multiple Research Fields" *J. Polym. Sci.*, v.50, pp. 3225-3258; Van Leeuwen, et al. (1983) "Hydroformylation of Less Reactive Olefins with Modified Rhodium Catalysts" *J. Organomet. Chem.*, v.258, pp. 343-350; A. Van Rooy, et al. (1996) "Rhodium-catalysed hydroformylation of branched 1-alkenes; bulky phosphite vs. triphenylphosphine as modifying ligand" *J. Organomet. Chem.*, v.507, pp. 69-73; P. Kalck, et al. (2009) "Cobalt-Catalyzed Hydroformylation of Alkenes: Generation and Recycling of the Carbonyl Species, and Catalytic Cycle." *Chem. Rev.*, v.109, pp. 4272-7282; R. Franke, (2012) "Applied Hydroformylation," *Chem. Rev.*, v.112(11), pp. 5675-5732; W.L. Arnarego, et al.(2003) "Purification of Laboratory Chemicals", 5th ed., Elsevier: Oxford; ASTM D445 "Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and Calculation of Dynamic Viscosity)"; ASTM D2270 "Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 and 100°C"; *Spartan '16*, version 2.0.7 Wavefunction, Inc.: Irvine California, 2016; US 8,383,869; JP 2005-298443A; US 5,068,047; US 3,933,659; US 4,176,074; US 4,105,571; US 3,779,928; US 3,778,375; US 3,852,205; US 3,879,306; US 3,932,290; US 4,028,258; US 4,344,853; and US 4,464,493.

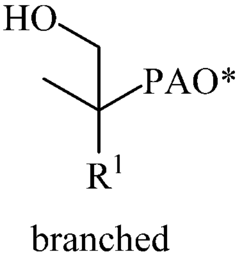
SUMMARY OF THE INVENTION

[0008] The present disclosure provides alcohol-polyalpha olefins, compositions comprising alcohol-polyalpha olefins, and methods for forming alcohol-polyalpha olefins.

[0009] In at least one embodiment, the present disclosure provides **alcohol-**polyalpha olefin represented by formula **(VIIa)** or **(VIIb)**:



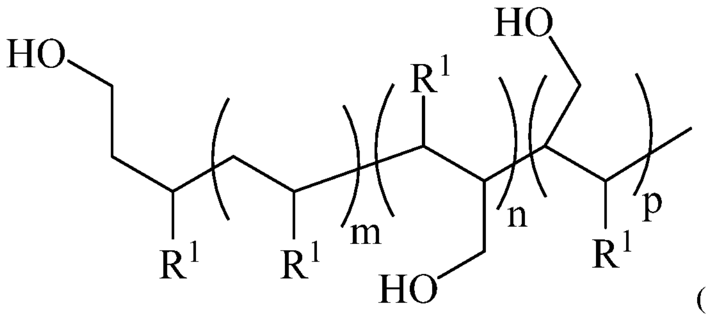
(VIIa)



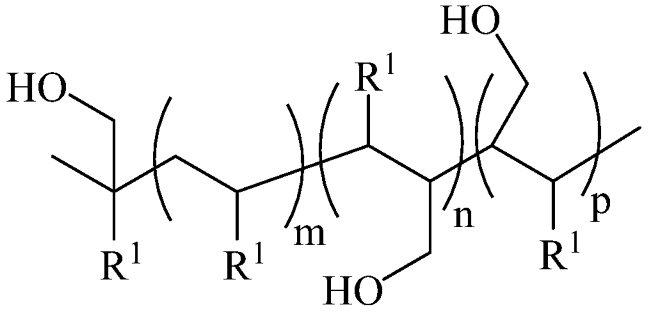
(VIIb),

where R^1 is hydrocarbyl, typically containing from 1 to 100 carbon atoms, and PAO* is a polymer having two or more alpha-olefin mer units, typically 2 to 400 mer units. The alcohol-polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** typically has a number average molecular weight of 500 g/mol or greater, such as from 500 g/mol to 10,000 g/mol.

[0010] In yet another embodiment, the present disclosure provides polyalpha olefins represented by formula **(VIIIa)** or **(VIIIb)**:



(VIIIa)



(VIIIb),

where R^1 is hydrocarbyl, typically containing from 1 to 100 carbon atoms, and m, n, and p are integers such that the number average molecular weight of the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** is 500 g/mol or greater, such as from 500 g/mol to 10,000 g/mol.

[0011] In yet another embodiment, the present disclosure provides methods for making terminal alcohol-containing polyalpha olefins.

[0012] In still another embodiment, the present disclosure provides compositions, such as oil compositions, comprising a terminal alcohol-containing polyalpha olefin.

BRIEF DESCRIPTION OF THE FIGURES

[0013] FIG. 1A is a representation illustrating a molecular model of an oxPAO-alcohol (polydecene), according to one embodiment.

[0014] FIG. 1B is a representation illustrating a molecular model of an internal beta-branched oxPAO-alcohol (polydecene), according to one embodiment.

[0015] FIG. 2 is a graph illustrating kinematic viscosity measurements (ASTM D445, 100°C) for uPAO-65 starting material, oxPAO-aldehyde, and oxPAO-alcohol, according to one embodiment.

[0016] FIG. 3A is an ^1H NMR ($CDCl_3$) spectrum of uPAO-65 starting material, according to one embodiment.

[0017] FIG. 3B is an ^1H NMR ($CDCl_3$) spectrum of uPAO-65 starting material, according to one embodiment.

[0018] FIG. 4A is an ^1H NMR ($CDCl_3$) spectrum of hydroformylated uPAO-aldehyde, according to one embodiment.

[0019] FIG. 4B is an ^1H NMR ($CDCl_3$) spectrum of hydroformylated uPAO-aldehyde, according to one embodiment.

[0020] FIG. 5A is an ^1H NMR ($CDCl_3$) spectrum of hydroformylated uPAO reduced to oxPAO-alcohol, according to one embodiment.

[0021] FIG. 5B is an ^1H NMR ($CDCl_3$) spectrum of hydroformylated uPAO reduced to oxPAO-alcohol, according to one embodiment.

DETAILED DESCRIPTION

[0022] The present disclosure provides alcohol-polyalpha olefins (referred to as oxPAO-alcohols), and methods thereof, that include a terminal alcohol group and can provide increased viscosity as compared to conventional PAOs. The viscosity increase can provide oxPAO-alcohols which can be used in a variety of end use applications, such as for viscosity modification of compositions, such as oils, particularly lubricating oils. The alcohol functional groups of oxPAO-alcohols can also provide additional chemical modification and/or or modulation of the physical or surfactant properties of the oxPAO-alcohols or blends thereof.

Definitions

[0023] As used herein, "molecular weight" refers to the number average molecular weight (Mn) unless otherwise specified.

[0024] In this disclosure, the article "a" or "an" means at least one, unless it is clearly specified or indicated by the context to mean one.

[0025] The term "alkyl group" or "alkyl" interchangeably refers to a saturated hydrocarbyl group consisting of carbon and hydrogen atoms. "Linear alkyl group" refers to a non-cyclic alkyl group in which all carbon atoms are covalently connected to no more than two carbon atoms. "Branched alkyl group" refers to a non-cyclic alkyl group in which at least one carbon atom is covalently connected to more than two carbon atoms. "Cycloalkyl group" refers to an alkyl group in which all carbon atoms form a ring structure comprising one or more rings.

[0026] The term "aryl group" refers to an unsaturated, cyclic hydrocarbyl group consisting of carbon and hydrogen atoms in which the carbon atoms join to form a conjugated π system. Non-limiting examples of aryl groups include phenyl, 1-naphthyl, 2-naphthyl, 3-naphthyl, and the like.

[0027] The term "arylalkyl group" refers to an alkyl group substituted by an aryl group or alkylaryl group. Non-limiting examples of arylalkyl group include benzyl, 2-phenylpropyl, 4-phenylbutyl, 3-(3-methylphenyl)propyl, 3-(*p*-tolyl)propyl, and the like.

[0028] The term "alkylaryl group" refers to an aryl group substituted by an alkyl group. Non-limiting examples of alkylaryl group include 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2-methyl-1-naphthyl, 6-phenylhexyl, 5-pentylphenyl, 4-butylphenyl, 4-terterybutylphenyl, 7-phenylheptanyl, 4-octylphenyl, and the like.

[0029] The term "cycloalkylalkyl group" refers to an alkyl group substituted by a cycloalkyl group or an alkylcycloalkyl group. An example of cycloalkylalkyl group is cyclohexylmethyl.

[0030] The term "alkylcycloalkyl group" refers to a cycloalkyl group substituted by an alkyl group. Non-limiting examples of alkylcycloalkyl group include 2-methylcyclohexyl, 3-methylcyclohexyl, 4-methylcyclohexyl, 4-tertiary butyl cyclohexyl, 4-phenylcyclohexyl, cyclohexylpentyl, and the like.

[0031] The term "hydrocarbyl group" or "hydrocarbyl" interchangeably refers to a group consisting of hydrogen and carbon atoms only. A hydrocarbyl group can be saturated or unsaturated, linear or branched, cyclic or acyclic, containing a cyclic structure or free of cyclic structure, and aromatic or non-aromatic.

[0032] "Cn" group or compound refers to a group or a compound comprising carbon atoms at total number thereof of n. Thus, "Cm-Cn" or "Cm to Cn" group or compound refers to a group or compound comprising carbon atoms at a total number thereof in the range from m to n. Thus, a C_1-C_{50} alkyl group refers to an alkyl group comprising carbon atoms at a total number thereof in the range from 1 to 50.

[0033] The term “carbon backbone” in an alkane or an alkyl group refers to the longest straight carbon chain in the molecule of the compound or the group in question.

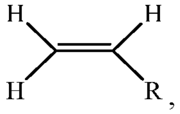
[0034] The term “carbon backbone” of an olefin is defined as the straight carbon chain therein including a C=C functionality having the largest number of carbon atoms.

[0035] The term “olefin” refers to an unsaturated hydrocarbon compound having a hydrocarbon chain containing at least one carbon-to-carbon double bond in the structure thereof, wherein the carbon-to-carbon double bond does not constitute a part of an aromatic ring. The olefin may be linear, branched linear, or cyclic. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have a "propylene" content of 35 wt% to 55 wt%, it is understood that the mer unit in the copolymer is derived from propylene in the polymerization reaction and said derived units are present at 35 wt% to 55 wt%, based upon the weight of the copolymer.

[0036] A “polymer” has two or more of the same or different mer units. (“Different” as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically.) A polymer can be a homopolymer or a copolymer.

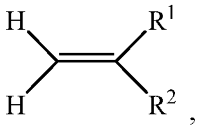
[0037] The term “terminal olefin” refers to an olefin having a terminal carbon-to-carbon double bond in the structure thereof ($(R^1R^2)\text{-}C{=}CH_2$, where R^1 and R^2 can be independently hydrogen or any hydrocarbyl group, such as R^1 is hydrogen, and R^2 is an alkyl group). A “linear terminal olefin” is a terminal olefin defined in this paragraph wherein R^1 is hydrogen, and R^2 is hydrogen or a linear alkyl group.

[0038] The term “vinyl” means an olefin having the following formula:



wherein R is a hydrocarbyl group, such as a saturated hydrocarbyl group such as an alkyl group.

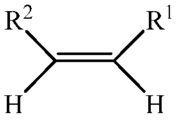
[0039] The term “vinylidene” means an olefin having the following formula:



wherein R^1 and R^2 are each independently a hydrocarbyl group, such as a saturated hydrocarbyl group such as alkyl group.

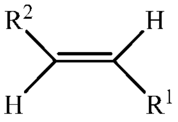
[0040] The term “1,2-di-substituted vinylene” means

(i) an olefin having the following formula:



; or

(ii) an olefin having the following formula:

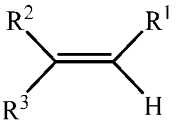


; or

(iii) a mixture of (i) and (ii) at any proportion thereof,

wherein R^1 and R^2, the same or different at each occurrence, are each independently a hydrocarbyl group, such as saturated hydrocarbyl group such as alkyl group.

[0041] The term "tri-substituted vinylene" means an olefin having the following formula:



,

wherein R^1, R^2, and R^3 are each independently a hydrocarbyl group, such as a saturated hydrocarbyl group such as alkyl group.

[0042] An "alpha olefin" is an olefin having a double bond at the alpha (or 1-) position. For the purposes of this disclosure, the term "alpha olefin" includes C_4-C_{20} olefins. Non-limiting examples of alpha olefins include 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-eicosene, 1-heneicosene, 1-docosene, 1-tricosene, 1-tetracosene, 1-pentacosene, 1-hexacosene, 1-heptacosene, 1-octacosene, 1-nonacosene, 1-triacontene, 4-methyl-1-pentene, 3-methyl-1-pentene, 5-methyl-1-nonene, 3,5,5-trimethyl-1-hexene, vinylcyclohexane, and vinylnorbornene.

[0043] A "polyalpha olefin" or "PAO" is a polymer having two or more alpha-olefin mer units. The term "polyalpha-olefin(s)" ("PAO(s)") includes one or more terminal (also referred to as alpha) olefin monomer(s). PAOs are produced from the polymerization reactions of terminal olefin monomer molecules in the presence of a catalyst system, optionally further hydrogenated to remove residual carbon-carbon double bonds therein. Thus, a PAO can be a dimer (resulting from two terminal olefin molecules), a trimer (resulting from three terminal olefin molecules), a tetramer (resulting from four terminal olefin molecules), or any other polymer comprising two or more structure (also referred to as "mer") units derived from one or more terminal olefin monomer(s). The PAO molecule can be highly regio-regular, such that the bulk material exhibits an isotacticity, or a syndiotacticity when measured by ^{13}C NMR. The

PAO molecule can be highly regio-irregular, such that the bulk material is substantially atactic when measured by ^{13}C NMR. A PAO material made by using a metallocene-based catalyst system is typically called a metallocene-PAO ("mPAO"), and a PAO material made by using traditional non-metallocene-based catalysts (e.g., Lewis acids, supported chromium oxide, and the like) is typically called a conventional PAO ("cPAO"). A PAO material that has not been hydrogenated and therefore is unsaturated is called an unhydrogenated/unsaturated PAO ("uPAO"). An oxPAO is a PAO containing an alcohol (-OH) or aldehyde (CH=O) group. An "oxPAO-alcohol" is a PAO containing an alcohol (-OH). An "oxPAO-aldehyde" is a PAO containing an aldehyde (CH=O) group. An alcohol-polyalpha olefin is a PAO having an -OH group attached thereto, also referred to as an oxPAO-alcohol. A "polyalpha olefin group" is a substituted or unsubstituted PAO. "Substituted" means that at least one hydrogen atom has been replaced with at a heteroatom, or a heteroatom containing group, such as halogen (such as Br, Cl, F or I) or at least one functional group such as $-NR^*_2$, $-OR^*$, $-SeR^*$, $-TeR^*$, $-PR^*_2$, $-AsR^*_2$, $-SbR^*_2$, $-SR^*$, $-BR^*_2$, $-SiR^*_3$, $-GeR^*_3$, $-SnR^*_3$, $-PbR^*_3$, and the like, where each R* is independently a hydrocarbyl or halocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted completely saturated, partially unsaturated, or aromatic cyclic or polycyclic ring structure, or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0044] TCB is 1,2,4-trichlorobenzene.

[0045] The term "rhodium carbonyl compounds" means compounds comprising rhodium covalently bonded to at least one carbonyl group. Non-limiting examples of rhodium carbonyl compounds include: $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, (acetylacetonato)dicarbonylrhodium(I), chlorodicarbonylrhodium dimer, chlorobis(ethylene)rhodium dimer, $HRh(CO)_4$, and $HRh(CO)PPh_3$.

[0046] The term "phosphine compound" refers to a phosphorous-containing organic compound having the formula PR_3, where R is a hydrocarbyl group, such as an aryl group, an alkylaryl group, an alkyl group, or an arylalkyl group.

[0047] The term "syngas" means a mixture of carbon monoxide and hydrogen, such as at a molar ratio of from 0.8:1 to 1.4:1, such as 1:1.

[0048] The term "selectivity" of a terminal olefin in a reaction toward a given product species means the percentage of the terminal olefin converted into the given product species on the basis of the all of the terminal olefin converted. Thus, if in a specific polymerization reaction, 5% of the terminal olefin monomer is converted into trimer, then the selectivity of the terminal olefin toward trimer in the polymerization reaction is 5%.

[0049] In this disclosure, all molecular weight data are reported in the units of grams per mole (g·mol^{-1}).

[0050] NMR spectroscopy provides key structural information about the synthesized polymers. Proton NMR (^{1}H-NMR) analysis of the unsaturated PAO product gives a quantitative breakdown of the olefinic structure types (viz. vinyl, 1,2-di-substituted, tri-substituted, and vinylidene). In this disclosure, compositions of mixtures of olefins comprising terminal olefins (vinyls and vinylidenes) and internal olefins (1,2-di-substituted vinylenes and tri-substituted vinylenes) are determined by using ^{1}H-NMR. Specifically, a NMR instrument of at least a 500 MHz is run under the following conditions: a 30° flip angle RF pulse, 120 scans, with a delay of 5 seconds between pulses; sample dissolved in any suitable deuterated solvent such as $CDCl_3$ (deuterated chloroform) or deuterated 1,2,4-trichlorobenzene (TCB); and signal collection temperature at 25°C. The following approach is taken in determining the concentrations of the various olefins among all of the olefins from an NMR spectrum. First, peaks corresponding to different types of hydrogen atoms in vinyls (T1), vinylidenes (T2), 1,2-di-substituted vinylenes (T3), and tri-substituted vinylenes (T4) are identified at the peak regions in TABLE 1 below. Second, areas of each of the above peaks (A1, A2, A3, and A4, respectively) are then integrated. Third, quantities of each type of olefins (Q1, Q2, Q3, and Q4, respectively) in moles are calculated (as A1/2, A2/2, A3/2, and A4, respectively). Fourth, the total quantity of all olefins (Qt) in moles is calculated as the sum total of all four types (Qt=Q1+Q2+Q3+Q4). Finally, the molar concentrations (C1, C2, C3, and C4, respectively, in mol%) of each type of olefin, on the basis of the total molar quantity of all of the olefins, is then calculated (in each case, Ci=100*Qi/Qt).

TABLE 1 (Determined using deuterated TCB)

Hydrogen Atoms		Peak Region (ppm)	Peak Area	Number of Hydrogen Atoms	Quantity of Olefin (mol)	Concentration of Olefin (mol%)
Type No.	Olefin Structure					
T1	CH_2=CH-R^1	4.95 - 5.10	A1	2	Q1=A1/2	C1
T2	CH_2=CR^1R^2	4.70 - 4.84	A2	2	Q2=A2/2	C2
T3	CHR^1=CHR^2	5.31 - 5.55	A3	2	Q3=A3/2	C3
T4	CR^1R^2=CH R^3	5.11 - 5.30	A4	1	Q4=A4	C4

[0051] All percentages in describing chemical compositions herein are by weight unless specified otherwise. “Wt%” means percent by weight.

[0052] All kinematic viscosity values in this disclosure are as determined pursuant to ASTM D445. Kinematic viscosity at 100°C is reported herein as KV100, and kinematic viscosity at 40°C is reported herein as KV40. Units of all Kinematic viscosity values herein are centistokes (cSt) unless otherwise specified.

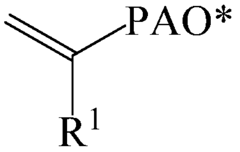
[0053] All viscosity index ("VI") values in this disclosure are as determined pursuant to ASTM D2270.

