

**LUBRICATING OIL COMPOSITION WITH VISCOSITY MODIFIER BASED ON
SYNDIOTACTIC PROPYLENE-BASED ETHYLENE- PROPYLENE COPOLYMERS
WITH IMPROVED PROPERTIES**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit under 35 U.S.C. §119(e) of the filing date of U.S. Provisional Patent Application No. 63/276,025, entitled LUBRICATING OIL COMPOSITION WITH VISCOSITY MODIFIER BASED ON SYNDIOTACTIC PROPYLENE-BASED ETHYLENE- PROPYLENE COPOLYMERS WITH IMPROVED PROPERTIES filed November 5, 2021, disclosure of which is incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to syndiotactic propylene-based ethylene-propylene copolymers in lubricating oils and uses thereof.

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 friction between 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 improvers (VII). Viscosity index improving components, many of which are derived from 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] Desirable VIIs generally exhibit adequate low-temperature viscosity properties such that a lubrication fluid comprising the VII would maintain adequately low viscosity at low

temperatures, as may be demonstrated by fluid measurements such as pour point, mini-rotary viscometry (MRV), and cold-cranking simulator (CCS) testing. In addition, it may be desirable to maximize thickening efficiency (TE), which is a measure of thickening ability of a polymer in a lubrication fluid (e.g., such that greater TE indicates a smaller amount of VII may be added to achieve desired properties). One challenge is that TE is interdependent with shear stability index (SSI), and SSI needs for various VIIs can vary across different lubricating oil grades and target end uses and/or markets. It would be desirable for a VII to provide a greater thickening efficiency (TE) at a given target or desired SSI (which, again, may be different for different target uses). This means that for a given SSI, desirable VIIs would be designed to increase or maximize TE at the given SSI.

[0007] As explained in U.S. Patent No. 9,139,794 and in U.S. Patent No. 9,127,151 (see, e.g., '151 Patent at column 5, lines 21-32), it is generally believed that the composition of olefin copolymer VII at a given SSI largely determines the TE, and that higher ethylene content is preferred because of its higher TE. On the other hand, the '151 Patent explains that while increasing the ethylene content of rheology modifiers leads to improved TE/SSI ratios, it can also lead to increased crystallinity of the olefin copolymer, which is thought to be detrimental because crystalline polymers tend to associate. These associations are apparent as regions (e.g., "lumps") of high viscosity which give the oil a non-uniform appearance. Therefore, it would appear that one must accept trade-offs in designing an olefin copolymer VII. In order to achieve greater TE, one must accept higher crystallinity, thereby sacrificing low-temperature performance due to, e.g., greater gelation tendency and/or detrimentally higher SSI. In practice, many of the commercial viscosity modifiers based on ethylene-propylene copolymer utilized less than 50% ethylene content so that the final polymer does not exhibit melting point as a solid or non-uniform appearance in lubrication oil composition.

[0008] This perceived trade-off can make it very difficult to achieve desired properties in certain olefin copolymer VIIs. In the past, propylene-based polymers and copolymers have been used as a viscosity index improvers, as described in WO Patent Application Publication 2016/018523 A1 and U.S. Patent Application Publication No. 2012/0015854A. The propylene-based copolymers comprise propylene as a main monomers and units derived from one or more other alpha olefins (e.g., ethylene). Due to low crystallinity, these viscosity modifiers generally demonstrated lower thickening power comparing to olefin copolymers with 50% or higher ethylene content. Therefore, there is a need for viscosity index improvers and lubricating oils comprising propylene-based copolymers that exhibit good viscometrics,

high thickening efficiency and good low temperature performance. Moreover, it may be particularly advantageous to identify desirable VIIs using propylene-based ethylene-propylene copolymers with low ethylene content.

SUMMARY OF DISCLOSURE

[0009] The present disclosure addresses the continuing need to develop viscosity index improvers and lubricating oils. More particularly, the present disclosure provides syndiotactic propylene-based ethylene-propylene copolymers that exhibit good viscometrics, high thickening efficiency and good low temperature performance. It has been surprisingly discovered that tacticity of propylene segments of ethylene-propylene copolymer plays an important role in the performance of viscosity index improvers and lubricating oil compositions.

[0010] The present disclosure is concerned with lubricant oil compositions comprising syndiotactic propylene-based ethylene-propylene copolymers comprising a) 2 to 20 % by weight of ethylene; b) 80 to 98 % by weight of propylene; c) 50 to 99% rr triads, and d) Mw (LS) of 10 to 250 kg/mol.

[0011] In another aspect, the present disclosure is concerned with a method of manufacturing a lubricant oil composition with improved low temperature performance, the method comprising: mixing a lubricant base oil, and 0.01 wt.% to 20 wt.% of a viscosity index improver, wherein the viscosity index improver comprises a syndiotactic propylene-based ethylene-propylene copolymer comprising: a) 2 to 20 % by weight of ethylene; b) 80 to 98 % by weight of propylene; c) 50 to 99% rr triads, and d) Mw (LS) of 10 to 250 kg/mol and wherein the lubricant base oil has a kinematic viscosity at 100°C of 1.4 to 20 mm²/s.

