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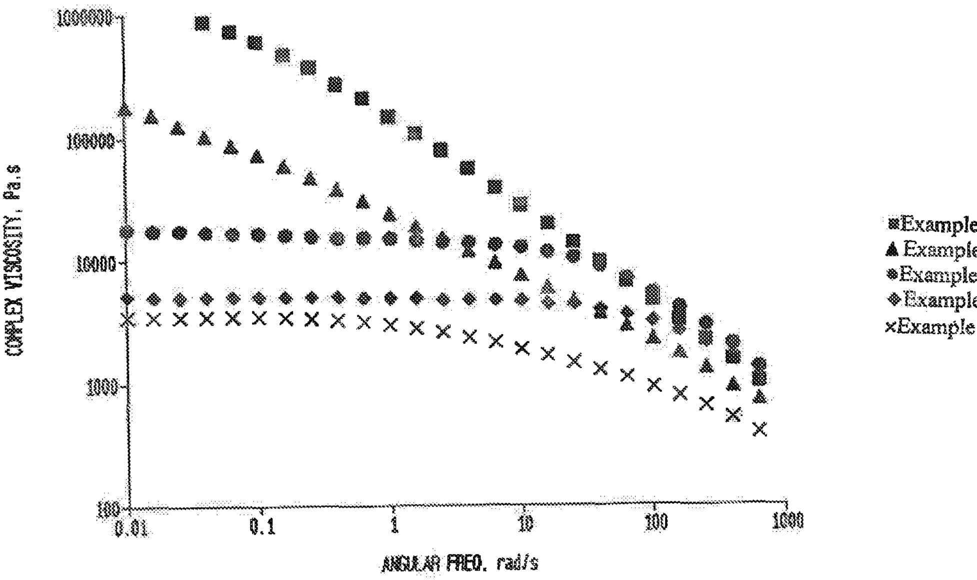

FIG. 1

(57) Abstract: In some embodiments, ethylene-propylene branched copolymers are synthesized with pyridyldiamido catalysts and a chain transfer agent, and their performance as viscosity modifiers in oil are detailed. In some embodiments, the present disclosure provides for ethylene-propylene branched copolymers having a shear thinning onset of less than about 0.01 rad/s and an HTHS value of less than about 3.3. In some embodiments, the ethylene-propylene branched copolymer is used as a viscosity modifier in a lubricating composition and a fuel composition.

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ETHYLENE-PROPYLENE BRANCHED COPOLYMERS AS VISCOSITY MODIFIERS WITH ENHANCED FUEL ECONOMY

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CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application 62/640,307, filed March 8, 2018.

FIELD

[0002] The present disclosure relates to a process to produce long chain branched polymers from pyridyldiamido transition metal complexes and the use of such polymers as lubricant additives, such as viscosity modifiers.

BACKGROUND

[0003] Lubrication fluids are applied between moving surfaces to reduce friction, thereby improving efficiency and reducing wear. Lubrication fluids also often function to dissipate the heat generated by moving surfaces.

[0004] One type of lubrication fluid is a petroleum-based lubrication oil used for internal combustion engines. Lubrication oils contain additives that help the lubrication oil to have a certain viscosity at a given temperature. In general, the viscosity of lubrication oils and fluids is inversely dependent upon temperature. When the temperature of a lubrication fluid is increased, the viscosity generally decreases, and when the temperature is decreased, the viscosity generally increases. For internal combustion engines, for example, it is desirable to have a lower viscosity at low temperatures to facilitate engine starting during cold weather, and a higher viscosity at higher ambient temperatures when lubrication properties typically decline.

[0005] Additives for lubrication fluids and oils include rheology modifiers, such as viscosity index (VI) improvers. VI improving components, many of which are derived from ethylene-alpha-olefin copolymers, 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.

[0006] 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.

[0007] The use of blends of amorphous and semi-crystalline ethylene-based copolymers for lubricant oil formulations has allowed for increased thickening efficiency, shear stability index, low temperature viscosity performance and pour point. See, e.g., U.S. Patent Nos. 7,402,235 and 5,391,617, and European Patent 0 638,611, the disclosures of which are incorporated herein by reference.

[0008] Currently, for olefin-based viscosity modifier applications, commercial materials are linear ethylene-propylene polymers (either random or blocks of ethylene- or propylene-rich). Other commercial materials such as SV and PMAs have different molecular architectures.

[0009] There remains a need, however, for novel rheology modifier compositions comprised of ethylene and alpha-olefin-based copolymers suitable for use as VI improvers which have good high temperature thermal-oxidative stability, high temperature corrosion resistance, low frictional property, low cold crank viscosity, and low gelation property while still having excellent low temperature solution rheological properties. Moreover, there remains a need for highly-branched ethylene-propylene- based polymer viscosity modifiers (EP-based VMs) which have close performance to other commercial products but at lower costs.

[0010] References of interest include: 1) U.S. Publication No. 2014/0256893; 2) U.S. Publication No. 2015/0141596; 3) U.S. Patent No. 8,053,529; 4) U.S. Patent No. 8,188,200; 5) U.S. Patent No. 8,338,557; 6) U.S. Publication No. 2015/0141601; 7) U.S. Patent No. 7,087,686; 8) U.S. Patent No. 7,928,164; 9) U.S. Patent No. 9,580,533; 10) U.S. Patent No. 6,300,451; 11) U.S. Patent No. 5,670,595; 12) *A. Valente, et al.*, Chem. Rev., 2013, 113, 3836-3857; 13) Vaughan, A; Davis, D.S.; Hagadorn, J. R. in Comprehensive Polymer Science, Vol. 3, Chapter 20, “Industrial catalysts for alkene polymerization”; 14) Gibson, V. C.; Spitzmesser, S. K. Chem. Rev. 2003, 103, 283; 15) Britovsek, G. J.P.; Gibson, V. C.; Wass, D. F. Angew. Chem. Int. Ed. 1999, 38, 428; 16) International Publication No. WO 2006/036748; 17) McGuire, R. et al. Coordination Chemistry Reviews, Vol 254, No. 21-22, pages 2574-2583 (2010); 18) U.S. Patent No. 4,540,753; 19) U.S. Patent No. 4,804,794; 20) P. Chem. Rev. 2013, 113, 3836-38-57; 21) J. Am. Chem. Soc. 2005, 127, 9913-9923; 22) Lub. Sci. 1989, 1, 265-280; 23) Lubricant Additives, Chemistry and Applications, pages 293-327, CRC Press, 2003; 24) Chemistry and Technology of Lubricants, 3rd edition, pages 153-187, Springer, 2010; 25) U.S. Publication No. 2013-0131294; 26) U.S. Publication No. 2002/0142912; 27) U.S. Patent No. 6,900,321; 28) U.S. Patent No. 6,103,657; 29)

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SUMMARY

[0011] The present disclosure relates to methods for olefin polymerization. More specifically, the present disclosure relates to the synthesis of ethylene-propylene (EP) branched copolymers using pyridyldiamido (PDA) catalyst and an added chain transfer agent (CTA) and their performance as viscosity modifiers in oil.

[0012] Methods include a two stage process where living polymer chains produced in a first polymerization stage are reacted in a subsequent polymerization stage with diene monomer to crosslink the living ends of the polymer chains to form long-chain branched polyolefin. This process yields polyolefin containing high levels of long-chain branching, but without the formation of gels that cause reactor fouling. The highly branched polymers can be combined with base stock oils, fuels, additives, or other similar materials. In such cases, the branched polymers act as viscosity modifiers.

[0013] In an embodiment, a method of making a lubricating oil composition includes: blending a base stock oil with a branched polymer having: an Mw(LS)/Mn(DRI) of from about 1.0 to about 6.0; an Mw(LS) of from about 3,000 to about 1,000,000 g/mol; a g'vis (branching index) of 0.90 or less; and an ethylene content of about 40% to about 80% or less.

[0014] In at least some embodiments, the method includes contacting ethylene and one or more C_3 to C_{40} alpha-olefins with a catalyst system comprising a non-metallocene catalyst, an activator, and a reversible chain transfer agent to form a first polymer; contacting the first polymer with a coupling agent in the presence of the first catalyst system or a second catalyst system comprising a second non-metallocene catalyst and a second activator; obtaining a second polymer; and blending the second polymer with a base stock oil.

[0015] In at least some embodiments, a method of making a lubricating oil composition includes: contacting ethylene and one or more C_3 to C_{40} alpha-olefins (which can include one or more mono-reactive dienes) with a catalyst system comprising a non-metallocene catalyst, an activator, and a reversible chain transfer agent in a first reactor to form a first polymer; transferring the first polymer and reactor effluent into a second reactor and contacting the first polymer and reactor effluent with a coupling agent (and optionally one or more alpha-olefins (which can include one or more dienes), and optionally a second catalyst and a second activator; obtaining a second polymer; and blending the second polymer with a base stock oil.

[0016] In at least some embodiments, the branched polymer has a high temperature, high shear (HTHS) viscosity of about 4.0 or less; and a kinematic viscosity (KV) at 100°C of about 15 cSt or less; and thickening efficiency is 5 or less to shear stability index (30 cycles) is 80 or less.

BRIEF DESCRIPTION OF THE FIGURE

[0017] So that the manner in which the above recited features of the present disclosure can be understood in detail, a more particular description of the disclosure, briefly summarized above, may be had by reference to embodiments, some of which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only exemplary embodiments and are therefore not to be considered limiting of its scope, for the disclosure may admit to other equally effective embodiments.

[0018] Fig. 1 is a dynamic frequency sweep on neat polymers at 190°C, according to one embodiment.

DETAILED DESCRIPTION

[0019] Viscosity modifiers, when added to oils, reduce the tendency of the oil to change its viscosity with temperature in order to improve its viscosity index (VI) and flow characteristics. Improving VI helps in maintaining constant the flow properties of the protective oil film. This means a high enough viscosity to avoid damage on engine parts when the temperature rises because of the engine heat and a low enough viscosity against the cold start and pumping.

[0020] To make sure the viscosity modifier (VM) is used in a cost-effective way, polymer thickening efficiency is important. 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 having a high value of TE indicates that it is a potent thickener.

[0021] TE is primarily a function of polymer chemistry and molecular weight. Large molecules are better thickeners than small ones and, at the same molecular weight, some polymer chemistries are better thickeners than others. There is a trade-off, though. While large molecules are good thickeners, they are also more easily broken, which impacts the shear stability of the oil. A polymer's shear stability index (SSI) is defined as its resistance to mechanical degradation under shearing stress.

[0022] Commercial olefin copolymer-based (OCP-based) viscosity modifiers are linear polymers.

[0023] Viscosity modifiers with branched structures have been discovered to provide better fuel economy than their linear counterparts. The novel branched OCPs of the present disclosure have improved fuel economy benefits over the commercial products.

[0024] Poly(ethylene-propylene) copolymers with high level of branching can be made via pyridyldiamido (PDA) catalysts and diethylzinc chain transfer agent (CTA) followed by the addition of dienes via a 2-staged coordinated chain transfer polymerization method. Blending the polymers with base oils, and optionally additives, provides novel lubricating compositions.

[0025] OCP characteristics that have been discovered to affect lubricant properties are the ratio of ethylene to propylene, the molecular weight of the polymer, and the molecular weight distribution of the polymer. Ethylene-propylene ratio mainly affects thickening power (TP) and low temperature properties (cold cranking simulator (CCS) and pour point (PP)). Molecular weight acts on thickening power (TP) and permanent shear stability index (PSSI). Molecular weight distribution has a major influence on PSSI.

[0026] The copolymer influences the viscometric properties of a base stock. Base stocks are affected by many properties including kinematic viscosity (KV), where an inverse relationship exists between KV and low-temperature fluidity, and VI, where a direct relationship exists between VI and low-temperature fluidity. Increasing the VI of a base stock by adding copolymers provides improved viscometrics under both low-temperature and high-temperature regimes. VI itself represents the change in viscosity over a temperature range from 40°C to 100°C. The higher the VI, the lower the oil's viscometric properties will change, and the flatter its profile will be over the temperature range. This can be extended to higher and lower temperatures.

[0027] In this disclosure, EP branched copolymers are synthesized from pyridyldiamido (PDA) catalyst and an added chain transfer agent (CTA) and are added to oil. In at least some embodiments, the EP copolymers produced by the methods disclosed herein have an Mw(LS) greater than about 100 kg/mol, more preferred greater than about 200 kg/mol, most preferred greater than about 400 kg/mol. In at least some embodiments, the ethylene content is preferred to be less than about 70 wt%, more preferred less than about 60 wt%, most preferred less than about 50 wt%.

[0028] For purposes herein, the numbering scheme for the Periodic Table Groups is used as described in CHEMICAL AND ENGINEERING NEWS, 63(5), pg. 27 (1985). For example, a "Group 4 metal" is an element from Group 4 of the Periodic Table, e.g., Hf, Ti, or Zr.

[0029] As used herein, an "olefin," alternatively referred to as "alkene," is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond. 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 an "ethylene" content of 35 wt% to 55 wt%, it is understood that the monomer ("mer") unit in the copolymer is derived from ethylene in the polymerization reaction and said derived units are present at 35 wt% to 55 wt%, based upon the weight of the copolymer.

[0030] A "polymer" has two or more of the same or different monomer ("mer") units. A "homopolymer" is a polymer having mer units that are the same. A "copolymer" is a polymer having two or more mer units that are different from each other. A "terpolymer" is a polymer having three mer units that are different from each other. "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. Accordingly, the definition of copolymer, as used herein, includes terpolymers.

[0031] For purposes of this disclosure, ethylene shall be considered an α-olefin.

[0032] As used herein, the term "substituted" means that a hydrogen group has been replaced with a heteroatom, or a heteroatom-containing group. For example, a "substituted hydrocarbyl" is a radical made of carbon and hydrogen where at least one hydrogen is replaced by a heteroatom or heteroatom-containing group.

[0033] As used herein, Mn is number average molecular weight, Mw is weight average molecular weight, and Mz is z average molecular weight, wt% is weight percent, and mol% is mole percent. Molecular weight distribution (MWD), also referred to as polydispersity (PDI), is defined to be Mw divided by Mn. Unless otherwise noted, all molecular weight units (e.g., Mw, Mn, Mz) are g/mol.

[0034] Copolymers (and terpolymers) of polyolefins have a comonomer, such as propylene, incorporated into the polyethylene backbone. These copolymers (and terpolymers) provide varying physical properties compared to polyethylene alone and are typically produced in a low pressure reactor, utilizing, for example, solution, slurry, or gas phase polymerization processes. The comonomer content of a polyolefin (e.g., wt% of comonomer incorporated into a polyolefin backbone) influences the properties of the polyolefin (and composition of the copolymers) and is dependent on the identity of the polymerization catalyst.

[0035] "Linear" means that the polymer has few, if any, long chain branches and typically has a g'vis value of 0.97 or above, such as 0.98 or above.

[0036] The term "cyclopentadienyl" refers to a 5-member ring having delocalized bonding within the ring and typically being bound to M through η^5-bonds, carbon typically making up the majority of the 5-member positions.

[0037] As used herein, a "catalyst" includes a single catalyst, or multiple catalysts with each catalyst being conformational isomers or configurational isomers. Conformational isomers include, for example, conformers and rotamers. Configurational isomers include, for example, stereoisomers.

[0038] The term "complex," may also be referred to as catalyst precursor, precatalyst, catalyst, catalyst compound, transition metal compound, or transition metal complex. These words are used interchangeably. Activator and cocatalyst are also used interchangeably.

[0039] Unless otherwise indicated, the term "substituted" generally means that a hydrogen of the substituted species has been replaced with a different atom or group of atoms. For example, methyl-cyclopentadiene is cyclopentadiene that has been substituted with a methyl group. Likewise, picric acid can be described as phenol that has been substituted with three nitro groups, or, alternatively, as benzene that has been substituted with one hydroxy and three nitro groups.

[0040] The following abbreviations may be used herein: dme is 1,2-dimethoxyethane, Me is methyl, Et is ethyl, Pr is propyl, cPr is cyclopropyl, nPr is normal propyl, iPr is isopropyl, Bu is butyl, nBu is normal butyl, iBu is isobutyl, sBu is sec-butyl, tBu is tert-butyl, p-tBu is para-tert-butyl, Ph is phenyl, Bn is benzyl (i.e., CH_2Ph), Oct is octyl, Cy is cyclohexyl, TMS is trimethylsilyl, TIBAL is triisobutylaluminum, TNOAL is tri(n-octyl)aluminum, MAO is methylalumoxane, p-Me is para-methyl, THF (also referred to as thf) is tetrahydrofuran, RT is room temperature (and is 23°C unless otherwise indicated), tol is toluene, and EtOAc is ethyl acetate.

[0041] An “anionic ligand” is a negatively charged ligand that donates one or more pairs of electrons to a metal ion. A “neutral donor ligand” is a neutrally charged ligand which donates one or more pairs of electrons to a metal ion.

[0042] As used herein, a “catalyst system” includes at least one catalyst compound and a support material. A catalyst system of the present disclosure can further include an activator and an optional co-activator. For the purposes of this disclosure and claims thereto, when catalyst systems are described as comprising neutral stable forms of the components, it is well understood by one of ordinary skill in the art, that the ionic form of the component is the form that reacts with the monomers to produce polymers. Furthermore, catalysts of the present disclosure represented by a Formula are intended to embrace ionic forms thereof of the compounds in addition to the neutral stable forms of the compounds. Furthermore, activators of the present disclosure are intended to embrace ionic/reaction product forms thereof of the activator in addition to ionic or neutral form.

[0043] A scavenger is a compound that can be added to a reactor to facilitate polymerization by scavenging impurities. Some scavengers may also act as chain transfer agents. Some scavengers may also act as activators and may be referred to as co-activators. A co-activator, that is not a scavenger, may also be used in conjunction with an activator in order to form an active catalyst. In some embodiments, a co-activator can be pre-mixed with the transition metal compound to form an alkylated transition metal compound. Examples of scavengers include trialkylaluminums, methylalumoxanes, modified methylalumoxanes such as MMAO-3A (Akzo Nobel), bis(diisobutylaluminum)oxide (Akzo Nobel), tri(n-octyl)aluminum, triisobutylaluminum, and diisobutylaluminum hydride.

[0044] As used herein, “alkoxides” include those where the alkyl group is a C_1 to C_{10} hydrocarbyl. The alkyl group may be straight chain, branched, or cyclic. The alkyl group may be saturated or unsaturated. In some embodiments, the alkyl group may include at least one aromatic group.

[0045] The terms “hydrocarbyl radical,” “hydrocarbyl,” “hydrocarbyl group,” “alkyl radical,” and “alkyl” are used interchangeably throughout this document. Likewise, the terms “group,” “radical,” and “substituent” are also used interchangeably in this document. For purposes of this disclosure, “hydrocarbyl radical” refers to C_1 to C_{100} radicals, that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic. Examples of such radicals include methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and their substituted analogues. Substituted analogues of hydrocarbyl radicals are radicals in which at least one hydrogen atom of the hydrocarbyl radical has been substituted with at least one halogen (such as Br, Cl, F or I) or at least one functional group such as C(O)R*, C(O)NR*$_2$, C(O)OR*, NR*$_2$, OR*, SeR*, TeR*, PR*$_2$, AsR*$_2$, SbR*$_2$, SR*, BR*$_2$, SiR*$_3$, GeR*$_3$, SnR*$_3$, and PbR*$_3$ (where R* is independently a hydrogen or hydrocarbyl radical, and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure), or where at least one heteroatom has been inserted within a hydrocarbyl ring.

[0046] The term “alkenyl” means a straight-chain, branched-chain, or cyclic hydrocarbon radical having one or more double bonds. These alkenyl radicals may be optionally substituted. Examples of suitable alkenyl radicals include ethenyl, propenyl, allyl, 1,4-butadienyl cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, cyclootenyl, including their substituted analogues. Substituted analogues of alkenyl radicals are radicals in which at least one hydrogen atom of the alkenyl radical has been substituted with at least one halogen (such as Br, Cl, F or I) or at least one functional group such as C(O)R*, C(O)NR*$_2$, C(O)OR*, NR*$_2$, OR*, SeR*, TeR*, PR*$_2$, AsR*$_2$, SbR*$_2$, SR*, BR*$_2$, SiR*$_3$, GeR*$_3$, SnR*$_3$, and PbR*$_3$ (where R* is independently a hydrogen or alkenyl radical, and two or more R* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure), or where at least one heteroatom has been inserted within an alkenyl ring.

[0047] The term “alkoxy” or “alkoxide” means an alkyl ether or aryl ether radical wherein the term alkyl is as defined above. Examples of suitable alkyl ether radicals include methoxy, ethoxy, n-propoxy, iso-propoxy, n-butoxy, iso-butoxy, sec-butoxy, tert-butoxy, and phenoxyl.

[0048] The term “aryl” or “aryl group” includes a C_4 to C_{20} aromatic ring, such as a six carbon aromatic ring, and the substituted variants thereof, including phenyl, 2-methyl-phenyl, xylyl, 4-bromo-xylyl. Likewise heteroaryl means an aryl group where a ring carbon atom (or two or three ring carbon atoms) has been replaced with a heteroatom, preferably N, O, or S. As used herein, the term “aromatic” also refers to pseudoaromatic heterocycles which are heterocyclic substituents that have similar properties and structures (nearly planar) to aromatic heterocyclic ligands, but are not by definition aromatic; likewise the term aromatic also refers to substituted aromatics.

[0049] Where isomers of a named alkyl, alkenyl, alkoxide, or aryl group exist (e.g., n-butyl, iso-butyl, iso-butyl, and tert-butyl) reference to one member of the group (e.g., n-butyl) shall expressly disclose the remaining isomers (e.g., iso-butyl, sec-butyl, and tert-butyl) in the family. Likewise, reference to an alkyl, alkenyl, alkoxide, or aryl group without specifying a particular isomer (e.g., butyl) expressly discloses all isomers (e.g., n-butyl, iso-butyl, sec-butyl, and tert-butyl).

[0050] For any particular compound disclosed herein, any general or specific structure presented also encompasses all conformational isomers, regioisomers, and stereoisomers that may arise from a particular set of substituents, unless stated otherwise. Similarly, unless stated otherwise, the general or specific structure also encompasses all enantiomers, diastereomers, and other optical isomers whether in enantiomeric or racemic forms, as well as mixtures of stereoisomers, as would be recognized by a skilled artisan.

[0051] The term "ring atom" means an atom that is part of a cyclic ring structure. By this definition, a benzyl group has six ring atoms and tetrahydrofuran has 5 ring atoms.