I. The uPAO Feed and Processes for Making uPAO's

I.1 General

[0054] uPAOs of the present disclosure are polyalpha olefins having high (>50 %) vinyl or vinylidene content and a molecular weight of 500 g/mol or greater, such as 1,000 g/mol or greater. In at least one embodiment, a uPAO has a molecular weight of from 500 g/mol to 10,000 g/mol, such as from 1,000 g/mol to 5,000 g/mol, such as from 1,000 g/mol to 3,000 g/mol, such as from 1,500 g/mol to 3,000 g/mol. Useful uPAOs also have a degree of internal unsaturation. In at least one embodiment, a uPAO has an internal unsaturation of less than 0.4 unsaturations per 1000 carbon atoms, such as less than 0.3, such as less than 0.2, such as from 0.01 to 0.4, such as from 0.01 to 0.3, such as from 0.01 to 0.2. Unsaturation (internal and terminal) in a polymer can be determined by ^{1}H NMR with reference to *Macromolecules* (2014), v.47, p. 3782 and *Macromolecules* (2005), v.38, p. 6988, but in event of conflict *Macromolecules* (2014), v.47, p. 3782 shall control. Peak assignments are determined referencing the solvent of tetrachloroethane-1,2 d_2 at 5.98 ppm. Specifically, percent internal unsaturation is determined by adding Vy1+Vy2+trisubstituted olefins then dividing by total unsaturation.

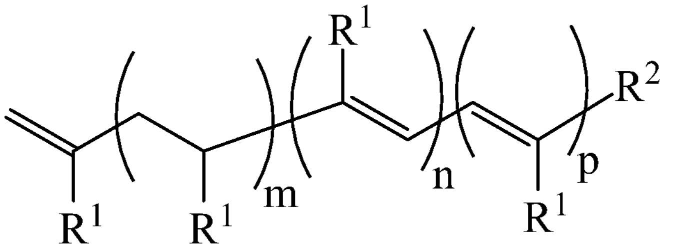
[0055] In at least one embodiment, a uPAO is represented by formula (**I**):



(**I**)

where R^1 is any hydrocarbyl group, such as an alkyl group, typically containing from 1 to 100 carbon atoms, such as a linear or branched alkyl group, such as a linear alkyl group. In at least one embodiment, R^1 comprises c1 to c2 carbon atoms, where c1 and c2 can be, independently, any integer between 1 and 60, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 68, or 70, and c1 is less than c2. In one embodiment, c1 is 2 and c2 is 40. Alternatively, c1 is 4 and c2 is 30. R^1 can have an even number of carbon atoms. Examples of R^1 include: ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl, *n*-icosyl, *n*-docosyl, *n*-tetracosyl, *n*-hexacosyl, and *n*-octacosyl. In one embodiment, R^1 is selected from: *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, and *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, and *n*-octadecyl. PAO* is a polyalpha olefin group having two or more alpha-olefin mer units, typically 2 to 400 mer units, such as 2 to 100 mer units. In one embodiment, PAO is selected from poly-1-pentenyl, poly-1-hexenyl, poly-1-heptenyl, poly-1-octenyl, poly-1-nonenyl, poly-1-decenyl, poly-1-undecenyl, poly-1-dodecenyl, poly-1-tridecenyl, poly-1-tetradecenyl, poly-1-pentadecenyl, and poly-1-hexadecenyl. The molecular weight of the uPAO of formula **(I)** is 500 g/mol or greater, such as 1,000 g/mol or greater. In at least one embodiment, a uPAO represented by formula **(I)** has a molecular weight of from 500 g/mol to 10,000 g/mol, such as from 1,000 g/mol to 5,000 g/mol, such as from 1,000 g/mol to 3,000 g/mol, such as from 1,500 g/mol to 3,000 g/mol. In at least one embodiment, a uPAO represented by formula **(I)** has an internal unsaturation of less than 0.4 unsaturations per 1000 carbon atoms, such as less than 0.3, such as less than 0.2, such as from 0.01 to 0.4, such as from 0.01 to 0.3, such as from 0.01 to 0.2.

[0056] In at least one embodiment, a uPAO is represented by formula **(II)**:



(II),

where each R^1, the same or different, can be independently any hydrocarbyl group, typically containing from 1 to 100 carbon atoms, such as an alkyl group, such as a linear or branched alkyl group, such as a linear alkyl group, R^2 is hydrogen or a hydrocarbyl group having 1 to 70 carbon atoms, and m, n, and p are integers such that the number average molecular weight of the uPAO represented by formula **(II)** is 500 g/mol or greater, typically 500 to 10,000 g/mol. The uPAO represented by formula **(II)** represents random and block configurations.

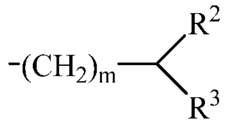
[0057] In at least one embodiment, each R^1, the same or different, comprises c1 to c2 carbon atoms, where c1 and c2 can be, independently, any integer between 1 and 60, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 68, or 70, and c1 is less than c2. In one embodiment, c1 is 2 and c2 is 40. Alternatively, c1 is 4 and c2 is 30. Each R^1, the same or different, can include an even number of carbon atoms. Examples of each R^1, the same or different, include: ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl, *n*-icosyl, *n*-docosyl, *n*-tetracosyl, *n*-hexacosyl, and *n*-octacosyl. R^1 can be *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, and *n*-octadecyl.

[0058] R^2 is hydrogen or comprises c1 to c2 carbon atoms, where c1 and c2 can be, independently, any integer between 1 and 60, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 68, or 70, and c1 is less than c2. In one embodiment, c1 is 1 and c2 is 10. In at least one embodiment, R^2 is selected from H, methyl, ethyl, propyl, and benzyl, such as H or methyl.

[0059] m, n, and p are integers such that the molecular weight of the uPAO of formula **(II)** is 500 g/mol or greater, such as 1,000 g/mol or greater. In at least one embodiment, each of n and p is, independently, 20 or less, such as 10 or less, such as 5 or less, such as 1, such as 0. Preferably each of n and p is, independently, 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15 16, 17, 18, 19, or 20.

[0060] In at least one embodiment, a uPAO represented by formula **(II)** has a molecular weight of from 500 g/mol to 10,000 g/mol, such as from 1,000 g/mol to 5,000 g/mol, such as from 1,000 g/mol to 3,000 g/mol, such as from 1,500 g/mol to 3,000 g/mol.

[0061] Each R^1, the same or different, can be a branched alkyl group, such as a branched alkyl group represented by formula **(III)**:



$$-(CH_2)_m-CH(R^2)(R^3)$$

(III),

where R^2 and R^3 are independently hydrocarbyl groups (preferably comprising from 1 to 50 carbon atoms), such as alkyl groups, such as linear or branched alkyl groups, such as linear alkyl groups, m is an integer and $m \geq 3$, such as $m \geq 4$, such as $m \geq 5$, such as $m \geq 6$, such as $m \geq 7$. In one embodiment, R^2 and R^3 each comprises c3 to c4 carbon atoms, where c3 and c4 can be, independently, any integer between 1 and 50, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, or 50, and c3 is less than c4. In one embodiment, c3 is 2 and c4 is 40. Alternatively, c3 is 4, and c4 is 30.

[0062] In one embodiment of the uPAO represented by formula **(II)**, the R^1 groups are identical. Thus, examples of uPAO represented by formula **(II)** can be: poly-1-pentene, poly-1-hexene, poly-1-heptene, poly-1-octene, poly-1-nonene, poly-1-decene, poly-1-undecene, poly-1-dodecene, poly-1-tridecene, poly-1-tetradecene, poly-1-pentadecene, poly-1-hexadecene, and mixtures thereof. In at least one embodiment, R^1 is a polydecene having a number average molecular weight of about 2,000 to 7500 g/mol (preferably from 2100 to 5000 g/mol, preferably about 2,240 gmol), >84% vinylidene, 1>% vinyl, >6% vinylene, and >8% trisubstituted alkene.

[0063] In at least one embodiment, the two R^1 groups in formula **(III)** differ in molar mass by no greater than 145 (or 130, 115, 100, 85, 70, 55, 45, 30, or even 15) grams per mole. In such embodiments, the two R^1 groups can differ in terms of total number of carbon atoms contained therein by no greater than 10 (or 9, 8, 7, 6, 5, 4, 3, 2, or even 1).

[0064] The uPAO having formula (**I**) or (**II**) can be advantageously made by polymerization of a monomer feed comprising a terminal olefin represented by formula (**IV**):

$$R^1\text{-CH=CH}_2 \quad \textbf{(IV)},$$

where R^1 is a hydrocarbyl group, typically containing from 1 to 100 carbon atoms.

[0065] The monomer feed can consist essentially of a single terminal olefin having a formula (**IV**). In such case, a single uPAO having a formula (**II**) where the R^1 groups are identical can be advantageously made in the process, which can be used as the uPAO feed in hydroformylation reactions for making alcohol products. It is contemplated that the monomer feed may comprise multiple terminal olefins having differing alpha olefins of formula (**IV**). In such case, as discussed below, multiple different uPAOs of formula (**II**) may be produced, which can be used together as the uPAO feed for making an alcohol product comprising multiple alcohol-containing compounds. In one embodiment, the monomer feed comprises multiple terminal olefins and the olefins differ in terms of molecular weight by no greater than 145 (or 130, 115, 100, 85, 70, 55, 45, 30, or even 15) grams per mole. The multiple terminal olefins contained in the monomer feed can differ in terms of total number of carbon atoms contained therein by no greater than 10 (or 9, 8, 7, 6, 5, 4, 3, 2, or even 1).

[0066] A uPAO represented by formula (**I**) or (**II**) feed used in a process of this disclosure for making gamma-branched alcohol is a uPAO having formula (**I**) or (**II**) having a content of gamma-branched alcohol of at least 60 wt%, such as at least 70 wt%, such as at least 80 wt%, such as at least 82 wt%, such as 84 wt%, such as at least 90 wt%, such at least 95 wt%, such as at least 99 wt%, based on the total weight of the olefins contained in the feed.

[0067] It is possible to use a mixture of two or more different uPAOs as the uPAO feed in the process for making a mixture of gamma-branched alcohols as the gamma-branched alcohol product. The individual uPAOs contained in the mixture can have similar number average (Mn) molecular weights, e.g., having molecular weights that differ by no more than, e.g., 500, 400, 300, 250, 225, 200, 175, 150, 140, or even 130 grams per mole. The individual uPAOs contained in the mixture can differ in terms of total number of carbon atoms contained therein, for example, by no more than 20, 16, 12, 10, 9, 8, 7, 6, 5, 4, 3, 2, or even 1. The individual uPAOs contained in the mixture can be structural isomers. The uPAOs having different chemical formulas and/or molecular weight can be converted into alcohol compounds having different chemical formulas and/or molecular weights under the same or similar reaction conditions. If the mixture of alcohols can be used for an intended application, the corresponding mixture of uPAO can be used as the uPAO feed for making the gamma-branched alcohol product by using a process of this disclosure.

[0068] The feed of vinylidene represented by formula (**I**) or (**II**) used in a process of this disclosure for making gamma-branched alcohol can include 1,2-di-substituted vinylene(s) and tri-substituted vinylene(s) as impurities, for example, at a total concentration no greater than 25 wt%, such as no greater than 20 wt%, such as no greater than 10 wt%, such as no greater than 5 wt%, such as no greater than 1 wt%, based on the total weight of olefins contained in the feed.

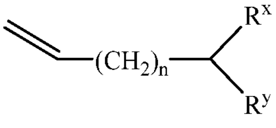
I.2 Terminal Olefins for PAO Formation

[0069] Terminal olefin monomers are olefins containing at least one vinyl C=C bond per monomer molecule, though those olefins containing additional C=C bonds per monomer molecule (such as two or more) can be used as well.

[0070] The terminal olefin monomer in a process for making the uPAOs of formulas (**I**) or (**II**) can include from n1 to n2 carbon atoms per molecule, where n1 and n2 can be, independently, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 58, 60, and n1 is less than n2. In one embodiment, n1 is 4 and n2 is 50; such as n1 is 6 and n2 is 40; such as n1 is 6 and n2 is 30; such as n1 is 6 and n2 is 20.

[0071] The terminal olefin monomer in a process for making the uPAO having formula (**I**) or (**II**) can be a linear terminal olefin. Examples of linear terminal olefins as the monomer for a process of this disclosure include: 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, 1-icosene, 1-henicosene, 1-docosene, 1-tricosene, 1-tetracosene, 1-pentacosene, 1-hexacosene, 1-heptacosene, 1-octacosene, 1-nonacosene, and 1-triacontene. In one embodiment, a linear terminal olefin as a monomer for a process of the present disclosure is selected from: 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene, and 1-icosene. In one embodiment, a linear terminal olefin as a monomer for a process of the present disclosure is selected from: 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-icosene. In one embodiment, a linear terminal olefin as a monomer for a process of the present disclosure is selected from: 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, and 1-octadecene. Linear terminal olefins having even number of carbon atoms can be advantageously manufactured by the polymerization of ethylene, as is typically done in the industry. Many of these linear terminal olefins with even number of carbon atoms are commercially available at large quantities.

[0072] Branched terminal olefins can be used as the monomer in the process as well. Branched terminal olefins can be those represented by the following formula:



, where R^x and R^y are independently any hydrocarbyl group, such as any C_1-C_{30} alkyl group, such as any C_1-C_{30} linear alkyl group, n is an integer, and $n \geq 2$, such as $n \geq 4$, such as $n \geq 5$. In one embodiment, $n \leq 30$, such as $n \leq 20$, such as $n \leq 15$.

[0073] The terminal olefin monomer may be fed as a neat material or as a solution in an inert solvent into the polymerization reactor. Non-limiting examples of the inert solvent include: benzene, toluene, a xylene, ethylbenzene, and mixtures thereof; *n*-pentane, *n*-hexane, cyclohexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane and branched isomers thereof, and mixtures thereof; Isopar™ solvent; and the like.

[0074] The terminal olefins used herein can be produced directly from ethylene growth process as practiced by several commercial production processes, or they can be produced from Fischer-Tropsch hydrocarbon synthesis from CO/H_2 syngas, or from metathesis of internal olefins with ethylene, or from cracking of petroleum or Fischer-Tropsch synthetic wax at high temperature, or any other terminal olefin synthesis routes. A feed for the present disclosure can be at least 80 wt% terminal olefin (such as linear alpha olefin), such as at least 90 wt% terminal olefin (such as linear alpha olefin), such as 100% terminal olefin (such as linear alpha olefin). The feed olefins can be the mixture of olefins produced from other linear terminal olefin process containing C_4 to C_{20} terminal olefins as described in Chapter 3 "Routes to Alpha-Olefins" of the book Alpha Olefins Applications Handbook, Edited by G. R. Lappin and J. D. Sauer, published by Marcel Dekker, Inc. N.Y. 1989.

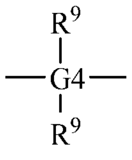
[0075] The terminal olefin feed and or solvents may be treated to remove catalyst poisons, such as peroxides, oxygen or nitrogen-containing organic compounds or acetylenic compounds before being supplied to the polymerization reactor. The treatment of the linear terminal olefin with an activated 13 Angstrom molecular sieve and a de-oxygenate catalyst, e.g., a reduced copper catalyst, can increase catalyst productivity (expressed in terms of quantity of PAO produced per micromole of the metallocene compound used), typically more than 10-fold. Alternatively, the feed olefins and or solvents are treated with an activated molecular sieve, such as 3 Angstrom, 4 Angstrom, 8 Angstrom or 13 Angstrom molecular sieve, and/or in combination with an activated alumina or an activated de-oxygenated catalyst. Such treatment can desirably increase catalyst productivity, typically 2- to 10-fold or more.

[0076] To form a compound represented by formula **(I)** or **(II)** having identical R^1 groups, a single terminal olefin monomer can be fed into the polymerization reactor. For example, 1-octene feed will result in a single vinyl terminated PAO having n-hexyl moieties along the PAO backbone.

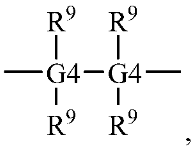
[0077] If two different terminal olefin monomers including a first monomer (R^a-CH=CH_2) and a second monomer (R^b-CH=CH_2, where R^b differs from R^a, and are independently substituted or unsubstituted alkyl having 1 to 100 carbon atoms) are fed into the polymerization reactor, multiple different vinyl terminated PAO compounds may be produced at various quantities, typically depending on the reactivity of the monomers.

I.3 Metallocene Compounds

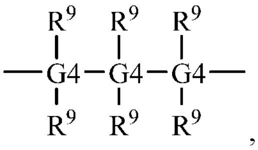
[0078] The metallocene compound in the catalyst system useful in a process for making a uPAO represented by formula **(I)** or **(II)** can be represented by the formula $Cp(Bg)_nMX_2Cp'$, where Cp and Cp', the same or different, represent a cyclopentadienyl, alkyl-substituted cyclopentadienyl, indenyl, alkyl-substituted indenyl, 4,5,6,7-tetrahydro-2*H*-indenyl, alkyl-substituted 4,5,6,7-tetrahydro-2*H*-indenyl, 9*H*-fluorenyl, or alkyl-substituted 9*H*-fluorenyl; Bg represents a bridging group linking Cp and Cp', and n is zero (0), one (1), or two (2), such as zero (0) or one (1), such as zero (0, i.e., where the metallocene compound is unbridged). Exemplary Bg can be represented by any of

(i) 

$$-\overset{R^9}{\underset{R^9}{G4}}-$$

, (ii) 

$$-\overset{R^9}{\underset{R^9}{G4}}-\overset{R^9}{\underset{R^9}{G4}}-$$

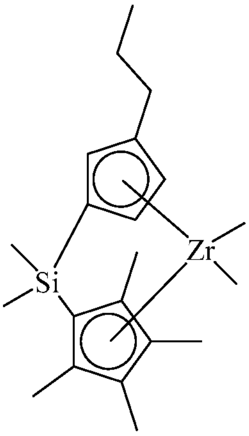
, and (iii) 

$$-\overset{R^9}{\underset{R^9}{G4}}-\overset{R^9}{\underset{R^9}{G4}}-\overset{R^9}{\underset{R^9}{G4}}-$$

,

where groups G4 are the same or different at each occurrence and are independently selected from carbon, silicon, and germanium, and each occurrence of R^9 is independently a C_1-C_{30} substituted or unsubstituted linear, branched, or cyclic hydrocarbyl groups, which may join together to form cyclic or multicyclic structures. R^9 can include substituted or unsubstituted methyl, ethyl, *n*-propyl, phenyl, and benzyl. In at least one embodiment, Bg is category (i) or (ii) above. For example, Bg is category (i) above. In at least one embodiment, all R^9's are identical.

[0079] M represents Hf or Zr. For example, M is Zr. X, the same or different at each occurrence, independently represents a halogen, such as C_l, or a hydrocarbyl (preferably a C_1 to C_{30} hydrocarbyl), such as linear or branched alkyl group, such as methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, branched isomeric groups thereof, and the like; a cycloalkyl group; a cycloalkylalkyl group; an alkylcycloalkyl group; an aryl group, such as phenyl; an arylalkyl group such as benzyl; an alkylaryl group such as tolyl and xylyl. In at least one embodiment, X is methyl or C_l; such as X is C_l. Without being bound by theory, it is believed that the use of the metallocene compound results in the formation of uPAO in the polymerization reaction. A Metallocene compound useful in a process for making the uPAOs represented by formula **(I)** or **(II)** is $Si(CH_3)_2$(3-propylCp)(tetramethylCp)$Zr(CH_3)_2$, and is represented by the following structure:



[0080] Alternatively, one group of metallocene compounds useful for a process for making a uPAO used in the process for making gamma-branched alcohol product of this disclosure are those unbridged metallocene compounds having a general formula Cp_2MX_2, where each Cp represents the same or different substituted or unsubstituted cyclopentadienyl ring (each Cp may independently be as defined for Cp' above), M is Zr or Hf (such as Zr), and X is as defined above, and, in at least one embodiment, is selected from C_l, C_1-C_{10} linear or branched alkyl groups, phenyl, and benzyl. $BisCpMX_2$, where the Cp groups are as defined above and are the same, M is Hf or Zr, and X is as defined above are also useful.