[0012] In yet another further aspect, the present disclosure is concerned with a method of lubricating an engine, comprising: supplying to the engine a lubricating oil composition comprising a major amount of a base oil of lubricating viscosity; a syndiotactic propylene-based ethylene-propylene copolymer comprising: a) 2 to 20 % by weight of ethylene; b) 80 to 98 % by weight of propylene; c) 50 to 99% rr triads; and d) Mw (LS) of 10 to 250 kg/mol; and wherein the lubricant base oil has a kinematic viscosity at 100°C of 1.4 to 20 mm²/s.

DETAILED DESCRIPTION

[0013] 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 2 wt.% to 20 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 2 wt.% to 20 wt.%, based upon the weight of the copolymer.

[0014] 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.

[0015] 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.

[0016] 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.

[0017] Olefin polymers and oligomers (“polyolefins” or “polyolefin polymers”), in general, and in particular poly-alpha-olefin polymers comprising propylene or other C3 or higher alpha-olefin monomers, comprise hydrocarbyl groups that are pendent from the polymer backbone chain. The pendent hydrocarbyl groups may be arranged in different stereochemical configurations determined relative to the polymer backbone chain. These arrangements include atactic, isotactic, and/or syndiotactic configurations.

[0018] As used herein, “tacticity” of a polymer reflects the stereochemical regularity of hydrocarbyl groups, which are pendent to the polymer molecule backbone. Tacticity may be related to the degree of crystallinity that an olefin polymer, in particular a poly-alpha-olefin polymer, can obtain. Three main types of tacticity have been described in poly-alpha-olefins: atactic, isotactic, and syndiotactic.

[0019] Atactic polyolefins are those wherein the hydrocarbyl groups pendent to the polymer molecule backbone assume no regular order with reference to the backbone. This random, or atactic, structure is represented by a polymer backbone of alternating methylene and methine carbons, with randomly oriented branches substituting the methine carbons. The methine carbons randomly have Rectus (“R”) and Sinister (“S”) configurations, creating adjacent pairs either of like configuration (a “meso” or “m” dyad) or of unlike configuration (a “racemic” or “r” dyad).

[0020] Isotactic polyolefins are characterized as having pendent hydrocarbyl groups ordered in space to the same side or plane of the polymer backbone chain. Using isotactic polypropylene as an example, the isotactic structure is typically described as having the pendent methyl groups attached to the ternary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the carbon backbone chain of the polymer, e.g., the methyl groups are all above or below the plane. The percentage of m dyads in the chain determines the degree of isotacticity of the polymer and is related to the crystallinity of the polymer.

[0021] Syndiotactic polyolefins are those wherein the hydrocarbyl groups pendent to the polymer molecular backbone alternate sequentially in order from one side or plane to the opposite side or plane relative to the polymer backbone. The percentage of r dyads in the chain determines the degree of syndiotacticity of the polymer and is related to the crystallinity of the polymer.

[0022] The molecular chain backbone of a syndiotactic polymer can be considered to be a copolymer of olefins with alternating stereochemical configurations. Highly syndiotactic polymers may be highly crystalline and thus may have defined melting points similar to their isotactic polymorphs and thus may be characterized in part by their melting point temperature.

[0023] The triad tacticity of a polymer is the relative tacticity of a sequence of three adjacent propylene units, a chain consisting of head to tail bonds, expressed as a binary combination of m and r sequences. It is usually expressed for the propylene-based polymers described as the ratio of the number of units of the specified tacticity to all of the propylene triads in the polymer. For example, an rr triad indicates 3 adjacent propylene units, wherein the stereochemistry of propylene units are alternating (e.g., RSR, SRS).

[0024] The tacticity of ethylene-propylene copolymer is measured by ^{13}C NMR including the concentration of isotactic and syndiotactic diads ([m] and [r]), and triads ([mm], [mr] and [rr]). The designation “m” or “r” describes the stereochemistry of pairs of contiguous propylene groups, “m” referring to meso and “r” to racemic. 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).

[0025] The “rr triad tacticity index” of a polymer is a measure of the relative syndiotacticity of a sequence of three adjacent propylene units connected in a head-to-tail configuration. More specifically, in the present invention, the rr triad tacticity index (also referred to as the “rr

Fraction”) of a polypropylene copolymer is expressed as the ratio of the number of units of racemic tacticity to all of the methyl triads in the copolymer:

$$rr \text{ Fraction} = \frac{[PP + EP(rr)]}{[PP + EP(rr)] + [PP + EP(mm)] + [PP + EP(mr)]}$$

[0026] The regions for PP+EP(mm), PP+EP(mr), and PP+EP(rr) are defined as

	Chemical shift range (ppm)
PP+EP(mm)	21.2 - 22.3
PP+EP(mr)	20.4 - 21.2
PP+EP(rr)	19.6 - 20.4

[0027] This triad tacticity calculation does not account for sequence, chain ends, or regio-defects present within these regions.