[0052] A heterocyclic ring is a ring having a heteroatom in the ring structure as opposed to a heteroatom-substituted ring where a hydrogen on a ring atom is replaced with a heteroatom. For example, tetrahydrofuran is a heterocyclic ring and 4-*N,N*-dimethylamino-phenyl is a heteroatom-substituted ring.

[0053] As used herein the term "aromatic" also refers to pseudoaromatic heterocycles which are heterocyclic substituents that have similar properties and structures (nearly planar) to aromatic heterocyclic ligands, but are not by definition aromatic; likewise, the term aromatic also refers to substituted aromatics.

[0054] The term "continuous" means a system that operates without interruption or cessation. For example a continuous process to produce a polymer would be one where the reactants are continually introduced into one or more reactors and polymer product is continually withdrawn during a polymerization process.

[0055] A solution polymerization means a polymerization process in which the polymer is dissolved in a liquid polymerization medium, such as an inert solvent or monomer(s) or their blends. A solution polymerization is typically homogeneous. A homogeneous polymerization is one where the polymer product is dissolved in the polymerization medium. Such systems are preferably not turbid as described in J. Vladimir Oliveira, C. Dariva and J. C. Pinto, Ind. Eng. Chem. Res., 2000, Vol. 29, p. 4627.

[0056] A bulk polymerization means a polymerization process in which the monomers and/or comonomers being polymerized are used as a solvent or diluent using little or no inert solvent as a solvent or diluent. A small fraction of inert solvent might be used as a carrier for catalyst and scavenger. A bulk polymerization system contains less than about 25 wt% of inert solvent or diluent, preferably less than about 10 wt%, preferably less than about 1 wt%, preferably about 0 wt%.

[0057] "Catalyst productivity" is a measure of how many grams of polymer (P) are produced using a polymerization catalyst comprising g (W) of catalyst (cat), over a period of time of T hours; and may be expressed by the following formula: P/(T x W) and expressed in units of $gPgcat^{-1}hr^{-1}$. "Conversion" is the amount of monomer that is converted to polymer product, and is reported as mol% and is calculated based on the polymer yield and the amount of monomer fed into the reactor. "Catalyst activity" is a measure of the level of activity of the catalyst and is reported as the mass of product polymer (P) produced per mole (or mmol) of catalyst (cat) used (kgP/molcat or gP/mmolCat), and catalyst activity can also be expressed per unit of time, for example, per hour (hr).

[0058] The term "pyridyldiamido complex" or "pyridyldiamide complex" or "pyridyldiamido catalyst" or "pyridyldiamide catalyst" refers to a class of coordination complexes described in U.S. Patent No. 7,973,116 B2, U.S. Publication Nos. 2012/0071616 Al, 2011/0224391 Al, and 2011/0301310 A1 that feature a dianionic tridentate ligand that is coordinated to a metal center through one neutral Lewis basic donor atom (e.g., a pyridine group) and a pair of anionic amido or phosphido (i.e., deprotonated amine or phosphine) donors. In these complexes the pyridyldiamido ligand is coordinated to the metal with the formation of one five membered chelate ring and one seven membered chelate ring. It is possible for additional atoms of the pyridyldiamido ligand to be coordinated to the metal without affecting the catalyst function upon activation; an example of this could be a cyclometalated substituted aryl group that forms an additional bond to the metal center.

[0059] Herein, "catalyst" and "catalyst complex" are used interchangeably.

Processes

[0060] The present disclosure provides methods for forming a lubricating oil composition. The method includes catalyst systems and polymerization processes. The catalyst systems described herein are useful in polymerizing unsaturated monomers conventionally known to undergo transition metal catalyzed coordinative polymerization. The catalyst systems may be used in a variety of polymerization processes such as solution, slurry, or gas-phase polymerizations; however, a solution polymerization process is preferred for the present application that requires reversible polymeryl group transfer between the catalyst and an added main-group metal chain transfer agent.

[0061] One or more reactors in series or in parallel may be used. The complexes, chain transfer agent, activator, and when desired, co-activator, may be delivered as a solution or slurry, either separately to the reactor, activated in-line just prior to the reactor, or preactivated and pumped as an activated solution or slurry to the reactor. Polymerizations are carried out in either single reactor operation, in which monomer, comonomers, catalyst/activator/co-activator, optional scavenger, and optional modifiers are added continuously to a single reactor or in series reactor operation, in which the above components are added to each of two or more reactors connected in series. The catalyst components can be added to the first reactor in the series. The catalyst component may also be added to both reactors, with one component being added to a first reactor and another component to other reactors. In one preferred embodiment, the complex is activated in the reactor in the presence of olefin.

[0062] Polymerization processes of the present disclosure can be carried out in any suitable manner known in the art. Any suspension, homogeneous, bulk, solution, slurry, or gas phase polymerization process known in the art can be used. Such processes can be run in a batch, semi-batch, or continuous mode. Homogeneous polymerization processes and slurry processes are preferred. (A homogeneous polymerization process is defined to be a process where at least about 90 wt% of the product is soluble in the reaction media.) A bulk homogeneous process is particularly preferred. (A bulk process is defined to be a process where monomer concentration in all feeds to the reactor is about 70 vol% or more.) Alternately, no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the carrier for the catalyst system or other additives, or amounts typically found with the monomer; e.g., propane in propylene). According to an embodiment, a method of polymerizing olefins to produce at least one polyolefin composition includes contacting at least one olefin with a catalyst system of the present disclosure; and obtaining a polyolefin. A method of polymerizing olefins can include introducing any catalyst system described herein into a reactor as a slurry.

[0063] Polymerization may be homogeneous (solution or bulk polymerization) or heterogeneous (slurry - in - liquid diluent, or gas phase - in - gaseous diluent). In the case of heterogeneous slurry or gas phase polymerization, the complex and activator may be supported.

[0064] In an embodiment, a method of making a lubricating oil composition is provided. The method includes: blending a base stock oil with a branched polymer having: an Mw(LS)/Mn(DRI) of from about 1.0 to about 6.0; an Mw(LS) of from about 3,000 to about 1,000,000 g/mol; a g'vis of 0.90 or less; and an ethylene content of about 40% to about 80% or less.

[0065] Alternately, in an embodiment, a method of making a lubricating oil composition includes: contacting ethylene and one or more C_3 to C_{40} alpha-olefins with a catalyst system comprising a non-metallocene catalyst, an activator, and a reversible chain transfer agent to form a first polymer; contacting the first polymer with a coupling agent in the presence of the first catalyst system or a second catalyst system comprising a second non-metallocene catalyst and a second activator; obtaining a second polymer; and blending the second polymer with a base stock oil. The second polymer can be a branched polymer.

[0066] In a first stage, one or more of the catalyst compounds of the present disclosure, one or more activators, one or more reversible chain transfer agents, and one or more C_2 to C_{40} alpha-olefins (including ethylene) are contacted to produce a first polymer. In a second stage, the mixture containing the first polymer is contacted with one or more coupling agents, optionally one or more of the catalyst compounds of the present disclosure, optionally one or more activators, and optionally one or more C_2 to C_{40} alpha-olefins (including ethylene), to form long-chain branched polymer. Preferably, a coupling agent is not introduced into the reactor during the first stage. Preferably, a reversible chain transfer agent is not introduced into the reactor during the second stage. Processes of the present disclosure provide reduced or eliminated gel formation, and mass recovery of about 50% by weight or greater based on the total weight of polymer product of a polymerization, as determined by gel permeation chromatography. Comparatively, a coupling agent present in the reactor during the first stage forms an intractable network gel with a low mass recovery of less than 30%.

[0067] In at least some embodiments, the catalyst system of the first stage and the catalyst system of the second stage each have one catalyst.

[0068] For the first stage and second stage, the catalyst compound and activator may be introduced to the reactors as separate solutions, slurries, or suspensions. Alternatively, the catalyst compound and activator may be combined together as a slurry, suspension, or solution prior to introduction to the reactors. The catalyst compound and activator are combined typically prior to contacting the catalyst system with the reversible chain transfer agent in the first stage. The catalyst compound and activator are combined typically prior to contacting the catalyst system with the coupling agent in the second stage. In some embodiments, additional catalyst and activator are not added during the second stage, and residual catalyst from the first stage is used to promote the crosslinking of the living polymer chains with the coupling agent.

[0069] The first stage and the second stage can (1) be performed in the same reactor or (2) be performed in different reactors where the ethylene polymer/copolymer of the first stage is transferred to a second reactor and the second stage is then performed. A catalyst compound of the first stage can be the same as or different than a catalyst compound of the second stage. Similarly, an activator of the first stage can be the same as or different than an activator of the second stage. For purposes of the present disclosure, one catalyst compound or activator is considered different from another if they differ by at least one atom. For example, $(iPrCp)(Cp)ZrCl_2$ is different that Cp_2ZrCl_2, which is different from $(iPrCp)_2ZrCl_2$.

[0070] The process described herein is a solution polymerization process that may be performed in a batchwise fashion or in a continuous process. Suitable reactors include tank, loop, and tube designs. In some embodiments, the process is performed in a continuous fashion and dual loop reactors in a series configuration are used. In some embodiments, the process is performed in a continuous fashion and dual continuous stirred-tank reactors (CSTRs) in a series configuration are used. In some embodiments, the process is performed in a continuous fashion and a tube reactor is used. In some embodiments, the process is performed in a continuous fashion and one loop reactor and one CSTR are used in a series configuration. In some embodiments, the process is performed in a batchwise fashion and a single stirred tank reactor is used.

[0071] In the first stage, one or more reactors in series or in parallel may be used. The complexes, activator, and reversible chain transfer agent, may be delivered as a solution, neat liquid, or slurry, either separately to the reactor, activated in-line just prior to the reactor, or preactivated and pumped as an activated solution or slurry to the reactor. Polymerizations are carried out in either single reactor operation, in which monomer, comonomers, catalyst/activator/co-activator, optional scavenger, reversible chain transfer agent, and optional modifiers are added continuously to a single reactor or in series reactor operation, in which the above components may be added to each of two or more reactors connected in series. The components can be added to the first reactor in the series. The components may also be added to both reactors, with one component, such as an activator, being added to the first reactor and another component, such as a coupling agent, to the second reactor. In one preferred embodiment, the complex is activated in the reactor in the presence of olefin.

[0072] In the second stage, one or more reactors in series or in parallel may be used. The coupling agent and optional catalyst and activator, may be delivered as a solution, neat liquid, or slurry, either separately to the reactor, activated in-line just prior to the reactor, or preactivated and pumped as an activated solution or slurry to the reactor. Polymerizations and crosslinkings are carried out in either single reactor operation, in which catalyst/activator/co-activator, coupling agent, monomer, optional comonomer, optional scavenger, and optional modifiers are added to a single reactor or in series reactor operation, in which the above components are added to each of two or more reactors connected in series. The components can be added to the first reactor in the series. The component may also be added to both reactors, with one component, such as an activator, being added to the first reactor and another component, such as a coupling agent, to the second reactor. If the reaction is performed in a single reactor then the addition of the crosslinking agent (i.e., second stage) occurs after the first stage of the polymerization has been completed. In one preferred embodiment, the complex is activated in the reactor in the presence of olefin.

[0073] Any suitable process may be used to prepare the polymers of the first stage of the polymerization or crosslinking process of the second stage including the use of a single continuous flow stirred tank reactor (CSTR). Other modifications, such as the use of two reactors in series or parallel to tailor the MWD of the polymer, are also contemplated.

[0074] In a preferred embodiment, the polymerization process of the first stage of the polymerization or crosslinking process of the second stage is performed in a batch reactor, semi-continuous batch reactor, a CSTR reactor or tubular reactor or a combination thereof.

[0075] In a particularly preferred embodiment, the polymerization process of the first stage of the polymerization and/or crosslinking process of the second stage is a continuous process.

[0076] Processes of the first stage and/or the second stage of the present disclosure can be carried out in any suitable manner, such as any suitable bulk, or solution polymerization process. Such processes can be run in a batch, semi-batch, or continuous mode. Solution phase polymerization processes are preferred. A solution process is a process where at least about 90 wt% of the product is soluble in the reaction media. A bulk process is a process where monomer concentration in all feeds to the reactor is about 70 volume% or more.

Alternatively, no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the carrier for the catalyst system or other additives, or amounts typically found with the monomer; e.g., propane in propylene).

[0077] Suitable diluents/solvents for polymerization and/or crosslinking include non-coordinating, inert diluents/solvents. Examples include straight and branched-chain hydrocarbons, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof, such as can be found commercially (Isopar™, which is isoparaffins); perhalogenated hydrocarbons, such as perfluorinated C_4 to C_{10} alkanes, chlorobenzene, and aromatic and alkylsubstituted aromatic compounds, such as benzene, toluene, mesitylene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, 1-butene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. In at least some embodiments, aliphatic hydrocarbon solvents are used as the solvent, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof. In some embodiments, the solvent is not aromatic, preferably aromatics are present in the solvent at less than about 1 wt%, preferably less than about 0.5 wt%, preferably about 0 wt% based upon the weight of the solvents.

[0078] In some embodiments, the feed concentration of the monomers and comonomers for the polymerization is from about 1 vol% in solvent to about 60 vol% in solvent, such as about 1 vol% in solvent to about 40 vol% in solvent, such as about 1 vol% in solvent to about 20 vol% in solvent, based on the total volume of the feedstream. In some embodiments, the polymerizations can be run in a bulk process.

[0079] Preferred processes of the first stage and/or second stage can be run at any temperature and/or pressure suitable to obtain the desired polymers. Typical temperatures and/or pressures include a temperature in the range of from about 0°C to about 300°C, such as about 50°C to 200°C, such as about 75°C to about 150°C, such as from about 85°C to about 100°C, such as from about 100°C to about 135°C; and at a pressure from about 0.20 MPa to about 1500 MPa, such as from about 0.20 MPa to about 25 MPa, such as from about 0.45 MPa to about 13 MPa, such as from about 1 MPa to about 12 MPa, such as from about 0.2 MPa to about 0.5 MPa, for example about 1.5 MPa or about 8 MPa.

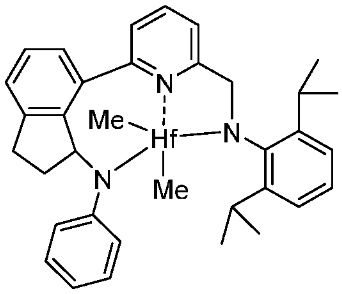
[0080] In typical processes of the first stage and/or second stage, the average residence time of the reaction in each reactor is from about 0 to about 300 minutes, such as from about 6 to about 60 minutes, such as from about 15 minutes to about 60 minutes, such as from about 10 to about 45 minutes, such as from about 10 to about 30 minutes. For a process using two continuous reactors (CSTR or loop) in series, each continuous reactor will preferably have a residence time of from about 15 to about 60 minutes. In at least some embodiments, an average period of time between the end of the first stage and the beginning of the second stage is from about 0 minutes to about 300 minutes, such as from about 0.1 minutes to about 100 minutes, such as from about 0.5 minutes to about 30 minutes, such as about from about 0.3 minutes to about 15 minutes, such as from about 1 minute to about 5 minutes.

[0081] In some embodiments hydrogen is present in the polymerization reactor at a partial pressure of about 0.000007 to about 0.7 MPa, preferably from about 0.007 to about 0.2 MPa, preferably from about 0.01 to about 0.1 MPa. In at least some embodiments, hydrogen is not present in the polymerization reactor (or kept below about 0.000007 MPa) while the first stage is being performed so as not to interfere with polymer chelation with the metal of the chain transfer agent, e.g., form unreactive “dead” polymer chains. In at least some embodiments, hydrogen is not present in the polymerization reactor (or kept below about 0.1 psig) while the second stage is being performed so as not to initiate the growth of new polymer chains in the presence of the coupling agent, which will increase the unwanted formation of reactor gels.

Solution Polymerization

[0082] A solution polymerization is a polymerization process in which the polymer is dissolved in a liquid polymerization medium, such as an inert solvent or monomer(s) or their blends. A solution polymerization is typically homogeneous. A homogeneous polymerization is one where the polymer product is dissolved in the polymerization medium. Such systems are preferably not turbid as described in J. Vladimir Oliveira, C. Dariva and J. C. Pinto, Ind. Eng, Chem. Res. 29, 2000, 4627. Generally, solution polymerization involves polymerization in a continuous reactor in which the polymer formed, the starting monomer and catalyst materials supplied are agitated to reduce or avoid concentration gradients and in which the monomer acts as a diluent or solvent or in which a hydrocarbon is used as a diluent or solvent. Suitable processes typically operate at temperatures from about 0°C to about 250°C, preferably from about 50°C to about 170°C, more preferably from about 80°C to about 150°C, more preferably from about 100°C to about 140°C and at pressures of about 0.1 MPa or more, preferably 2 MPa or more. The upper pressure limit is not critically constrained but typically can be about 200 MPa or less, preferably 120 MPa or less, preferably 30 MPa or less. Temperature control in the reactor can generally be obtained by balancing the heat of polymerization and with reactor cooling by reactor jackets or cooling coils to cool the contents of the reactor, auto refrigeration, pre-chilled feeds, vaporization of liquid medium (diluent, monomers or solvent) or combinations of all three. Adiabatic reactors with pre-chilled feeds can also be used. The purity, type, and amount of solvent can be optimized for the maximum catalyst productivity for a particular type of polymerization. The solvent can be also introduced as a catalyst carrier. The solvent can be introduced as a gas phase or as a liquid phase depending on the pressure and temperature. Advantageously, the solvent can be kept in the liquid phase and introduced as a liquid. Solvent can be introduced in the feed to the polymerization reactors.

[0083] In at least some embodiments, the pyridyldiamido transition metal complex is Catalyst 1:



(Catalyst 1); and the activator is N,N-dimethylanilinium tetra(perfluorophenyl)borate.

Alpha-Olefin Monomers

[0084] Monomers and comonomers useful for the first and/or second stage include substituted or unsubstituted C_2 to C_{40} alpha-olefins, alternatively C_2 to C_{20} alpha-olefins, alternatively C_2 to C_{12} alpha-olefins, preferably ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, styrene, p-methylstyrene, norbornene, 1,4-hexadiene, and 5-ethylidene-2-norbornene) and isomers thereof, and combinations thereof.

[0085] In some embodiments one or more dienes are present in the polymer produced herein at up to about 10 wt%, preferably at about 0.00001 to about 5.0 wt%, preferably about 0.002 to about 2 wt%, preferably at about 0.03 to about 1 wt%, even more preferably about 0.03 to about 0.2 wt%, based upon the total weight of the composition. In some embodiments about 500 ppm or less of diene is added to the polymerization, preferably about 400 ppm or less, preferably about 300 ppm or less. In other embodiments at least about 50 ppm of diene is added to the polymerization, or about 100 ppm or more, or about 150 ppm or more. Preferred diolefin monomers useful in the present disclosure include any hydrocarbon structure, preferably C_4 to C_{30}, having at least two unsaturated bonds, wherein at least two of the unsaturated bonds are readily incorporated into a polymer by either a stereospecific or a non-stereospecific catalyst(s). It is further preferred that the diolefin monomers be selected from alpha, omega-diene monomers (i.e., di-vinyl monomers). More preferably, the diolefin monomers are linear di-vinyl monomers, most preferably those containing from 4 to 30 carbon atoms. Examples of preferred dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene, tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene, triacontadiene, particularly preferred dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, and low molecular weight polybutadienes (Mw less than about 1000 g/mol). Preferred cyclic dienes include cyclopentadiene, vinylnorbornene, norbornadiene, ethylidene norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions.

[0086] The complexes described herein are particularly effective for the polymerization of ethylene and at least one other alpha-olefin monomer, such as a C_3 to C_{20} alpha-olefin, and particularly a C_3 to C_{12} alpha-olefin. Examples of preferred alpha-olefin monomers to copolymerize with ethylene include propylene, 1-butene, 1-pentene; 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-dodecene, 4-methylpentene; 1,3-methylpent-1-ene, 3,5,5-trimethylhex-1-ene, and 5-ethylnon-1-ene.

[0087] In at least some embodiments the preferred alpha-olefins are C_2 to C_{20} alpha-olefins that exclude dienes.

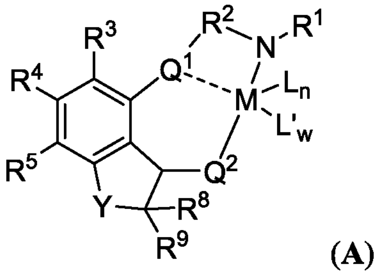
Catalysts

[0088] The present disclosure provides a method for forming lubricating compositions. The method includes polymerization processes where, in a first stage, one or more catalyst compounds, one or more activators, one or more reversible chain transfer agents, one or more C_2 to C_{40} alpha-olefins are contacted to produce a first polymer that has a substantially linear backbone. In a second stage, the first polymer is contacted with one or more coupling agents, optionally one or more catalysts and activators, and optionally one or more C_2 to C_{40} alpha-olefins, to form a long-chain branched polymer. Catalyst compounds of the present disclosure for the first stage and/or the second stage can be any suitable coordinative chain transfer polymerization (CCTP) catalysts. Preferably, a catalyst is a non-metallocene catalyst.

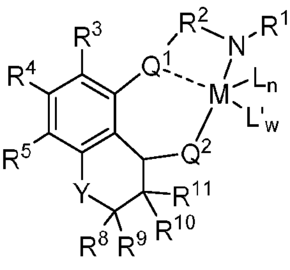
[0089] Without being bound by theory, catalyst systems that are suitable for use in the present disclosure are those that are capable of behaving as living alpha-olefin polymerization catalysts in the presence of a reversible chain transfer agent. The catalyst should not undergo significant beta-hydride elimination or beta-hydride transfer to monomer during the process. This will allow nearly all of the living polymer chains produced in the first stage to be crosslinked in the second stage in a head-to-head fashion. The coupling of polymer chains in a head-to-head fashion prevents the formation of extended network gels. Metallocenes, in particular group 4 metallocenes, are known to be susceptible to beta-hydride elimination or beta-hydride transfer to monomer processes under typical polymerization conditions.

[0090] The transition-metal catalyst and activator are added to the first stage of the polymerization. In the second stage of the polymerization (e.g., the crosslinking stage), additional catalyst and activator may be added to the reactor, but it may not be needed if the catalyst mixture from the first stage is still active. The first stage catalyst/activator may be the same or different from the second stage catalyst/activator. Additionally, mixtures of catalysts and activators may be used in each stage. Transition metal catalysts may be linked together by covalent or non-covalent bonds to form bimetallic or multimetallic catalysts.