[0081] In a process for making a uPAO represent by formula **(I)** or **(II)**, the terminal olefin monomer (or multiple co-monomers) are fed into the polymerization reactor at a first feeding rate of R(to) moles per hour, and the metallocene compound is fed into the reactor at a second feeding rate of R(mc) moles per hour. The ratio of the first feeding rate to the second feeding rate R(to)/R(mc) can be in the range from x1 to x2, where x1 and x2 can be, independently, 100, 150, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, or 1,000, as long as x1 is less than x2. In at least one embodiment, x1 is 300, and x2 is 800, such as x1 is 400, and x2 is 750, such as x1 is 500 and x2 is 750.

[0082] The metallocene compound can be dissolved or dispersed in an inert solvent and then fed into the reactor as a solution or a dispersion. Such inert solvent for the metallocene compound can be, e.g., benzene, toluene, any xylene, ethylbenzene, and mixtures thereof; *n*-

pentane, *n*-hexane, cyclohexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and branched isomers thereof, and mixtures thereof; Isopar™ solvent; and the like.

[0083] One or more metallocene compound(s) may be used in the process for making the uPAO represented by formula (**I**) or (**II**).

I.4a Activators (Alumoxanes)

[0084] The alumoxane used in the process of this disclosure functions as activator of the metallocene compound and/or scavenger for impurities (such as water). Alumoxanes can be obtained by partial hydrolysis of alkyl aluminum compounds. Thus, non-limiting examples of alumoxanes useful in the process of this disclosure include those made by partial hydrolysis of trimethyl aluminum, triethyl aluminum, tri(*n*-propyl)aluminum, tri(isopropyl)aluminum, tri(*n*-butyl)aluminum, tri(isobutyl)aluminum, tri-(tert-butyl)aluminum, tri(*n*-pentyl)aluminum, tri(*n*-hexyl)aluminum, tri(*n*-octyl)aluminum, and mixtures thereof. Alumoxanes for the process of this disclosure can be methylalumoxane ("MAO") made from partial hydrolysis of trimethyl aluminum.

[0085] The alumoxane feed supplied into the polymerization reactor is advantageously substantially free of metal elements other than aluminum, alkali metals, alkaline earth metals, and the metal(s) contained in the metallocene compound(s) described above. In at least one embodiment, the alumoxane feed used in a process of this disclosure comprises metal elements other than aluminum, alkali metals, alkaline earth metals, Zr, and Hf at a total concentration of no greater than x1 ppm by mole, based on the total moles of all metal atoms in the alumoxane feed, where x1 can be 50,000, 40,000, 30,000, 20,000, 10,000, 8,000, 6,000, 5,000, 4,000, 2,000, 1,000, 800, 600, 500, 400, 200, 100, 80, 60, 50, 40, 20, or even 10. For example, the alumoxane feed used in a process of this disclosure comprises metal elements other than aluminum, Zr, and Hf at a total concentration of no greater than x2 ppm by mole, based on the total moles of all metal atoms in the alumoxane feed, where x2 can be 50,000, 40,000, 30,000, 20,000, 10,000, 8,000, 6,000, 5,000, 4,000, 2,000, 1,000, 800, 600, 500, 400, 200, 100, 80, 60, 50, 40, 20, or even 10. The alumoxane feed fed into the reactor can be free of all metals other than aluminum and the metal(s) contained in the metallocene compound(s) described above.

[0086] A portion or the entirety of the alumoxane fed into the polymerization reactor may be mixed with a portion or the entirety of the metallocene compound(s) described above, such as dissolved and/or dispersed into an inert solvent, before it is fed into the reactor. In such case, the stream carrying a portion or the entirety of alumoxane fed into the reactor may contain the metal element(s) contained in the metallocene compound(s).

[0087] The alumoxane may be introduced into the reactor as a stream separate from the terminal olefin monomer stream and the metallocene compound stream. Alternatively or in addition, at least a portion of the alumoxane may be combined with the terminal olefin monomer and supplied into the reactor together. Mixing alumoxane with the olefin monomer before being supplied into the reactor can result in the scavenging of catalyst poisons contained in the monomer feed before such poisons have a chance to contact the metallocene compound inside the reactor. It is also possible to combine at least a portion of the alumoxane with at least a portion of the metallocene compound in a mixture, and supply the mixture as a catalyst stream into the reactor.

[0088] The alumoxane can be dissolved or dispersed in an inert solvent before being fed into the reactor or before being combined with the monomer feed and/or the metallocene compound. Examples of inert solvent can be: benzene, toluene, any xylene, ethylbenzene, *n*-pentane, *n*-hexane, cyclohexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and branched isomers thereof, and mixtures thereof, Isopar™ solvent, and the like.

I.4b Activators (Non-Coordination Anion)

[0089] The term "non-coordinating anion" (NCA) means an anion which either does not coordinate to a cation or which is only weakly coordinated to a cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral transition metal compound and a neutral by-product from the anion. Non-coordinating anions can include those that are compatible, stabilize the transition metal cation in the sense of balancing its ionic charge at +1, and yet retain sufficient lability to permit displacement during polymerization.

[0090] It is within the scope of the present disclosure to use an ionizing activator, neutral or ionic, such as tri (n-butyl) ammonium tetrakis (pentafluorophenyl) borate, a tris perfluorophenyl boron metalloid precursor or a tris perfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 1998/043983), boric acid (US 5,942,459), or combination thereof. It is also within the scope of the present disclosure to use neutral or ionic activators alone or in combination with alumoxane or modified alumoxane activators.

[0091] For descriptions of useful activators please see US 8,658,556 and 6,211,105.

[0092] Exemplary activators include N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(3,5-

bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, $[Me_3NH^+][B(C_6F_5)_4^-]$, 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium; sodium tetrakis(pentafluorophenyl)borate, potassium tetrakis(pentafluorophenyl)borate, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridinium, sodium tetrakis(perfluorophenyl)aluminate, and N,N-dimethylanilinium tetrakis(perfluorophenyl)aluminate.

[0093] In at least one embodiment, the activator comprises a triaryl carbonium (such as triphenylcarbenium tetraphenylborate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

[0094] In another embodiment, the activator comprises one or more of trialkylammonium tetrakis(pentafluorophenyl)borate, N,N-dialkylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate, trialkylammonium tetrakis-(2,3,4,6-tetrafluorophenyl) borate, N,N-dialkylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trialkylammonium tetrakis(perfluoronaphthyl)borate, N,N-dialkylanilinium tetrakis(perfluoronaphthyl)borate, trialkylammonium tetrakis(perfluorobiphenyl)borate, N,N-dialkylanilinium tetrakis(perfluorobiphenyl)borate, trialkylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate, (where alkyl is methyl, ethyl, propyl, n-butyl, sec-butyl, or t-butyl).

[0095] An activator-to-catalyst ratio, e.g., all NCA activators-to-catalyst ratio can be about a 1:1 molar ratio. Alternate ranges include from 0.1:1 to 100:1, alternatively from 0.5:1 to 200:1, alternatively from 1:1 to 500:1 alternatively from 1:1 to 1000:1. A particularly useful range is from 0.5:1 to 10:1, such as 1:1 to 5:1.

I.5 Polymerization Reaction Conditions

[0096] In a process for making the uPAO represented by formula (**I**) or (**II**), the terminal olefin monomer (or multiple co-monomers) is introduced into the polymerization reactor at a first feeding rate of R(to) moles per hour, and the metallocene compound is introduced into the reactor at a second feeding rate of R(mc) moles per hour, and the alumoxane is introduced into the reactor at a third feeding rate corresponding to R(Al) moles of aluminum atoms per hour.

[0097] A ratio of the third feeding rate to the second feeding rate R(Al)/R(mc) can be in the range from y1 to y2, where y1 and y2 can be, independently, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12.0, 12.5, 13.0, 13.5, 14.0, 14.5, 15.0, as long as y1 is less than y2. In at least one embodiment, y1 is 2.0, and y2 is 12.0, such as y1 is 2.0, and y2 is 10.0, such as y1 is 2.0, and y2 is 7.0, such as y1 is 2.0, and y2 is 5.0.

[0098] The polymerization reaction in a process of this disclosure can be carried out at a mild temperature in the range from t1 to t2°C, where t1 and t2 can be, independently, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, or 90, as long as t1 is less than t2. In at least one embodiment, t1 is 40, and t2 is 80, such as t1 is 50, and t2 is 75.

[0099] The polymerization reaction may be carried out at a residence time in the range from rt1 to rt2 hours, where rt1 and rt2 can be, independently, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.0, 10, 12, 15, 18, 24, 30, 36, 42, or 48, as long as rt1 is less than rt2. In at least one embodiment, rt1 is 3 and rt2 is 8, such as rt1 is 4 and rt2 is 8, such as rt1 is 5 and rt2 is 7.

[0100] The polymerization reaction can be carried out in the presence of mechanical stirring of the reaction mixture such that a substantially homogeneous reaction mixture with a steady composition is withdrawn from the reactor once the reactor reaches steady state.

[0101] Advantageously the polymerization reaction of a process of this disclosure is carried out under mild pressure. Because the polymerization reaction is sensitive to water and oxygen, the reactor is typically protected by an inert gas atmosphere such as nitrogen. To prevent air leakage into the reactor, it is desirable that the total pressure inside the reactor is slightly higher than the ambient pressure.

[0102] The polymerization reaction can be carried out in the presence of a quantity of inert solvent. Non-limiting examples of such solvent include: benzene, toluene, any xylene, ethylbenzene, and mixtures thereof, *n*-pentane, *n*-hexane, cyclohexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and branched isomers thereof, and mixtures thereof; Isopar® solvent; and the like.

[0103] Due to the nature of the metallocene compound and the alumoxane used in a process of this disclosure, in the polymerization reaction, a high selectivity of the terminal olefin toward uPAOs represented by formula **(I)** or **(II)** (e.g., at least 95%, 96%, 97%, 98%, or even 99%) can be achieved. Thus, the PAOs thus made tend to be predominantly vinylidene and can be advantageously used as a vinylidene without further purification in applications where vinylidenes are desired.

[0104] In addition to the high selectivity of the terminal olefin monomer toward PAO in the polymerization reaction, the process of this disclosure also exhibits a high conversion of the terminal olefin monomer, e.g., a conversion of at least 40%, 45%, 50%, 55%, 60%, 65%, or 70%, can be achieved in a single pass polymerization reaction. With recycling of unreacted monomer separated from the polymerization reaction mixture to the polymerization reactor, the overall conversion can be even higher, making the process of this disclosure particularly economic.

[0105] Because the alumoxane introduced into the reaction system in a process of this disclosure is substantially free of metals other than aluminum, metals contained in the metallocene compound, alkali metals, and alkaline earth metals, the terminal olefin monomer does not undergo significant isomerization.

I.6 Post-Polymerization Treatment

[0106] The polymerization reaction mixture stream withdrawn from the reactor typically comprises the unreacted terminal olefin monomer(s), uPAO represented by formula **(I)** or **(II)**, -metallocene compound, -activator (such as alumoxane), contact product(s) of metallocene compound and activator, and optional solvent.

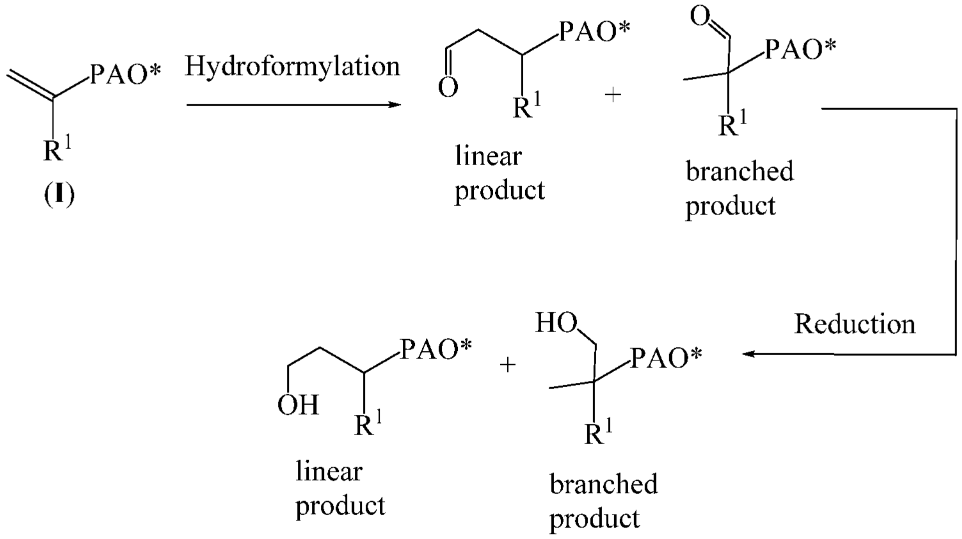
[0107] Once the polymerization reaction mixture stream leaves the reactor, typically a stream of quenching agent is injected into the stream to terminate the polymerization reactions. Non-limiting examples of quenching agents include: water, methanol, ethanol, CO_2, and mixtures thereof. In at least one embodiment, a quenching agent is water.

[0108] The metal elements contained in the polymerization mixture, including aluminum and Zr or Hf, can be removed from the mixture. Removal thereof can be achieved through mechanical filtration using a filtration aid such as Celite. Upon filtration, the liquid mixture can contain aluminum at a concentration no higher than 50 ppm by weight (such as no higher than 30 ppm, such as no higher than 20 ppm, such as no higher than 10, such as no higher than 5 ppm), based on the total weight of the liquid mixture.

[0109] Upon filtration, a mixture comprising monomer, the uPAO represented by formula **(I)** or **(II)** and the optional solvent is obtained. The monomer and solvent can be removed by flashing or distillation at an elevated temperature and/or optionally under vacuum. Because isomerization of the monomer is avoided in (i) in the polymerization reaction due to the lack of Lewis acid capable of catalyzing isomerization reaction and (ii) in the flashing/distillation step due to the removal of aluminum and other metal elements from the liquid mixture at the earlier filtration step, the monomer reclaimed form the mixture consists essentially of the terminal olefin monomer as introduced into the reactor. As such, the reclaimed monomer can be recycled to the polymerization reactor as a portion of the monomer stream.

II. Formation of Alcohol-Containing PolyAlpha Olefins from Vinyl-Terminated PAOs

[0110] Scheme 1 illustrates formation of an alcohol-containing polyalpha olefin (oxPAO-alcohol) from a vinyl-terminated PAO, such as a vinyl-terminated PAO represented by formula **(I)**. In a carbonylation stage, the vinyl-terminated PAO undergoes hydroformylation to form a linear carbonylated PAO and or a branched carbonylated PAO (oxPAO-aldehyde). Some or all of the carbonyl moiety(ies) of the oxPAO-aldehyde undergo a reduction to produce a linear alcohol-containing polyalpha olefin and or a branched alcohol-containing polyalpha olefin (both of which are referred to as an "oxPAO-alcohol"). The reaction process of Scheme 1 can also be performed using a vinyl-terminated PAO represented by formula **(II)**.



Scheme 1

II. Hydroformylation

II.1 Catalysts

[0111] Using a catalyst, such as a rhodium-containing carbonylation catalyst, in combination with a phosphine compound, one can produce oxPAO. In the carbonylation stage, the uPAO molecule reacts with syngas (CO and H_2) to produce a carbonylated derivative of the uPAO. Without intending to be bound by a particular theory, it is believed that an aldehyde is formed as a result.

[0112] Examples of the rhodium-containing catalysts include the following of rhodium at any suitable oxidation state (e.g., (I), (II) or (III)) and mixtures thereof: oxides; inorganic salts such as rhodium fluoride, rhodium chloride, rhodium bromide, rhodium iodide, rhodium nitrate, and rhodium sulfate; rhodium salts of carboxylic acids such as rhodium acetate, di-rhodium tetracetate, rhodium acetylacetonate, rhodium(II) isobutyrate, rhodium(II) 2-ethylhexanoate;

rhodium carbonyl compounds such as $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, (acetylacetonato)dicarbonylrhodium(I), (acetylacetonato)rhodium(I)(cyclooctadiene), $HRh(CO)_4$, $HRh(CO)PPh_3$, chlorodicarbonylrhodium dimer, chlorobis(ethylene)rhodium dimer, hexarhodiumhexadecylcarbonyl, tetrarhodiumdodecylcarbonyl, and the like.

[0113] A catalyst can include a cobalt-containing catalyst at any suitable oxidation state (e.g., (I), (II) or (III)) and mixtures thereof: oxides; inorganic salts such as cobalt fluoride, cobalt chloride, cobalt bromide, cobalt iodide, cobalt nitrate, and cobalt sulfate; cobalt salts of carboxylic acids such as cobalt acetate, di-cobalt tetracetate, cobalt acetylacetonate, cobalt(II) isobutyrate, cobalt(II) 2-ethylhexanoate; cobalt carbonyl compounds such as Co_2CO_8, $HCo(CO)_4$, $HCo(CO)_3PPh_3$, and the like.

[0114] Catalytically effective amounts of a catalyst can range from n1 to n2 micromoles of the catalyst per mole of the uPAO to be converted, where n1 and n2 can be, independently, 200, 250, 300, 350, 400, 450, 500, 550, 650, 700, 750, 800, 850, 900, 950, 1,000, 1,100, 1,200, 1,300, 1,400, 1,500, 1,600, 1,700, 1,800, 1,900, 2,000, 2,100, 2,200, 2,300, 2,400, 2,500, 2,600, 2,700, 2,800, 2,900, or 3,000, as long as n1 is less than n2. For example, n1 is 300 and n2 is 2,500, such as n1 is 500 and n2 is 2,000, such as n1 is 600 and n2 is 1,800.

[0115] A portion of the catalyst can be solubilized in an inert solvent, or dispersed in an inert liquid medium and then introduced into the reactor. Alternatively or additionally, a portion of the catalyst can be dispersed in the uPAO to be converted as a suspension. The reactor is equipped with a mechanical stirrer, such that the reaction is conducted with continuous stirring to achieve a uniform distribution of the catalyst in the reaction media.

II.2 The Phosphine Compound

[0116] Presence of a phosphine compound in the reaction system can provide a high-purity of reaction product oxPAO-aldehydes and ultimately oxPAO-alcohols.

[0117] Non-limiting examples of phosphine compounds in the hydroformylation of uPAO in a process of this disclosure include: triphenyl phosphine; tri-(n-butyl) phosphine; tri-(tert-butyl) phosphine; tri-(n-pentyl) phosphine; tri-(n-hexyl) phosphine; tri(n-heptyl) phosphine; tri-(n-octyl) phosphine; tri(n-nonyl) phosphine; tri-(n-decyl) phosphine; and any mixture of two or more thereof, and the like.

[0118] A catalytically effective amount of the phosphine compound can range from n1 to n2 micromoles of the phosphine compound per mole of the uPAO to be converted, where n1 and n2 can be, independently, 1,000, 1,500, 2,000, 2,500, 3,000, 3,500, 4,000, 4,500, 5,000, 5,500, and 6,000, and n1 is less than n2. In at least one embodiment, n1 is 1,500 and n2 is 5,000, such as n1 is 2,000 and n2 is 4,000.