[0028] Similarly, m diads and r diads can be calculated as follows where mm, mr and rr are defined above:

$$m = mm + \frac{1}{2} mr$$

$$r = rr + \frac{1}{2} mr$$

[0029] ¹³C NMR can be used to determine monomer content and sequence distribution for the ethylene-propylene copolymers using a procedure adapted from J.C. Randall’s paper: *Polymer Reviews*, **1989**, vol.29(2), pp. 201-317. Included in the paper are measurement and calculations for 1,2 propylene addition triad sequence distributions termed EEE, EEP, PEP, EPE, EPP and PPP and reported as mole fractions.

[0030] The present disclosure relates to syndiotactic propylene-based ethylene-propylene copolymers in lubricating oil and uses thereof. The syndiotactic propylene-based ethylene-propylene copolymers allow for improved performance of lubricating oils, such as good viscometrics, high thickening efficiency and good low temperature performance.

[0031] According to an embodiment, the syndiotactic propylene-based syndiotactic propylene-based ethylene-propylene copolymer employed in the lubricant oil compositions of the present disclosure includes a syndiotactic propylene-based ethylene-propylene copolymers comprising a) 2 to 20 % by weight of ethylene; b) 80 to 98 % by weight of propylene; c) 50 to 99% rr triads, and d) Mw (LS) of 10 to 250 kg/mol.

[0032] In some embodiments, the syndiotactic propylene-based ethylene-propylene copolymer may range from 4 to 18 % by weight of ethylene, 5 to 15% by weight of ethylene,

6 to 12 % by weight of ethylene, and 7 to 9 % by weight of ethylene.

[0033] In some embodiments, the syndiotactic propylene-based ethylene-propylene copolymer has 82 to 96% by weight of propylene, 85 to 95% by weight of propylene, 88 to 94% by weight of propylene, 91 to 93% by weight of propylene.

[0034] In an embodiment, the syndiotactic-rich ethylene-propylene copolymers produced herein have syndiotactic stereo-regular propylene crystallinity. The term "stereo-regular" as used herein means that the predominant number, i.e. greater than 50%, of the propylene residues in the polypropylene segments in a polymer chain exclusive of any other monomer such as ethylene, has the same 1,2 insertion and the stereo-chemical orientation of the pendant methyl groups is the same, either meso or racemic.

[0035] Propylene copolymers produced herein may have an rr triad tacticity index of three propylene units, as measured by ^{13}C NMR, of 55% or greater, 60% or greater, 65% or greater, 70% or greater. In some embodiments, the syndiotactic propylene-based ethylene-propylene copolymer may range from 60 to 90% rr triads, 65 to 90% rr triads, 70 to 90% rr triads, 75 to 90% rr triads, and 80 to 90% rr triads. In other embodiments, the copolymer may range from 65 to 85% rr triads, and 70 to 80% rr triads.

[0036] In some embodiments, the Mw (LS) may range from 20 to 150 kg/mol, 30 to 140 kg/mol, 40 to 120 kg/mol, 50 to 100 kg/mol, and 60 to 90 kg/mol.

[0037] The present disclosure includes a syndiotactic propylene-based ethylene-propylene copolymer having MFR of 0.1 to 450 g/10 min. measured at 2.16 kg and 230°C. The MFR measured at 2.16 kg and 230°C may range from 1 to 400 g/10 min., 10 to 300 g/10 min., 50 to 200 g/10 min., and 75 to 150 g/10 min.

[0038] The syndiotactic propylene-based ethylene-propylene copolymers employed in the lubricant oil compositions of the present disclosure can be prepared by any suitable manner known in the art.

[0039] In some embodiments, the syndiotactic-rich ethylene-propylene copolymer has a glass transition temperature of 20°C or less, alternatively 10°C or less, alternatively 0°C or less, alternatively -5°C or less, or alternatively -10 °C or less. In another embodiment, the syndiotactic ethylene-propylene copolymer has a T_g (°C) from DSC and ethylene content (C2 wt%) from FTIR relationship of: $-0.5263 \cdot T_g - 4.8158 < \text{C2wt\%} < -0.5714 \cdot T_g + 0.9857$.

[0040] In some embodiments, the syndiotactic-rich ethylene-propylene copolymer displays no substantial melting peak, wherein the heat of fusion of the peak is 5 J/g or less as determined by differential scanning calorimetry at a scan rate of 10 °C/min (ASTM D3418-03). In some

embodiments, the syndiotactic-rich ethylene-propylene copolymer displays no endotherm peak during the second heating cycle of the DSC measurement at a scan rate of 10 °C/min. Alternatively, the syndiotactic-rich ethylene-propylene copolymer has no melting peak in the second heating cycle of the DSC measurement according to the procedure described herein.

[0041] In embodiments where the syndiotactic-rich ethylene-propylene copolymer is a blended polymer, the rr triad tacticity index of the first polymer component may be 70% or less, 65% or less, or even 60% or less. The rr triad tacticity index of the second polymer component may be 70% or more, 75% or more, or even 80% or more.