[0091] In at least some embodiments, the catalyst of the first stage and/or the second stage is a pyridyldiamido transition metal complex represented by the formula (A), (B), (C), or (D):



(A)



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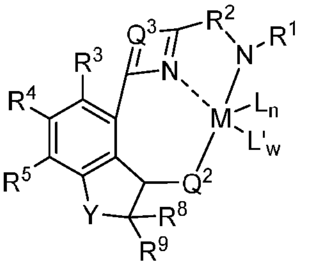

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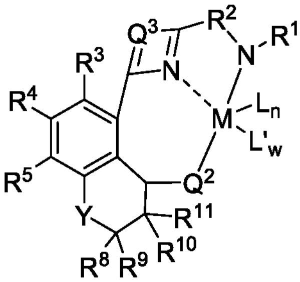


(D)

wherein:

M is a Group 3 or 4 metal (preferably a Group 4 metal, preferably Ti, Zr, or Hf);

Q^1 is a three atom bridge with the central of the three atoms being a Group 15 or 16 element (said Group 15 element may or may not be substituted with an R^{30} group) that preferably forms a dative bond to M, preferably represented by the formula: $-G^1-G^2-G^3-$ where G^2 is a Group 15 or 16 atom (said Group 15 element may be substituted with a R^{30} group), G^1 and G^3 are each a Group 14, 15 or 16 atom (each Group 14, 15 and 16 element may or may not be substituted with one or more R^{30} groups), where G^1, G^2 and G^3, or G^1 and G^2, or G^1 and G^3, or G^2 and G^3 may form a singular or multi ring system, where each R^{30} group is independently a hydrogen, a C_1 to C_{100} hydrocarbyl radical, or a silyl radical;

Q^2 is $-NR^{17}$ or $-PR^{17}$, where R^{17} is a hydrocarbyl radical, a substituted hydrocarbyl radical, a silyl radical, or a germyl radical;

Q^3 is $-(TT)-$ or $-(TTT)-$ where each T is carbon or a heteroatom (preferably C, O, S, or N), and said carbon or heteroatom may be unsubstituted or substituted with one or more R^{30} groups that together with the "$-C-Q^3=C-$" fragment, forms a 5- or 6-membered cyclic group or a polycyclic group including the 5- or 6-membered cyclic group;

R^1 is a hydrocarbyl radical, a substituted hydrocarbyl radical, or a silyl radical;

each of R^3, R^4, and R^5 is independently a hydrogen, a hydrocarbyl radical, a substituted hydrocarbyl radical, an aryl radical, a substituted aryl radical, an alkoxy radical, an aryloxy radical, a halogen, an amino radical, or a silyl radical, or two or more adjacent R^3, R^4, and R^5 groups may independently join together to form a substituted or unsubstituted hydrocarbyl ring or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;

R^2 is $-E(R^{12})(R^{13})-$ where E is carbon, silicon, or germanium (preferably carbon or silicon, more preferably carbon) and R^{12} and R^{13} as described herein;

Y is oxygen, sulfur, or $-E^*(R^6)(R^7)-$, wherein E* is carbon, silicon, or germanium (preferably carbon or silicon, more preferably carbon) and R^6 and R^7 as described herein;

each of R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} is independently a hydrogen, a hydrocarbyl radical, a substituted hydrocarbyl radical, an alkoxy radical, a halogen, an amino radical, or a silyl radical, or two or more adjacent R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} groups may independently join together to form a saturated, substituted or unsubstituted hydrocarbyl ring or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;

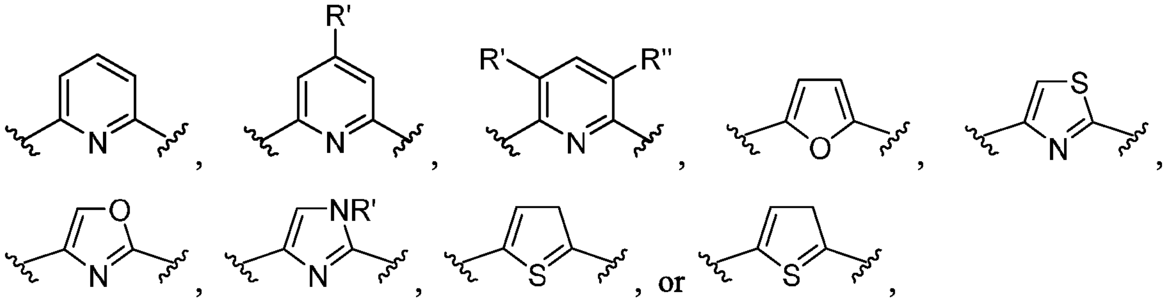
L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group; in an embodiment, L'_w and L_n may be joined;

n is 1 or 2 (preferably 2);

L' is neutral Lewis base; and

w is 0, 1, 2, 3 or 4 (preferably 0 or 1);

[0092] In some embodiments, Q^1 is:



wherein:

the ⸙ indicates the connections to R^2 and the aromatic ring, and

each of R' and R" is an alkyl group, such as a hydrocarbyl, such as a C_1 to C_{20} alkyl group, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, and dodecyl.

[0093] In some embodiments, each L is independently a halide, alkyl, aryl, alkoxy, amido, hydrido, phenoxy, hydroxy, silyl, allyl, alkenyl, triflate, alkylsulfonate, arylsulfonate, or alkynyl and/or each L' is independently an ether, thio-ether, amine, nitrile, imine, pyridine, or phosphine.

[0094] In some embodiments, G^1 is carbon, nitrogen, oxygen, silicon, or sulfur, preferably carbon.

[0095] In some embodiments, G^2 is nitrogen, phosphorous, oxygen, sulfur, or selenium, preferably nitrogen, oxygen, or sulfur.

[0096] In some embodiments, G^3 is carbon, nitrogen, oxygen, silicon, or sulfur, preferably carbon.

[0097] In some embodiments, Q^2 is $–NR^{17}$, $–PR^{17}$, or oxygen, preferably $–NR^{17}$.

[0098] In some embodiments, Q^3 is CHCHCH, CHCH, CHN(R'), CH–S, CHC(R')CH, C(R')CHC(R''), CH–O, NO, preferably CHCHCH, CHCH, CHN(R'), CHN(Me), CH–S, preferably the R' is a C_1 to C_{20} hydrocarbyl, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl.

[0099] In some embodiments, R^1 is a hydrocarbyl, substituted hydrocarbyls, or silyl radical (preferably alkyl, aryl, heteroaryl, and silyl groups, more preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, phenyl, substituted phenyl, 2,6-disubstitutedphenyl, 2,6-diisopropylphenyl, 2,4-6-trisubstituted aryl, 2,4,6-triisopropylphenyl, and isomers thereof, including cyclohexyl).

[0100] In some embodiments, R^{17} is a hydrogen, hydrocarbyl, substituted hydrocarbyl, silyl, or germyl group (preferably alkyl, aryl, heteroaryl, and silyl groups, more preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, cycloalkyl, cyclooctyl, cyclododecyl, phenyl, substituted phenyl, 2-substituted phenyl, ortho-tolyl, 2,6-disubstitutedphenyl, or isomers thereof, including cyclohexyl).

[0101] In some embodiments, each R^{30} group is a hydrogen, a C_1 to C_{100} hydrocarbyl radical, or a silyl radical (preferably alkyl, aryl, and silyl groups, more preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, phenyl, or isomers thereof, including cyclohexyl).

[0102] In some embodiments, R^2 contains 1 to 20 carbons, preferably R^2 is CH_2, CH(aryl), CH(2-isopropylphenyl), CH(2,6-dimethylphenyl), CH(2,4-6-trimethylphenyl), CH(alkyl), CMe_2, $SiMe_2$, $SiEt_2$, or $SiPh_2$.

[0103] In some embodiments, each of E and E* are, independently, carbon, silicon, or germanium (preferably carbon or silicon, more preferably carbon). In a preferred embodiment, E and E* are both carbon.

[0104] In some embodiments, each of R^{12}, R^{13}, R^6, and R^7 is independently a hydrogen, a hydrocarbyl radical, a substituted hydrocarbyl radical, an aryl radical, a substituted aryl radical, an alkoxy radical, a halogen, an amino radical, or phosphino, or R^{12} and R^{13} and/or R^6 and R^7 may be joined to form a saturated, substituted or unsubstituted hydrocarbyl ring, where the ring has 4, 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings, or R^{12} and R^{13} and/or R^6 and R^7 may be joined to form a saturated heterocyclic ring, or a saturated substituted heterocyclic ring where substitutions on the ring can join to form additional rings.

[0105] In some embodiments, at least one of R^{12} and R^{13} is a C_1 to C_{100} (preferably C_6 to C_{40}, more preferably C_7 to C_{30}, even more preferably C_8 to C_{20}) substituted or unsubstituted hydrocarbyl group (preferably aryl, phenyl, substituted phenyl, alkyl or aryl substituted phenyl, C_2 to C_{30} alkyl or aryl substituted phenyl, 2-substituted phenyl, 2-isopropylphenyl, or 2,4,6-trimethylphenyl).

[0106] In some embodiments, at least one of R^6 and R^7 is a C_1 to C_{100} (preferably C_6 to C_{40}, more preferably C_7 to C_{30}, even more preferably C_8 to C_{20}) substituted or unsubstituted hydrocarbyl group (preferably aryl, phenyl, substituted phenyl, alkyl or aryl substituted phenyl, C_2 to C_{30} alkyl or aryl substituted phenyl, 2-substituted phenyl, 2-isopropylphenyl, or 2,4,6-trimethylphenyl).

[0107] In some embodiments, each of R^3, R^4, and R^5 is independently a hydrogen, a hydrocarbyl radical, a substituted hydrocarbyl radical, an alkoxy radical, an aryloxy radical, a halogen, an amino radical, or a silyl radical, or two or more adjacent R^3, R^4, and R^5 groups may independently join together to form a substituted or unsubstituted hydrocarbyl ring or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings. Preferably, each of R^3, R^4, and R^5 is independently a hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, phenyl, substituted phenyl, or isomers thereof.

[0108] In some embodiments, each of R^8, R^9, R^{10}, and R^{11} is independently a hydrogen, a hydrocarbyl radical, a substituted hydrocarbyl radical, an aryl radical, a substituted aryl radical, an alkoxy radical, a halogen, an amino radical, or a silyl radical, or two or more adjacent R^8, R^9, R^{10}, and R^{11} groups may independently join together to form a saturated, substituted or unsubstituted hydrocarbyl ring or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings. Preferably, each of R^8, R^9, R^{10}, and R^{11} is independently hydrogen, methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, phenyl, substituted phenyl, or isomers thereof.

[0109] Preferably, any of the R groups above and other R groups mentioned hereafter, contain up to 30 carbon atoms, preferably no more than 30 carbon atoms, especially from 2 to 20 carbon atoms.

[0110] Preferably, M is Ti, Zr, or Hf and/or E and/or E* is carbon, with Zr or Hf based complexes being especially preferred.

[0111] In some embodiments, R^1 and R^{17} are phenyl groups that are variously substituted with between zero to five substituents that include F, Cl, Br, I, CF_3, NO_2, alkoxy, dialkylamino, aryl, and alkyl groups with between one to ten carbons.

[0112] In some embodiments, each L may be a halide, alkyl, aryl, alkoxy, amido, hydrido, phenoxy, hydroxy, silyl, allyl, alkenyl, triflate, alkylsulfonate, arylsulfonate, and alkynyl. The selection of the leaving groups depends on the synthesis route adopted for arriving at the complex and may be changed by additional reactions to suit the later activation method in polymerization. For example, alkyl is preferred when using non-coordinating anions such as N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate or tris(pentafluorophenyl)borane. The "n" indicates the number of L groups present.

[0113] In some embodiments, two L groups may be linked to form a dianionic leaving group, for example, oxalate.

[0114] In some embodiments, each L' is independently an ether, thio-ether, amine, nitrile, imine, pyridine, or phosphine, preferably ethers. The "w" indicates the number of L' groups present.

[0115] In some embodiments, M is preferably a Group 4 metal, more preferably Zr or Hf.

[0116] In some embodiments, E and/or E* is preferably carbon.

[0117] Preferably, in some embodiments, R^6 and R^7 are the same.

[0118] In some embodiments, R^1, R^3, R^4, R^8, and R^{17} may each contain no more than 30 carbon atoms.

[0119] In some embodiments, E and E* is carbon, and each of R^1 and R^{17} is independently a phenyl group that is substituted with 0, 1, 2, 3, 4, or 5 substituents, the substituents comprising F, Cl, Br, I, CF_3, NO_2, alkoxy, dialkylamino, hydrocarbyl, and substituted hydrocarbyl groups with from one to ten carbons.

[0120] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (A), the formula (B), the formula (C), the formula (D), or combinations thereof.

[0121] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (A) above and at least one of R^6 and R^7 is a group containing from 1 to 100 (preferably 6 to 40, more preferably 7 to 30) carbons.

[0122] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (A) above, and M is a Group 4 metal preferably Zr or Hf, more preferably Hf.

[0123] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (B) above, and M is a Group 4 metal preferably Zr or Hf, preferably Hf.

[0124] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (A) above, and G^2 is oxygen, and G^1 and G^3 are carbon atoms that are joined to each other by two to six additional atoms to form a cyclic structure.

[0125] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (B) above, and G^2 is oxygen, and G^1 and G^3 are carbon atoms that are joined to each other by two to six additional atoms to form a cyclic structure.

[0126] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (A) above, and G^2 is nitrogen, and G^1 and G^3 are carbon atoms that are joined to each other by two to six additional atoms to form a cyclic structure.

[0127] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (B) above, and G^2 is nitrogen, and G^1 and G^3 are carbon atoms that are joined to each other by two to six additional atoms to form a cyclic structure.

[0128] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (A) above, and G^2 is sulfur, and G^1 and G^3 are carbon atoms that are joined to each other by two to six additional atoms to form a cyclic structure.

[0129] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (B) above, and G^2 is sulfur, and G^1 and G^3 are carbon atoms that are joined to each other by two to six additional atoms to form a cyclic structure.

[0130] In a the preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (C) above, and Q^3 is C(H)C(H)C(H), R^1 is 2,6-diisopropylphenyl, and R^{17} is phenyl.

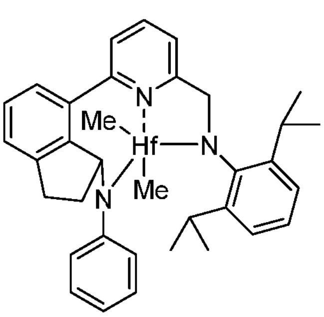
[0131] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (D) above, R^6 is H, R^7 is a group containing between 1 to 100 (preferably 6 to 40, more preferably 7 to 30) carbons, M is a Group 4 metal (preferably Zr or Hf, more preferably Hf), and E is carbon.

[0132] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (A) above, and R^1 is a 2,6-disubstituted aryl group where the substituents are selected from isopropyl, 3-pentyl, or cyclic aliphatic hydrocarbons containing between 4-20 carbons.

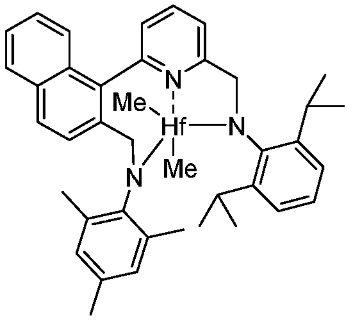
[0133] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (A) above, and Q^1 is three atoms of a pyridine, imidazole, tetrahydrofuran, dioxane, dihydrothiazole, oxathiolane, tetrahydropyran, dihydrooxazole, or phosphinine group that is substituted at the adjacent positions.

[0134] In a preferred embodiment, the pyridyldiamido transition metal complex is represented by the formula (A) above, and R^2 is CH(aryl) with the aryl group containing between 7 and 20 carbon atoms.

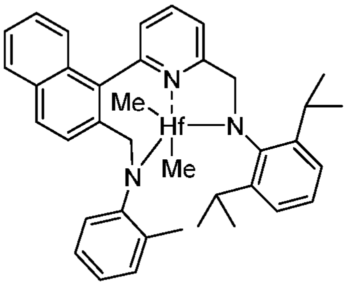
[0135] In a preferred embodiment, the pyridyldiamido transition metal complex is one or more of the compounds represented by formula the (1), (2), and (3):



(1),

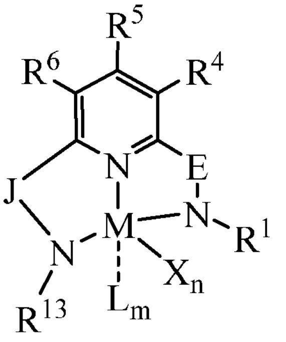


(2), and

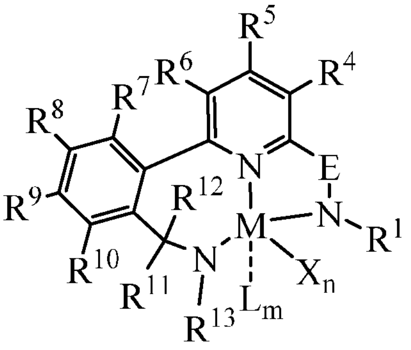


(3).

In at least one embodiment, a catalyst is a pyridyldiamido or quinolinyldiamido transition metal complex represented by formula **(I)** or **(II)**;



(I)



(II)

wherein:

M is a Group 3, 4, 5, 6, 7, 8, 9, or 10 metal (preferably M is Zr or Hf);

E is $C(R^2)$ or $C(R^3)(R^{3'})$;

X is an anionic leaving group (preferably X is methyl, chloride, or dialkylamido);

n is 1 or 2;

L is a neutral Lewis base (preferably L is ether, amine, phosphine, or thioether);

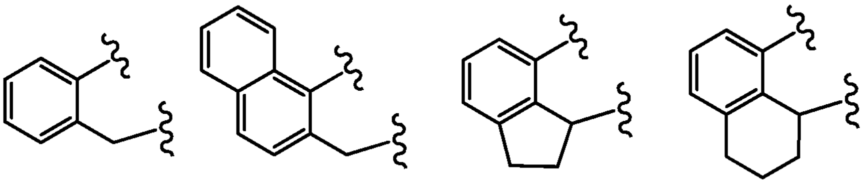
m is 0, 1, or 2;

R^1 and R^{13} are independently selected from substituted or unsubstituted hydrocarbyl or silyl groups (preferably R^1 and R^{13} are aryl groups, preferably R^1 is 2,6-disubstituted aryl, more preferably R^1 is 2,6-diisopropylphenyl, preferably R^{13} is 2-substituted aryl, more preferably R^{13} is phenyl, preferably R^1 is 2,6-disubstituted aryl group and R^{13} is an aryl group that is unsubstituted in the 2 and 6 positions);

R^2 is a group containing 1-10 carbon atoms that is optionally joined with R^4 to form an aromatic ring (preferably R^2 and R^4 are joined to form a six membered aromatic ring);

R^3, $R^{3'}$, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} are each independently selected from hydrogen, substituted or unsubstituted hydrocarbyl, alkoxy, silyl, amino, aryloxy, halogen, and phosphino (preferably R^3 and $R^{3'}$ are hydrogen);

J is a divalent group that forms a three-atom-length bridge between the pyridine ring and the amido nitrogen (preferably J is selected from:



);

and

two X groups may be joined to form a dianionic group;

two L groups may be joined to form a bidentate Lewis base;

an X group may be joined to an L group to form a monoanionic bidentate group;

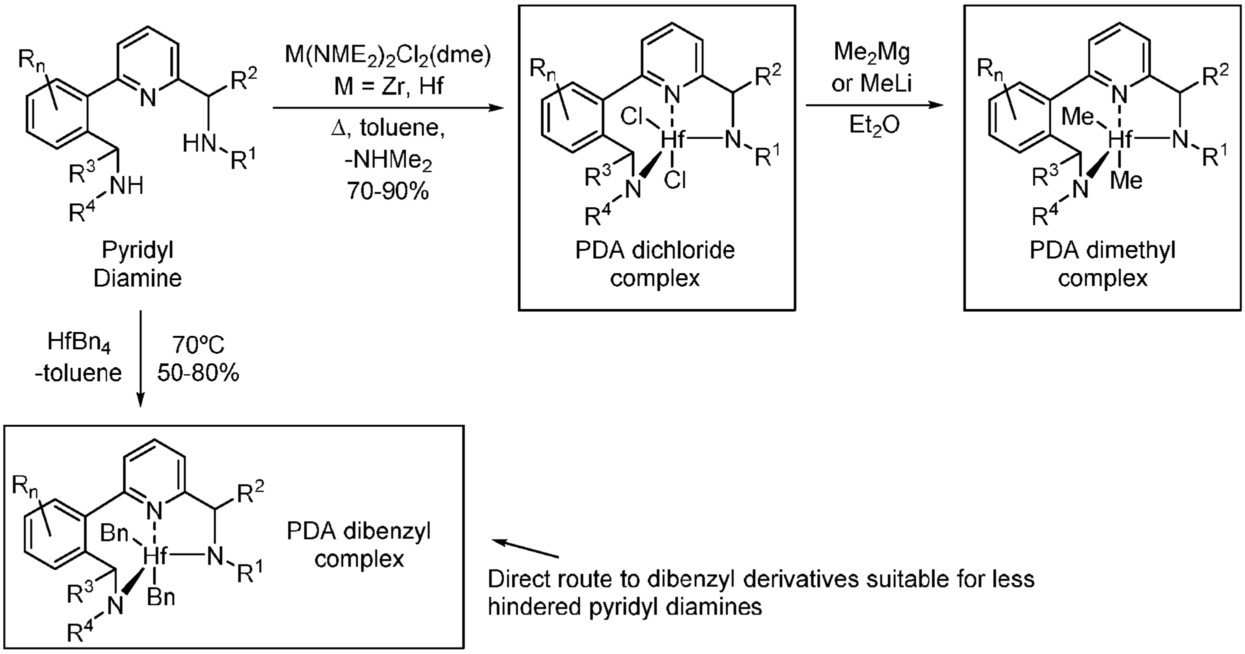
adjacent groups from the following R^3, $R^{3'}$, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, and R^{12} may be joined to form a ring (preferably R^7 and R^8 are joined to form an aromatic ring, preferably R^7 and R^8 are joined to form cyclopentyl or cyclohexyl, preferably R^{10} and R^{11} are joined to form a five- or six-membered ring, more preferably R^{10} and R^{11} are joined to form cyclopentyl or cyclohexyl).