[0119] Without intending to be bound by a particular theory, it is believed that the phosphine compound introduced into the carbonylation reaction mixture functions as a ligand to the catalyst during reaction, which favorably catalyzes the desired carbonylation conducive to the formation of the oxPAO-aldehyde of this disclosure.

[0120] The phosphine compound may be introduced into the carbonylation reactor separately from the catalyst. Alternatively or additionally, a portion of the phosphine compound may be combined with a portion of the catalyst to form a mixture comprising a catalyst-phosphine complex and then the mixture can be introduced into the reactor.

II.3 The Carbonylation Reaction

[0121] The carbonylation reaction of the uPAO can be conducted in the presence of an atmosphere comprising CO and hydrogen at a molar ratio of H_2:CO of from 0.8:1 to 1.4:1, such as about 1:1 at an absolute total partial pressure of CO and H_2 in a range from p1 to p2 MPa (million Pascal), where p1 and p2 can be, independently, 0.1, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5, 10, 20, or 30 and p1 is less than p2. For example, p1 is 0.1 and p2 is 5.0, such as p1 is 0.5 and p2 is 3.0. A high total partial pressure of CO/H_2 is conducive to a high conversion of the vinylidene. In one embodiment, the conversion of vinylidene in the carbonylation reaction is at least 30%, such as at least 50%, such as at least 55%, such as at least 60%.

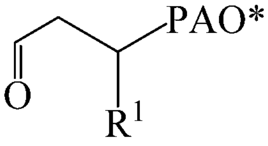
[0122] The carbonylation reaction of the uPAO can be conducted at a relatively mild temperature in a range from t1°C to t2°C, where t1 and t2 can be, independently, 40, 45, 50, 55, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, or 180, and t1 is less than t2. For example, t1 is 60 and t2 is 150, such as t1 is 80 and t2 is 120. Reaction time can range from 0.5 hour to 96 hours, such as 24 hour to 72 hours.

[0123] The carbonylation can be conducted in a batch reactor configured to withstand a high internal pressure. At the end of the reaction, the reactor is cooled down and depressurized, and the carbonylation product mixture, comprising the oxPAO-aldehyde product and other undesired by-products (if any), can be reduced in the next stage without the need of purification.

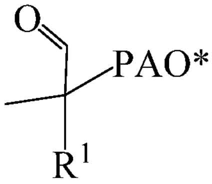
[0124] The carbonylation reaction of the vinylidene can be conducted with or without an inert solvent. Inert solvents for use in this stage can include: *n*-pentane, *n*-hexane, cyclohexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and branched isomers thereof, and mixtures thereof, and the like.

II.3.a Aldehyde Functional PolyAlpha Olefins (oxPAO-aldehydes)

[0125] In at least one embodiment, an aldehyde functional polyalpha olefin (oxPAO-aldehyde) is represented by formula **(Va)** or **(Vb)**:



linear (**Va**)



branched (**Vb**)

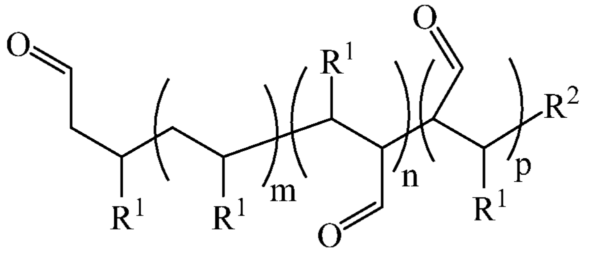
where R^1 is any hydrocarbyl group, typically containing from 1 to 100 carbon atoms, such as an alkyl group, such as a linear or branched alkyl group, such as a linear alkyl group. In at least one embodiment, R^1 comprises c1 to c2 carbon atoms, where c1 and c2 can be, independently, any integer between 1 and 60, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 68, or 70, and c1 is less than c2. In one embodiment, c1 is 2 and c2 is 40. Alternatively, c1 is 4 and c2 is 30. R^1 can include an even number of carbon atoms. Examples of R^1 include: ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl, *n*-icosyl, *n*-docosyl, *n*-tetracosyl, *n*-hexacosyl, and *n*-octacosyl. In one embodiment, R^1 is selected from: *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, and *n*-octadecyl. PAO* is a polyalpha olefin group having two or more alpha-olefin mer units, typically 2 to 400 mer units, such as 2 to 100 mer units. In one embodiment, PAO* is selected from poly-1-pentenyl, poly-1-hexenyl, poly-1-heptenyl, poly-1-octenyl, poly-1-nonenyl, poly-1-decenyl, poly-1-undecenyl, poly-1-dodecenyl, poly-1-tridecenyl, poly-1-tetradecenyl, poly-1-pentadecenyl, and poly-1-hexadecenyl. The molecular weight of the oxPAO-aldehyde of formula (**Va**) or (**Vb**) is 500 g/mol or greater, such as 1,000 g/mol or greater. In at least one embodiment, an oxPAO-aldehyde of formula (**Va**) or (**Vb**) has a molecular weight of from 500 g/mol to 10,000 g/mol, such as from 1,000 g/mol to 5,000 g/mol, such as from 1,000 g/mol to 3,000 g/mol, such as from 1,500 g/mol to 3,000 g/mol. In at least one embodiment, an oxPAO-aldehyde of formula (**Va**) or (**Vb**) has an internal unsaturation of less than 0.4 unsaturations per 1,000 carbon atoms, such as less than 0.1, such as less than 0.01, such as from 0.01 to 0.4, such as from 0.01 to 0.3, such as from 0.01 to 0.2.

[0126] In at least one embodiment, a composition comprises one or more oxPAO-aldehydes of formula (**Va**) and one or more oxPAO-aldehydes of (**Vb**). A molar ratio of oxPAO-aldehydes of formula (**Va**) to oxPAO-aldehydes of formula (**Vb**) (i.e., a ratio of linear to branched oxPAO-aldehydes) can be 5:1 or greater, such as 8:1 or greater, such as 10:1 or greater, such as 15:1 or greater, such as 20:1 or greater.

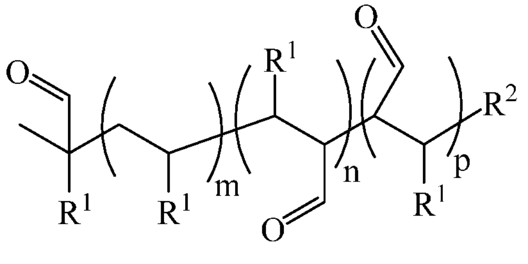
[0127] oxPAO-aldehydes of the present disclosure have a higher viscosity than their corresponding uPAOs. Without being bound by theory, it is believed that the increase in viscosity of oxPAO-aldehydes of the present disclosure, as compared to their corresponding aldehyde derivatives (oxPAO-aldehydes), demonstrates that the oxPAO-aldehydes have a terminal aldehyde moiety capable of receiving hydrogen bonds with another oxPAO-aldehyde.

[0128] An oxPAO-aldehyde of formula **(Va)** or **(Vb)** (or composition thereof) can have a kinematic viscosity @ 100°C of 50 cSt or greater according to ASTM D445, such as 70 cSt or greater, such as 85 cSt or greater, such as from 90 cSt to 1,000 cST, such as from 90 cSt to 300 cST, such as from 90 cSt to 200 cST, such as from 90 cST to 100 cSt.

[0129] In at least one embodiment, an oxPAO-aldehyde is represented by formula **(VIa)** or **(VIb)**:



linear **(VIa)**



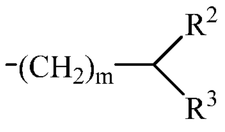
branched **(VIb)**,

where each R^1, the same or different, can be independently any hydrocarbyl group, typically containing from 1 to 100 carbon atoms, such as an alkyl group, such as a linear or branched alkyl group, such as a linear alkyl group, R^2 is hydrogen or a hydrocarbyl group having 1 to 70 carbon atoms, and m, n, and p are integers such that the number average molecular weight of the oxPAO-aldehyde represented by formula **(VIa)** or **(VIb)** is 500 g/mol or greater, typically 500 to 10,000 g/mol. The oxPAO-aldehyde represented by formula **(VIa)** or **(VIb)** represents random and block configurations. In at least one embodiment, each R^1, the same or different, comprises c1 to c2 carbon atoms, where c1 and c2 can be, independently, any integer between 1 and 60, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 68, or 70, and c1 is less than c2. In at least one embodiment, c1 is 2 and c2 is 40. Alternatively, c1 is 4 and c2 is 30. Each R^1, the same or different, can include an even number of carbon atoms. Examples of each R^1, the same or different, include: ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl, *n*-icosyl, *n*-docosyl, *n*-tetracosyl, *n*-hexacosyl, and *n*-octacosyl. In at least one embodiment, R^1 is *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, or *n*-octadecyl. R^2 is hydrogen or comprises c1 to c2 carbon atoms, where c1 and c2 can be, independently, any integer between 1 and 60, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 68, or 70, and c1 is less than c2. In one embodiment, c1 is 1 and c2 is 10. In at least one embodiment, R^2 is selected from H, methyl, ethyl, propyl, and benzyl, such as H or methyl. m, n, and p are integers such that the molecular weight of the oxPAO-aldehyde represented by formula **(VIa)** or **(VIb)** is 500 g/mol or greater, such as 1,000 g/mol or greater. In at least one embodiment, each of n and p is 20 or less, such as 10 or less, such as 5 or less, such as 1, such as 0. In at least one embodiment, an oxPAO-aldehyde represented by formula **(VIa)** or **(VIb)** has a molecular weight of from 500 g/mol to 10,000 g/mol, such as from 1,000 g/mol to 5,000 g/mol, such as from 1,000 g/mol to 3,000 g/mol, such as from 1,500 g/mol to 3,000 g/mol.

[0130] In at least one embodiment, a composition comprises one or more oxPAO-aldehydes of formula **(VIa)** and one or more oxPAO-aldehydes of **(VIb)**. A molar ratio of oxPAO-aldehydes of formula **(VIa)** to oxPAO-aldehydes of formula **(VIb)** (i.e., a ratio of linear to branched oxPAO-aldehydes) can be 5:1 or greater, such as 8:1 or greater, such as 10:1 or greater, such as 15:1 or greater, such as 20:1 or greater.

[0131] An oxPAO-aldehyde of formula **(VIa)** or **(VIb)** (or composition thereof) can have a kinematic viscosity @ 100°C of 50 cSt or greater according to ASTM D445, such as 70 cSt or greater, such as 85 cSt or greater, such as from 90 cSt to 1,000 cST, such as from 90 cSt to 300 cST, such as from 90 cSt to 200 cST, such as from 90 cST to 100 cSt.

[0132] For each oxPAO-aldehyde of formula **(Va)**, **(Vb)**, **(VIa)**, and **(VIb)**, each R^1, the same or different, can be a branched alkyl group, such as a branched alkyl group represented by formula **(III)**:



(III),

where R^2 and R^3 are independently hydrocarbyl groups, such as alkyl groups, such as linear or branched alkyl groups, such as linear alkyl groups, m is an integer and $m \geq 3$, such as $m \geq 4$, such as $m \geq 5$, such as $m \geq 6$, such as $m \geq 7$. In one embodiment, R^2 and R^3 each comprises c3 to c4 carbon atoms, where c3 and c4 can be, independently, any integer between 1 and 50, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, or 50, and c3 is less than c4. In one embodiment, c3 is 2 and c4 is 40. Alternatively, c3 is 4, and c4 is 30.

II.4 Reduction of the Carbonylation Product (oxPAO)

[0133] Reduction of the carbonylated derivative (such as an aldehyde) of the oxPAO-aldehyde obtained in the carbonylation stage results in the formation of an oxPAO-alcohol, such as an oxPAO-alcohol.

[0134] Such reduction can be performed by combining the oxPAO-aldehyde (after removal of solid materials by, e.g., filtration) with a reducing agent under reducing conditions. Non-limiting examples of the reducing agent include: $NaBH_4$, $NaAlH_4$, and $LiAlH_4$.

[0135] A reducing agent in a process of this disclosure can be molecular hydrogen (a hydrogenation catalyst). Reduction by contacting hydrogen can be performed in the presence of a hydrogenation catalyst under hydrogenation conditions. The hydrogenation catalyst can include a hydrogenation metal such as Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt, and combinations thereof which can be supported on an inorganic substrate such as activated carbon, silica, alumina, and the like. Hydrogenation conditions can include a hydrogen partial pressure in a range from p3 to p4 MPa, where p3 and p4 can be, independently, 5.0, 6.0, 7.0, 8.0, 9.0, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, or 20, as long as p3 is less than p4. For example, p3 is 7 and p4 is 18, such as p3 is 8 and p4 is 15.

[0136] Reduction conditions can be performed at a temperature in the range from t3 to t4°C, where t3 and t4 can be, independently, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, or 200, as long as t3 is less than t4. In at least one embodiment, t3 is 60 and t4 is 180, such as t3 is 70 and t4 is 150.

[0137] The hydrogenation reaction may be conducted with or without the presence of an inert solvent. Non-limiting examples of inert solvent useful for this stage include: *n*-pentane *n*-hexane, cyclohexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane and branched isomers thereof, and mixtures thereof, and the like.

[0138] At the end of the reduction reaction, oxPAO-aldehydes present in the carbonylation product mixture are converted to oxPAO-alcohol(s). Any olefins, including unreacted uPAO, present in the carbonylation product mixture, can also be hydrogenated into corresponding alkanes. Thus, a hydrogenation product mixture comprising the oxPAO-alcohol and byproducts such as alkane of the uPAO is obtained at the end of the reduction reaction.

[0139] The reduction product mixture can be separated to remove the light components such as alkane of the uPAO to obtain an alcohol product comprising primarily the oxPAO-alcohol product(s).

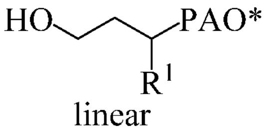
[0140] In a process of this disclosure, the oxPAO-alcohol product can have a purity (after purification) of at least 96 wt%, or at least 97 wt% or at least 98 wt%, or even at least 99 wt%, based on the total weight of the alcohol product.

[0141] If components heavier than the oxPAO-alcohol are present at quantities higher than a level acceptable for the intended application of the alcohol, one may further purify the product by using one or more of distillation, adsorption, liquid chromatography, gas chromatography, and the like, to obtain a substantially pure oxPAO-alcohol.

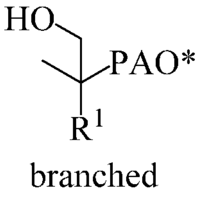
[0142] The combination of the hydroformylation process of this disclosure can provide a high conversion, high selectivity process for making the oxPAO-alcohol from a terminal olefin feed and CO/H_2 syngas mixture.

III. Alcohol Functional PolyAlpha Olefins (oxPAO-alcohols)

[0143] In at least one embodiment, an alcohol functional polyalpha olefin (oxPAO-alcohol) is represented by formula **(VIIa)** or **(VIIb)**:



(VIIa)



(VIIb)

where R^1 is any hydrocarbyl group, typically containing from 1 to 100 carbon atoms, such as an alkyl group, such as a linear or branched alkyl group, such as a linear alkyl group. In at least one embodiment, R^1 comprises c1 to c2 carbon atoms, where c1 and c2 can be, independently, any integer between 1 and 60, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 68, or 70, and c1 is less than c2. In one embodiment, c1 is 2 and c2 is 40. Alternatively, c1 is 4 and c2 is 30. R^1 can include an even number of carbon atoms. Examples of R^1 include: ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl, *n*-icosyl, *n*-docosyl, *n*-tetracosyl, *n*-hexacosyl, and *n*-octacosyl. In one embodiment, R^1 is selected from: *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, and *n*-octadecyl. PAO* is a polyalpha olefin group having two or more alpha-olefin mer units, typically 2 to 400 mer units, such as 2 to 100 mer units. In one embodiment, PAO* is selected from poly-1-pentenyl, poly-1-hexenyl, poly-1-heptenyl, poly-1-octenyl, poly-1-nonenyl, poly-1-decenyl, poly-1-undecenyl, poly-1-dodecenyl, poly-1-tridecenyl, poly-1-tetradecenyl, poly-1-pentadecenyl, or poly-1-hexadecenyl. The molecular weight of the oxPAO-alcohol of formula **(VIIa)** or **(VIIb)** is 500 g/mol or greater, such as 1,000 g/mol or greater. In at least one embodiment, an oxPAO-alcohol of formula **(VIIa)** or **(VIIb)** has a molecular weight of from 500 g/mol to 10,000 g/mol, such as from 1,000 g/mol to 5,000 g/mol, such as from 1,000 g/mol to 3,000 g/mol, such as from 1,500 g/mol to 3,000 g/mol. In at least one embodiment, an oxPAO-alcohol of formula **(VIIa)** or **(VIIb)** has an internal unsaturation of less than 0.4 unsaturations per 1,000 carbon atoms, such as less than 0.1, such as less than 0.01, such as from 0.01 to 0.4, such as from 0.01 to 0.3, such as from 0.01 to 0.2.

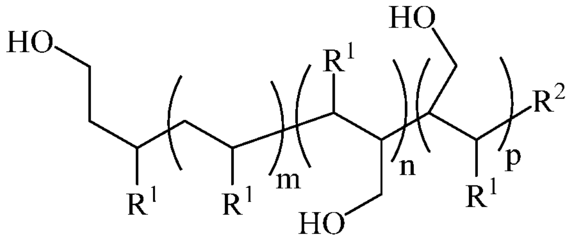
[0144] In at least one embodiment, a composition comprises one or more oxPAO-alcohols of formula **(VIIa)** and one or more oxPAO-alcohols of **(VIIb)**. A molar ratio of oxPAO-alcohols of formula **(VIIa)** to oxPAO-alcohols of formula **(VIIb)** (i.e., a ratio of linear to branched oxPAO-alcohols) can be 5:1 or greater, such as 8:1 or greater, such as 10:1 or greater, such as 15:1 or greater, such as 20:1 or greater.

[0145] oxPAO-alcohols of the present disclosure have a higher viscosity than their corresponding aldehyde derivatives (oxPAO-aldehydes). Without being bound by theory, it is believed that the increase in viscosity of oxPAO-alcohols of the present disclosure, as compared to their corresponding aldehyde derivatives (oxPAO-aldehydes), demonstrates that the oxPAO-alcohols have a terminal hydroxyl moiety capable of donating and or receiving hydrogen bonds with another oxPAO-alcohol. Comparatively, an oxPAO-alcohol having an alcohol moiety located toward or along the middle of the PAO backbone (e.g., an "internal" hydroxyl moiety) does not provide an increase in viscosity, as compared to both its corresponding aldehyde derivative and an oxPAO-alcohol having an alcohol moiety having a terminal hydroxyl moiety. Without being bound by theory, it is believed this result is due to the alkyl groups along the PAO backbone acting to shield a hydroxyl group located toward or along the middle of the PAO backbone from interacting with adjacent molecules/moieties.

[0146] An oxPAO-alcohol of formula **(VIIa)** or **(VIIb)** (or composition thereof) can have a kinematic viscosity @ 100°C of 95 cSt or greater according to ASTM D445, such as 100 cSt or greater, such as 105 cSt or greater, such as from 95 cSt to 1,000 cST, such as from 100 cSt to 500 cST, such as from 110 cSt to 300 cST, such as from 120 cST to 200 cSt.

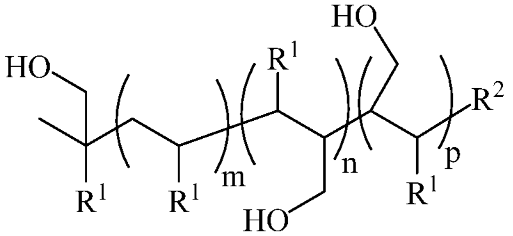
[0147] Furthermore, the viscosity and chemical structure(s) of oxPAO-alcohols of the present disclosure can provide a polarity such that the oxPAO-alcohols do not phase separate in the presence of non-polar molecules, such as oil. Accordingly, oxPAO-alcohols of the present disclosure can be suitable as viscosity modifiers.