[0042] In embodiments where the syndiotactic-rich ethylene-propylene copolymer is a blended polymer, the ethylene content of the first syndiotactic-rich ethylene-propylene copolymer component may be less than 10 wt%, alternatively less than 7 wt%, alternatively less than 5 wt%, alternatively less than 3 wt% based upon the total weight of the first polymer component. The ethylene content of the second syndiotactic-rich ethylene-propylene copolymer component may be greater than 5 wt%, alternatively greater than 7 wt%, alternatively greater than 10 wt%, alternatively greater than 15 wt%, alternatively greater than 20 wt% with an upper limit of 25 wt% based upon the total weight of the second polymer component.

[0043] In embodiments, the weight average molecular weight of the first copolymer component is greater than that of the second copolymer component. In embodiments, the weight average molecular weight of the first copolymer component is greater than about 150,000 g/mol, or about 200,000 g/mol, or about 250,000 g/mol. Alternatively, the weight average molecular weight of the second copolymer component is less than about 150,000 g/mol, or about 100,000 g/mol, or about 50,000 g/mol to less than about 20,000 g/mol.

[0044] The syndiotactic-rich ethylene-propylene copolymers according to various embodiments can be a blend of at least two syndiotactic-rich ethylene-propylene copolymers. In one embodiment of the invention, the blend has a bimodal molecular weight distribution or wide molecular weight distribution with $MWD > 3.0$. The blend can also have a bimodal composition distribution or wide composition distribution. Alternatively, one component has ethylene content in the range of 0.2 to 5 wt% and M_w in the range of 100,000 to 400,000 g/mol, and one component has ethylene content in the range of 2 to 15 wt% and M_w in the range of 10,000 to 150,000 g/mol.

Catalyst

[0045] The syndiotactic propylene-based ethylene-propylene copolymers of the present disclosure can be prepared by any suitable catalysts known in the art. The catalyst compounds described herein are used to polymerize olefinic monomers including propylene and ethylene to form syndiotactic propylene-based ethylene-propylene copolymers. As used herein, the terms “hydrocarbyl radical,” “hydrocarbyl,” and “hydrocarbyl group” are used interchangeably throughout the present disclosure. Likewise, the terms “group,” “radical,” and “substituent” are also used interchangeably throughout the present disclosure. For purposes of this disclosure, “hydrocarbyl radical” is defined to be a C1-C100 radical and may be linear, branched, or cyclic. When cyclic, the hydrocarbyl radical may be aromatic or non-aromatic. “Hydrocarbyl radical” is defined to include substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, silylcarbyl radicals, and germylcarbyl radicals as these terms are defined below. Substituted hydrocarbyl radicals are radicals in which at least one hydrogen atom has been substituted with at least one functional group such as NR^*_2 , OR^* , SeR^* , TeR^* , PR^*_2 , AsR^*_2 , SbR^*_2 , SR^* , BR^*_2 , SiR^*_3 , GeR^*_3 , SnR^*_3 , PbR^*_3 and the like or where at least one non-hydrocarbon atom or group has been inserted within the hydrocarbyl radical, such as —O— , —S— , —Se— , —Te— , $\text{—N(R}^*\text{)—}$, =N— , $\text{—P(R}^*\text{)—}$, =P— , $\text{—As(R}^*\text{)—}$, =As— , $\text{—Sb(R}^*\text{)—}$, =Sb— , $\text{—B(R}^*\text{)—}$, =B— , $\text{—Si(R}^*)_2\text{—}$, $\text{—Ge(R}^*)_2\text{—}$, $\text{—Sn(R}^*)_2\text{—}$, $\text{—Pb(R}^*)_2\text{—}$ and the like, where R^* is independently a hydrocarbyl or halocarbyl 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.

[0046] Halocarbyl radicals are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one halogen (e.g. F, Cl, Br, I) or halogen-containing group (e.g., CF_3).

[0047] Substituted halocarbyl radicals are radicals in which at least one halocarbyl hydrogen or halogen atom has been substituted with at least one functional group such as NR^*_2 , OR^* , SeR^* , TeR^* , PR^*_2 , AsR^*_2 , SbR^*_2 , SR^* , BR^*_2 , SiR^*_3 , GeR^*_3 , SnR^*_3 , PbR^*_3 and the like or where at least one non-carbon atom or group has been inserted within the halocarbyl radical such as —O— , —S— , —Se— , —Te— , $\text{—N(R}^*\text{)—}$, =N— , $\text{—P(R}^*\text{)—}$, =P— , $\text{—As(R}^*\text{)—}$, =As— , $\text{—Sb(R}^*\text{)—}$, =Sb— , $\text{—B(R}^*\text{)—}$, =B— , $\text{—Si(R}^*)_2\text{—}$, $\text{—Ge(R}^*)_2\text{—}$, $\text{—Sn(R}^*)_2\text{—}$, $\text{—Pb(R}^*)_2\text{—}$ and the like, where R^* is independently a hydrocarbyl or halocarbyl radical provided that at least one halogen atom remains on the original halocarbyl radical. Additionally, two or more R^* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure.