[0136] The pyridyl diamine ligands described herein are generally prepared in multiple steps. One key step involves the preparation of a suitable "linker" group(s) containing both an aryl boronic acid (or acid ester) and an amine group. Examples of these include compounds of the general formula: 7-(boronic acid)-2,3-dihydro-lH-inden-1-(amine), 7-(boronic acid ester)-2,3-dihydro-1H-1-(amine), 7-(boronic acid)-1,2,3,4-tetrahydronaphthalen-1-(amine), 7-(boronic acid ester)-1,2,3,4-tetrahydronaphthalen-1-(amine), which include various boronic acids, boronic acid esters, and amines. The linker groups may be prepared in high yield from arylhalide precursors containing amine functionality by first deprotonation of the amine group with 1.0 molar equivalents of n-BuLi, followed by transmetalation of an arylhalide with t-BuLi and subsequent reaction with a boron-containing reagent. This amine-containing linker is then coupled with a suitable pyridine containing species, such as 6-bromo-2-pyridinecarboxaldehyde. This coupling step typically uses a metal catalyst (e.g., $Pd(PPh_3)_4$) in less than 5 mol% loading. Following this coupling step, the new derivative, which can be described as amine-linker-pyridine-aldehyde, is then reacted with a second amine to produce the imine derivative amine-linker-pyridine-imine in a condensation reaction. This can then be reduced to the pyridyl diamine ligand by reaction with a suitable aryl anion, alkyl anion, or hydride source. This reaction is generally performed in etherial solvents at temperatures between about -100°C and about 50°C when aryllithium or alkyllithium reagents are employed. This reaction is generally performed in methanol at reflux when sodium cyanoborohydride is employed.

[0137] The preparation of pyridyl diamide metal complexes from pyridyl diamines may be accomplished using typical protonolysis and methylation reactions. In the protonolysis reaction, the pyridyl diamine is reacted with a suitable metal reactant to produce a pyridyldiamide metal complex. A suitable metal reactant will feature a basic leaving group that will accept a proton from the pyridiyl diamine and then generally depart and be removed from the product. Suitable metal reactants include, but are not limited to, $HfBn_4$ (Bn =

CH_2Ph), $ZrBn_4$, $TiBn_4$, $ZrBn_2Cl_2(OEt_2)$, $HfBn_2Cl_2(OEt_2)_2$, $Zr(NMe_2)_2Cl_2$(dimethoxyethane), $Hf(NMe_2)_2Cl_2$(dimethoxyethane), $Hf(NMe_2)_4$, and $Hf(NEt_2)_4$. Pyridyldiamide metal complexes that contain metal-chloride groups, such as the PDA dichloride complex in Scheme 1 below, can be alkylated by reaction with an appropriate organometallic reagent. Suitable reagents include organolithium and organomagnesium, and Grignard reagents. The alkylations are generally performed in etherial or hydrocarbon solvents or solvent mixtures at temperatures typically ranging from about -100°C to about 50°C.

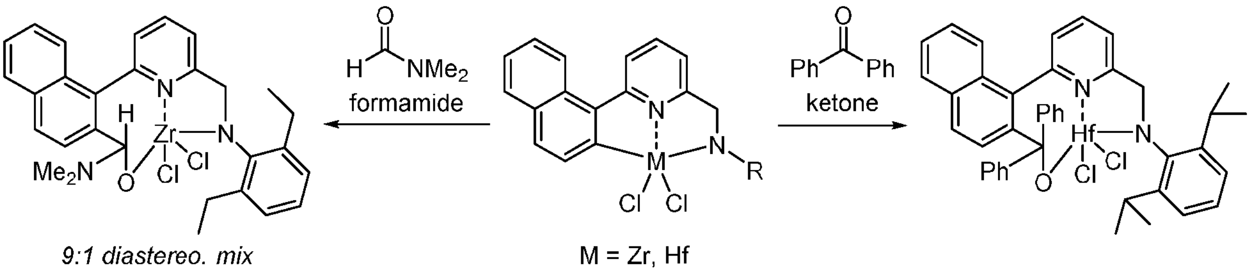
Scheme 1



Direct route to dibenzyl derivatives suitable for less hindered pyridyl diamines

[0138] In Scheme 1, each of R, R^1, R^2, R^3, R^4 is independently a hydrogen, a hydrocarbyl radical (such as alkyl radical and aryl radical), substituted hydrocarbyl radicals (such as heteroaryls), or silyl radical, and R_n indicates a hydrogen, a hydrocarbyl radical, or substituted hydrocarbyl radical, which may be joined to form a polycyclic aromatic ring and n is 1, 2, 3, or 4.

[0139] Another route to pyridyl diamide and other complexes of interest as catalysts involves the insertion of an unsaturated molecule into a covalent metal-carbon bond where the covalently bonded group is part of a multidentate ligand structure, such as that described by Boussie et al. in U.S. Patent No. 6,750,345. The unsaturated molecule will generally have a carbon-X double or triple bond where X is a Group 14 or Group 15 or Group 16 element. Examples of unsaturated molecules include alkenes, alkynes, imines, nitriles, ketones, aldehydes, amides, formamides, carbon dioxide, isocyanates, thioisocyanates, and carbodiimides. Examples showing the insertion reactions involving benzophenone and N,N-dimethylformamide are below.



Reversible Chain Transfer Agents (RCTAs)

[0140] In embodiments of the first stage of processes of the present disclosure, the term “reversible chain transfer agent” (RCTA) is defined as a Group 12 or 13 organometallic compound, or mixture of such compounds, which is capable of reversibly transferring/receiving an alkyl group, including polymeryl groups (long alkyl group produced by polymerizing monomers), between the Group 12 or 13 metal center and the activated transition metal polymerization catalyst. The chain transfer process provides transfer of alkyl or polymeryl groups between the Group 12 or 13 metal and the metal center of the activated polymerization catalyst. The term “reversible chain transfer agent” does not include chain transfer agents that irreversibly react with a growing polymer chain to form a dead chain that does not participate in any further growth. Based on this distinction, hydrogen and silanes are not reversible chain transfer agents. Reversible chain transfer agents (RCTA) useful herein include triakyl aluminum compounds and dialkyl zinc compounds (where the alkyl is preferably a C_1 to C_{40} alkyl group, more preferably a C_2 to C_{20} alkyl group, even more preferably a C_2 to C_{12} alkyl group, especially preferably a C_2 to C_8 group, such as methyl, ethyl, propyl (including isopropyl and n-propyl), butyl (including n-butyl, sec-butyl, and iso-butyl) pentyl, hexyl (including n-hexyl and iso-hexyl), heptyl (including n-heptyl and iso-heptyl), and octyl (including n-octyl and iso-octyl), and isomers or analogs thereof). Preferably the alkyl groups are unbranched alkyl groups, such as ethyl, n-propyl, n-hexyl, n-octyl, n-decyl, and n-dodecyl. Preferred agents are trialkyl aluminum compounds having unbranched alkyl groups that contain from 3 to 12 carbons each; also preferred are dialkyl zinc compounds having unbranched alkyl groups that contain from 1 to 12 carbons each. Specific examples of preferred agents include: triethylaluminum, tri(i-butyl)aluminum, tri(n-hexyl)aluminum, tri(n-octyl)aluminum (TNOAL or TNOA), diethylzinc, di(n-propyl)zinc, and di(n-octyl)zinc. Most preferred agents for the use of the present disclosure are diethyl zinc and tri(n-octyl)aluminum.

[0141] In a preferred embodiment, one or more triakyl aluminum compounds and one or more dialkyl zinc compounds (where the alkyl is preferably a C_1 to C_{40} alkyl group, preferably a C_2 to C_{20} alkyl group, preferably a C_2 to C_{12} alkyl group, preferably a C_2 to C_8 group, such as methyl, ethyl, propyl (including isopropyl and n-propyl), butyl (including n-butyl, sec-butyl and iso-butyl) pentyl, hexyl, heptyl, octyl, and isomers or analogs thereof) are used as the RCTA. Preferred combinations include TIBAL, and/or TNOAL with Et_2Zn, preferably TIBAL and Et_2Zn, or TNOAL and Et_2Zn. Preferably, the molar ratio of dialkyl zinc to trialkyl aluminum compounds (i.e., Zn/Al) present in the reaction is from about 0.5 to about 1,000, such as from about 1 to about 100, such as from about 10 to about 50. In at least some embodiments, the molar ratio of trialkylaluminum to dialkylzinc compounds (i.e., Al/Zn) is about 0.5 or more, about 1 or more, about 10 or more, about 50 or more, about 100 or more, about 1000 or more. In at least some embodiments, trialkylaluminum is the only RCTA used. In at least some embodiments, dialkylzinc is the only RCTA used.

[0142] The reversible chain transfer agent(s) are typically present in the reaction at a molar ratio of metal of the reversible chain transfer agent to transition metal (from the transition metal complex) of about 5 or more, preferably from about 10 to about 10000, preferably from about 20 to 4000, preferably from about 100 to about 4000, preferably from about 200 to 3000, preferably from about 50 to about 2000.

[0143] Without being bound by theory, addition of a reversible chain transfer agent to a reactor during the first stage of processes of the present disclosure provides a stabilized metal-capped first polymer (metal of the reversible chain transfer agent), allowing the first polymer to remain as a "living" polymer, e.g., capable of reacting with a coupling agent in the presence of a catalyst and activator in the second stage of processes of the present disclosure.

Coupling Agents

[0144] In embodiments of the second stage of processes of the present disclosure, the term "coupling agent" includes a compound that in the presence of an olefin polymerization catalyst couples two or more polymers by covalent bonding to form a larger polymer and the coupling agent is incorporated into the backbone of the larger polymer.

[0145] In at least some embodiments, a coupling agent is a dual-reactive diene. A dual-reactive diene can be conjugated or non-conjugated. Preferably, a dual-reactive diene is non-conjugated and is an α,ω-diene. Preferably, a dual-reactive diene is an α,ω-diene containing 5 to 30 carbons, more preferably 6 to 20 carbons, even more preferably 8 to 16 carbons. An α,ω-diene has each end of the molecule terminating in a vinyl group, such as 1,7-octadiene or 1,9-decadiene. Other exemplary dienes include 1,3-butadiene, 1,4-pentadiene, 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, 1,14-pentadecadiene, 1,15-hexadecadiene, 1,16-heptadecadiene, 1,17-octadecadiene, 1,18-nonadecadiene, 1,19-icosadiene, 1,20-heneicosadiene, 1,21-docosadiene, 1,22-tricosadiene, 1,23-tetracosadiene, 1,24-pentacosadiene, 1,25-hexacosadiene, 1,26-heptacosadiene, 1,27-octacosadiene, 1,28-nonacosadiene, 1,29-triacontadiene, and low molecular weight polybutadienes (Mw less than about 1000 g/mol), and combinations thereof. Dual-reactive dienes that feature cyclic groups include cyclopentadiene, norbornadiene, 5-vinyl-2-norbornene, divinylbenzene, diallylbenzene, 1-vinyl-4-allylbenzene, 1-vinyl-3-buten-1-ylbeznene, bis(4-methylphenyl)di-2-propenylsilane, 1-methyl-4-(methyldi-2-propen-1-ylsilyl)benzene, 1,1-di-2-propen-1-ylsilacyclopentane, 1,1’-(di-2-propen-1-ylsilylene)bisbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions, and combinations thereof. Coupling agents can also include higher linear or cyclic polyenes, for example, 1,5,10-undecatriene, 1,4,9-decatriene, 1,5,9-decatriene, 1,4,8-nonatriene, 1,3-diethenyl-1,2,3,3a,4,6a-hexahydropentalene, 4,5-diethenylcyclohexene, 5,6-diethenylcyclooctene, trivinylbenzene, 1,2-ethanediylbis[tri-2-propenyl]silane, triallylsilylbenzene, triallylmethylsilane, tetraallylsilane, bis(1-methylethyl)di-2-propen-1-ylsilane, dimethyldiallylsilane, or combinations thereof.

[0146] Most preferred coupling agents include 1,7-octadiene, 1,8-nonadiene, and 1,9-decadiene.

[0147] The coupling agent(s) are typically present in the reaction at a molar ratio of coupling agent to transition metal (from the transition metal complex) of about 5 or more, preferably from about 10 to about 2000, preferably from about 20 to about 1000, preferably from about 25 to about 800, preferably from about 50 to about 700, preferably from about 100 to about 600.

[0148] Without being bound by theory, contacting the first polymer with a coupling agent in a second stage provides controllable crosslinking via head-to-head couplings between first polymers to form a long-chain branched polymer. Unlike olefin polymerization processes that use diene crosslinking agents in a single reaction stage, the processes of the present disclosure have reduced or eliminated gel-formation in a reactor, providing mass recovery of polymer products of about 50% by weight or greater based on the total weight of polymer product of a polymerization, as determined by gel permeation chromatography. In at least some embodiments, mass recovery of polymer products of the present disclosure is about 60% or greater by weight, such as about 70% or greater by weight, such as about 80% or greater by weight, such as about 90% or greater by weight, such as about 95% or greater by weight, such as about 100% by weight based on the total weight of polymer product of a polymerization, as determined by gel permeation chromatography. Observed mass recovery percentage determined by GPC may be affected a modest amount by the presence of vinyl or other unsaturated groups and the presence of extremely high MW polymer chains. Therefore, mass recovery percentage data of the present disclosure encompasses such high MW polymer content and unsaturation content present in a polymer sample. Mass recovery percentage in combination with other metrics, such as melt index data and observable gel formation in a reactor, provide valuable data indicative of gel formation or lack thereof of a polymerization process.

[0149] Polymers formed during the first stage of processes of the present disclosure can be highly linear (e.g., g'vis of about 0.9 or greater). However, after treatment with a coupling agent during the second stage, polymers of the present disclosure can have g'vis values of about 0.9 or less, such as from about 0.4 to about 0.8, as determined by GPC-3D. Furthermore, in embodiments where the coupling agent is an α,ω-diene, polymers of the present disclosure can have a vinyl unsaturation content of about 0.8 or greater vinyls/1000 carbons, as determined by ^{1}H NMR, which provides reactive end groups of the polymers for functionalization.

Activators

[0150] The terms “cocatalyst” and “activator” are used herein interchangeably and are defined to be any compound which can activate any one of the catalyst compounds described above by converting the neutral catalyst compound to a catalytically active catalyst compound cation.

[0151] After the complexes have been synthesized, catalyst systems may be formed by combining the complexes with activators in any suitable manner including by supporting them for use in slurry or gas phase polymerization. The catalyst systems may also be added to or generated in solution polymerization or bulk polymerization (in the monomer). The catalyst system typically includes a complex as described above and an activator such as alumoxane or a non-coordinating anion.

[0152] Non-limiting activators, for example, include alumoxanes, aluminum alkyls, ionizing activators, which may be neutral or ionic, and conventional-type cocatalysts. Preferred activators typically include alumoxane compounds, modified alumoxane compounds, and ionizing anion precursor compounds that abstract a reactive, σ-bound, metal ligand making the metal complex cationic and providing a charge-balancing non-coordinating or weakly coordinating anion.

Alumoxane Activators

[0153] In an embodiment, alumoxane activators are utilized as an activator in the catalyst system. The alumoxane may be used with another activator. Alumoxanes are generally oligomeric compounds containing $-Al(R^1)-O-$ sub-units, where R^1 is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane, and isobutylalumoxane. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the abstractable ligand is an alkyl, halide, alkoxide or amide. Mixtures of different alumoxanes and modified alumoxanes may also be used. It may be preferable to use a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from the cloudy solution. A useful alumoxane is a modified methyl alumoxane (MMAO) cocatalyst type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A, covered under U.S. Patent No. 5,041,584). In a preferred embodiment, the activators are non-coordinating anions.

[0154] Another useful alumoxane is solid polymethylaluminoxane as described in U.S. Patent Nos. 9,340,630; 8,404,880; and 8,975,209.

[0155] When the activator is an alumoxane (modified or unmodified), some embodiments include the maximum amount of activator typically at up to about a 5000-fold molar excess Al/M over the catalyst compound (per metal catalytic site). The minimum activator-to-catalyst-compound is about a 1:1 molar ratio. Alternate preferred ranges include from about 1:1 to about 500:1, alternately from about 1:1 to about 200:1, alternately from about 1:1 to about 100:1, or alternately from about 1:1 to about 50:1. In an alternate embodiment, little or no alumoxane is used in the polymerization processes described herein. Preferably, alumoxane is present at about zero mole%, alternately the alumoxane is present at a molar ratio of aluminum to catalyst compound transition metal less than about 500:1, preferably less than about 300:1, more preferably less than about 100:1, even more preferably less than about 20:1.

Non-Coordinating Anion Activators

[0156] A non-coordinating anion (NCA) is defined to mean an anion either that does not coordinate to the catalyst metal cation or that does coordinate to the metal cation, but only weakly. The term NCA is also defined to include multicomponent NCA-containing activators, such as N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, that contain an acidic cationic group and the non-coordinating anion. The term NCA is also defined to include neutral Lewis acids, such as tris(pentafluorophenyl)boron, that can react with a catalyst to form an activated species by abstraction of an anionic group. An NCA coordinates weakly enough that a neutral Lewis base, such as an olefinically or acetylenically unsaturated monomer can displace it from the catalyst center. Any metal or metalloid that can form a compatible, weakly coordinating complex may be used or contained in the non-coordinating anion. Suitable metals include aluminum, gold, and platinum. Suitable metalloids include boron, aluminum, phosphorus, and silicon.

[0157] "Compatible" non-coordinating anions can be those which are not degraded to neutrality when the initially formed complex decomposes, and the anion does 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 useful in accordance with this present disclosure are 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.

[0158] 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 98/43983), 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.

[0159] The catalyst systems of the present disclosure can include at least one non-coordinating anion (NCA) activator.

[0160] In a preferred embodiment, boron containing NCA activators represented by the formula below can be used:

$$Z_d^+ (A^{d-})$$

where: Z is (L–H) or a reducible Lewis acid; L is a neutral Lewis base; H is hydrogen; $(L–H)^+$ is a Brønsted acid; A^{d-} is a non-coordinating anion, for example a boron containing non-coordinating anion having the charge d-; and d is 1, 2, or 3.

[0161] The cation component, Z_d^+ may include Brønsted acids such as protons or protonated Lewis bases or reducible Lewis acids capable of protonating or abstracting a moiety, such as an alkyl or aryl, from the bulky ligand containing transition metal catalyst precursor, resulting in a cationic transition metal species.

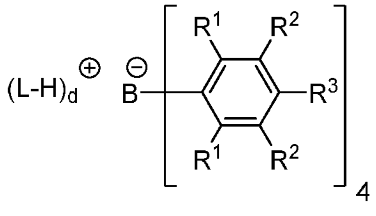
[0162] The activating cation Z_d^+ may also be a moiety such as silver, tropylium, carboniums, ferroceniums and mixtures, preferably carboniums and ferroceniums. Most preferably Z_d^+ is triphenyl carbonium. Preferred reducible Lewis acids can be any triaryl carbonium (where the aryl can be substituted or unsubstituted, such as those represented by the formula: (Ar_3C^+), where Ar is aryl substituted with a C_1 to C_{40} hydrocarbyl or with a substituted C_1 to C_{40} hydrocarbyl, or a heteroaryl substituted with a C_1 to C_{40} hydrocarbyl, or with a substituted C_1 to C_{40} hydrocarbyl; preferably the reducible Lewis acids in "Z" include those represented by the formula: (Ph_3C), where Ph is a substituted or unsubstituted phenyl, preferably substituted with C_1 to C_{40} hydrocarbyls or substituted a C_1 to C_{40} hydrocarbyls, more preferably C_1 to C_{20} alkyls or aromatics or substituted C_1 to C_{20} alkyls or aromatics, preferably Z is a triphenylcarbonium.

[0163] When Z_d^+ is the activating cation $(L–H)_d^+$, it is preferably a Brønsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof, preferably ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, dioctadecylmethylamine, methyldiphenylamine, pyridine, p-bromo-N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, phosphoniums from triethylphosphine, triphenylphosphine, and diphenylphosphine, oxoniums from ethers such as dimethyl ether diethyl ether, tetrahydrofuran and dioxane, sulfoniums from thioethers, such as diethyl thioethers, tetrahydrothiophene, and mixtures thereof.

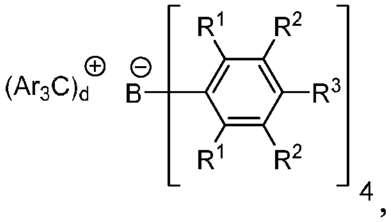
[0164] The anion component A^{d-} includes those having the formula $[M^{k+}Q_n]^{d-}$ wherein k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6 (preferably 1, 2, 3, or 4); n - k = d; M is an element selected from Group 13 of the Periodic Table of the Elements, preferably boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxide, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstitutedhydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than 1 occurrence is Q a halide. Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably each Q is a pentafluoryl aryl group. Examples of suitable A^{d-} also include diboron compounds as disclosed in U.S. Patent No. 5,447,895, which is fully incorporated herein by reference.

[0165] Examples of boron compounds which may be used as an activating cocatalyst include the compounds described as (and particularly those specifically listed as) activators in U.S. Patent No. 8,658,556, which is incorporated by reference herein.

[0166] Bulky activators are also useful herein as NCAs. "Bulky activator" as used herein refers to anionic activators represented by the formula:



or



wherein:

each R^1 is, independently, a halide, preferably a fluoride,

Ar is a substituted or unsubstituted aryl group (preferably a substituted or unsubstituted phenyl), preferably substituted with C_1 to C_{40} hydrocarbyls, more preferably C_1 to C_{20} alkyls or aromatics,

each R^2 is, independently, a halide, a C_6 to C_{20} substituted aromatic hydrocarbyl group or a siloxy group of the formula $-O-Si-R^a$, where R^a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl group (preferably R^2 is a fluoride or a perfluorinated phenyl group),

each R^3 is a halide, C_6 to C_{20} substituted aromatic hydrocarbyl group or a siloxy group of the formula $-O-Si-R^a$, where R^a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl group (preferably R^3 is a fluoride or a C_6 perfluorinated aromatic hydrocarbyl group); wherein R^2 and R^3 can form one or more saturated or unsaturated, substituted or unsubstituted rings (preferably R^2 and R^3 form a perfluorinated phenyl ring), and

L is a neutral Lewis base; $(L-H)^+$ is a Brønsted acid; d is 1, 2, or 3,

wherein the anion has a molecular weight of greater than 1020 g/mol, and wherein at least three of the substituents on the B atom each have a molecular volume of greater than 250 cubic Å, alternately greater than 300 cubic Å, or alternately greater than 500 cubic Å.