[0148] In at least one embodiment, an oxPAO-alcohol is represented by formula **(VIIIa)** or **(VIIIb)**:



linear

(VIIIa)



branched

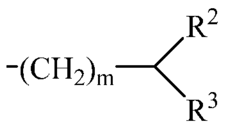
(VIIIb),

where each R^1, the same or different, can be independently any hydrocarbyl group, typically containing from 1 to 100 carbon atoms, such as an alkyl group, such as a linear or branched alkyl group, such as a linear alkyl group, R^2 is hydrogen or a hydrocarbyl group having 1 to 70 carbon atoms, and m, n, and p are integers such that the number average molecular weight of the oxPAO-alcohol represented by formula **(VIIIa)** or **(VIIIb)** is 500 g/mol or greater, typically 500 to 10,000 g/mol. The oxPAO-alcohol represented by formula **(VIIIa)** or **(VIIIb)** represents random and block configurations. In at least one embodiment, each R^1, the same or different, comprises c1 to c2 carbon atoms, where c1 and c2 can be, independently, any integer between 1 and 60, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 68, or 70, and c1 is less than c2. In at least one embodiment, c1 is 2 and c2 is 40. Alternatively, c1 is 4 and c2 is 30. Each R^1, the same or different, can include an even number of carbon atoms. Examples of each R^1, the same or different, include: ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl, *n*-icosyl, *n*-docosyl, *n*-tetracosyl, *n*-hexacosyl, and *n*-octacosyl. In at least one embodiment, R^1 is *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, or *n*-octadecyl. R^2 is hydrogen or comprises c1 to c2 carbon atoms, where c1 and c2 can be, independently, any integer between 1 and 60, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, 50, 52, 54, 56, 68, or 70, and c1 is less than c2. In one embodiment, c1 is 1 and c2 is 10. In at least one embodiment, R^2 is selected from H, methyl, ethyl, propyl, and benzyl, such as H or methyl. m, n, and p are integers such that the molecular weight of the oxPAO-alcohol represented by formula **(VIIIa)** or **(VIIIb)** is 500 g/mol or greater, such as 1,000 g/mol or greater. In at least one embodiment, each of n and p is 20 or less, such as 10 or less, such as 5 or less, such as 1, such as 0. In at least one embodiment, an oxPAO-alcohol represented by formula **(VIIIa)** or **(VIIIb)** has a molecular weight of from 500 g/mol to 10,000 g/mol, such as from 1,000 g/mol to 5,000 g/mol, such as from 1,000 g/mol to 3,000 g/mol, such as from 1,500 g/mol to 3,000 g/mol.

[0149] In at least one embodiment, a composition comprises one or more oxPAO-alcohols of formula **(VIIIa)** and one or more oxPAO-alcohols of **(VIIIb)**. A molar ratio of oxPAO-alcohols of formula **(VIIIa)** to oxPAO-alcohols of formula **(VIIIb)** (i.e., a ratio of linear to branched oxPAO-alcohols) can be 5:1 or greater, such as 8:1 or greater, such as 10:1 or greater, such as 15:1 or greater, such as 20:1 or greater.

[0150] An oxPAO-alcohol of formula **(VIIIa)** or **(VIIIb)** (or composition thereof) can have a kinematic viscosity @ 100°C of 95 cSt or greater according to ASTM D445, such as 100 cSt or greater, such as 105 cSt or greater, such as from 95 cSt to 1,000 cST, such as from 100 cSt to 500 cST, such as from 110 cSt to 300 cST, such as from 120 cST to 200 cSt.

[0151] For each oxPAO-alcohol of formula **(VIIa)**, **(VIIb)**, **(VIIIa)**, and **(VIIIb)**, each R^1, the same or different, can be a branched alkyl group, such as a branched alkyl group represented by formula **(III)**:



(III),

where R^2 and R^3 are independently hydrocarbyl groups, such as alkyl groups, such as linear or branched alkyl groups, such as linear alkyl groups, m is an integer and $m \geq 3$, such as $m \geq 4$, such as $m \geq 5$, such as $m \geq 6$, such as $m \geq 7$. In one embodiment, R^2 and R^3 each comprises c3 to c4 carbon atoms, where c3 and c4 can be, independently, any integer between 1 and 50, such as 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 14, 16, 18, 20, 22, 24, 26, 28, 30, 32, 34, 36, 38, 40, 42, 44, 46, 48, or 50, and c3 is less than c4. In one embodiment, c3 is 2 and c4 is 40. Alternatively, c3 is 4, and c4 is 30.

End Uses

[0152] One or more of the polyalpha olefin compounds of the present disclosure, such as the foregoing oxPAO-alcohols or blends thereof, may be used in a variety of end-use applications. Polyalpha olefin compounds of the present disclosure can be used as a surfactant, a detergent, a solvent, a wetting agent, a solubilizing agent, an emulsifier, as an intermediate for making derivatives such as esters and ethers that can be used as surfactants, solvents, wetting agents, solubilizing agents, emulsifiers, detergents, and lubricant base stocks or additives. Polyalpha olefin compounds of the present disclosure can be used as a friction modifier, an anti-corrosion coating, a viscosity modifier or synthetic base stock.

Viscosity Modifiers -- Lubrication Oil Compositions and Fuel Oil Compositions

[0153] Additives for lubrication fluids and oils include rheology modifiers, such as viscosity index (VI) improvers. VI improving components modify the rheological behavior of a lubricant to increase viscosity and promote a more constant viscosity over the range of temperatures at which the lubricant is used.

[0154] It is anticipated that the performance of VI improvers can be substantially improved, as measured by the thickening efficiency (TE) and the shear stability index (SSI), by appropriate and careful manipulation of the structure of the VI improver. Thickening efficiency (TE) describes the boost in kinematic viscosity at 100°C of an oil following the addition of a specific amount of polymer. A polymer's shear stability index (SSI) is defined as its resistance to mechanical degradation under shearing stress.

[0155] Lubricating oil compositions containing a polyalpha olefin, such as an oxPAO-alcohol, produced herein and one or more base oils (or base stocks) are also provided. The base stock can be or include natural or synthetic oils of lubricating viscosity, whether derived from hydrocracking, hydrogenation, other refining processes, unrefined processes, or re-refined processes. The base stock can be or include used oil. Natural oils include animal oils, vegetable oils, mineral oils and mixtures thereof. Synthetic oils include hydrocarbon oils, silicon-based oils, and liquid esters of phosphorus-containing acids. Synthetic oils may be produced by Fischer-Tropsch gas-to-liquid synthetic procedure as well as other gas-to-liquid oils.

[0156] In at least one embodiment, in addition to an oxPAO-aldehyde or oxPAO-alcohol of the present disclosure, the base stock is or includes a polyalphaolefin (PAO) including a PAO-2, PAO-4, PAO-5, PAO-6, PAO-7 or PAO-8 (the numerical value relating to Kinematic Viscosity at 100°C, ASTM D445). In one embodiment, the PAO can be prepared from dodecene and or decene. Generally, the polyalphaolefin suitable as an oil of lubricating viscosity has a viscosity less than that of a PAO-20 or PAO-30 oil. In one or more embodiments, the base stock can be defined as specified in the American Petroleum Institute (API) Base Oil Interchangeability Guidelines. For example, the base stock can be or include an API Group I, II, III, IV, and V oil or mixtures thereof.

[0157] PAOs useful herein are commercially available as SpectraSyn™ and SpectraSyn Ultra™ from ExxonMobil Chemical in Houston, Texas (previously sold under the SHF and SuperSyn™ tradenames by ExxonMobil Chemical Company), some of which are summarized in Table 2 below. Other useful PAOs include those sold under the tradenames Synfluid™ available from Chevron Phillips Chemical Company (Pasadena, Texas), Durasyn™ available from Innovene (Chicago, Illinois), Nexbase™ available from Neste Oil (Keilaniemi, Finland), and Synton™ available from Chemtura Corporation (Middlebury, Connecticut).

Table 2

	KV100 (cSt)	KV40 (cSt)	VI	Pour Point[1] (°C)	Specific Gravity[2]	Flash Point[3] (°C)	APHA Color[4]
SpectraSyn 4	4	19	126	-66	0.820	220	10
SpectraSyn Plus 4	4	17	122	-60	0.820	228	10
SpectraSyn6	6	31	138	-57	0.827	246	10
SpectraSyn Plus 6	6	30	140	-54	0.827	246	10
SpectraSyn 8	8	48	139	-48	0.833	260	10
SpectraSyn 10	10	66	137	-48	0.835	266	10
SpectraSyn 40	39	396	147	-36	0.850	281	10
SpectraSyn 100	100	1240	170	-30	0.853	283	60
SpectraSyn Ultra	150	1500	218	-33	0.850	> 265	10
SpectraSyn Ultra 300	300	3100	241	-27	0.852	> 265	20
SpectraSyn Ultra 1000	1000	10000	307	-18	0.855	> 265	30

[1]ASTM D97; [2]ASTM D4052 (15.6, 15.6°C); [3]ASTM D92; [4]ASTM D1209

[0158] In one or more embodiments, the base stock can include oil or blends thereof conventionally utilized as crankcase lubricating oils. For example, suitable base stocks can include crankcase lubricating oils for spark-ignited and compression-ignited internal combustion engines, such as automobile and truck engines, marine and railroad diesel engines, and the like. Suitable base stocks can also include those oils conventionally employed in and/or adapted for use as power transmitting fluids such as automatic transmission fluids, tractor fluids, universal tractor fluids and hydraulic fluids, heavy duty hydraulic fluids, power steering fluids and the like. Suitable base stocks can also be or include gear lubricants, industrial oils, pump oils and other lubricating oils.

[0159] In one or more embodiments, the base stock can include not only hydrocarbon oils derived from petroleum, but also include synthetic lubricating oils such as esters of dibasic acids; complex esters made by esterification of monobasic acids, polyglycols, dibasic acids and alcohols; polyolefin oils, etc. Thus, the lubricating oil compositions described can be suitably incorporated into synthetic base oil base stocks such as alkyl esters of dicarboxylic acids, polyglycols and alcohols; polyalphaolefins; polybutenes; alkyl benzenes; organic esters of phosphoric acids; or polysilicone oils.

[0160] A lubrication oil composition comprising an oxPAO-aldehyde or oxPAO-alcohol can have a thickening efficiency greater than about 1.5, or greater than about 1.7, or greater than about 1.9, or greater than about 2.2, or greater than about 2.4 or greater than about 2.6. The lubrication oil composition can have a shear stability index less than about 55, or less than about 45, or less than about 35, or less than about 30, or less than about 25, or less than about 20, or less than about 15. The lubrication oil composition can have a complex viscosity at about -35°C or less than about 500, or less than about 450, or less than about 300, or less than about 100, or less than about 50, or less about 20, or less than about 10 centistokes, as used herein, the term "complex viscosity" means a frequency-dependent viscosity function determined during forced small amplitude harmonic oscillation of shear stress, in units of Pascal-seconds, that is equal to the difference between the dynamic viscosity and the out-of-phase viscosity. For purposes of this disclosure, complex viscosity is determined using Anton-Parr Low Temperature Solution Rheology (low temperature rheology). Experiments are done on an Anton-Parr Model MCR501 rheometer using a 1" cone and plate setup. The cone has a nominal 1 degree angle and 50 micron gap. About 100 microliters of sample is deposited on the bottom plate using a syringe-pipette. The cone is then lowered onto the plate so that the volume between the cone and plate is fully occupied by solution. The temperature is then lowered at a cooling rate of about 1.5°C/min. while measuring the complex viscosity at an angular frequency of about 0.1 rad/sec applying about a 10% strain and recording a value every minute. The viscosity at about 0.1 rad/sec is then plotted as a function of temperature to observe the effect of gelation.

[0161] A lubrication oil composition comprising an oxPAO-aldehyde or oxPAO-alcohol can have a Mini Rotary Viscometer (MRV) viscosity at about -35°C in a 10W-50 formulation of less than about 60,000 cps according to ASTM 1678. The lubrication oil composition can have any suitable combination of desired properties. As a non-limiting example, the lubrication oil composition can have a thickening efficiency of about 1.5 or greater, such as 2.6 or greater, a shear stability index of 55 or less, such as 35 or less, such as 25 or less, a complex viscosity at about -35°C of 500 cSt or less, such as 300 cSt or less, such as 50 cSt or less, and/or a Mini Rotary Viscometer (MRV) viscosity at about -35°C in a 10W-50 formulation of 60,000 cps or less according to ASTM D1678.

[0162] Thickening efficiency (TE) is a measure of the thickening ability of the polymer in oil, and is defined as: $TE = 2/c \times \ln((kv_{(polymer+oil)})/kv_{oil})/\ln(2)$, where c is the concentration of the oxPAO-aldehyde or oxPAO-alcohol and kv is kinematic viscosity at 100°C according to ASTM D445. The shear stability index (SSI) is an indication of the resistance of polymers to permanent mechanical shear degradation in an engine. The SSI can be determined by passing a polymer-oil solution for 30 cycles through a high shear Bosch diesel injector according to the procedures listed in ASTM D6278.

[0163] In at least one embodiment, a lubrication oil composition comprises from 0.1 wt% to 2.5 wt%, such as from 0.25 wt% to 1.5 wt%, such as from 0.5 wt% to 1.0 wt% of the oxPAO-aldehyde or oxPAO-alcohol produced herein. In some embodiments, the amount of the oxPAO-aldehyde or oxPAO-alcohol produced herein in the lubrication oil composition can range from 0.5 wt%, 1 wt%, or 2 wt% to 2.5 wt%, 3 wt%, 5 wt%, or 10 wt%.

Oil Additives

[0164] The lubricating oil compositions can optionally contain one or more conventional additives, such as, for example, pour point depressants, antiwear agents, antioxidants, other viscosity-index improvers, dispersants, corrosion inhibitors, anti-foaming agents, detergents, rust inhibitors, friction modifiers, and the like.

[0165] Corrosion inhibitors, also known as anti-corrosive agents, promote the mechanical integrity of the metallic parts contacted by the lubricating oil composition. Illustrative corrosion inhibitors include phosphosulfurized hydrocarbons and the products obtained by reaction of a phosphosulfurized hydrocarbon with an alkaline earth metal oxide or hydroxide, such as in the presence of an alkylated phenol or of an alkylphenol thioester, and also can be in the presence of carbon dioxide. Phosphosulfurized hydrocarbons are prepared by reacting a suitable hydrocarbon such as a terpene, a heavy petroleum fraction of a C_2 to C_6 olefin polymer such as polyisobutylene, with from about 5 wt% to about 30 wt% of a sulfide of phosphorus for about 1/2 to about 15 hours, at a temperature in the range of about 66°C to about 316°C. Neutralization of the phosphosulfurized hydrocarbon may be effected in the manner known by those skilled in the art.

[0166] Oxidation inhibitors, or antioxidants, reduce the tendency of mineral oils to deteriorate in service, as evidenced by the products of oxidation such as sludge and varnish-like deposits on the metal surfaces, and by viscosity growth. Such oxidation inhibitors include alkaline earth metal salts of alkylphenolthioesters having C_5 to C_{12} alkyl side chains, e.g., calcium nonylphenate sulfide, barium octylphenate sulfide, dioctylphenylamine, phenylalphanaphthylamine, phosphosulfurized or sulfurized hydrocarbons, etc. Other useful oxidation inhibitors or antioxidants include oil-soluble copper compounds, such as described in US 5,068,047.

[0167] Friction modifiers serve to impart the proper friction characteristics to lubricating oil compositions such as automatic transmission fluids. Representative examples of suitable friction modifiers are found in US 3,933,659, which discloses fatty acid esters and amides;

US 4,176,074, which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; US 4,105,571, which discloses glycerol esters of dimerized fatty acids; US 3,779,928, which discloses alkane phosphonic acid salts; US 3,778,375, which discloses reaction products of a phosphonate with an oleamide; US 3,852,205, which discloses S-carboxyalkylene hydrocarbyl succinimide, S-carboxyalkylene hydrocarbyl succinamic acid and mixtures thereof; US 3,879,306, which discloses N-(hydroxyalkyl)alkenyl-succinamic acids or succinimides; US 3,932,290, which discloses reaction products of di-(lower alkyl) phosphites and epoxides; and US 4,028,258, which discloses the alkylene oxide adduct of phosphosulfurized N-(hydroxyalkyl) alkenyl succinimides. Exemplary friction modifiers are succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides and thiobis-alkanols, such as described in US 4,344,853.

[0168] Dispersants maintain oil insolubles, resulting from oxidation during use, in suspension in the fluid, thus preventing sludge flocculation and precipitation or deposition on metal parts. Suitable dispersants include high molecular weight N-substituted alkenyl succinimides, the reaction product of oil-soluble polyisobutylene succinic anhydride with ethylene amines such as tetraethylene pentamine and borated salts thereof. High molecular weight esters (resulting from the esterification of olefin substituted succinic acids with mono or polyhydric aliphatic alcohols) or Mannich bases from high molecular weight alkylated phenols (resulting from the condensation of a high molecular weight alkylsubstituted phenol, an alkylene polyamine and an aldehyde such as formaldehyde) are also useful as dispersants.

[0169] Pour point depressants (“ppd”), otherwise known as lube oil flow improvers, lower the temperature at which the fluid will flow or can be poured. Any suitable pour point depressant known in the art can be used. For example, suitable pour point depressants include, but are not limited to, one or more C_8 to C_{18} dialkylfumarate vinyl acetate copolymers, polymethyl methacrylates, alkylmethacrylates and wax naphthalene. A lubrication oil composition can include a base stock and one or more oxPAO-aldehydes or oxPAO-alcohols produced herein, and optionally, a pour point depressant.

[0170] Foam control can be provided by any one or more anti-foamants. Suitable antifoamants include polysiloxanes, such as silicone oils and polydimethyl siloxane.

[0171] Anti-wear agents reduce wear of metal parts. Representatives of conventional antiwear agents are zinc dialkyldithiophosphate and zinc diaryldithiosphate, which can also serve as an antioxidant.

[0172] Detergents and metal rust inhibitors include the metal salts of sulphonic acids, alkyl phenols, sulfurized alkyl phenols, alkyl salicylates, naphthenates and other oil soluble mono-and dicarboxylic acids. Highly basic (viz, overbased) metal salts, such as highly basic alkaline earth metal sulfonates (especially Ca and Mg salts) are frequently used as detergents.

[0173] Compositions containing these conventional additives can be blended with the base stock in amounts effective to provide their normal attendant function. Thus, typical formulations can include, in amounts by weight, a VI improver (from about 0.01% to about 12%); a corrosion inhibitor (from about 0.01% to about 5%); an oxidation inhibitor (from about 0.01% to about 5%); depressant (of from about 0.01% to about 5%); an anti-foaming agent (from about 0.001% to about 3%); an anti-wear agent (from about 0.001% to about 5%); a friction modifier (from about 0.01% to about 5%); a detergent/rust inhibitor (from about 0.01% to about 10%); and a base oil.

[0174] When other additives are used, it may be desirable, although not necessary, to prepare additive concentrates that include concentrated solutions or dispersions of the VI improver (in concentrated amounts), together with one or more of the other additives, such a concentrate denoted an “additive package,” whereby several additives can be added simultaneously to the base stock to form a lubrication oil composition. Dissolution of the additive concentrate into the lubrication oil can be facilitated by solvents and by mixing accompanied with mild heating, but this is not essential. The additive-package can be formulated to contain the VI improver and optional additional additives in proper amounts to provide the desired concentration in the final formulation when the additive-package is combined with a predetermined amount of base oil.