[0048] Hydrocarbylsilyl groups, also referred to as silylcarbyl groups (also referred to as hydrocarbyl silyl groups), are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one SiR^*_3 containing group or where at least one $-\text{Si}(\text{R}^*)_2-$ has been inserted within the hydrocarbyl radical where R^* is independently a hydrogen, a hydrocarbyl or halocarbyl 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. Silylcarbyl radicals can be bonded via a silicon atom or a carbon atom.

[0049] Substituted silylcarbyl radicals are silylcarbyl radicals in which at least one hydrogen atom has been substituted with at least one functional group such as NR^*_2 , OR^* , SeR^* , TeR^* , PR^*_2 , AsR^*_2 , SbR^*_2 , SR^* , BR^*_2 , GeR^*_3 , SnR^*_3 , PbR^*_3 and the like or where at least one non-hydrocarbon atom or group has been inserted within the silylcarbyl radical, such as $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$, $-\text{Te}-$, $-\text{N}(\text{R}^*)-$, $=\text{N}-$, $-\text{P}(\text{R}^*)-$, $=\text{P}-$, $-\text{As}(\text{R}^*)-$, $=\text{As}-$, $-\text{Sb}(\text{R}^*)-$, $=\text{Sb}-$, $-\text{B}(\text{R}^*)-$, $=\text{B}-$, $-\text{Ge}(\text{R}^*)_2-$, $-\text{Sn}(\text{R}^*)_2-$, $-\text{Pb}(\text{R}^*)_2-$ and the like, where R^* is independently a hydrogen, a hydrocarbyl or halocarbyl 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.

[0050] Germylcarbyl radicals, also referred to as germylcarbyl groups (also referred to as hydrocarbyl germyl groups), are radicals in which one or more hydrocarbyl hydrogen atoms have been substituted with at least one GeR^*_3 containing group or where at least one $-\text{Ge}(\text{R}^*)_2-$ has been inserted within the hydrocarbyl radical where R^* is independently a hydrogen, a hydrocarbyl or halocarbyl 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. Germylcarbyl radicals can be bonded via a germanium atom or a carbon atom.

[0051] Substituted germylcarbyl radicals are germylcarbyl radicals in which at least one hydrogen atom has been substituted with at least one functional group such as NR^*_2 , OR^* , SeR^* , TeR^* , PR^*_2 , AsR^*_2 , SbR^*_2 , SR^* , BR^*_2 , GeR^*_3 , SnR^*_3 , PbR^*_3 and the like or where at least one non-hydrocarbon atom or group has been inserted within the germylcarbyl radical, such as $-\text{O}-$, $-\text{S}-$, $-\text{Se}-$, $-\text{Te}-$, $-\text{N}(\text{R}^*)-$, $=\text{N}-$, $-\text{P}(\text{R}^*)-$, $=\text{P}-$, $-\text{As}(\text{R}^*)-$, $=\text{As}-$, $-\text{Sb}(\text{R}^*)-$, $=\text{Sb}-$, $-\text{B}(\text{R}^*)-$, $=\text{B}-$, $-\text{Ge}(\text{R}^*)_2-$, $-\text{Sn}(\text{R}^*)_2-$, $-\text{Pb}(\text{R}^*)_2-$ and the like, where R^* is independently a hydrogen, a hydrocarbyl or halocarbyl 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.

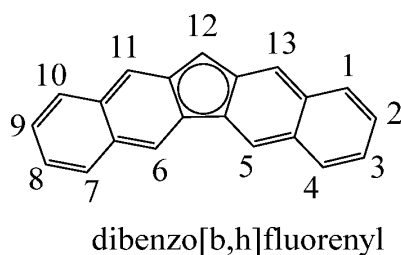
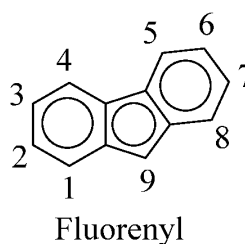
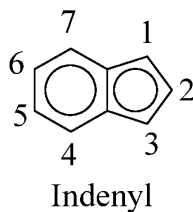
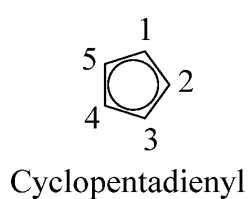
[0052] “Polar radicals” (or “polar groups”) are groups in which a heteroatom functionality is bonded directly to the indicated atom or atoms. Polar radicals include heteroatoms of groups 1-17 of the Periodic Table (except carbon and hydrogen) either alone or connected to other elements by covalent bonds or other interactions such as ionic bonds, van der Waals forces, or hydrogen bonding. Examples of functional heteroatom containing groups include carboxylic acids, acid halides, carboxylic esters, carboxylic salts, carboxylic anhydrides, aldehydes and their chalcogen (group 14) analogues, alcohols and phenols, ethers, peroxides and hydroperoxides, carboxylic amides, hydrazides and imides, amidines and other nitrogen analogues of amides, nitriles, amines and imines, azos, nitros, other nitrogen compounds, sulfur acids, selenium acids, thiols, sulfides, sulfoxides, sulfones, phosphines, phosphates, other phosphorus compounds, silanes, boranes, borates, alanes, aluminates. Examples of polar groups include NR^*_2 , OR^* , SeR^* , TeR^* , PR^*_2 , AsR^*_2 , SbR^*_2 , SR^* , BR^*_2 , SnR^*_3 , PbR^*_3 and the like where R^* is independently a hydrocarbyl, substituted hydrocarbyl, halocarbyl or substituted halocarbyl radical as defined above and two R^* may join together to form a substituted or unsubstituted saturated, partially unsaturated or aromatic cyclic or polycyclic ring structure.