[0167] Preferably $(Ar_3C)_d^+$ is $(Ph_3C)_d^+$, where Ph is a substituted or unsubstituted phenyl, preferably substituted with C_1 to C_{40} hydrocarbyls or substituted C_1 to C_{40} hydrocarbyls, more preferably C_1 to C_{20} alkyls or aromatics or substituted C_1 to C_{20} alkyls or aromatics.

[0168] "Molecular volume" is used herein as an approximation of spatial steric bulk of an activator molecule in solution. Comparison of substituents with differing molecular volumes allows the substituent with the smaller molecular volume to be considered "less bulky" in comparison to the substituent with the larger molecular volume. Conversely, a substituent with a larger molecular volume may be considered "more bulky" than a substituent with a smaller molecular volume.

[0169] Molecular volume may be calculated as reported in "A Simple 'Back of the Envelope' Method for Estimating the Densities and Molecular Volumes of Liquids and Solids," Journal of Chemical Education, Vol. 71, No. 11, November 1994, pp. 962-964. Molecular volume (MV), in units of cubic Å, is calculated using the formula: $MV = 8.3V_S$, where V_S is the scaled volume. V_S is the sum of the relative volumes of the constituent atoms, and is calculated from the molecular formula of the substituent using the following table of relative volumes. For fused rings, the V_S is decreased by 7.5% per fused ring.

Element	Relative Volume
H	1
1st short period, Li to F	2
2nd short period, Na to Cl	4
1st long period, K to Br	5
2nd long period, Rb to I	7.5
3rd long period, Cs to Bi	9

[0170] For a list of particularly useful Bulky activators as described in U.S. Patent No. 8,658,556, which is incorporated by reference herein.

[0171] In at least some embodiments, one or more of the NCA activators is chosen from the activators described in U.S. Patent No. 6,211,105.

[0172] Preferred activators include N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorophenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, $[Ph_3C^+][B(C_6F_5)_4^-]$, $[Me_3NH^+][B(C_6F_5)_4^-]$, 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine.

[0173] In a preferred embodiment, the activator includes a triaryl carbonium (such as triphenylcarbenium tetraphenylborate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate.

[0174] In at least some embodiments, the activator includes 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, iso-butyl, or t-butyl).

[0175] Most preferably, the ionic activator Z_d^+ (A^{d-}) is one or more of N,N-dimethylanilinium tetrakis(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)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 tetra(perfluorophenyl)borate, trimethylammonium tetrakis(perfluoronaphthyl)borate, triethylammonium tetrakis(perfluoronaphthyl)borate, tripropylammonium tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate, tri(*t*-butyl)ammonium tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, and tropillium tetrakis(perfluoronaphthyl)borate.

[0176] The typical activator-to-catalyst ratio, e.g., all NCA activators-to-catalyst ratio is about a 1:1 molar ratio. Alternate preferred ranges include from about 0.1:1 to about 100:1, alternately from about 0.5:1 to about 200:1, alternately from about 1:1 to about 500:1, alternately from about 1:1 to about 1000:1. A particularly useful range is from about 0.5:1 to about 10:1, preferably about 1:1 to about 5:1.

[0177] It is also within the scope of the present disclosure that the catalyst compounds can be combined with combinations of alumoxanes and NCA's (see for example, U.S. Patent Nos. 5,153,157, 5,453,410, European Patent No. 0 573 120 B1, International Publication Nos. WO 94/07928, and WO 95/14044 which discuss the use of an alumoxane in combination with an ionizing activator).

Scavengers

[0178] In some embodiments, when using the complexes described herein, particularly when they are immobilized on a support, the catalyst system will additionally comprise one or more scavenging compounds ("scavengers"). Here, the term scavenging compound means a compound that removes polar impurities from the reaction environment. These impurities adversely affect catalyst activity and stability. Typically, the scavenging compound will be an organometallic compound such as the Group 13 organometallic compounds of U.S. Patent Nos. 5,153,157; 5,241,025; International Publication Nos. WO-A-91/09882; WO-A-94/03506; WO-A-93/14132; and that of WO 95/07941. Exemplary compounds include triethyl aluminum, triethyl borane, tri-iso-butyl aluminum, methyl alumoxane, modified methylalumoxanes, bis(diisobutylaluminum)oxide, iso-butyl alumoxane, and tri-n-octyl aluminum. Those scavenging compounds having bulky or C_6-C_{20} linear hydrocarbyl substituents connected to the metal or metalloid center usually minimize adverse interaction with the active catalyst. Examples include triethylaluminum, but more preferably, bulky compounds such as tri-iso-butyl aluminum, tri-iso-prenyl aluminum, and long-chain linear alkyl-substituted aluminum compounds, such as tri-n-hexyl aluminum, tri-n-octyl aluminum, or tri-n-dodecyl aluminum. When alumoxane is used as the activator, any excess over that needed for activation will scavenge impurities and additional scavenging compounds may be unnecessary. Alumoxanes (methylalumoxane), aluminum oxides (e.g., bis(diisobutylaluminum)oxide), and modified alumoxanes (e.g., MMAO-3A) also may be added in scavenging quantities with other activators such as $[Me_2HNPh]^+[B(pfp)_4]^-$ or $B(pfp)_3$ (perfluorophenyl = pfp = C_6F_5).

Polymers

[0179] The present disclosure provides compositions of matter that can be produced by the methods herein. The compositions of matter include polymers of the present disclosure and oils and fuels containing polymers of the present disclosure that can be used as viscosity modifiers in the oils and fuels.

[0180] In at least some embodiments, after the second stage of a process of the present disclosure, a polymer is an ethylene copolymer having a comonomer content of from about 99 (percent by weight of the polymer) wt% to about 1 wt%, such as from about 80 wt% to about 10 wt%, such as from about 95 wt% to about 20 wt%, such as from about 95 wt% to about 30 wt%, such as from about 95 wt% to about 40 wt% based on the weight of the polymer. The balance of the polymer comprises ethylene. Alternatively, a polymer is an ethylene copolymer having a comonomer content of from about 1 wt% to about 99 wt%, such as from about 5 wt% to about 90 wt%, such as from about 10 wt% to about 80 wt%, such as from about 20 wt% to about 70 wt%, such as from about 30 wt% to about 60 wt% based on the weight of the polymer. The balance of the polymer comprises ethylene. In at least some embodiments, the comonomer is propylene.

[0181] A polymer of the present disclosure may have an ethylene content of from about 1 wt% to about 100 wt%, such as from about 2 wt% to about 20 wt%, such as from about 30 wt% to about 98 wt%, such as from about 40 wt% to about 97 wt%, such as from about 50 wt% to about 96 wt%, based on the weight of the polymer. The balance of the polymer comprises one or more comonomers.

[0182] In a preferred embodiment, the ethylene content of the polymer is from about 40% to 80% or less, or less than about 70 wt%, more preferred about 60 wt% or less, most preferred about 50 wt% ± 5 wt%.

[0183] In at least some embodiments, after the second stage of a process of the present disclosure, a polymer has a diene content of from about 0.1 wt% to about 10 wt%, such as from about 0.1 wt% to about 5 wt%, such as from about 0.1 wt% to about 2 wt%, such as from about 0.1 wt% to about 1 wt%, such as from about 0.1 wt% to about 0.5 wt%, based on the weight of the polymer. The balance of the polymer comprises ethylene and an optional comonomer.

[0184] In some embodiments, a polymer of the present disclosure can have a weight average molecular weight (Mw), as determined using light scattering detector (LS), of about 5,000,000 g/mol or less, a number average molecular weight (Mn), as determined using differential refractive index detector (DRI), of about 3,000,000 g/mol or less, a z-average molecular weight (Mz), as determined using a light scattering detector, of about 10,000,000 g/mol or less, and a g'vis average value of about 0.95 or less, all of which may be determined by gel permeation chromatography with three detectors (GPC-3D). A polymer of the present disclosure may have an Mn(LS) of from about 5,000 g/mol to about 1,000,000 g/mol, such as from about 10,000 to about 800,000 g/mol, such as from about 20,000 g/mol to about 500,000 g/mol. A polymer of the present disclosure may have an Mw(LS) of from about 3,000 g/mol to about 1,000,000 g/mol, such as from about 20,000 g/mol to about 500,000 g/mol, such as from about 30,000 g/mol to about 450,000 g/mol, such as from about 60,000 g/mol to about 500,000 g/mol, or from about 100,000 g/mol to about 600,000 g/mol. In a preferred embodiment, the preferred Mw (LS) is greater than about 100 kg/mol, more preferred greater than 200 kg/mol, most preferred greater than 400 kg/mol.

[0185] A polymer of the present disclosure may have an Mz (LS) of from about 50,000 g/mol to about 10,000,000 g/mol, such as from about 50,000 g/mol to about 6,000,000 g/mol, such as from about 100,000 g/mol to about 6,000,000 g/mol, such as from about 100,000 g/mol to about 2,000,000 g/mol, such as about 50,000 g/mol to about 1,000,000 g/mol, such as from about 100,000 g/mol to about 1,000,000 g/mol.

[0186] In some embodiments, the polymer has a PDI (Mw(LS)/Mn(DRI)) greater than about 1.0, more preferably greater than 2.0, more preferably greater than about 3.0, most preferably greater than about 4.0. In a preferred embodiment, the PDI is from about 1.0 to about 6.0.

[0187] In some embodiments, a polymer of the present disclosure may have a g'vis average value of about 0.95 or less, such as about 0.8 or less, or about 0.6 or less. Polymers of the present disclosure can have g'vis values of about 0.9 or less, such as from about 0.3 to about 0.9, such as from about 0.4 to about 0.8, such as from about 0.4 to about 0.6.

[0188] In some embodiments, a polymer of the present disclosure may have a melt index (MI, g/10 min, 190°C, 2.16 kg weight) of about 100 g/10 min or less, as determined in accordance with ASTM D1238 at 190°C. Preferably the MI is about 20 g/10 min or less, is about 5 g/10 min or less, about 3 g/10 min or less, about 2 g/10 min or less, about 1 g/10 min or less, about 0.2 g/10 min or less, about 0.1 g/10 min or less, about 0.05 g/10 min or less.

[0189] In some embodiments, the copolymer has thickening efficiency from about 0.5 to about 6 (preferably about 1 to about 5, preferably about 1.5 to about 4, most preferably about 2 to about 3). In some embodiments, the copolymer has a shear stability index at 30 cycles of less than about 60.

[0190] In some embodiments, the copolymer has a high temperature, high shear (HTHS) viscosity (cP) of from about 1.0 cP to about 4.5 cP, preferably about 3.5 cP or less, more preferably about 3.3 cP or less.

[0191] In some embodiments, the copolymers described herein also have a kinematic viscosity at 100°C (KV100), as measured by ASTM D445, of about 0 cSt to about 20 cSt, preferably about 5 cSt to about 15 cSt, more preferably about 8 cSt to about 14 cSt.

[0192] In some embodiments, the copolymers described herein also have a kinematic viscosity at 40°C (KV40), as measured by ASTM D445, of about 20 cSt to about 200 cSt, preferably 20 cSt to about 120 cSt, more preferably about 50 cSt to about 100 cSt.

[0193] Further, in some embodiments, the copolymers described herein have a thickening efficiency of from about 1.0 to about 20.0 or less, preferably about 3.0 or less, more preferably about 2.5 or less, even more preferably about 2.25 or less.

[0194] Further, in some embodiments, the copolymers described herein have a viscosity index (VI) as calculated of about 100 or greater, for example about 120 or more, preferably about 125 or more.

[0195] In some embodiments, the second (neat) polymer has a shear thinning onset of from about 0.001 rad/s to about 10 rad/s, preferably about 1.0 rad/s or less, more preferably about 0.1 rad/s or less, most preferred about 0.01 rad/s or less.

[0196] Peak melting point, T_m, (also referred to as melting point), peak crystallization temperature, T_c, (also referred to as crystallization temperature), glass transition temperature (T_g), heat of fusion (ΔH_f or H_f), and percent crystallinity are determined using the following DSC procedure according to ASTM D3418-03. Differential scanning calorimetric (DSC) data can be obtained using a TA Instruments model Q200 machine. Samples weighing approximately 5-10 mg are sealed in an aluminum hermetic sample pan. The DSC data are recorded by first gradually heating the sample to 200°C at a rate of 10°C/minute. The sample is kept at 200°C for 2 minutes, then cooled to -90°C at a rate of 10°C/minute, followed by an isothermal for 2 minutes and heating to 200°C at 10°C/minute. Both the first and second cycle thermal events were recorded. Areas under the endothermic peaks were measured and used to determine the heat of fusion and the percent of crystallinity. The percent crystallinity is calculated using the formula, [area under the melting peak (Joules/gram)/B(Joules/gram)]*100, where B is the heat of fusion for the 100% crystalline homopolymer of the major monomer component. These values for B are to be obtained from the Polymer Handbook, Fourth Edition, published by John Wiley and Sons, New York 1999, provided; however, a value of 290 J/g is used for the heat of fusion for 100% crystalline polyethylene. The crystallization temperatures reported here were obtained during the second heating/cooling cycle unless otherwise noted.

[0197] In a preferred embodiment the polymer produced herein has a unimodal or multimodal molecular weight distribution as determined by Gel Permeation Chromatography (GPC). By "unimodal" is meant that the GPC trace has one peak or inflection point. By "multimodal" is meant that the GPC trace has at least two peaks or inflection points. An inflection point is that point where the second derivative of the curve changes in sign (e.g., from negative to positive or vice versa).

[0198] Unless otherwise indicated, measurements of the moments of molecular weight, i.e., weight average molecular weight (Mw), number average molecular weight (Mn), and z average molecular weight (Mz) are determined by Gel Permeation Chromatography (GPC) as described in Macromolecules, 2001, Vol. 34, No. 19, pg. 6812, which is fully incorporated herein by reference, including that, a High Temperature Size Exclusion Chromatograph (SEC, Waters Alliance 2000), equipped with a differential refractive index detector (DRI) equipped with three Polymer Laboratories PLgel 10 mm Mixed-B columns is used. The instrument is operated with a flow rate of about 1.0 cm^3/min, and an injection volume of about 300 µL. The various transfer lines, columns, and differential refractometer (the DRI detector) are housed in an oven maintained at about 145°C. Polymer solutions are prepared by heating about 0.75 to about 1.5 mg/ml of polymer in filtered 1,2,4-trichlorobenzene (TCB) containing ~1000 ppm of butylated hydroxy toluene (BHT) at about 160°C for about 2 hours with continuous agitation. A sample of the polymer containing solution is injected into to the GPC and eluted using filtered 1,2,4-trichlorobenzene (TCB) containing ~1000 ppm of BHT. The separation efficiency of the column set is calibrated using a series of narrow MWD polystyrene standards reflecting the expected Mw range of the sample being analyzed and the exclusion limits of the column set. Seventeen individual polystyrene standards, obtained from Polymer Laboratories (Amherst, MA) and ranging from Peak Molecular Weight (Mp) ~580 to 10,000,000, were used to generate the calibration curve. The flow rate is calibrated for each run to give a common peak position for a flow rate marker (taken to be the positive inject peak) before determining the retention volume for each polystyrene standard. The flow marker peak position is used to correct the flow rate when analyzing samples. A calibration curve (log(Mp) vs. retention volume) is generated by recording the retention volume at the peak in the DRI signal for each PS standard, and fitting this data set to a 2nd-order polynomial. The equivalent polyethylene molecular weights are determined by using the Mark-Houwink coefficients shown in Table B.

Table B

Mark-Houwink coefficients		
Material	K (dL/g)	α
PS	1.75×10^{-4}	0.67
PE	5.79×10^{-4}	0.695

[0199] In at least some embodiments, the polymer produced is a tactic polymer, preferably an isotactic or highly isotactic polymer. In at least some embodiments, the polymer produced is isotactic polypropylene, such as highly isotactic polypropylene.

[0200] The term “isotactic polypropylene” (iPP) is defined as having at least about 10% or more isotactic pentads. The term “highly isotactic polypropylene” is defined as having about 50% or more isotactic pentads. The term “syndiotactic polypropylene” is defined as having about 10% or more syndiotactic pentads. The term “random copolymer polypropylene” (RCP), also called propylene random copolymer, is defined to be a copolymer of propylene and about 1 to about 10 wt% of an olefin chosen from ethylene and C_4 to C_8 alpha-olefins. Preferably, isotactic polymers (such as iPP) have at least about 20% (preferably at least about 30%, preferably at least about 40%) isotactic pentads. A polyolefin is “atactic,” also referred to as “amorphous” if it has less than about 10% isotactic pentads and syndiotactic pentads.

[0201] Polypropylene microstructure is determined by ^{13}C NMR spectroscopy, including the concentration of isotactic and syndiotactic diads ([m] and [r]), triads ([mm] and [rr]), and pentads ([mmmm] and [rrrr]). The designation “m” or “r” describes the stereochemistry of pairs of contiguous propylene groups, “m” referring to meso and “r” to racemic. Samples are dissolved in d_2-1,1,2,2-tetrachloroethane, and spectra recorded at 125°C using a 100 MHz (or higher) NMR spectrometer. Polymer resonance peaks are referenced to mmmm = 21.8 ppm. Calculations involved in the characterization of polymers by NMR are described by F. A. Bovey in POLYMER CONFORMATION AND CONFIGURATION (Academic Press, New York 1969) and J. Randall in POLYMER SEQUENCE DETERMINATION, ^{13}C-NMR METHOD (Academic Press, New York, 1977).

End Uses

[0202] Articles made using polymers produced herein may include, for example, molded articles (such as containers and bottles, e.g., household containers, industrial chemical containers, personal care bottles, medical containers, fuel tanks, and storage ware, toys, sheets, pipes, tubing) films, and non-wovens. It should be appreciated that the list of applications above is merely exemplary, and is not intended to be limiting.

[0203] In other embodiments, the ethylene copolymers produced herein are used in lubricating compositions or in fuel compositions, typically as viscosity modifiers.

<u>Lubrication Oil Compositions and Fuel Oil Compositions</u>

[0204] Lubricating oil compositions containing a copolymer 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.

[0205] In some embodiments, 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). Preferably, the polyalphaolefin 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.

[0206] 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 A 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).

	KV100 (cSt)	KV40 (cSt)	VI	Pour Point (°C)	Specific Gravity	Flash Point (°C)	APHA Color
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

[0207] In one or more embodiments, the base stock can include oil or blends thereof conventionally employed 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. 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. Suitable base stocks can also be or include gear lubricants, industrial oils, pump oils and other lubricating oils.

[0208] 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 hydrocarbons, alkyl esters of dicarboxylic acids, polyglycols, alcohols, polyalphaolefins, polybutenes, alkyl benzenes, organic esters of phosphoric acids, polysilicone oils, or combinations thereof.

[0209] The lubrication oil composition can include a base stock and one or more copolymers produced herein, and optionally, a pour point depressant. The lubrication oil composition 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 of 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 (imaginary part of “complex viscosity”). For purposes of this disclosure and the claims thereto, steady shear viscosity measurements are done on a TA Instruments Model ARES-G2 rheometer using a 25mm parallel-plate fixture at a temperature of about 190°C and a frequency of about 0.01 to 628 rad/s. All measurements were made within the linear regime as confirmed from strain sweep experiments. After loading and every temperature change, the samples were equilibrated at constant temperature during approximately 30 min until normal forces were completely relaxed. In the course of the measurements, the sample were kept under nitrogen protection to avoid thermal degradation.

[0210] 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 polymer 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.

[0211] The lubrication oil composition preferably comprises about 0.01 wt% to about 12 wt%, 0.1 to about 2.5 wt%, or about 0.25 to about 1.5 wt%, or about 0.5 wt% or about 1.25 wt% of the polymer produced herein. In some embodiments, the amount of the polymer produced herein in the lubrication oil composition can range from a low of about 0.5 wt%, about 1 wt%, or about 2 wt% to a high of about 2.5 wt%, about 3 wt%, about 5 wt%, or about 10 wt%.

Oil Additives

[0212] The lubricating oil compositions can optionally contain 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, or combinations thereof.

[0213] 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, preferably in the presence of an alkylated phenol or of an alkylphenol thioester, and also preferably 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.

[0214] 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. Other useful oxidation inhibitors or antioxidants include oil-soluble copper compounds, such as described in U.S. Patent No. 5,068,047.

[0215] 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 U.S. Patent No. 3,933,659, which discloses fatty acid esters and amides; U.S. Patent No. 4,176,074, which describes molybdenum complexes of polyisobutenyl succinic anhydride-amino alkanols; U.S. Patent No. 4,105,571, which discloses glycerol esters of dimerized fatty acids; U.S. Patent No. 3,779,928, which discloses alkane phosphonic acid salts; U.S. Patent No. 3,778,375, which discloses reaction products of a phosphonate with an oleamide; U.S. Patent No. 3,852,205, which discloses S-carboxyalkylene hydrocarbyl succinimide, S-carboxyalkylene hydrocarbyl succinamic acid and mixtures thereof; U.S. Patent No. 3,879,306, which discloses N-(hydroxyalkyl)alkenyl-succinamic acids or succinimides; U.S. Patent No. 3,932,290, which discloses reaction products of di-(lower alkyl) phosphites and epoxides; and U.S. Patent No. 4,028,258, which discloses the alkylene oxide adduct of phosphosulfurized N-(hydroxyalkyl) alkenyl succinimides. Preferred friction modifiers are succinate esters, or metal salts thereof, of hydrocarbyl substituted succinic acids or anhydrides and thiobis-alkanols, such as described in U.S. Patent No. 4,344,853.

[0216] 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.

[0217] 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.

[0218] Foam control can be provided by any one or more anti-foamants. Suitable antifoamants include polysiloxanes, such as silicone oils and polydimethyl siloxane.

[0219] Anti-wear agents reduce wear of metal parts. Representatives of conventional antiwear agents are zinc dialkyldithiophosphate and zinc diaryldithiosphate, which also serve as an antioxidant.

[0220] 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.

[0221] 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.

[0222] 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

[0223] Conventional blending methods are described in U.S. Patent No. 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. The pelletized, solid polymer of the present described, as described above, can be added by blending directly with the base oil so as give directly viscosity for the VI improver, so that the complex multi-step process of the prior art is not needed. The solid polymer composition can be dissolved in the base stock without the need for additional shearing and degradation processes.

[0224] The polymer compositions will 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.