Blending with Base Stock Oils

[0175] Conventional blending methods are described in US 4,464,493, which is incorporated by reference herein. This conventional process typically involves passing the polymer through an extruder at elevated temperature for degradation of the polymer and circulating hot oil across the die face of the extruder while reducing the degraded polymer to particle size upon issuance from the extruder and into the hot oil. An oxPAO-aldehyde or oxPAO-alcohol of the present disclosure can be added by blending directly with the base oil so that the complex multi-step conventional process is not needed. The oxPAO-aldehyde or oxPAO-alcohol can be dissolved in the base stock to form a without a need for additional shearing and degradation processes.

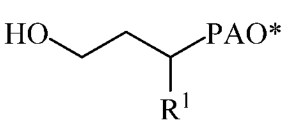
[0176] The oxPAO-aldehyde or oxPAO-alcohol can be soluble at room temperature in lube oils at up to about 10% concentration in order to prepare a viscosity modifier concentrate. Such concentrates, including eventually an additional additive package including the typical additives used in lube oil applications as described above, are generally further diluted to the final concentration (usually around 1%) by multi-grade lube oil producers. In this case, the concentrate will be a pourable homogeneous solid-free solution.

[0177] The oxPAO-aldehydes or oxPAO-alcohols produced herein can have a shear stability index of SSI (determined according to ASTM D6278, 30 cycles) of from 6 to 50, such as 10 to 40, such as 10 to 20.

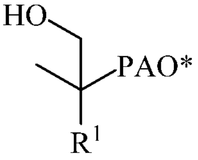
[0178] The oxPAO-aldehydes or oxPAO-alcohols produced herein can have a shear stability index of SSI (determined according to ASTM D6278 and D7109, 90 cycles) of from 8 to 65, such as 10 to 50, such as 10 to 40.

[0179] This invention further relates to:

1. An alcohol-polyalpha olefin represented by formula **(VIIa)** or **(VIIb)**:



linear **(VIIa)**



branched **(VIIb)**,

where R^1 is a C_1 to C_{100} hydrocarbyl and PAO* is an alpha-olefin polymer having two to 400 mer units,

wherein the alcohol-polyalpha olefin has a molecular weight of 500 g/mol or greater.

2. The polyalpha olefin of paragraph 1, wherein R^1 is linear alkyl.

3. The polyalpha olefin of paragraphs 1 or 2, wherein R^1 comprises from c1 to c2 carbon atoms, wherein each of c1 and c2 is independently an integer from 1 to 60, and c1 is less than c2.

4. The polyalpha olefin of paragraph 3, wherein c1 is 4 and c2 is 30.

5. The polyalpha olefin of any of paragraphs 1 to 4, wherein R^1 is selected from ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl, *n*-icosyl, *n*-docosyl, *n*-tetracosyl, *n*-hexacosyl, and *n*-octacosyl.

6. The polyalpha olefin of any of paragraphs 1 to 5, wherein PAO* is selected from poly-1-pentenyl, poly-1-hexenyl, poly-1-heptenyl, poly-1-octenyl, poly-1-nonenyl, poly-1-decenyl, poly-1-undecenyl, poly-1-dodecenyl, poly-1-tridecenyl, poly-1-tetradecenyl, poly-1-pentadecenyl, or poly-1-hexadecenyl.

7. The polyalpha olefin of any of paragraphs 1 to 6, wherein the polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** has a molecular weight of 1,000 g/mol to 10,000 g/mol.

8. The polyalpha olefin of any of paragraphs 1 to 7, wherein the polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** has a molecular weight of from 1,000 g/mol to 3,000 g/mol.

9. The polyalpha olefin of any of paragraphs 1 to 8, wherein the polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** has a molecular weight of from 1,500 g/mol to 3,000 g/mol.

10. The polyalpha olefin of any of paragraphs 1 to 9, wherein the polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** has a kinematic viscosity @ 100°C of 95 cSt or greater according to ASTM D445.

11. The polyalpha olefin of paragraph 10, wherein the polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** has a kinematic viscosity @ 100°C of from 110 cSt to 300 cSt according to ASTM D445.

12. A composition according to paragraphs 1 to 11 comprising alcohol-polyalpha olefin represented by formula **(VIIa)** and alcohol-polyalpha olefin represented by formula **(VIIb)**.

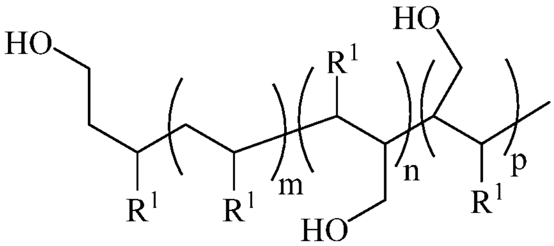
13. The composition of paragraph 12, wherein a molar ratio of the polyalpha olefin represented by formula **(VIIa)** to polyalpha olefin represented by formula **(VIIb)** is 5:1 or greater.

14. The composition of paragraph 13, wherein the molar ratio of the polyalpha olefin represented by formula **(VIIa)** to polyalpha olefin represented by formula **(VIIb)** is 10:1 or greater.

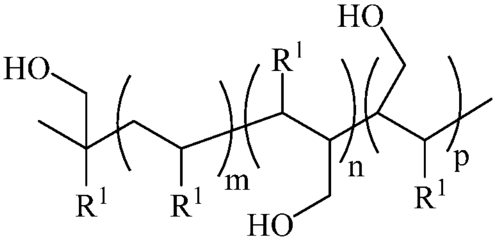
15. The composition of any of paragraphs 12 to 14, wherein the composition has a kinematic viscosity @ 100°C of 95 cSt or greater according to ASTM D445.

16. The composition of paragraph 15, wherein the composition has a kinematic viscosity @ 100°C of from 110 cSt to 300 cSt according to ASTM D445.

17. An alcohol-polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)**:



(VIIIa)



(VIIIb),

wherein:

R^1 is C_1 to C_{100} hydrocarbyl, and m, n, and p are integers such that the molecular weight of the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** is 500 g/mol or greater.

18. The polyalpha olefin of paragraph 17, wherein each of n and p is 20 or less.

19. The polyalpha olefin of paragraphs 17 or 18, wherein each of n and p is 10 or less.

20. The polyalpha olefin of any of paragraphs 17 to 19, wherein each of n and p is 5 or less.

21. The polyalpha olefin of any of paragraphs 17 to 21, wherein R^1 is linear alkyl.

22. The polyalpha olefin of any of paragraphs 17 to 21, wherein R^1 comprises from c1 to c2 carbon atoms, wherein each of c1 and c2 is independently an integer from 1 to 60, and c1 is less than c2.

23. The polyalpha olefin of paragraph 22, wherein c1 is 4 and c2 is 30.

24. The polyalpha olefin of any of paragraphs 17 to 23, wherein R^1 is selected from ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl, *n*-icosyl, *n*-docosyl, *n*-tetracosyl, *n*-hexacosyl, and *n*-octacosyl.

25. The polyalpha olefin of any of paragraphs 17 to 24, wherein the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** has a molecular weight of 1,000 g/mol or greater.

26. The polyalpha olefin of any of paragraphs 17 to 25, wherein the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** has a molecular weight of from 1,000 g/mol to 10,000 g/mol.

27. The polyalpha olefin of any of paragraphs 17 to 26, wherein the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** has a molecular weight of from 1,500 g/mol to 3,000 g/mol.

28. The polyalpha olefin of any of paragraphs 17 to 27, wherein the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** has a kinematic viscosity @ 100°C of 95 cSt or greater according to ASTM D445.

29. The polyalpha olefin of paragraph 28, wherein the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** has a kinematic viscosity @ 100°C of from 110 cSt to 300 cSt according to ASTM D445.

30. A composition according to paragraphs 17 to 29 comprising:

alcohol-polyalpha olefin represented by formula **(VIIIa)**; and
alcohol-polyalpha olefin represented by formula **(VIIIb)**.

31. The composition of paragraph 30, wherein a molar ratio of the polyalpha olefin represented by formula **(VIIIa)** to polyalpha olefin represented by formula **(VIIIb)** is 5:1 or greater.

32. The composition of paragraph 31, wherein the molar ratio of the polyalpha olefin represented by formula **(VIIIa)** to polyalpha olefin represented by formula **(VIIIb)** is 10:1 or greater.

33. The composition of any of paragraphs 30 to 32, wherein the composition has a kinematic viscosity @ 100°C.

Experimental

Experimental Details

[0180] Unless otherwise specified, all materials were obtained from commercial sources and purified by standard techniques. All manipulations were conducted with rigorous exclusion of air and water unless otherwise noted. ^{1}H NMR spectroscopy was performed using a Bruker 400 MHz NMR spectrometer. The uPAO-65 was dried over 3Å molecular sieves and degassed by bubbling dry dinitrogen through the viscous mixture for 2 days. All manipulations involving rhodium were conducted with rigorous exclusion of air and water. Rh(acac)COD and PPh_3 were obtained from commercial sources. Hydroformylation conversion values were determined by relative integration of the residual vinylidene content relative to the intensity of resonances corresponding to –C*H*O (aldehyde) or OH-C*H*2-R (alcohol).

[0181] **Kinematic Viscosity ("KV") Testing**: Kinematic viscosity and viscosity index determinations were made using a Canon automatic viscometer in accordance with ASTM methods D445 and D227, respectively. Viscosity measurements were made at temperatures using instrument controlled temperature baths (± 0.02°C). Each reported KV measurement was taken as an average of two independent runs on the same sample. The instrument is calibrated to report kinematic viscosity measurements with an error less than 0.65 % when compared to standards of known viscosity at 40°C and 100°C.

[0182] **Preparation of uPAO-65**: In a representative reaction, uPAO-65 was prepared in a 2-gallon CSTR at 57.1°C. Polydecene was fed at a rate of 2,080 g/h with a reactor pressure of 25 psi (nitrogen). TNOAl (6.25 wt% toluene) was utilized as scavenger and fed at a rate of 0.163 mL/min. The catalyst ($Si(CH_3)_2$(3-propylCp)(tetramethylCp)$Zr(CH_3)_2$) was activated with *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate and added as a toluene solution at a rate of 0.19 mL/min. Reactor residence time was 3 hours. The reactor was allowed to equilibrate for 9 hours prior to uPAO-65 collection from the reactor.

[0183] This high viscosity (KV 100 = 66 cST) uPAO material was estimated by ^{1}H NMR spectroscopy to have a number average molecular weight (Mn) of 2240 g/mol (~16 repeat units). The uPAO-65 material typically contains a single olefinic unsaturation per chain. Average olefinic composition was determined to be 84% vinylidene (H2C=C<), 1% vinyl (H2C=CH-), 6 % vinylene (-HC=CH-), and 8 % trisubstituted olefins (-HC=C<).

[0184] **Hydroformylation:** uPAO-65 (~300 mL) was charged into a 0.65 L Parr reactor fitted with a magnetic stir bar. To this viscous material, a toluene solution of PPh_3/Rh(acac)COD (ligand:Rh = 2.3:1; 20 mL; 0.1-1 wt%) was added as a bright orange mixture. The Parr reactor was then closed, sealed and pressurized to a desired pressure (100-450 PSIG) with synthesis gas (H_2:CO; 1:1). The reactor was then heated to a desired temperature and allowed to react for a period of time, typically 24 or 48 hours. Following the reaction, the mixture was cooled to room temperature and vented. The viscous reaction mixture, now brown in coloration, was combined with isohexane (100-200 mL) to reduce material viscosity. The material was then filtered, in air, through a silica plug to remove catalyst residue and other colored contaminates. Bulk volatiles were then removed from the filtrate by rotary evaporation. The resulting viscous oxPAO was heated to 50°C and placed under reduced pressure (150 mTorr) to remove any residual volatile materials. Conversion was estimated with ^{1}H NMR spectroscopy ($CDCl_3$) by relative integration of vinylidene resonances to the product aldehydes (linear and branched).

[0185] Table 3 illustrates results from batch hydroformylations with single or multiple passes. Entries 7-10 contain hydroformylation run results for partially converted uPAO/oxPAO materials that were blended from batches generated in entries 1-6. Conversion and *l:b* ratios were determined by relative integration of ^{1}H NMR ($CDCl_3$) spectroscopy. Conversion was determined by relative integration of –CHO and –CH_2-OH intensity versus residual vinylidene intensity. *l:b* ratio was determined by relative integration of linear vs. branched aldehyde intensity. For each run, the catalyst utilized was Rh(acac)COD/PPh_3 with a ligand to metal ratio of 2.3. Catalyst loadings were calculated using an approximate density of 0.85 g/mL for uPAO-65. Reactor volume limited to 0.64 L. A typical run utilized a syngas H_2:CO ratio of approximately 1:1.

Table 3

Entry	Batch #	Pass #	Starting Conversion (%)	End Conversion (%)	1:b ratio	Volume PAO (mL)
1	1	1	0	62.4	6.1	250
2	2	1	0	57.85	7.8	250
3	3	1	0	32.5	8.33	250
4	4	1	0	39.3	7.1	400
5	2	2	57.85	89.7	11.1	250
6	4	2	39.3	60.7	9.09	400
7	5 – 50/50 blend of batch 1 & 4	2	61.55	91.7	11.1	400
8	6 – 50/50 blend of batch 3 & 4	2	46.6	84.8	11.1	400
9	7 – 50/50 blend of batch 6 & 3	3	58.65	77.5	11.2	400
10	8 – 50/50 blend of 5 & 4	3	90.7	85	11.1	400
1	1	1	0.13	24	450	100
2	2	1	0.13	40	400	120
3	3	1	0.39	72	100	120
4	4	1	0.08	20	500	110
5	2	2	0.13	48	400	120
6	4	2	0.08	48	150	100
7	5 – 50/50 blend of batch 1 & 4	2	0.08	72	400	120
8	6 – 50/50 blend of batch 3 & 4	2	0.08	72	400	120
9	7 – 50/50 blend of batch 6 & 3	3	0.08	72	400	120
10	8 – 50/50 blend of 5 & 4	3	0.09	48	400	120

[0186] **Reduction**: Under a nitrogen atmosphere and in a 1 L flask, two batches of oxPAO-aldehyde (material from entries 9 and 10 of Table 3; 500 mL) were combined with tetrahydrofuran (400 mL) and dimethoxyethane (100 mL). This afforded a mixture with reduced viscosity. The mixture was fitted with a magnetic stir bar and allowed to stir for 5 min until a homogeneous solution was obtained. Thereafter, $NaBH_4$ (18 g, ~ 4 equiv) was slowly added. The mixture was stirred at room temperature for 1 hour then heated to 70°C and allowed to react for 24 hours. The mixture was then removed from an inert atmosphere environment, transferred to a 2L reaction vessel, diluted with isohexane (200 mL) and combined with water (300 mL). The resulting biphasic mixture was allowed to stir for 5 hours at room temperature. The mixture was then slowly neutralized to pH ~7 with HCl (3M). The resulting mixture was then subjected to an aqueous workup utilizing isohexane as organic diluent. The organic portions were combined, dried with Na_2SO_4 and filtered through silica. The filtrate was concentrated to a colorless oil by rotary evaporation. The crude oil was transferred to a round bottom flask under an inert atmosphere. The material was then heated to 120°C and placed under vacuum (300 mTorr) to remove volatiles. It was filtered an additional time through a medium porosity fritted funnel packed with Celite. ^1H NMR spectroscopy ($CDCl_3$) was used to confirm the composition by integration the oxPAO-alcohol methylene proton resonances located on carbon located alpha to the hydroxyl moiety (e.g., HO-C*H2*-R) relative to residual vinylidene resonances.

[0187] **Molecular Modelling and Conformational Search**: Molecular models of hydroxyl functionalized PAO's were generated using Spartan 16', version 2.0.7 available from Wavefunction, Inc. of Irvine California. (Monte Carlo conformational search, MMFF94.) (Visualization performed with Mercury 3.7.) A geometry optimization was conducted using a conformational search (1,000 conformations for linear oxPAO-alcohols, 100 conformations for branched hydroxyl functionalized polydecene). Figure 1A illustrates the molecular model of an oxPAO-alcohol (polydecene), and Figure 1B illustrates the molecular model of an internal beta-branched oxPAO-alcohol (polydecene). Figure 1A demonstrates that terminal alcohol-containing oxPAO is exposed to an external environment, rendering the molecule capable of interacting with, for example, a nearby terminal alcohol-containing oxPAO, providing an increased kinematic viscosity, as compared to the internal beta-branched alcohol-containing oxPAO of Figure 1B where the alcohol moiety is crowded by alkyl moieties along the oxPAO backbone.

Material Characterization

[0188] Figure 2 is a graph illustrating kinematic viscosity measurements (ASTM D445, 100°C) for uPAO-65 starting material, oxPAO-aldehyde (> 80% aldehyde), and oxPAO-alcohol (>80% alcohol). Kinematic viscosity testing (100°C) showed a marked increase relative to the uPAO-65 starting material (See Figure 2 and Table 4). This increase in viscosity is consistent with the presence of polar end groups capable of engaging in hydrogen bonding interactions.

[0189] Table 4 illustrates kinematic viscosity results for uPAO-65 and oxPAO samples. Standard error for kinematic values determined by ASTM D445 is +/- 0.7. ASTM D2270 was utilized for viscosity index determination.

Table 4

Entry	Sample	Test	Units	ASTM Method	Value
1	uPAO-65	KV @ 100°C	cSt	D445	66.65
		KV @ 40°C	cSt	D445	562.8
		Viscosity Index	N/A	D2270	194.0
2	oxPAO-aldehyde	KV @ 100°C	cSt	D445	92.59
3	oxPAO-alcohol	KV @ 100°C	cSt	D445	122.5
		KV @ 40°C	cSt	D445	1241
		Viscosity Index	N/A	D2270	201.6

[0190] Corroborating this spectroscopic data, oxPAO-aldehyde materials exhibit ^{1}H NMR spectroscopic signals consistent with the presence of linear (major) and minor (branched) aldehyde products (Figures 3A and 3B). Figure 4A illustrates the ^{1}H NMR ($CDCl_3$) spectrum of hydroformylated uPAO showing aldehyde. Figure 4B illustrates the ^{1}H NMR ($CDCl_3$) spectrum of hydroformylated uPAO showing aldehyde. Figure 5A illustrates the ^{1}H NMR ($CDCl_3$) spectrum of hydroformylated uPAO reduced to oxPAO-alcohol. Figure 5B illustrates the ^{1}H NMR ($CDCl_3$) spectrum of hydroformylated uPAO reduced to oxPAO-alcohol showing alcohol $-CH_2$-OH resonances.

[0191] Utilizing this knowledge, it was discovered that high viscosity unsaturated polyalpha olefins (uPAO) can undergo hydroformylation to afford aldehyde or hydroxyl terminated PAO's. It was discovered that unsaturated poly decene (uPAO) of moderate viscosity (65 cST) was selectively hydroformylated to afford aldehyde and alcohol functionalized polyalpha olefin materials (oxPAO's). This was achieved under comparatively mild conditions with good linear to branch (*l*:*b*) selectivity, reasonable per pass conversion and low rhodium catalyst loadings. These materials are of interest because the polar functionality (e.g., -CHO, OH) at the end of the oligo decene chain can provide a "bottlebrush structure" with a hyrophillic head group (e.g., see Figure 1A). The resulting gamma branched alcohol is unique relative to internal or beta branched alcohols, of comparable size, that might be accessed from metathetical methods or by Guerbet type chemistry (Figure 1B). This is demonstrated by molecular simulations of conformational minima for the oxPAO-alcohols versus a beta branched internal alcohols. In the case of an internal alcohol, the polar functionality is buried within a network of sterically encumbering alkyl chains limiting the ability of the hydroxyl functionality to influence material properties and interact with surfaces or substrates.