[0053] In using the terms “substituted or unsubstituted cyclopentadienyl ligand”, “substituted or unsubstituted indenyl ligand”, and “substituted or unsubstituted tetrahydroindenyl ligand”, the substitution to the aforementioned ligand may be hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl, or germylcarbyl. The substitution may also be within the ring giving heterocyclopentadienyl ligands, heteroindenyl ligands or heterotetrahydroindenyl ligands, each of which can additionally be substituted or unsubstituted.

[0054] The hydrocarbyl radical may be independently selected from methyl, ethyl, ethenyl, and isomers of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, nonadecyl, eicosyl, heneicosyl, docosyl, tricosyl, tetracosyl, pentacosyl, hexacosyl, heptacosyl, octacosyl, nonacosyl, triacontyl, propenyl, butenyl, pentenyl, hexenyl, heptenyl, octenyl, nonenyl, decenyl, undecenyl, dodecenyl, tridecenyl, tetradecenyl, pentadecenyl, hexadecenyl, heptadecenyl, octadecenyl, nonadecenyl, eicosenyl, heneicosenyl, docosenyl, tricosenyl, tetracosenyl, pentacosenyl, hexacosenyl, heptacosenyl, octacosenyl, nonacosenyl, triacontenyl, propynyl, butynyl, pentynyl, hexynyl, heptynyl, octynyl, nonynyl, decynyl, undecynyl, dodecynyl, tridecynyl, tetradecynyl, pentadecynyl, hexadecynyl, heptadecynyl, octadecynyl,

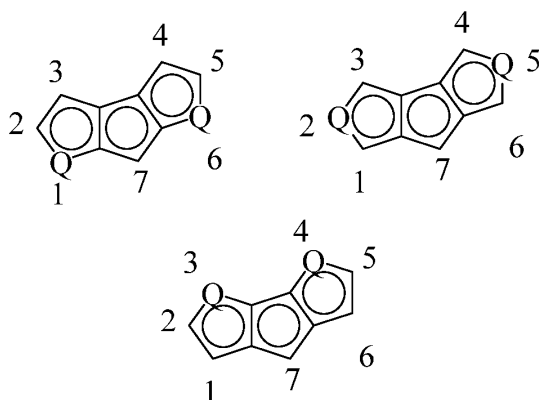
nonadecynyl, eicosynyl, heneicosynyl, docosynyl, tricosynyl, tetracosynyl, pentacosynyl, hexacosynyl, heptacosynyl, octacosynyl, nonacosynyl, triacontynyl, butadienyl, pentadienyl, hexadienyl, heptadienyl, octadienyl, nonadienyl, and decadienyl. Also included are isomers of saturated, partially unsaturated and aromatic cyclic and polycyclic structures wherein the radical may additionally be subjected to the types of substitutions described above. Examples include phenyl, methylphenyl, dimethylphenyl, ethylphenyl, diethylphenyl, propylphenyl, dipropylphenyl, benzyl, methylbenzyl, naphthyl, anthracenyl, cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl, methylcyclohexyl, cycloheptyl, cycloheptenyl, norbornyl, norbornenyl, adamantyl and the like. For this disclosure, when a radical is listed, it indicates that radical type and all other radicals formed when that radical type is subjected to the substitutions defined above. Alkyl, alkenyl and alkynyl radicals listed include all isomers including where appropriate cyclic isomers, for example, butyl includes n-butyl, 2-methylpropyl, 1-methylpropyl, tert-butyl, and cyclobutyl (and analogous substituted cyclopropyls); pentyl includes n-pentyl, cyclopentyl, 1-methylbutyl, 2-methylbutyl, 3-methylbutyl, 1-ethylpropyl, and neopentyl (and analogous substituted cyclobutyls and cyclopropyls); butenyl includes E and Z forms of 1-butenyl, 2-butenyl, 3-butenyl, 1-methyl-1-propenyl, 1-methyl-2-propenyl, 2-methyl-1-propenyl and 2-methyl-2-propenyl (and cyclobutenyls and cyclopropenyls). Cyclic compounds having substitutions include all isomer forms, for example, methylphenyl would include ortho-methylphenyl, meta-methylphenyl and para-methylphenyl; dimethylphenyl would include 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2,5-dimethylphenyl, 2,6-dimethylphenyl, 3,4-dimethylphenyl, and 3,5-dimethylphenyl.