[0225] The copolymers produced herein preferably have a shear stability index of SSI (determined according to ASTM D6278, 30 cycles) of from about 6 to about 50, preferably about 10 to about 40, more preferably about 10 to about 20.

[0226] The copolymers produced herein preferably have a shear stability index of SSI (determined according to ASTM D6278=) of from about 8 to about 65, more preferably about 10 to about 70, even more preferably about 10 to about 60.

[0227] The following further embodiments are contemplated as within the scope of the present invention.

Embodiment A

A method of making a lubricating oil composition comprising:

(a) combining a base stock oil with a branched polymer having:

an Mw(LS)/Mn(DRI) of from about 1.0 to about 6.0;

an Mw(LS) of from about 3,000 to about 1,000,000 g/mol;

a g'vis of about 0.90 or less; and

an ethylene content of about 40% to about 80% or less; and

(b) recovering a lubricating oil composition.

Embodiment B

The method of Embodiment A, wherein the branched polymer is formed by: contacting ethylene and one or more C_3 to C_{40} alpha-olefins with a catalyst system comprising a non-metallocene catalyst, an activator, and a reversible chain transfer agent to recover a first polymer; and

contacting the first polymer with a coupling agent in the presence of the first catalyst system or a second catalyst system comprising a second non-metallocene catalyst and a second activator to recover the branched polymer.

Embodiment C

The method of any one of Embodiments A or B, wherein the base stock oil comprises a hydrocarbon, polyalphaolefin (PAO), alkyl esters of dicarboxylic acids, polyglycols, alcohols, polybutenes, alkylbenzenes, organic esters of phosphoric acids, polysilicone oils, or combinations thereof.

Embodiment D

The method of any one of Embodiments A to C, further comprising blending the base stock oil and the polymer with an oil additive.

Embodiment E

The method of Embodiment D, wherein the oil additive is a pour point depressant, anti-wear agent, antioxidant, other viscosity-index improver, dispersant, corrosion inhibitor, anti-foaming agent, detergent, rust inhibitor, friction modifier, or a combination thereof.

Embodiment F

The method of any one of Embodiments A to E, wherein the lubricating oil composition comprises about 0.01 wt% to about 12 wt% of the polymer based on the composition.

Embodiment G

The method of any one of Embodiments B to F, further comprising transferring the first polymer from a first reactor to a second reactor.

Embodiment H

The method of any one of Embodiments B to G, wherein the first catalyst system comprises isohexane.

Embodiment I

The method of any one of Embodiments B to H, wherein the one or more C_3 to C_{20} alpha-olefins is propylene.

Embodiment J

The method of any one of Embodiments B to I, wherein the contacting ethylene and the contacting the first polymer occurs at a temperature of about 0°C to about 300°C, at a pressure in the range of from about 0.20 MPa to about 1500 MPa, and at a time up to about 300 min.

Embodiment K

The method of any one of Embodiments B to J, wherein the reversible chain transfer agent comprises one or more of trialkyl aluminum or dialkyl zinc.

Embodiment L

The method of Embodiment K, wherein the reversible chain transfer agent comprises trialkyl aluminum is triethylaluminum, tri(i-butyl) aluminum, tri(n-hexyl) aluminum, tri(n-octyl) aluminum, and the dialkyl zinc is diethyl zinc, di(n-propyl)zinc, and di(n-octyl)zinc.

Embodiment M

The method of any one of Embodiments B to L, wherein the coupling agent is an α,ω-diene.

Embodiment N

The method of any one of Embodiments B to M, wherein the coupling agent is 1,6-heptadiene; 1,7-octadiene; 1,8-nonadiene; 1,9-decadiene; 1,10-undecadiene; 1,11-dodecadiene; 1,12-tridecadiene; 1,13-tetradecadiene, or combinations thereof.

Embodiment O

The method of any one of Embodiments A to N, wherein the branched polymer ha

a high temperature, high shear (HTHS) viscosity of about 4.0 or less; and

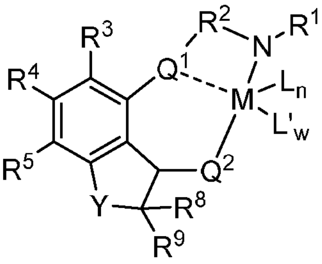
a kinematic viscosity (KV) at 100°C of about 15 cSt or less; and a ratio of thickening efficiency to shear stability index (30 cycles) of from about 1:5 to about 1:20.

Embodiment P

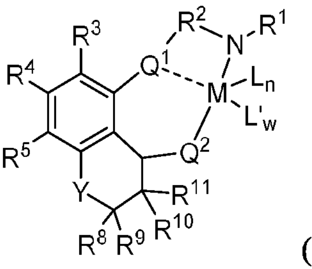
The method of any one of Embodiments A to O, wherein the kinematic viscosity at 100°C of the lubricating oil is increased by at least about 50% upon blending with 1.15 wt% of the branched polymer.

Embodiment Q

The method of any one of Embodiments B to P, wherein the non-metallocene catalyst is a pyridyldiamido transition metal complex represented by the formula (A), (B), (C), or (D):



(A)



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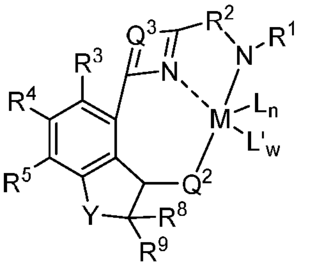

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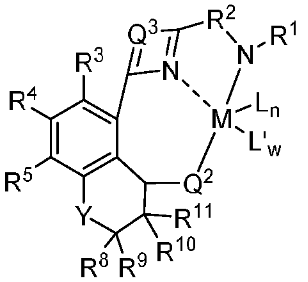


(D),

wherein:

M is a Group 3 or 4 metal;

Q^1 is a three atom bridge with the central of the three atoms being a group 15 or 16 element (said group 15 element may or may not be substituted with an R^{30} group) represented by the formula: $-G^1-G^2-G^3-$ where G^2 is a group 15 or 16 atom (said group 15 element may be substituted with a R^{30} group), G^1 and G^3 are each a group 14, 15 or 16 atom (each group 14, 15 and 16 element may or may not be substituted with one or more R^{30} groups), where G^1, G^2 and G^3, or G^1 and G^2, or G^1 and G^3, or G^2 and G^3 may form a singular or multi ring system;

each R^{30} group is independently a hydrogen, a C_1 to C_{100} hydrocarbyl radical, or a silyl radical;

Q^2 is $-NR^{17}$ or $-PR^{17}$, where R^{17} is a hydrocarbyl radical, a substituted hydrocarbyl radical, a silyl radical, or a germyl radical;

Q^3 is $-(TT)-$ or $-(TTT)-$ where each T is carbon or a heteroatom, and said carbon or heteroatom may be unsubstituted or substituted with one or more R^{30} groups that together with the "$-C-Q^3=C-$" fragment, forms a 5- or 6-membered cyclic group or a polycyclic group including the 5- or 6-membered cyclic group;

R^1 is a hydrocarbyl radical, a substituted hydrocarbyl radical, or a silyl radical;

each of R^3, R^4, and R^5 is independently a hydrogen, a hydrocarbyl radical, a substituted hydrocarbyl radical, an aryl radical, a substituted aryl radical, an alkoxy radical, an aryloxy radical, a halogen, an amino radical, or a silyl radical, or two or more adjacent R^3, R^4, and R^5 groups may independently join together to form a substituted or unsubstituted hydrocarbyl ring or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings; R^2 is $-E(R^{12})(R^{13})-$ where E is carbon, silicon, or germanium; Y is oxygen, sulfur, or $-E^*(R^6)(R^7)-$, wherein E* is carbon, silicon, or germanium; each of R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} is independently a hydrogen, a hydrocarbyl radical, a substituted hydrocarbyl radical, an aryl radical, a substituted aryl radical, an alkoxy radical, a halogen, an amino radical, or a silyl radical, or two or more adjacent R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} groups may independently join together to form a saturated, substituted or unsubstituted hydrocarbyl ring or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;

L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;

n is 1 or 2;

L' is neutral Lewis base; and

w is 0, 1, 2, 3 or 4.

<u>Embodiment R</u>

The method of any one of Embodiments B to Q, wherein M is Ti, Zr, or Hf.

Embodiment S

The method of any one of Embodiments B to R, wherein R^2 is CH_2, CH(aryl), CH(2-isopropylphenyl), CH(2,6-dimethylphenyl), CH(2,4-6-trimethylphenyl), CH(alkyl), CMe_2, $SiMe_2$, $SiEt_2$, or $SiPh_2$.

Embodiment T

The method of any one of Embodiments B to S, wherein E and E* are carbon and each of R^6, R^7, R^{12}, and R^{13} is a C_6 to C_{30} substituted or unsubstituted aryl group.

Embodiment U

The method of any one of Embodiments B to T, wherein Q^2 is $–NR^{17}$.

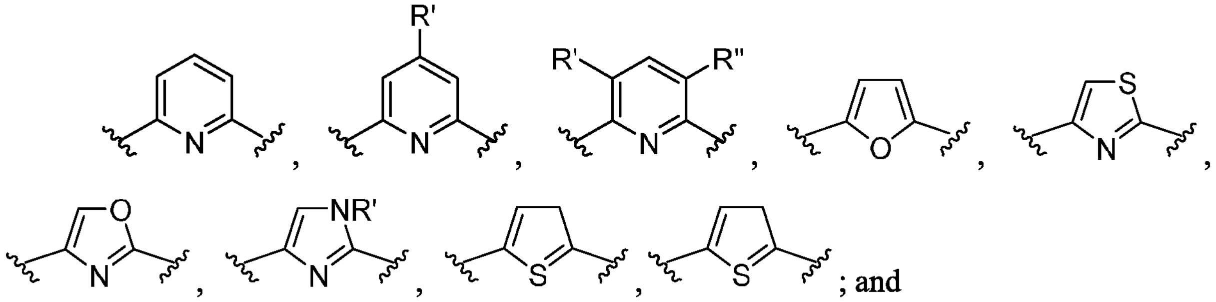
Embodiment V

The method of any one of Embodiments B to U, wherein each of E and E* is carbon and each of R^1 and R^{17} is independently phenyl groups that are substituted with 0, 1, 2, 3, 4, or 5 substituents, the substituents comprising F, Cl, Br, I, CF_3, NO_2, alkoxy, dialkylamino, hydrocarbyl, and substituted hydrocarbyl groups with from one to ten carbons.

Embodiment W

The method of any one of Embodiments B to V, wherein:

Q^1 is:



; and

Q^3 is CHCHCH, CHCH, CHN(R'), CH–S, CHC(R')CH, C(R')CHC(R''), CH-O, or NO, wherein the ⌇ indicates the connections to R^2 and the aromatic ring, and R' and R'' is a hydrocarbyl.

Embodiment X

The method of any one of Embodiments B to W, wherein the activator comprises alkylalumoxane.

Embodiment Y

The method of any one of Embodiments B to X, wherein the activator is represented by the formula:

$$(Z)_d^+(A^{d-})$$

wherein Z is (L–H) or a reducible Lewis acid, L is a neutral base; H is hydrogen; $(L\text{–}H)^+$ is a Brønsted acid; A^{d-} is a non-coordinating anion having the charge d-; and d is an integer from 1 to 3.

Embodiment Z

The method of any one of Embodiments B to Y, wherein the catalyst system further comprises an activator represented by the formula:

$$(Z)_d^+(A^{d-})$$

wherein A^{d-} is a non-coordinating anion having the charge d-; and d is an integer from 1 to 3; and Z is a reducible Lewis acid represented by the formula: (Ar_3C^+), wherein Ar is aryl substituted with a C_1 to C_{40} hydrocarbyl or with a substituted C_1 to C_{40} hydrocarbyl, or a heteroaryl substituted with a C_1 to C_{40} hydrocarbyl, or with a substituted C_1 to C_{40} hydrocarbyl.

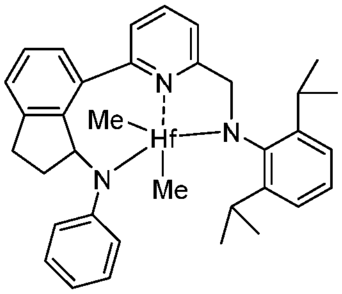
Embodiment AA

The method of any one of Embodiments B to Z, wherein the activator comprises one or more of:

N,N-dimethylanilinium tetrakis(perfluorophenyl)borate,
N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-dimethylanilinium tetrakis(perfluorobiphenyl)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 tetra(perfluorophenyl)borate,
trimethylammonium tetrakis(perfluoronaphthyl)borate,
triethylammonium tetrakis(perfluoronaphthyl)borate,
tripropylammonium tetrakis(perfluoronaphthyl)borate,
tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, and
tropillium tetrakis(perfluoronaphthyl)borate.

Embodiment AB

The method of any one of Embodiments B to AA, wherein

the pyridyldiamido transition metal complex is  ; and the activator is N,N-dimethylanilinium tetra(perfluorophenyl)borate.

Embodiment AC

The method of any one of Embodiments B to AB, further comprising introducing the catalyst represented by the formula (A), (B), (C), or (D) into a reactor as a slurry.

Embodiment AD

The method of any one of Embodiments A to AC, wherein the branched polymer has a viscosity index of about 120 or more.

Embodiment AE

The method of any one of Embodiments A to AD, wherein the branched polymer has a shear thinning onset of about 0.01 rad/s or less.

Embodiment AF

A lubricating oil composition comprising a copolymer having:
an Mw(LS)/Mn(DRI) is from about 2.0 to about 6.0;
an Mw(LS) is from about 50,000 to about 1,000,000 g/mol;
a g'vis of less than about 0.90;
an ethylene content of about 40% to about 60% or less;
a thickening efficiency of about 1.2 or more; and
a shear stability index (30 cycles) less than about 40.

Experimental

[0228] Polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity from Sigma-Aldrich) containing 2,6-di-tertbutyl-4-methylphenol (BHT, 99% from Aldrich) at 165°C in a shaker oven for approximately

3 hours. The typical concentration of polymer in solution was between 0.1 to 0.9 mg/ml with a BHT concentration of 1.25 mg BHT/ml of TCB.

Determination by GPC-IR Hyphenated with Multiple Detectors

[0229] Unless otherwise indicated, the distribution and the moments of molecular weight (Mw, Mn, Mw/Mn, etc.), the comonomer content (C2, C3, C6, etc.) and the branching index (g'vis) are determined by using a high temperature Gel Permeation Chromatography (Polymer Char GPC-IR) equipped with a multiple-channel band-filter based Infrared detector IR5, an 18-angle light scattering detector and a viscometer. Three Agilent PLgel 10-µm Mixed-B LS columns are used to provide polymer separation. Aldrich reagent grade 1,2,4-trichlorobenzene (TCB) with 300 ppm antioxidant butylated hydroxytoluene (BHT) is used as the mobile phase. The TCB mixture is filtered through a 0.1-µm Teflon filter and degassed with an online degasser before entering the GPC instrument. The nominal flow rate is 1.0 ml/min and the nominal injection volume is 200 µL. The whole system including transfer lines, columns, and detectors are contained in an oven maintained at 145°C. The polymer sample is weighed and sealed in a standard vial with 80-µL flow marker (Heptane) added to it. After loading the vial in the autosampler, polymer is automatically dissolved in the instrument with 8 ml added TCB solvent. The polymer is dissolved at 160°C with continuous shaking for about 1 hour for most PE samples or 2 hour for PP samples. The TCB densities used in concentration calculation are 1.463 g/ml at room temperature and 1.284 g/ml at 145°C. The sample solution concentration is from 0.2 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples. The concentration (c), at each point in the chromatogram is calculated from the baseline-subtracted IR5 broadband signal intensity (I), using the following equation:

$$c = \beta I$$

where β is the mass constant.

[0230] The mass recovery is calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume. The conventional molecular weight (IR MW) is determined by combining universal calibration relationship with the column calibration which is performed with a series of monodispersed polystyrene (PS) standards ranging from 700 to 10M gm/mole. The MW at each elution volume is calculated with following equation

$$\log M = \frac{\log(K_{PS}/K)}{a+1} + \frac{a_{PS}+1}{a+1}\log M_{PS}$$

where the variables with subscript "PS" stand for polystyrene while those without a subscript are for the test samples. In this method, $\alpha_{PS} = 0.67$ and $K_{PS} = 0.000175$ while α and K are for other materials as calculated and published in literature (Sun, T. et al. *Macromolecules* 2001, *34*, 6812), except that for purposes of the present disclosure, α = 0.695 and K = 0.000579 for linear ethylene polymers, α = 0.705 and K = 0.0002288 for linear propylene polymers, α = 0.695 and K = 0.000181 for linear butene polymers, α is 0.695 and K is 0.000579*(1-0.0087*w2b+0.000018*(w2b)^2) for ethylene–butene copolymer where w2b is a bulk weight percent of butene comonomer, α is 0.695 and K is 0.000579*(1-0.0075*w2b) for ethylene–hexene copolymer where w2b is a bulk weight percent of hexene comonomer, and α is 0.695 and K is 0.000579*(1-0.0077*w2b) for ethylene–octene copolymer where w2b is a bulk weight percent of octene comonomer. Concentrations are expressed in g/cm^3, molecular weight is expressed in g/mole, and intrinsic viscosity (hence K in the Mark–Houwink equation) is expressed in dL/g unless otherwise noted.

[0231] The comonomer composition is determined by the ratio of the IR5 detector intensity corresponding to CH_2 and CH_3 channel calibrated with a series of PE and PP homo/copolymer standards whose nominal value are predetermined by NMR or FTIR. In particular, this provides the methyls per 1000 total carbons (CH_3/1000TC) as a function of molecular weight. The short-chain branch (SCB) content per 1000TC (SCB/1000TC) is then computed as a function of molecular weight by applying a chain-end correction to the CH_3/1000TC function, assuming each chain to be linear and terminated by a methyl group at each end. The weight% comonomer is then obtained from the following expression in which *f* is 0.3, 0.4, 0.6, 0.8, and so on for C3, C4, C6, C8, and so on comonomers, respectively.

$$w2 = f * \text{SCB/1000TC}.$$

[0232] The bulk composition of the polymer from the GPC-IR and GPC-4D analyses is obtained by considering the entire signals of the CH_3 and CH_2 channels between the integration limits of the concentration chromatogram. First, the following ratio is obtained

$$\text{Bulk IR ratio} = \frac{\text{Area of CH}_3\text{ signal within integration limits}}{\text{Area of CH}_2\text{ signal within integration limits}}.$$

[0233] Then the same calibration of the CH_3 and CH_2 signal ratio, as mentioned previously in obtaining the CH3/1000TC as a function of molecular weight, is applied to obtain the bulk CH3/1000TC. A bulk methyl chain ends per 1000TC (bulk CH3end/1000TC) is obtained by weight-averaging the chain-end correction over the molecular-weight range. Then

$$w2b = f * \text{bulk CH3/1000TC}$$

$$\text{bulk SCB/1000TC} = \text{bulk CH3/1000TC} - \text{bulk}\frac{\text{CH3end}}{\text{1000TC}}$$

and bulk SCB/1000TC is converted to bulk $w2$ in the same manner as described above.

[0234] The LS detector is the 18-angle Wyatt Technology High Temperature DAWN HELEOSII. The LS molecular weight (*M*) at each point in the chromatogram is determined by analyzing the LS output using the Zimm model for static light scattering (*Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press, 1972.):

$$\frac{K_o c}{\Delta R(\theta)} = \frac{1}{MP(\theta)} + 2A_2 c \; .$$

[0235] Here, ΔR(θ) is the measured excess Rayleigh scattering intensity at scattering angle θ, c is the polymer concentration determined from the IR5 analysis, A_2 is the second virial coefficient, P(θ) is the form factor for a monodisperse random coil, and K_o is the optical constant for the system:

$$K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

where N_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system. The refractive index, n=1.500 for TCB at 145 °C and λ=665 nm. For analyzing polyethylene homopolymers, ethylene-hexene copolymers, and ethylene-octene copolymers, dn/dc=0.1048 ml/mg and A_2=0.0015; for analyzing ethylene-butene copolymers, dn/dc=0.1048*(1-0.00126*w2) ml/mg and A_2=0.0015 where w2 is weight percent butene comonomer.

[0236] A high temperature Agilent (or Viscotek Corporation) viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_S, for the solution flowing through the viscometer is calculated from their outputs. The intrinsic viscosity, [η], at each point in the chromatogram is calculated from the equation $[\eta] = \eta_S/c$, where c is concentration and is determined from the IR5 broadband channel output. The viscosity MW at each point is calculated as

$$M = K_{PS} M^{\alpha_{PS}+1} / [\eta],$$

where α_{ps} is 0.67 and K_{PS} is 0.000175.

[0237] The branching index (g'_{vis}) is calculated using the output of the GPC-IR5-LS-VIS method as follows. The average intrinsic viscosity, $[\eta]_{avg}$, of the sample is calculated by:

$$[\eta]_{avg} = \frac{\sum c_i [\eta]_i}{\sum c_i}$$

where the summations are over the chromatographic slices, i, between the integration limits.

[0238] The branching index g'_{vis} is defined as

$$g'_{vis} = \frac{[\eta]_{avg}}{K M_v^{\alpha}},$$

where M_V is the viscosity-average molecular weight based on molecular weights determined by LS analysis and the K and α are for the reference linear polymer, which are, for purposes of the present disclosure, α = 0.695 and K = 0.000579 for linear ethylene polymers, α = 0.705 and K = 0.0002288 for linear propylene polymers, α = 0.695 and K = 0.000181 for linear butene polymers, α is 0.695 and K is 0.000579*(1-0.0087*w2b+0.000018*(w2b)^2) for ethylene–butene copolymer where w2b is a bulk weight percent of butene comonomer, α is 0.695 and K is 0.000579*(1-0.0075*w2b) for ethylene–hexene copolymer where w2b is a bulk weight percent of hexene comonomer, and α is 0.695 and K is 0.000579*(1-0.0077*w2b) for ethylene–octene copolymer where w2b is a bulk weight percent of octene comonomer. Concentrations are expressed in g/cm^3, molecular weight is expressed in g/mole, and intrinsic viscosity (hence K in the Mark–Houwink equation) is expressed in dL/g unless otherwise noted. Calculation of the w2b values is as discussed above.

[0239] Experimental and analysis details not described above, including how the detectors are calibrated and how to calculate the composition dependence of Mark-Houwink parameters and the second-virial coefficient, are described by T. Sun, P. Brant, R. R. Chance, and W. W. Graessley (*Macromolecules*, 2001, Vol. 34(19), pp. 6812-6820).