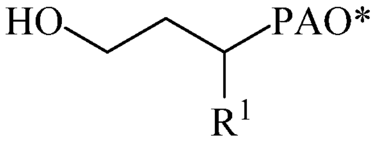
[0192] Overall, oxPAO-alcohols, and methods thereof, of the present disclosure include a terminal alcohol group and can provide increased viscosity as compared to conventional PAOs. The viscosity increase can provide oxPAO-alcohols which can be used in a variety of end use applications, such as for viscosity modification of compositions, such as oils.

[0193] All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with this text. As is apparent from the foregoing general description and the specific embodiments, while forms of the present disclosure have been illustrated and described, various modifications can be made without departing from the spirit and scope of the present disclosure. Accordingly, it is not intended that the present disclosure be limited thereby. Likewise, the term "comprising" is considered synonymous with the term "including." Likewise whenever a composition, an element or a group of elements is preceded with the transitional phrase "comprising", it is understood that we also contemplate the same composition or group of elements with transitional phrases "consisting essentially of," "consisting of", "selected from the group of consisting of," or "is" preceding the recitation of the composition, element, or elements and vice versa.

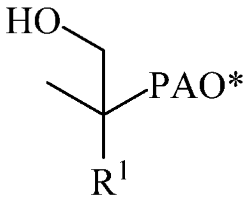
CLAIMS:

What is claimed is:

1. An alcohol-polyalpha olefin represented by formula **(VIIa)** or **(VIIb)**:



linear **(VIIa)**



branched **(VIIb)**,

where R^1 is a C_1 to C_{100} hydrocarbyl and PAO* is an alpha-olefin polymer having two to 400 mer units.

2. The polyalpha olefin of claim 1, wherein R^1 is linear C_1-C_{100} alkyl.

3. The polyalpha olefin of claim 1 or 2, wherein R^1 comprises from c1 to c2 carbon atoms, wherein each of c1 and c2 is independently an integer from 1 to 60, and c1 is less than c2.

4. The polyalpha olefin of claim 3, wherein c1 is 4 and c2 is 30.

5. The polyalpha olefin of any of claims 1-4, wherein R^1 is selected from ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl, *n*-icosyl, *n*-docosyl, *n*-tetracosyl, *n*-hexacosyl, and *n*-octacosyl.

6. The polyalpha olefin of any of claims 1-5, wherein PAO* is selected from poly-1-pentenyl, poly-1-hexenyl, poly-1-heptenyl, poly-1-octenyl, poly-1-nonenyl, poly-1-decenyl, poly-1-undecenyl, poly-1-dodecenyl, poly-1-tridecenyl, poly-1-tetradecenyl, poly-1-pentadecenyl, or poly-1-hexadecenyl.

7. The polyalpha olefin of any of claims 1-6, wherein the polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** has a molecular weight of 1,000 g/mol to 10,000 g/mol.

8. The polyalpha olefin of any of claims 1-7, wherein the polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** has a molecular weight of from 1,000 g/mol to 3,000 g/mol.

9. The polyalpha olefin of any of claims 1-8, wherein the polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** has a molecular weight of from 1,500 g/mol to 3,000 g/mol.

10. The polyalpha olefin of any of claims 1-9, wherein the polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** has a kinematic viscosity @ 100°C of 95 cSt or greater according to ASTM D445.

11. The polyalpha olefin of claim 10, wherein the polyalpha olefin represented by formula **(VIIa)** or **(VIIb)** has a kinematic viscosity @ 100°C of from 110 cSt to 300 cSt according to ASTM D445.

12. A composition according to any of claims 1-11 comprising alcohol-polyalpha olefin represented by formula **(VIIa)**; and alcohol-poly alpha olefin represented by formula **(VIIb)**.

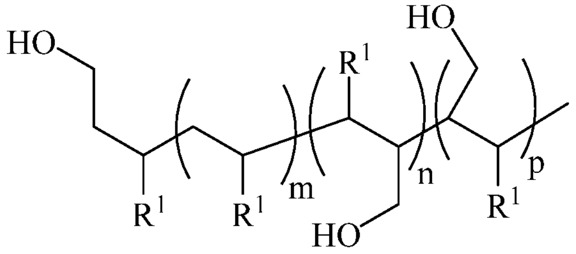
13. The composition of claim 12, wherein a molar ratio of the polyalpha olefin represented by formula **(VIIa)** to polyalpha olefin represented by formula **(VIIb)** is 5:1 or greater.

14. The composition of claim 13, wherein the molar ratio of the polyalpha olefin represented by formula **(VIIa)** to polyalpha olefin represented by formula **(VIIb)** is 10:1 or greater.

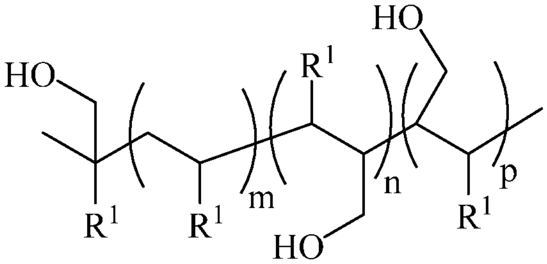
15. The composition of any of claims 12-14, wherein the composition has a kinematic viscosity @ 100°C of 95 cSt or greater according to ASTM D445.

16. The composition of claim 15, wherein the composition has a kinematic viscosity @ 100°C of from 110 cSt to 300 cSt according to ASTM D445.

17. An alcohol polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)**:



(VIIIa)



(VIIIb),

wherein:

R^1 is C_1 to C_{100} hydrocarbyl, and m, n, and p are integers such that the molecular weight of the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** is 500 g/mol or greater.

18. The polyalpha olefin of claim 17, wherein each of n and p is 20 or less.

19. The polyalpha olefin of claim 17 or 18, wherein each of n and p is 10 or less.

20. The polyalpha olefin of any of claims 17-19, wherein each of n and p is 5 or less.

21. The polyalpha olefin of any of claims 17 -20, wherein R^1 is linear C_1-C_{100} alkyl.

22. The polyalpha olefin of any of claims 17-21, wherein R^1 comprises from c1 to c2 carbon atoms, wherein each of c1 and c2 is independently an integer from 1 to 60, and c1 is less than c2.

23. The polyalpha olefin of claim 22, wherein c1 is 4 and c2 is 30.

24. The polyalpha olefin of any of claims 17-23, wherein R^1 is selected from ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, *n*-octyl, *n*-decyl, *n*-dodecyl, *n*-tetradecyl, *n*-hexadecyl, *n*-octadecyl, *n*-icosyl, *n*-docosyl, *n*-tetracosyl, *n*-hexacosyl, and *n*-octacosyl.

25. The polyalpha olefin of any of claims 17-24, wherein the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** has a molecular weight of 1,000 g/mol or greater.

26. The polyalpha olefin of any of claims 17-25, wherein the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** has a molecular weight of from 1,000 g/mol to 10,000 g/mol.

27. The polyalpha olefin of any of claims 17-26, wherein the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** has a molecular weight of from 1,500 g/mol to 3,000 g/mol.

28. The polyalpha olefin of any of claims 17-27, wherein the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** has a kinematic viscosity @ 100°C of 95 cSt or greater according to ASTM D445.

29. The polyalpha olefin of claim 28, wherein the polyalpha olefin represented by formula **(VIIIa)** or **(VIIIb)** has a kinematic viscosity @ 100°C of from 110 cSt to 300 cSt according to ASTM D445.

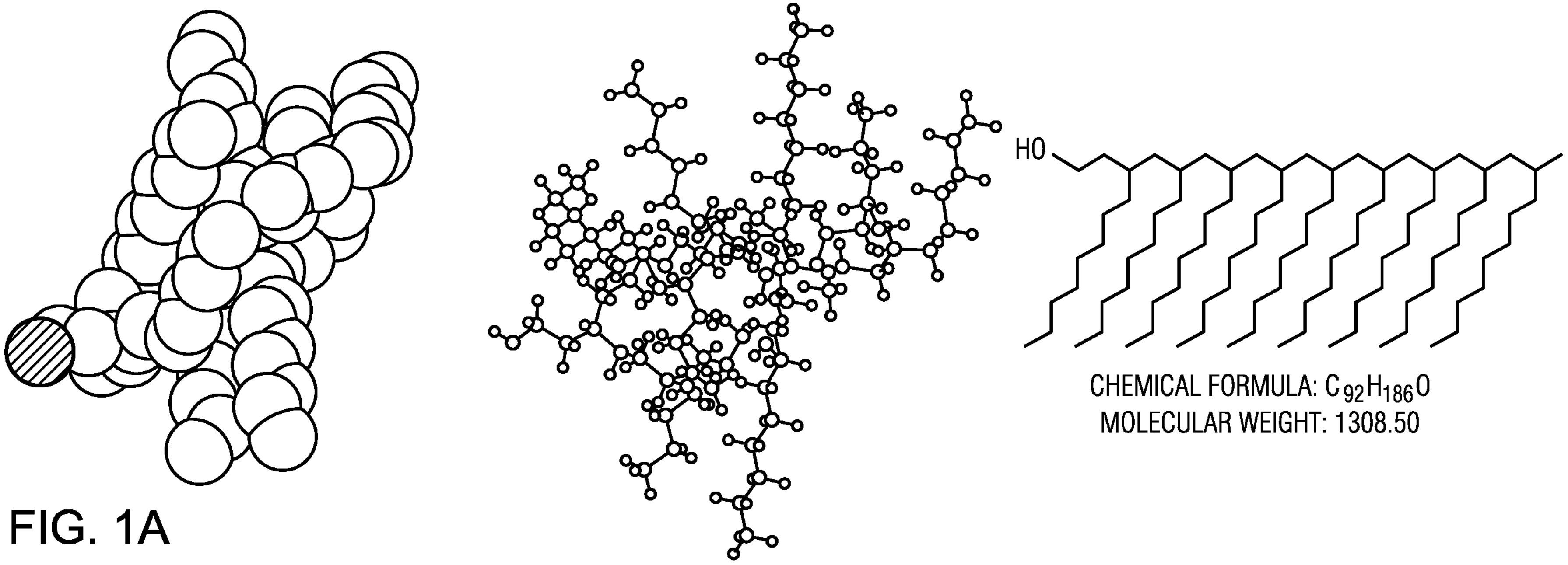
30. A composition according to any of claims 17-29 comprising:
alcohol-polyalpha olefin represented by formula **(VIIIa)**; and
alcohol-polyalpha olefin represented by formula **(VIIIb)**.

31. The composition of claim 30, wherein a molar ratio of the polyalpha olefin represented by formula **(VIIIa)** to polyalpha olefin represented by formula **(VIIIb)** is 5:1 or greater.

32. The composition of claim 31, wherein the molar ratio of the polyalpha olefin represented by formula **(VIIIa)** to polyalpha olefin represented by formula **(VIIIb)** is 10:1 or greater.

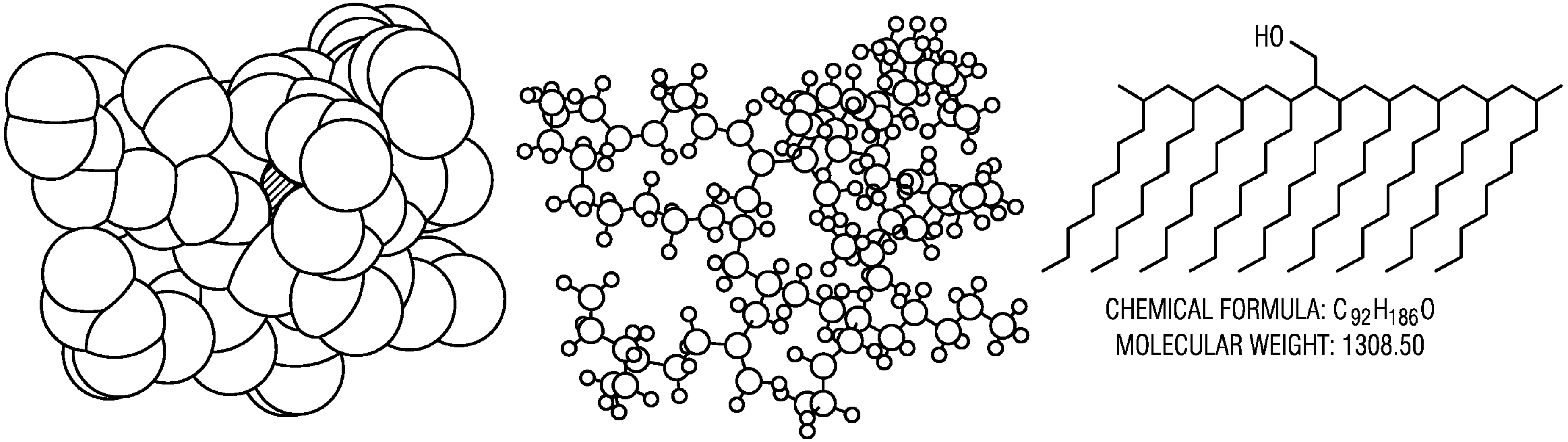
33. The composition of any of claims 30-32, wherein the composition has a kinematic viscosity @ 100°C of 95 cSt or greater according to ASTM D445.

34. The composition of claim 33, wherein the composition has a kinematic viscosity @ 100°C of from 110 cSt to 300 cSt according to ASTM D445.



CHEMICAL FORMULA: $C_{92}H_{186}O$
MOLECULAR WEIGHT: 1308.50

FIG. 1A



CHEMICAL FORMULA: $C_{92}H_{186}O$
MOLECULAR WEIGHT: 1308.50

FIG. 1B

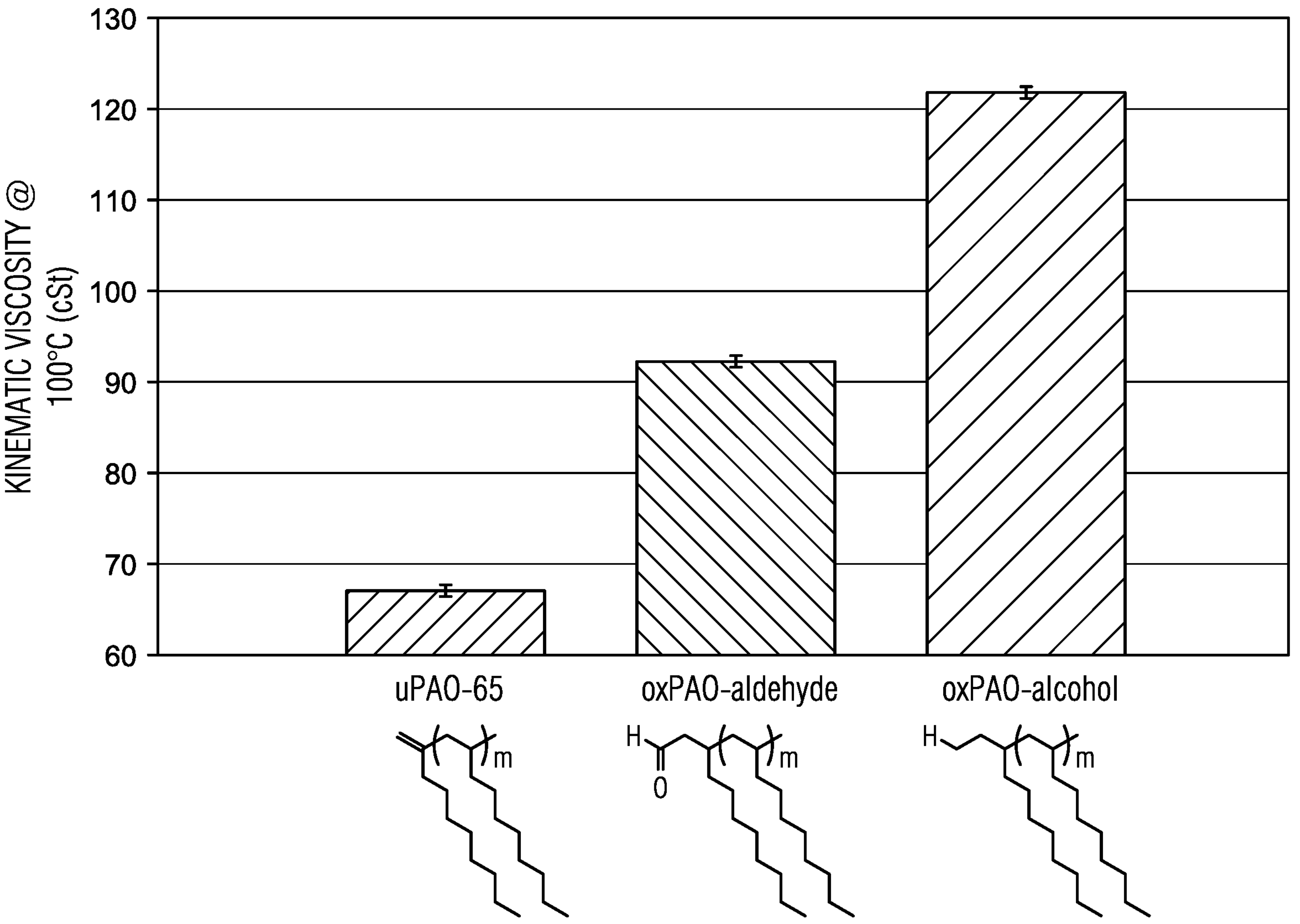

KINEMATIC VISCOSITY @ 100°C (cSt)
130
120
110
100
90
80
70
60
uPAO-65
oxPAO-aldehyde
oxPAO-alcohol
m
H
O
m
H
m

FIG. 2

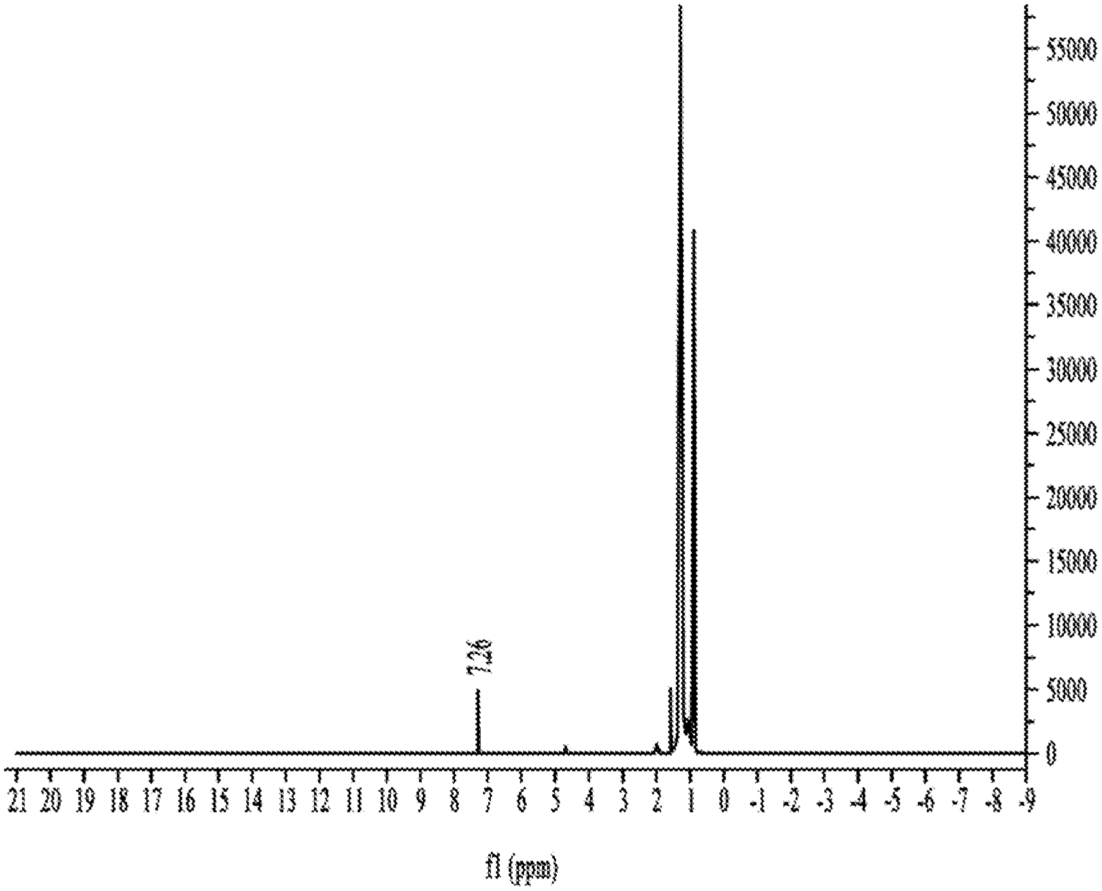

7.26
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5 -6 -7 -8 -9
f1 (ppm)