[0055] Examples of cyclopentadienyl and indenyl ligands are illustrated below as anionic ligands. The ring numbering scheme is also illustrated. When a cyclopentadienyl ligand has one bridging substituent, the bridging substituent is in the one position. When a cyclopentadienyl ligand has two bridging substituents, the bridging substituents are in the one and two positions. When a fluorenyl ligand has a bridging substituent, the bridging substituent is in the nine position. When dibenzo[b,h]fluorene has a bridging substituent, the bridging substituent is in the twelve position.

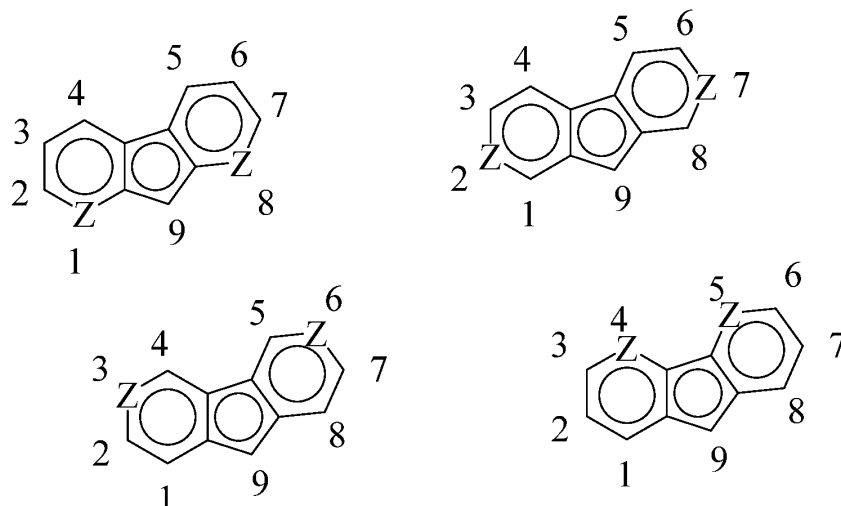


[0056] A similar numbering and nomenclature scheme is used for heterocyclopentapentalenyls, heterofluorenyls, and the like, as illustrated below. Each structure illustrated is drawn as an anion.

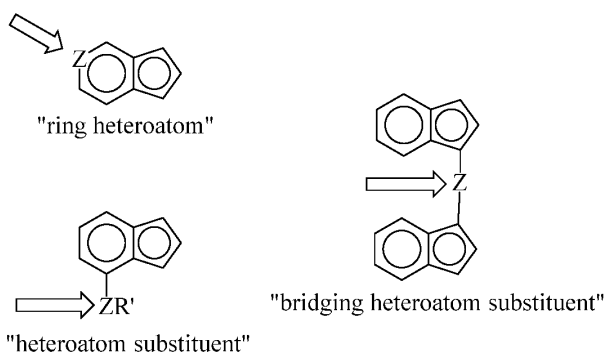
[0057] Non-limiting examples of heterocyclopentapentalenyls include the following, where Q represents the heteroatoms O, S, Se, or Te, or heteroatom groups, NR^{**}, PR^{**}, AsR^{**}, or SbR^{**} where R^{**} is hydrogen, or a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl, or germylcarbyl substituent. When a heterocyclopentapentalenyl ligand has a bridging substituent, the bridging substituent is in the seven position.



[0058] Non-limiting examples of heterofluorenyls where Z represents the heteroatoms N or P include the following. When a heterofluorenyl ligand has a bridging substituent, the bridging substituent is in the nine position.



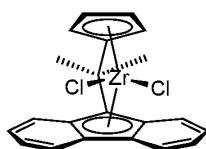
[0059] A “ring heteroatom” is a heteroatom that is within a cyclic ring structure. A “heteroatom substituent” is a heteroatom containing group that is directly bonded to a ring structure through the heteroatom. A “bridging heteroatom substituent” is a heteroatom or heteroatom group that is directly bonded to two different ring structures through the heteroatom. The terms “ring heteroatom”, “heteroatom substituent”, and “bridging heteroatom substituent” are illustrated below where Z and R' are as defined above.



[0060] A “ring carbon atom” is a carbon atom that is part of a cyclic ring structure. For example, an indenyl ligand has nine ring carbon atoms; a cyclopentadienyl ligand has five ring carbon atoms.

[0061] Transition metal compounds have symmetry elements and belong to symmetry groups. These elements and groups are well established and can be referenced from Chemical

Applications of Group Theory (2nd Edition) by F. Albert Cotton, Wiley-Interscience, 1971. Compounds with C_s symmetry possess a mirror plane. For example, the structure below has a C_s symmetric plane that bisects the zirconium center, the carbon bridge and the cyclopentadienyl and fluorenyl ligands.