[0240] All molecular weights are weight average unless otherwise noted. All molecular weights are reported in g/mol unless otherwise noted.

[0241] Methyl groups per 1000 carbons (CH_3/1000Carbons) is determined by ^{1}H NMR.

[0242] Melt Index (MI, also referred to as I2) is measured according to ASTM D1238 at 190°C, under a load of 2.16 kg unless otherwise noted. The units for MI are g/10 min or dg/min.

[0243] High Load Melt Index (HLMI, also referred to as I21) is the melt flow rate measured according to ASTM D1238 at 190°C, under a load of 21.6 kg. The units for HLMI are g/10 min or dg/min.

[0244] Melt Index Ratio (MIR) is the ratio of the high load melt index to the melt index, or I21/I2.

[0245] Average wt% of ethylene (C2 content) is determined by ^{1}H NMR and ^{13}C NMR.

[0246] To determine various molecular weight related values by GPC, high temperature size exclusion chromatography was performed using GPC-IR (Polymer Char). The IV (intrinsic viscosity) molecular weights presented in the examples are relative to linear polystyrene standards whereas the LS (light scattering) and TR (infrared) molecular weights are absolute.

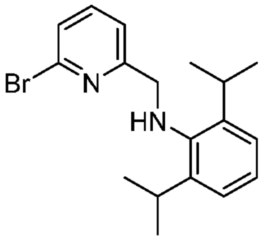
Differential Scanning Calorimetry

[0247] Crystallization temperature (T_c) and melting temperature (or melting point, T_m) are measured using Differential Scanning Calorimetry (DSC) on a commercially available instrument (e.g., TA Instruments 2920 DSC). Typically, 6 to 10 mg of molded polymer or plasticized polymer is sealed in an aluminum pan and loaded into the instrument at room temperature. Melting data (first heat) is acquired by heating the sample to at least 30°C above its melting temperature, typically 220°C for polyethylene, at a heating rate of 10°C/min. The sample is held for at least 5 minutes at this temperature to destroy its thermal history. Crystallization data are acquired by cooling the sample from the melt to at least 50°C below the crystallization temperature, typically -100°C for polyethylene, at a cooling rate of 10°C/min. The sample is held at this temperature for at least 5 minutes, and finally heated at 10°C/min to acquire additional melting data (second heat). The endothermic melting transition (first and second heat) and exothermic crystallization transition are analyzed according to standard procedures. The melting temperatures reported are the peak melting temperatures from the second heat unless otherwise specified.

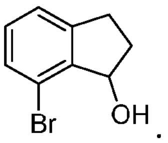
[0248] For polymers displaying multiple peaks, the melting temperature is defined to be the peak melting temperature from the melting trace associated with the largest endothermic calorimetric response (as opposed to the peak occurring at the highest temperature). Likewise, the crystallization temperature is defined to be the peak crystallization temperature from the crystallization trace associated with the largest exothermic calorimetric response (as opposed to the peak occurring at the highest temperature). Areas under the DSC curve are used to determine the heat of transition (heat of fusion, H_f, upon melting or heat of crystallization, H_c, upon crystallization), which can be used to calculate the degree of crystallinity (also called the percent crystallinity). The percent crystallinity (X%) is calculated using the formula:

$$(X\%) = [\text{area under the curve (in J/g)} / H^o \text{ (in J/g)}] * 100$$

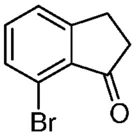
where H^o is the ideal heat of fusion for a perfect crystal of the homopolymer of the major monomer component. These values for H^o are to be obtained from the *Polymer Handbook, Fourth Edition,* published by John Wiley and Sons, New York 1999, except that a value of 290 J/g is used for H^o (polyethylene), a value of 140 J/g is used for H^o (polybutene), and a value of 207 J/g is used for H^o (polypropylene).



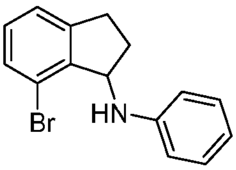
[0249] Preparation of N-[(6-bromopyridin-2-yl)methyl]-2,6-diisopropylaniline. A solution of 6-bromopyridine-2-carbaldehyde (85.0 g, 457 mmol) and 2,6-diisopropylaniline (80.9 g, 457 mmol) ethanol (1000 ml) was refluxed for 8 h. The obtained solution was evaporated to dryness, and the residue was recrystallized from 200 ml of methanol. In an argon atmosphere, to thus obtained 113.5 g (329 mmol) of N-[(1E)-(6-bromopyridin-2-yl)methylene]-2,6-diisopropylaniline were added $NaBH_3CN$ (33.16 g, 526 mmol), acetic acid (9 ml) and methanol (1000 ml). This mixture was refluxed for 12 h, cooled to room temperature, poured into 1000 ml of water, and the crude product was extracted with ethyl acetate (3 x 200 ml). The combined extract was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm, eluent: hexane-ethyl acetate = 10:1, vol.). Yield 104.4 g (66%) of a yellow oil. Anal. calc. for $C_{18}H_{23}BrN_2$: C, 62.25; H, 6.68; N, 8.07. Found: C, 62.40; H, 6.87; N, 7.90. ^1H NMR ($CDCl_3$): δ 7.50 (m, 1H, 4-H in Py), 7.38 (m, 1H, 5-H in Py), 7.29 (m, 1H, 3-H in Py), 7.05-7.12 (m, 3H, 3,4,5-H in 2,6-$iPr_2C_6H_3$), 4.18 (s, 2H, CH_2NH), 3.94 (br.s, 1H, NH), 3.33 (sept, J = 6.8 Hz, 2H, $CHMe_2$), 1.23 (d, J = 6.8 Hz, 12H, $CHMe_2$).



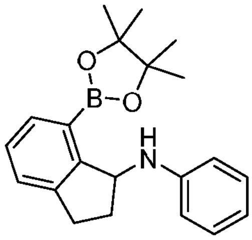
[0250] Preparation of 7-bromoindan-1-ol. To a mixture of indan-1-ol (100 g, 746 mmol), N,N,N’,N’-tetramethylethylenediamine (250 ml, 1.64 mol), and pentane (3000 ml) cooled to a temperature of -20°C, 2.5M nBuLi in hexanes (655 ml, 1.64 mol) was added. The reaction mixture was then refluxed for 12 h and then cooled to -80°C. Then, 1,2-dibromotetrafluoroethane (225 ml, 1.87 mol) of was added, and the resulting mixture was allowed to warm to room temperature. This mixture was stirred for 12 h, and then 100 ml of water was added. The resulting mixture was diluted with 2000 ml of water, and the organic layer was separated. The aqueous layer was extracted with toluene (3 x 400 ml). The combined organic extract was dried over Na_2SO_4 and evaporated to dryness. The residue was distilled using a Kugelrohr apparatus, b.p. 120-140°C/1mbar. The resulting yellow oil was dissolved in 50 ml of triethylamine, and the obtained solution added dropwise to a stirred solution of 49.0 ml (519 mmol) of acetic anhydride and 4.21 g (34.5 mmol) of 4-(dimethylamino)pyridine in 70 ml of triethylamine. The resulting mixture was stirred for 5 min, then 1000 ml of water was added, and stirring was continued for 12 h. Then, the reaction mixture was extracted with ethyl acetate (3 x 200 ml). The combined organic extract was washed with aqueous Na_2CO_3, dried over Na_2SO_4, and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm, eluent: hexane-ethyl acetate = 30:1, vol.). The resulting ester was dissolved in 1000 ml of methanol, KOH (50.5 g, 900 mmol) was added, and this mixture was refluxed for 3 h. The reaction mixture was then cooled to room temperature and poured into 4000 ml of water. The crude product was extracted with dichloromethane (3 x 300 ml). The combined organic extract was dried over Na_2SO_4 and evaporated to dryness. Yield 41.3 g (26%) of a white crystalline solid. Anal. Calc for C_9H_9BrO: C 50.73; H 4.26. Found: C 50.85; H 4.48. ^1H NMR ($CDCl_3$): δ 7.34 (d, J = 7.6 Hz, 1H, 6-H); 7.19 (d, J = 7.4 Hz, 1H, 4-H); 7.12 (dd, J = 7.6 Hz, J = 7.4 Hz, 1H, 5-H); 5.33 (dd, J = 2.6 Hz, J = 6.9 Hz, 1H, 1-H), 3.18-3.26 (m, 1H, 3- or 3’-H), 3.09 (m, 2H, 3,3’-H); 2.73 (m, 2H, 2,2’-H).



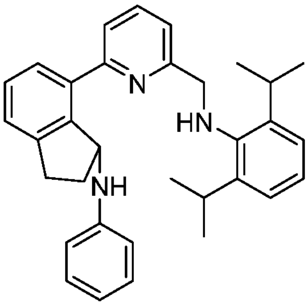
[0251] Preparation of 7-bromoindan-1-one. To a solution of 7-bromoindan-1-ol (37.9 g, 177 mmol) in dichloromethane (3500 ml) was added pyridinium chlorochromate (194 g, 900 mmol). The resulting mixture was stirred at room temperature for 5 h, then passed through a silica gel pad (500 ml), and the elute was evaporated to dryness. Yield 27.6 g (74%) of a white crystalline solid. Anal. Calc for C_9H_7BrO: C 51.22; H 3.34. Found: C 51.35; H 3.41. ^{1}H NMR ($CDCl_3$): δ 7.51 (m, 1H, 6-H); 7.36-7.42 (m, 2H, 4,5-H); 3.09 (m, 2H, 3,3'-H); 2.73 (m, 2H, 2,2'-H).



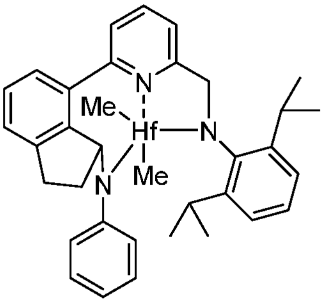
[0252] Preparation of 7-bromo-N-phenyl-2,3-dihydro-1H-inden-1-amine. To a stirred solution of aniline (10.4 g, 112 mmol) in toluene (60 ml) was added $TiCl_4$ (5.31 g, 28.0 mmol) for 30 min at room temperature in an argon atmosphere. The resulting mixture was stirred at 90°C for 30 min followed by an addition of 7-bromoindan-1-one (6.00 g, 28.0 mmol). The resulting mixture was stirred for 10 min at 90°C, poured into 500 ml of water, and the crude product was extracted with ethyl acetate (3 x 100 ml). The organic layer was separated, dried over Na_2SO_4, and then evaporated to dryness. The residue was crystallized from 10 ml of ethyl acetate at -30°C. The resulting solid was separated and dried in vacuum. After that it was dissolved in 100 ml of methanol, $NaBH_3CN$ (2.70 g, 42.9 mmol) and glacial acetic acid (0.5 ml) was added. The resulting mixture was refluxed for 3 h in an argon atmosphere. The resulting mixture was cooled to room temperature and then evaporated to dryness. The residue was diluted with 200 ml of water, and crude product was extracted with ethyl acetate (3 x 50 ml). The combined organic extract was dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm, eluent: hexane-ethyl acetate-triethylamine = 100:10:1, vol.). Yield 5.50 g (68%) of a yellow oil. Anal. calc. for $C_{15}H_{14}BrN$: C, 62.52; H, 4.90; N 4.86. Found: C, 62.37; H, 5.05; N 4.62. ^{1}H NMR ($CDCl_3$): δ 7.38 (m, 1H, 6-H in indane); 7.22 (m, 3H, 3,5-H in phenyl and 4-H in indane); 7.15 (m, 1H, 5-H in indane); 6.75 (m, 1H, 4-H in indane); 6.69 (m, 2H, 2,6-H in phenyl); 4.94 (m, 1H, 1-H in indane); 3.82 (br.s, 1H, NH); 3.17-3.26 (m, 1H, 3- or 3'-H in indane); 2.92-2.99 (m, 2H, 3'- or 3-H in indane); 2.22-2.37 (m, 2H, 2,2'-H in indane).



[0253] Preparation of N-phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1H-inden-1-amine. To a solution of 7-bromo-N-phenyl-2,3-dihydro-1H-inden-1-amine (2.50 g, 8.70 mmol) in THF (50 ml) was added 2.5M n-BuLi in hexanes (3.50 ml, 8.70 mmol) at -80°C in an argon atmosphere. The reaction mixture was then stirred for 1 h at this temperature. Then, 1.7M t-BuLi in pentane (11.1 ml, 17.8 mmol) was added, and the reaction mixture was stirred for 1 hour. Then, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.23 g, 17.4 mmol) was added. Then, the cooling bath was removed, and the resulting mixture was stirred for 1 h at room temperature. To the formed mixture 10 ml of water was added, and the resulting mixture was evaporated to dryness. The residue was diluted with 200 ml of water, and the title product was extracted with ethyl acetate (3 x 50 ml). The combined organic extract was dried over Na_2SO_4 and evaporated to dryness. Yield 2.80 g (96%) of a light yellow oil. Anal. calc. For $C_{21}H_{26}BNO_2$: C 75.24; H 7.82; N 4.18. Found: C 75.40; H 8.09; N 4.02. ^1H NMR ($CDCl_3$): δ 7.63 (m, 1H, 6-H in indane); 7.37-7.38 (m, 1H, 4-H in indane); 7.27-7.30 (m, 1H, 5-H in indane); 7.18 (m, 2H, 3,5-H in phenyl); 6.65-6.74 (m, 3H, 2,4,6-H in phenyl); 5.20-5.21 (m, 1H, 1-H in indane); 3.09-3.17 (m, 1H, 3- or 3'-H in indane); 2.85-2.92 (m, 1H, 3'- or 3-H in indane); 2.28-2.37 (m, 1H, 2- or 2'-H in indane); 2.13-2.19 (m, 1H, 2'- or 2-H in indane); 1.20 (s, 6-H, 4,5-Me in BPin); 1.12 (s, 6H, 4',5'-Me in BPin).



[0254] Preparation of 7-(6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)-N-phenyl-2,3-dihydro-1H-inden-1-amine. A solution of Na_2CO_3 (2.21 g, 21.0 mmol) in a mixture of water (80 ml) and methanol (25 ml) was purged with argon for 30 min. The obtained solution was added to a mixture of N-phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2,3-dihydro-1H-inden-1-amine (2.80 g, 8.40 mmol), N-[(6-bromopyridin-2-yl)methyl]-2,6-diisopropylaniline (2.90 g, 8.40 mmol), $Pd(PPh_3)_4$ (0.48 g, 0.40 mmol), and toluene (120 ml). This mixture was stirred for 12 h at 70°C, then cooled to room temperature. The organic layer was separated, the aqueous layer was extracted with ethyl acetate (3 x 50 ml). The combined organic extract was washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography on silica gel 60 (40-63 μm, eluent: hexane-ethyl acetate-triethylamine = 100:5:1, vol.). Yield 2.00 g (50%) of a yellow oil. Anal. calc. For $C_{33}H_{37}N_3$: C 83.33; H 7.84; N 8.83. Found: C 83.49; H 7.66; N 8.65. ^1H NMR ($CDCl_3$): δ 7.56-7.61 (m, 3H, 6-H in indane and 4.5-H in Py); 7.46-7.51 (m, 2H, 3,5-H in phenyl); 7.14-7.16 (m, 1H, 4-H in indane); 7.08-7.12 (m, 5H, 3-H in Py, 3,4,5-H in 2,6-diisopropylphenyl and 5-H in indane); 6.65 (m, 1H, 4-H in phenyl); 6.53 (m, 2H, 2,6-H in phenyl); 5.21-5.22 (m, 1H, 1-H in indane); 3.95-4.15 (m, 4H, CH_2NH and NH-phenyl and NH-2,6-diisopropylphenyl); 3.31 (sept, J=6.8 Hz, 2H, CH in 2,6-diisopropylphenyl); 3.16-3.24 (m, 1H, 3- or 3'-H in indane); 2.91-2.97 (m, 1H, 3'- or 3-H in indane); 2.21-2.37 (m, 2H, 2,2'-H in indane); 1.19-2.21 (m, 12H, CH_3 in 2,6-diisopropylaniline).



(Catalyst 1)

[0255] Preparation of Catalyst 1. Toluene (5 ml) was added to 7-(6-(((2,6-diisopropylphenyl)amino)methyl)pyridin-2-yl)-N-phenyl-2,3-dihydro-1H-inden-1-amine (0.296 g, 0.623 mmol) and $Hf(NMe_2)_2Cl_2(dme)$ (0.267 g, 0.623 mmol) to form a clear colorless solution. The mixture was loosely capped with aluminum foil and heated to 95°C for 3 hours. The mixture was then evaporated to a solid and washed with Et_2O (5 ml) to afford 0.432 g of the presumed (pyridyldiamide) $HfCl_2$ complex. This was dissolved in CH_2Cl_2 (5 ml) and cooled to -50°C. An Et_2O solution of dimethylmagnesium (3.39 ml, 0.747 mmol) was added dropwise and the mixture was allowed to warm to ambient temperature. After 30 minutes the volatiles were removed by evaporation and the residue was extracted with CH_2Cl_2 (10 ml) and filtered. The solution was concentrated to 2 ml and pentane (4 ml) was added. Cooling to -10°C overnight afforded colorless crystals that were isolated and dried under reduced pressure. Yield = 0.41 g, 92%. ^{1}H NMR (CD_2Cl_2, 400 MHz): 8.00 (t, 1H), 6.85-7.65 (13H), 5.06 (d, 1H), 4.91 (dd, 1H), 4.50 (d, 1H), 3.68 (sept, 1H), 3.41 (m, 1H), 2.85 (m, 1H), 2.61 (sept, 1H), 2.03 (m, 1H), 1.85 (m, 1H), 1.30 (m, 2H), 1.14 (d, 3H), 1.06 (d, 3H), 0.96 (d, 3H), 0.68 (3, 3H), -0.48 (s, 3H), -0.84 (s, 3H).

Polymerization

[0256] Details of polymerization conditions and polymers formed are reported in Tables 1 and 2. Batch polymerizations were performed in either a stirred 2 L autoclave reactor. All solvents, monomers, and gases were purified using 3 angstrom molecular sieves, oxygen scavenger, and/or sodium-potassium alloy, as required.

Example 1 - Ethylene/propylene/1,9-decadiene terpolymerization. The polymerization was performed in a 2 L autoclave reactor. A scavenger (bis(diisobutylaluminum)oxide) (1.25 mL of 0.2 M hexanes solution, 0.25 mmol), diethylzinc (0.5 mL of 1 M in hexanes, 0.5 mmol) and isohexane (1000 mL) were added to the reactor followed by propylene (150 mL). The reactor was sealed and the mixture was warmed to 90°C while stirring rapidly (ca. 700 rpm). The pressure inside the reactor at this time was noted and the ethylene feed regulator was adjusted to a value 100 psi above this pressure. Then a mixture of Catalyst 1 (3000 nmol), N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate (3000 nmol), and toluene (6 mL) was pushed into the reactor with a chaser of isohexane (200 mL). Immediately ethylene was opened to the reactor. An exotherm of 20°C was observed and the polymerization was continued with ethylene pressure being maintained. After 5 minutes, the ethylene flow was blocked and 1,9-decadiene (30 mL) was added to the reactor using high pressure nitrogen to push in the charge. Ethylene was reintroduced at this time (50 psi over reactor pressure after 1,9-decadiene addition) and the polymerization was allowed to continue with ethylene flow for an additional 18 minutes. Ethanol (2.5 mL) was then added to the reactor using high pressure nitrogen to quench the polymerization. The reactor was then cooled and vented. A toluene solution of octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076) (0.1 g, 5 mL) was added to the solution. The polymer was recovered following evaporation of the volatiles and drying at 50°C in a vacuum oven. Yield: 129 g.

Example 2 - Ethylene/propylene/1,9-decadiene terpolymerization. The polymerization was performed in a 2 L autoclave reactor. Bis(diisobutylaluminum)oxide (1.25 mL of 0.2 M hexanes solution, 0.25 mmol), diethylzinc (4 mL of 1 M in hexanes, 4 mmol) and isohexane (1000 mL) were added to the reactor followed by propylene (150 mL). The reactor was sealed and the mixture was warmed to 90°C while stirring rapidly (ca. 700 rpm). The pressure inside the reactor at this time was noted and the ethylene feed regulator was adjusted to a value 100 psi above this pressure. Then a mixture of Catalyst 1 (3000 nmol), N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate (3000 nmol), and toluene (6 mL) was pushed into the reactor with a chaser of isohexane (200 mL). Immediately ethylene was opened to the reactor. An exotherm of 13°C was observed and the polymerization was continued with ethylene pressure being maintained. After 5 minutes, the ethylene flow was blocked and 1,9-decadiene (30 mL) was added to the reactor using high pressure nitrogen to push in the charge. Ethylene was reintroduced at this time (50 psi over reactor pressure after 1,9-decadiene addition) and the polymerization was allowed to continue with ethylene flow for an additional 18 minutes. Ethanol (2.5 mL) was then added to the reactor using high pressure nitrogen to quench the polymerization. The reactor was then cooled and vented. A toluene solution of octadecyl 3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate (Irganox 1076) (0.1 g, 5 mL) was added to the solution. The polymer was recovered following evaporation of the volatiles and drying at 50°C in a vacuum oven. Yield: 143 g.

Table 1

Example	Catalyst 1 (nmol)	Propylene (ml)	Ethylene (psi)	1,9-decadiene (ml)	$ZnEt_2$ (mmol)	Polym. Temp (°C)	Yield (g)	Catalyst activity (g/g)
1	3000	150	100	30	0.5	90	129	42,850
2	3000	150	100	30	4	90	143	47,633

Table 2

Example	wt% C2 (^{1}H NMR)	MI (dg/min)	Mn$_{(DRI)}$ (g/mol)	Mw$_{(DRI)}$ (g/mol)	Mz$_{(DRI)}$ (g/mol)	Mn$_{(LS)}$ (g/mol)	Mw$_{(LS)}$ (g/mol)	Mz$_{(LS)}$ (g/mol)	[η] (dL/g)	g'vis	Mw$_{(LS)}$/ Mn$_{(DRI)}$
1	45.8	TLTM	79,884	193,186	462,078	178,267	412,369	1,724,844	1.34	0.45	5.16
2	59.4	2.5	34,476	45,843	60,424	88,193	145,223	1,502,505	0.68	0.47	4.21
3*										0.15	
4*										1.01	
5*										1.01	
6*										0.99	

MI is collected at 190°C and 2.16 kg. TLTM means the value is too low to measure. * Presented as a comparative example.