FIG. 3A

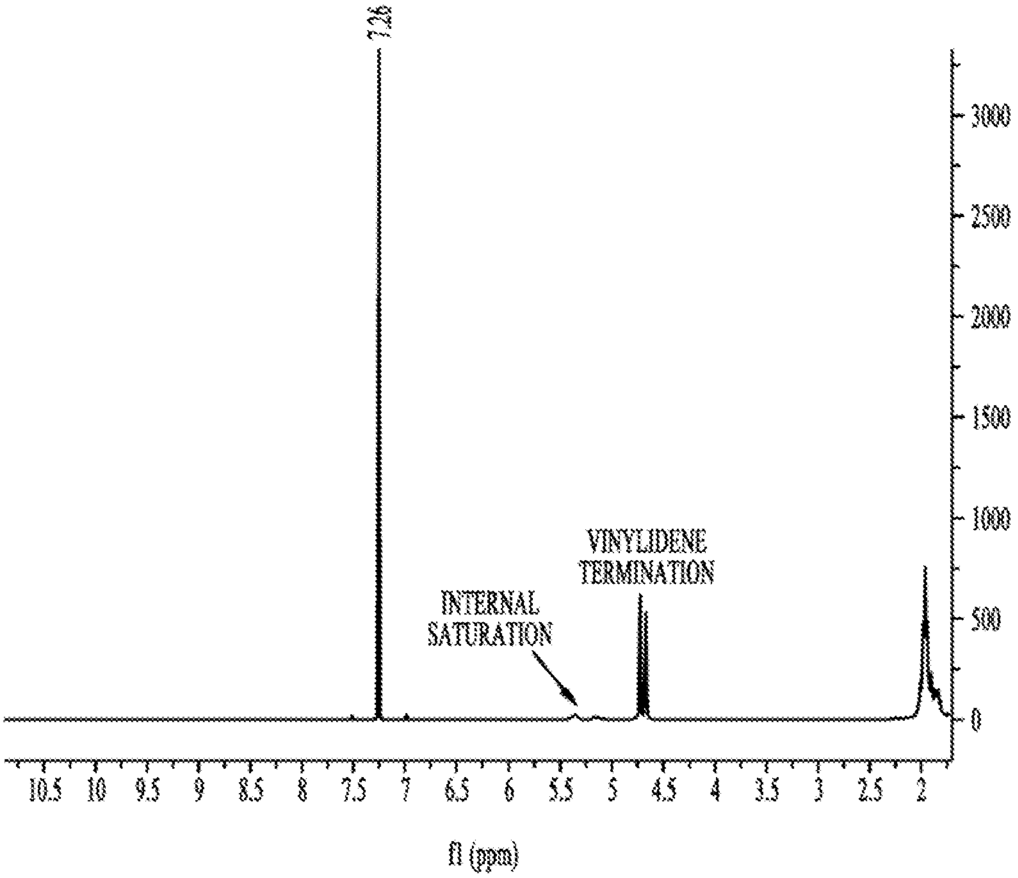

7.26
INTERNAL SATURATION
VINYLIDENE TERMINATION
3000
2500
2000
1500
1000
500
0
10.5
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
2
f1 (ppm)

FIG. 3B

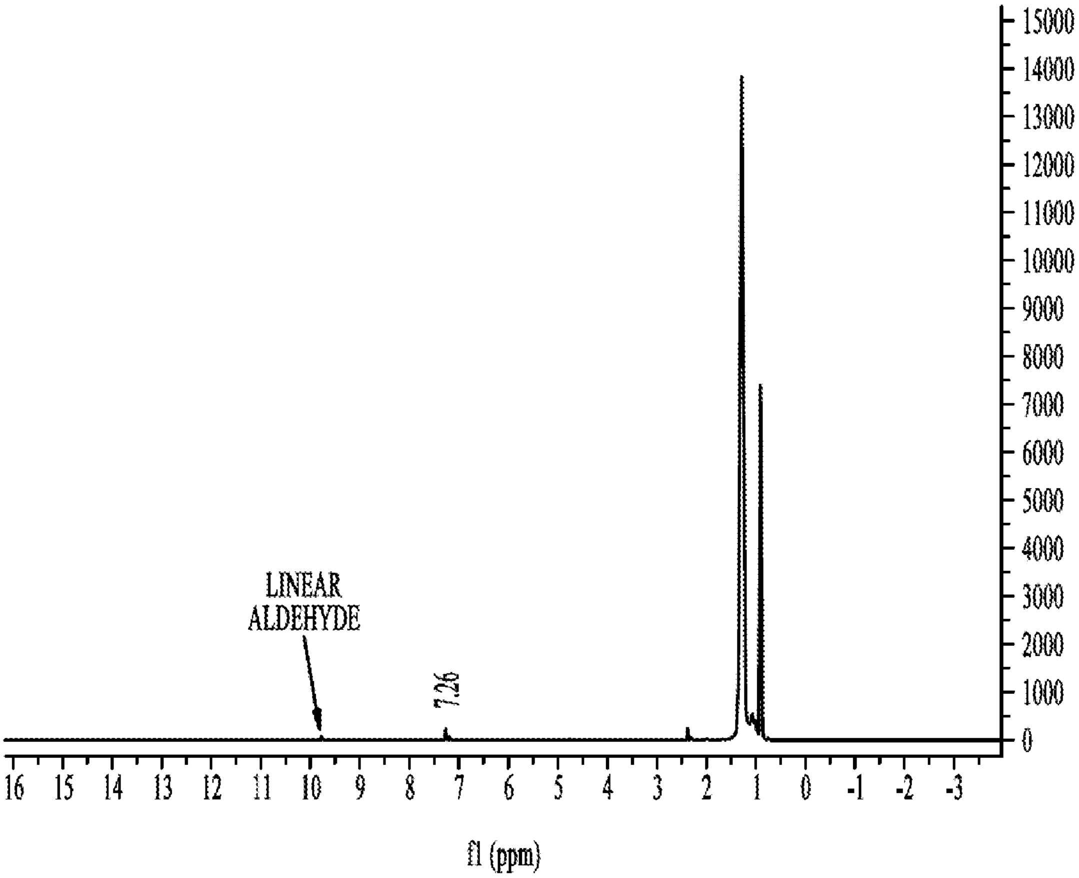
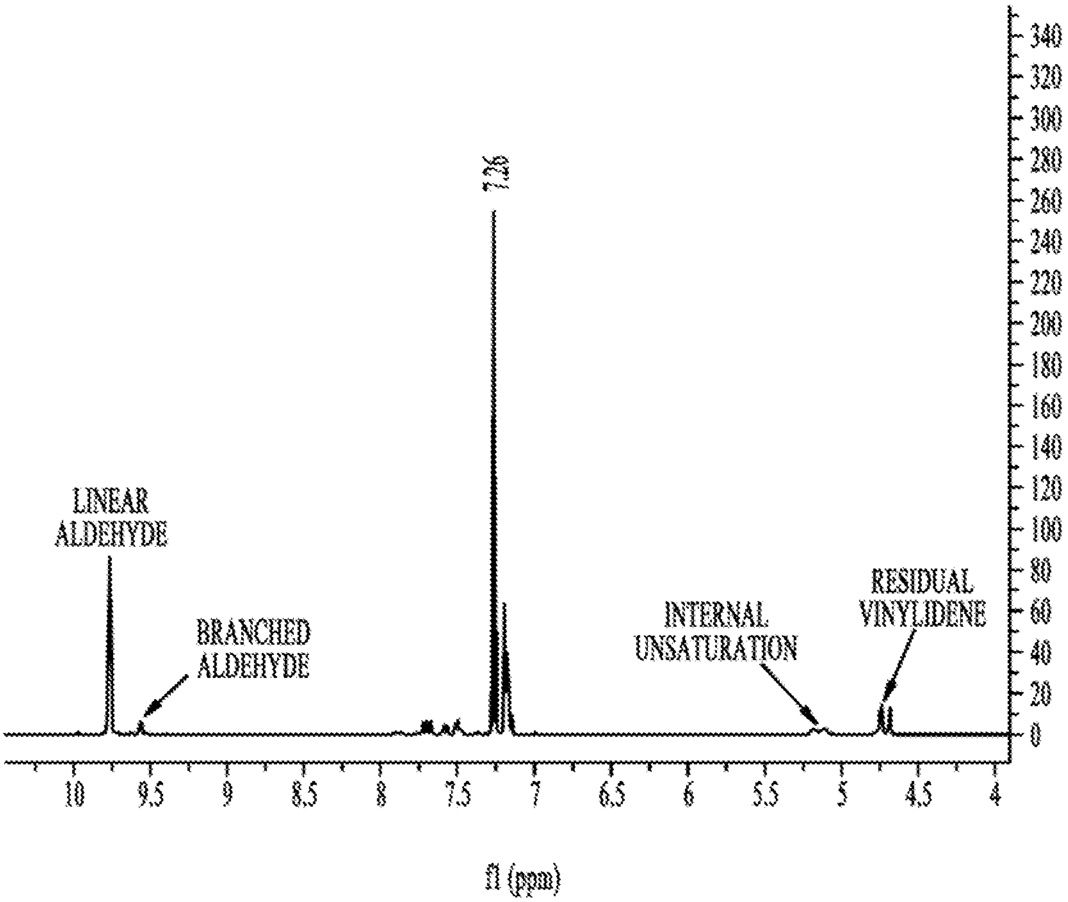

LINEAR ALDEHYDE
7.26
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

FIG. 4A



7.26
LINEAR ALDEHYDE
BRANCHED ALDEHYDE
INTERNAL UNSATURATION
RESIDUAL VINYLIDENE
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
f1 (ppm)

FIG. 4B

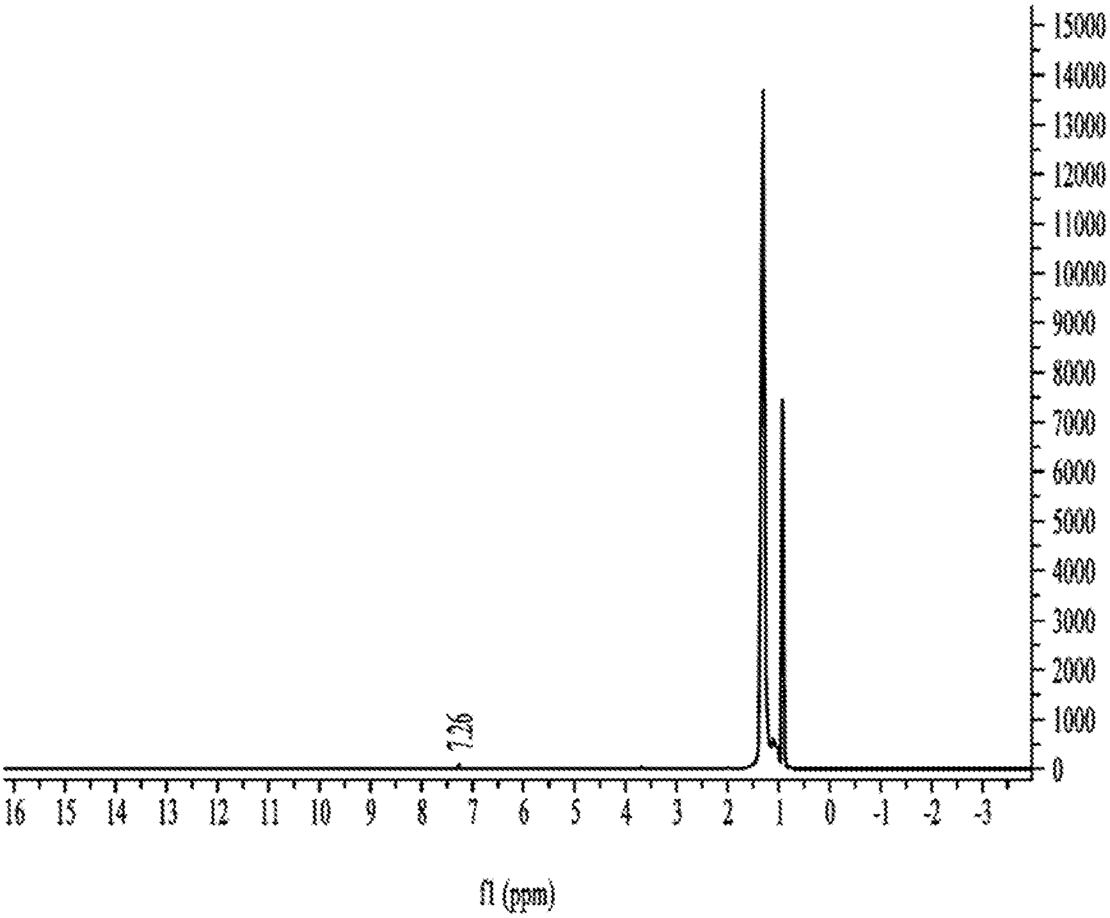

7.26
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)

FIG. 5A

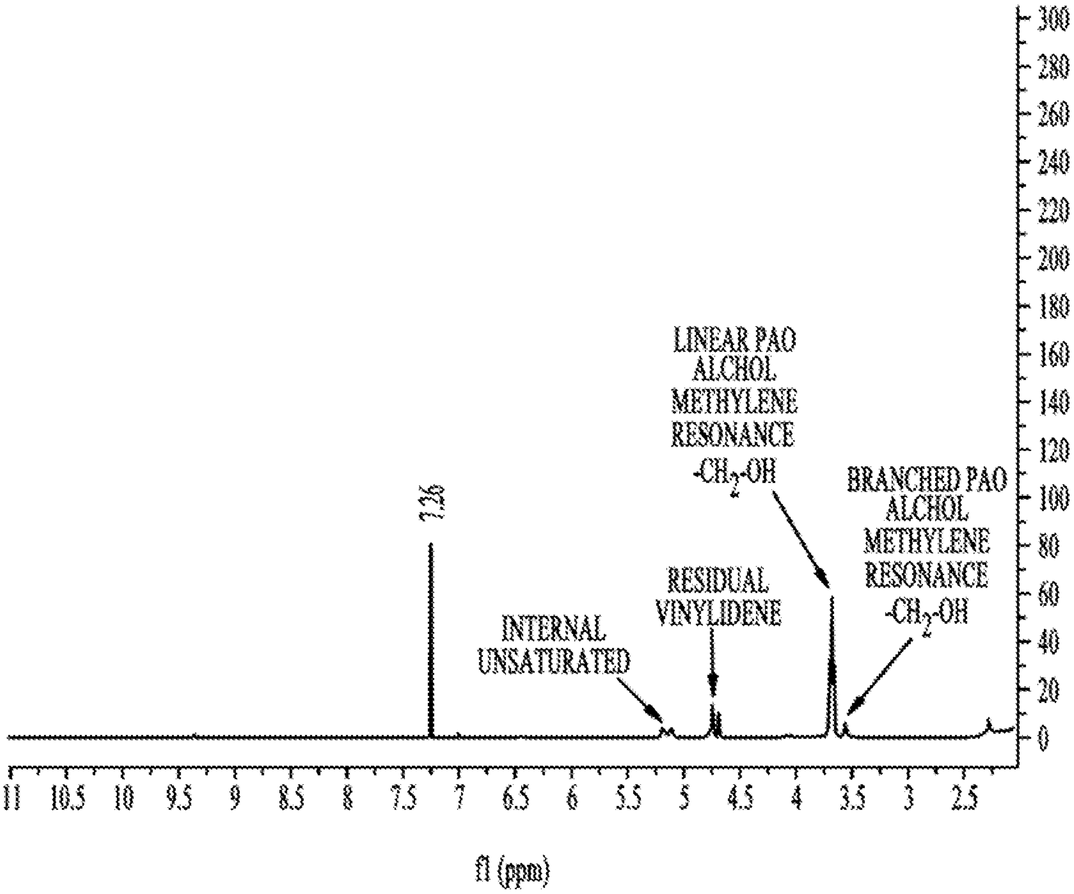

7.26
LINEAR PAO ALCHOL METHYLENE RESONANCE $-CH_2-OH$
BRANCHED PAO ALCHOL METHYLENE RESONANCE $-CH_2-OH$
RESIDUAL VINYLIDENE
INTERNAL UNSATURATED
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
11
10.5
10
9.5
9
8.5
8
7.5
7
6.5
6
5.5
5
4.5
4
3.5
3
2.5
f1 (ppm)

FIG. 5B

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/034968

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M129/90 C08F8/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M C08F C10N

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 919 869 A (THALER WARREN A [US] ET AL) 6 July 1999 (1999-07-06) Example 2, sample (3) starting from polybutene-1 column 1, lines 13-17 column 2, line 65 - column 3, line 37 column 4, lines 20-45 -----	1-34
A	US 2009/270296 A1 (PATIL ABHIMANYU ONKAR [US] ET AL) 29 October 2009 (2009-10-29) paragraphs [0001], [0006] - [0010], [0038], [0039], [0052], [0056] paragraph [0066]; examples 2-6; tables I, II ----- -/--	1-34

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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

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"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 4 September 2019	Date of mailing of the international search report 24/09/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Bork, Ana-Maria

1

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	NICOLE M. G. FRANSSEN ET AL: "Synthesis of functional 'polyolefins': state of the art and remaining challenges", CHEMICAL SOCIETY REVIEWS, vol. 42, no. 13, 1 January 2013 (2013-01-01), page 5809, XP055272709, UK ISSN: 0306-0012, DOI: 10.1039/c3cs60032g cited in the application Paragraph 4.3; Schemes 35, 37 -----	1-34
A	US 2018/037521 A1 (ISLAM MD SAFATUL [US] ET AL) 8 February 2018 (2018-02-08) cited in the application paragraphs [0009], [0046], [0047], [0070], [0074] paragraphs [0077] - [0081], [0083]; examples 1-11; tables II, III -----	1-34

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2019/034968

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5919869 A	06-07-1999	AU 1973895 A	25-09-1995
		BR 9507050 A	02-09-1997
		CA 2183270 A1	14-09-1995
		DE 69509760 D1	24-06-1999
		DE 69509760 T2	21-10-1999
		EP 0750643 A1	02-01-1997
		JP H09510241 A	14-10-1997
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		US 5880219 A	09-03-1999
		US 5919869 A	06-07-1999
		WO 9524431 A1	14-09-1995
US 2009270296 A1	29-10-2009	US 2009270296 A1	29-10-2009
		WO 2009131765 A1	29-10-2009
US 2018037521 A1	08-02-2018	NONE	