Table 3

Example	1	2	3	4	5	6
AC-150 (wt%)	98.83	98.83	98.83	98.83	98.83	98.83
Irganox™ 1076 (wt%)	0.015	0.015	0.015	0.015	0.015	0.015
Irgafos™ 168 (wt%)	0.005	0.005	0.005	0.005	0.005	0.005
$T_{c, DSC}$ (°C)	-	-24.0	-	27.5	28.9	14.2
KV40 (cSt)	80.69	55.31	124.38	143.23	120.83	51.91
KV100 (cSt)	12.0	8.8	18.42	19.0	15.7	11.9
VI	143	136	166	146	132	108
Thickening Efficiency	2.14	1.35	3.21	3.29	2.74	2.12
SSI-30	33.9	16.9	52	53.3	35.7	23.2
HTHS (cP)	3.19	2.69	3.8	3.95	3.85	3.39

[0257] The examples were formulated and tested as viscosity modifiers in lubricants. The samples were blended at about 1 wt% concentration (based upon the weight of the final blended solution) with Irganox 1076 and Irgafos 168 (commercially available antioxidants from BASF) in a Group I mineral oil base (AC-150 base oil). The formulated oils were then tested in a diesel injector equipped shear stability tester according to ASTM D7109.

[0258] AC-150™ base oil is a commercial Group I base oil available from ExxonMobil Chemical Co.

[0259] SSI-90 is Shear Stability Index as determined according to sheared viscosity via diesel injector at 90 cycles, as determined by ASTM D6278 and ASTM D7109 at 90 cycles.

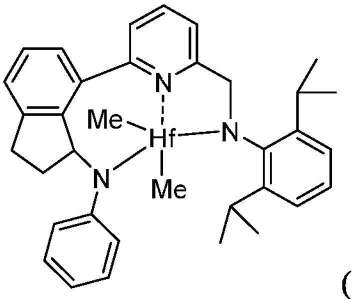
[0260] SSI-30 is Shear Stability Index as determined according to sheared viscosity via diesel injector at 30 cycles according to ASTM D6278.

[0261] Thickening Efficiency is determined according to ASTM D445.

[0262] VI is viscosity index and is determined according to ASTM D2270.

[0263] KV is Kinematic Viscosity as determined by ASTM D445 (KV40 is determined at 40°C, and KV100 is determined at 100°C).

[0264] Characterization of selected ethylene copolymers are shown in Table 2. The polymers were produced under the conditions of Table 1 in a 2 L batch reactor. The two branched polymers were made with Catalyst 1, activator N,N-dimethylanilinium tetra(perfluorophenyl)borate, and diethylzinc as the chain transfer agent. Catalyst 1 is



(1).

[0265] In the first stage, ethylene and propylene were added with catalyst 1 and an NCA in isohexane. The scavenger was bis(diisobutylaluminum)oxide. In the second stage, 1,9-decadiene was added concentrated at the end of the polymer chain. Coupling the dienes leads to the formation of EP copolymers at high molecular weight with high level of branching. Examples 3 to 6 are linear commercial olefin copolymers (OCPs).

[0266] Table 2 shows characterization of the ethylene copolymers for Example 1, Example 2, and Examples 3 to 6 (OCPs).

[0267] The C2 wt% for Example 1 and Example 2 are less than about 60 wt%, with Example 1 being less than about 50 wt% at 45.8. The Mw (LS) for Example 1 and Example 2 is 412,369 g/mol and 145,223 g/mol, respectively. The PDI (Mw(LS)/Mn(DRI)) for Example 1 and Example 2 is 5.16 and 4.21, respectively. Example 1 and Example 2 have g'vis values of 0.45 and 0.47, respectively, whereas the comparative linear EP copolymers are approximately 1. Taken together, these data indicate that the inventive examples have a high molecular weight component that contains long chain branching.

[0268] Table 3 shows the viscosity modifier performance for commercial copolymers, Example 3, Example 4, Example 5, and Example 6, and the two inventive branched EP copolymers, Example 1 and Example 2. The individual compositions are in AC-150 Group I base oil with antioxidant. High temperature high shear (HTHS) viscosity is related to fuel economy, and a lower HTHS value indicates better fuel economy.

[0269] Example 6 and Example 1 have similar kinematic viscosity at 100°C (KV100) but the HTHS for Example 1 is 3.19 cP which is significantly lower than that of Example 6 at 3.39 cP. In addition, the viscosity index for Example 1 is 143, which is much higher than that of Example 6 at 108. Both suggest that Example 1 has enhanced fuel economy benefits than the commercial Example 6.

[0270] Figure 1 is a graph illustrating the dynamic frequency sweep on the neat polymers at 190°C for Example 1 and four commercial VM grades, Example 3, Example 4, Example 5 and Example 6. Example 1 shows much stronger shear thinning with viscosity decreasing across several orders of magnitude than the commercial grades. The plateau region for Example 1 is less than 0.01 rad/s, indicating a much earlier shear thinning onset than the three commercial grades. Both indicate enhanced fuel economy performance of Example 1 compared with the existing commercial grades.

[0271] Overall, the branched EP products show high level of branching as suggested by the GPC data. The branched EP polymers provide enhanced high temperature high shear (HTHS) viscosity than existing commercial grades, which translates to better fuel economy. The neat polymer rheological results demonstrate strong shear thinning and much earlier shear thinning onset, which also translate to better fuel economy. The thickening efficiency and mechanical shear stability is comparable with existing products.

[0272] 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

We claim:

1. A method of making a lubricating oil composition comprising:

(a) combining a base stock oil with a branched polymer having:

an Mw(LS)/Mn(DRI) of from about 1.0 to about 6.0;

an Mw(LS) of from about 3,000 to about 1,000,000 g/mol;

a g'vis of about 0.90 or less; and

an ethylene content of about 40% to about 80% or less; and

(b) recovering a lubricating oil composition.

2. The method of claim 1, wherein the branched polymer is formed by:

contacting ethylene and one or more C_3 to C_{40} alpha-olefins with a catalyst system comprising a non-metallocene catalyst, an activator, and a reversible chain transfer agent to recover a first polymer; and

contacting the first polymer with a coupling agent in the presence of the first catalyst system or a second catalyst system comprising a second non-metallocene catalyst and a second activator to recover the branched polymer.

3. The method of claim 1 or 2, wherein the base stock oil comprises a hydrocarbon, polyalphaolefin (PAO), alkyl esters of dicarboxylic acids, polyglycols, alcohols, polybutenes, alkylbenzenes, organic esters of phosphoric acids, polysilicone oils, or combinations thereof.

4. The method of claim 1 or 2, further comprising blending the base stock oil and the polymer with an oil additive.

5. The method of claim 4, wherein the oil additive is a pour point depressant, anti-wear agent, antioxidant, other viscosity-index improver, dispersant, corrosion inhibitor, anti-foaming agent, detergent, rust inhibitor, friction modifier, or a combination thereof.

6. The method of claim 1 or 2, wherein the lubricating oil composition comprises about 0.01 wt% to about 12 wt% of the polymer based on the composition.

7. The method of claim 2, further comprising transferring the first polymer from a first reactor to a second reactor.

8. The method of claim 2, wherein the first catalyst system comprises isohexane.

9. The method of claim 2, wherein the one or more C_3 to C_{20} alpha-olefins is propylene.

10. The method of claim 2, wherein the contacting ethylene and the contacting the first polymer occurs at a temperature of about 0°C to about 300°C, at a pressure in the range of from about 0.20 MPa to about 1500 MPa, and at a time up to about 300 min.

11. The method of claim 2, wherein the reversible chain transfer agent comprises one or more of trialkyl aluminum or dialkyl zinc.

12. The method of claim 11, wherein the reversible chain transfer agent comprises trialkyl aluminum is triethylaluminum, tri(i-butyl) aluminum, tri(n-hexyl) aluminum, tri(n-octyl) aluminum, and the dialkyl zinc is diethyl zinc, di(n-propyl)zinc, and di(n-octyl)zinc.

13. The method of claim 2, wherein the coupling agent is an α,ω-diene.

14. The method of claim 2, wherein the coupling agent is 1,6-heptadiene; 1,7-octadiene; 1,8-nonadiene; 1,9-decadiene; 1,10-undecadiene; 1,11-dodecadiene; 1,12-tridecadiene; 1,13-tetradecadiene, or combinations thereof.

15. The method of claim 1 or 2, wherein the branched polymer has

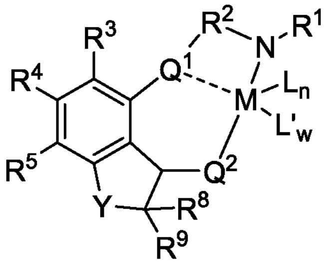
a high temperature, high shear (HTHS) viscosity of about 4.0 or less;

a kinematic viscosity (KV) at 100°C of about 15 cSt or less; and

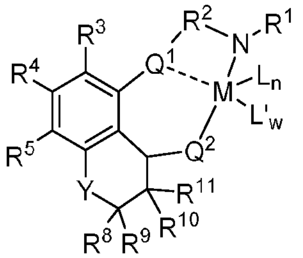
a ratio of thickening efficiency to shear stability index (30 cycles) of from about 1:5 to about 1:20.

16. The method of claim 1 or 2, wherein the kinematic viscosity at 100°C of the lubricating oil is increased by at least about 50% upon blending with 1.15 wt% of the branched polymer.

17. The method of claim 2, wherein the non-metallocene catalyst is a pyridyldiamido transition metal complex represented by the formula (A), (B), (C), or (D):



(A)



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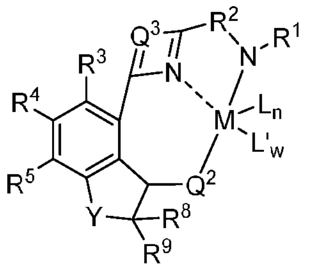
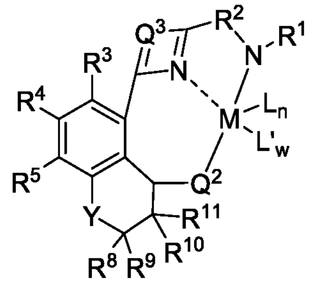


(C)



(D),

wherein

M is a Group 3 or 4 metal;

Q^1 is a three atom bridge with the central of the three atoms being a group 15 or 16 element (said group 15 element may or may not be substituted with an R^{30} group) represented by the formula: $-G^1-G^2-G^3-$ where G^2 is a group 15 or 16 atom (said group 15 element may be substituted with a R^{30} group), G^1 and G^3 are each a group 14, 15 or 16 atom (each group 14, 15 and 16 element may or may not be substituted with one or more R^{30} groups), where G^1, G^2 and G^3, or G^1 and G^2, or G^1 and G^3, or G^2 and G^3 may form a singular or multi ring system;

each R^{30} group is independently a hydrogen, a C_1 to C_{100} hydrocarbyl radical, or a silyl radical;

Q^2 is $-NR^{17}$ or $-PR^{17}$, where R^{17} is a hydrocarbyl radical, a substituted hydrocarbyl radical, a silyl radical, or a germyl radical;

Q^3 is –(TT)– or –(TTT)– where each T is carbon or a heteroatom, and said carbon or heteroatom may be unsubstituted or substituted with one or more R^{30} groups that together with the "–C–Q^3=C–" fragment, forms a 5- or 6-membered cyclic group or a polycyclic group including the 5- or 6-membered cyclic group;

R^1 is a hydrocarbyl radical, a substituted hydrocarbyl radical, or a silyl radical;

each of R^3, R^4, and R^5 is independently a hydrogen, a hydrocarbyl radical, a substituted hydrocarbyl radical, an aryl radical, a substituted aryl radical, an alkoxy radical, an aryloxy radical, a halogen, an amino radical, or a silyl radical, or two or more adjacent R^3, R^4, and R^5 groups may independently join together to form a substituted or unsubstituted hydrocarbyl ring or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring atoms and where substitutions on the ring can join to form additional rings;

R^2 is –E(R^{12})(R^{13})– where E is carbon, silicon, or germanium;

Y is oxygen, sulfur, or –E*(R^6)(R^7)–, wherein E* is carbon, silicon, or germanium;

each of R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} is independently a hydrogen, a hydrocarbyl radical, a substituted hydrocarbyl radical, an aryl radical, a substituted aryl radical, an alkoxy radical, a halogen, an amino radical, or a silyl radical, or two or more adjacent R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, and R^{13} groups may independently join together to form a saturated, substituted or unsubstituted hydrocarbyl ring or heterocyclic ring, where the ring has 5, 6, 7, or 8 ring carbon atoms and where substitutions on the ring can join to form additional rings;

L is an anionic leaving group, where the L groups may be the same or different and any two L groups may be linked to form a dianionic leaving group;

n is 1 or 2;

L' is neutral Lewis base; and

w is 0, 1, 2, 3 or 4.

18. The method of claim 2, wherein M is Ti, Zr, or Hf.

19. The method of claim 2, wherein R^2 is CH_2, CH(aryl), CH(2-isopropylphenyl), CH(2,6-dimethylphenyl), CH(2,4-6-trimethylphenyl), CH(alkyl), CMe_2, $SiMe_2$, $SiEt_2$, or $SiPh_2$.

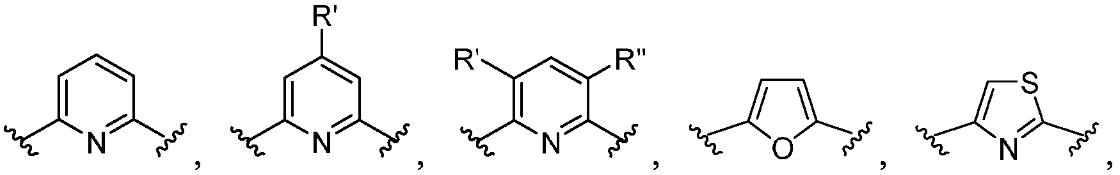
20. The method of claim 2, wherein E and E* are carbon and each of R^6, R^7, R^{12}, and R^{13} is a C_6 to C_{30} substituted or unsubstituted aryl group.

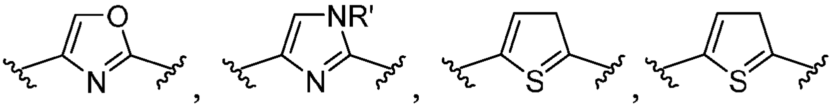
21. The method of claim 2, wherein Q^2 is $-NR^{17}$.

22. The method of claim 2, wherein each of E and E* is carbon and each of R^1 and R^{17} is independently phenyl groups that are substituted with 0, 1, 2, 3, 4, or 5 substituents, the substituents comprising F, Cl, Br, I, CF_3, NO_2, alkoxy, dialkylamino, hydrocarbyl, and substituted hydrocarbyl groups with from one to ten carbons.

23. The method of claim 2, wherein:

Q^1 is:





; and

Q^3 is CHCHCH, CHCH, CHN(R'), CH–S, CHC(R')CH, C(R')CHC(R''), CH-O, or NO, wherein the ~ indicates the connections to R^2 and the aromatic ring, and R' and R'' is a hydrocarbyl.

24. The method of claim 2, wherein the activator comprises alkylalumoxane.

25. The method of claim 2, wherein the activator is represented by the formula:

$$(Z)_d^+(A^{d-})$$

wherein Z is (L–H) or a reducible Lewis acid, L is a neutral base; H is hydrogen; $(L–H)^+$ is a Brønsted acid; A^{d-} is a non-coordinating anion having the charge d-; and d is an integer from 1 to 3.

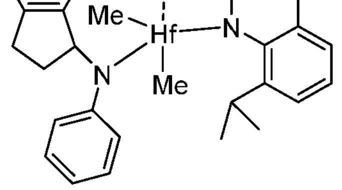
26. The method of claim 2, wherein the catalyst system further comprises an activator represented by the formula:

$$(Z)_d^+(A^{d-})$$

wherein A^{d-} is a non-coordinating anion having the charge d-; and d is an integer from 1 to 3; and Z is a reducible Lewis acid represented by the formula: (Ar_3C^+), wherein Ar is aryl substituted with a C_1 to C_{40} hydrocarbyl or with a substituted C_1 to C_{40} hydrocarbyl, or a heteroaryl substituted with a C_1 to C_{40} hydrocarbyl, or with a substituted C_1 to C_{40} hydrocarbyl.

27. The method of claim 2, wherein the activator comprises one or more of:
N,N-dimethylanilinium tetrakis(perfluorophenyl)borate,
N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-dimethylanilinium tetrakis(perfluorobiphenyl)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 tetra(perfluorophenyl)borate,
trimethylammonium tetrakis(perfluoronaphthyl)borate,
triethylammonium tetrakis(perfluoronaphthyl)borate,
tripropylammonium tetrakis(perfluoronaphthyl)borate,
tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
tri(t-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, and
tropillium tetrakis(perfluoronaphthyl)borate.

28. The method of claim 2, wherein:

the pyridyldiamido transition metal complex is  ;and the activator is N,N-dimethylanilinium tetra(perfluorophenyl)borate.

29. The method of claim 2, further comprising introducing the catalyst represented by the formula (A), (B), (C), or (D) into a reactor as a slurry.

30. The method of claim 1 or 2, wherein the branched polymer has a viscosity index of about 120 or more.

31. The method of claim 1 or 2, wherein the branched polymer has a shear thinning onset of about 0.01 rad/s or less.

32. A lubricating oil composition comprising a copolymer having:
an Mw(LS)/Mn(DRI) is from about 2.0 to about 6.0;
an Mw(LS) is from about 50,000 to about 1,000,000 g/mol;
a g'vis of less than about 0.90; an ethylene content of about 40% to about 60% or less;
a thickening efficiency of about 1.2 or more; and
a shear stability index (30 cycles) less than about 40.

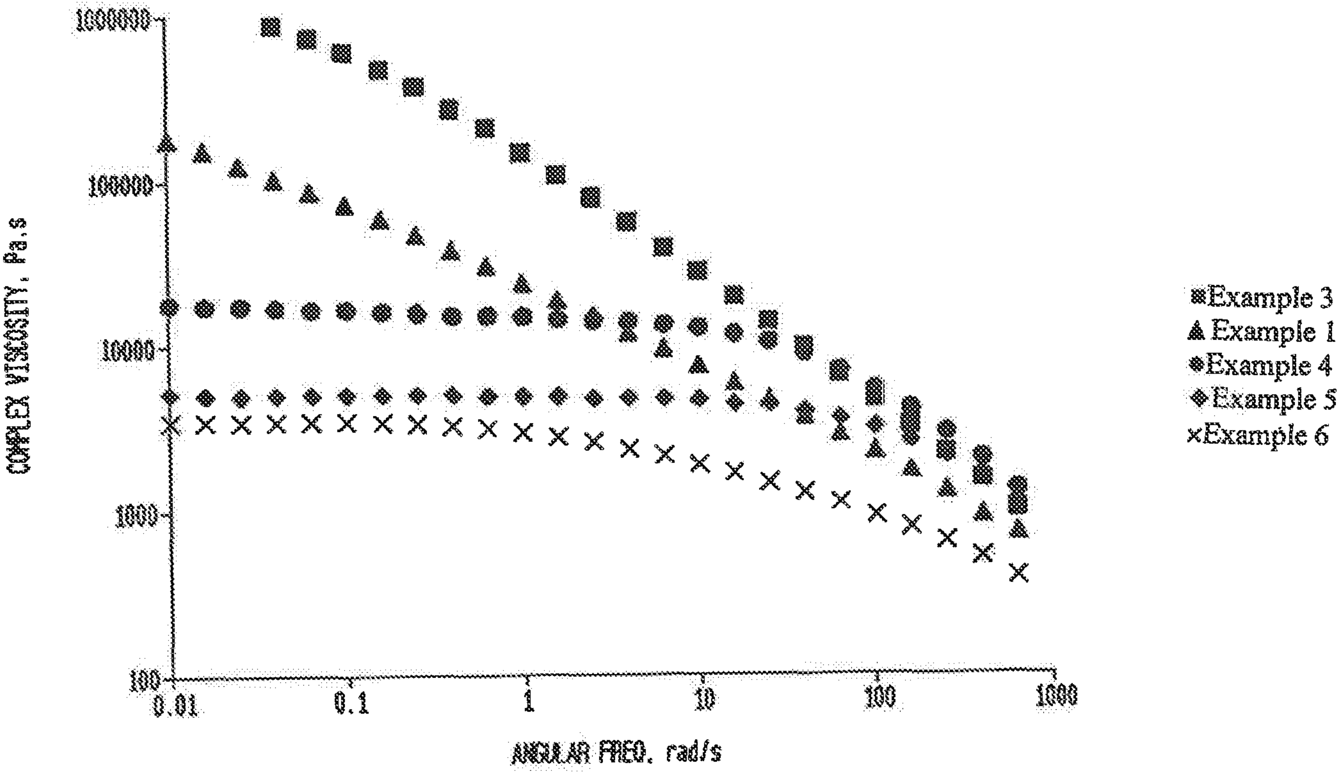

1000000
100000
10000
1000
100
COMPLEX VISCOSITY, Pa.s
0.01
0.1
1
10
100
1000
ANGULAR FREQ. rad/s
Example 3
Example 1
Example 4
Example 5
Example 6

FIG. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/021173

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10M143/04 C10M143/14 C08F4/64 C08F210/16
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 C10N C08F

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2006/281647 A1 (HAZELTON RONALD L [US] ET AL) 14 December 2006 (2006-12-14) paragraphs [0001], [0004], [0040], [0052]; claims 17, 18, 29; table 1 paragraph [0029] - paragraph [0037] -----	1-32
A	WO 2004/000900 A1 (EXXONMOBIL CHEM PATENTS INC [US]; RAVISHANKAR PERIAGARAM S [US]) 31 December 2003 (2003-12-31) claim 1; examples 3, 4, 5 -----	1-32
X	US 2011/269656 A1 (BURRINGTON JAMES D [US] ET AL) 3 November 2011 (2011-11-03) paragraph [0050] -----	1-32
A	WO 2015/073157 A1 (EXXONMOBIL CHEM PATENTS INC [US]) 21 May 2015 (2015-05-21) cited in the application claims 1, 34 -----	1-32

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

☒ See patent family annex.

* Special categories of cited documents :

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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

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"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 16 May 2019	Date of mailing of the international search report 23/05/2019
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 Klaes, Daphne

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2019/021173

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WO 2015073157 A1	21-05-2015	NONE	