[0062] Symmetric substituents are substituents that retain the C_s symmetry of the transition. For example, *t*-butyl groups substituted in the 2 and 7 positions of a fluorenyl ligand would be symmetric substituents.

[0063] Compounds with pseudo- C_s symmetry are similar with the exception that the bridging group, the labile ligands, and distant substituents of similar size on the cyclopentadienyl ligand or fluorenyl ligand are not included in determining the symmetry of the compound. These compounds, while not truly C_s -symmetric, are considered to have C_s -symmetric active sites for olefin polymerization. Therefore, a compound, for example having a MeEtSi or MePhSi bridging ligand, is considered to have a pseudo C_s -plane of symmetry given the appropriate remaining ligand structure. Likewise, a compound, for example having one Me and one Cl labile ligand, is considered to have a pseudo C_s -plane of symmetry given the appropriate remaining ligand structure. Non-limiting examples of pseudo C_s symmetric compounds are illustrated below:

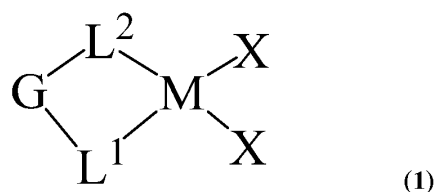


[0064] Compounds with pseudo- C_s symmetry can also have unlike substituents on the non-labile ligands (i.e., cyclopentadienyl or fluorenyl ligands) if the substituents are distant from the active site. Substituents of this type, referred to as pseudo symmetric substituents, are typically adjacent to the bridging group and do not substantially differ in size from one another. Typically, the size difference of these substituents is within 2 non-hydrogen atoms of each other. Thus, a cyclopentadienyl substituted at the 2 and the 5 positions with methyl and ethyl, respectively, or a cyclopentadienyl substituted at the 2 position with methyl and not substituted

in the 5 position, or a fluorenyl substituted at the 1 and the 8 positions with hexyl and octyl, respectively, would be considered to have pseudo- C_s symmetry.

[0065] In general, those catalysts both capable of producing syndiotactic polypropylene and capable of reacting with hydrogen to terminate the growing polymer chain, are catalysts that are useful for producing the syndiotactic polypropylene homopolymers and syndiotactic propylene-based ethylene-propylene copolymers described herein.

[0066] Catalysts useful for making the syndiotactic polypropylene homopolymers and syndiotactic propylene-rich ethylene-propylene copolymers include metallocene compounds (pre-catalysts) having the structure represented by formula (1) having C_s or pseudo- C_s symmetry:



wherein:

M is zirconium or hafnium;

L^1 is a unsubstituted fluorenyl, heterocyclopentapentalenyl, or heterofluorenyl, or a substituted fluorenyl, heterocyclopentapentalenyl, or heterofluorenyl ligand with one or more symmetric or pseudo symmetric substituents, each substituent group being, independently, a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germlylcarbyl, and optionally two or more adjacent substituents may join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent;

L^2 is a cyclopentadienyl ring or a substituted cyclopentadienyl ring with one or more symmetric or pseudo symmetric substituents in the 2 and 5 positions of the ring, each substituent group being, independently, a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germlylcarbyl;

G is a bridging group;

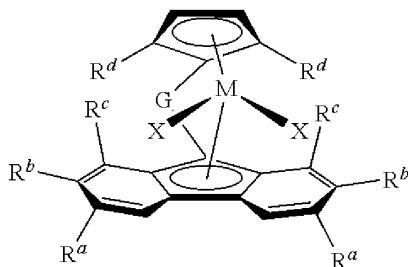
each X is, independently, a hydride radical, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germlylcarbyl; or both X are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand; both X may,

independently, be a halogen, alkoxide, aryloxy, amide, phosphide or other univalent anionic ligand or both X can also be joined to form a dianionic chelating ligand.

[0067] In some embodiments of formula (1), L^1 is fluorenyl or substituted fluorenyl; such as fluorenyl, 2,7-dimethylfluorenyl, 2,7-diethylfluorenyl, 2,7-dipropylfluorenyl, 2,7-dibutylfluorenyl, 2,7-diphenylfluorenyl, 2,7-dichlorofluorenyl, 2,7-dibromofluorenyl, 3,6-dimethylfluorenyl, 3,6-diethylfluorenyl, 3,6-dipropylfluorenyl, 3,6-dibutylfluorenyl, 3,6-diphenylfluorenyl, 3,6-dichlorofluorenyl, 3,6-dibromofluorenyl, 2,7-di-tertbutyl fluorenyl, or 1,1,4,4,7,7,10,10-octamethyl-octahydrodibenzofluorenyl. Most preferably 2,7-di-tert-butylfluorenyl or fluorenyl. In some embodiments, L^2 is cyclopentadienyl. In some embodiments, G is methylene, dimethylmethylene, diphenylmethylene, dimethylsilylene, diphenylsilylene, di(4-triethylsilylphenyl)silylene, ethylene, or di(para-triethylsilylphenyl)methylene, most preferably dimethylmethylene, diphenylmethylene or di(para-triethylsilylphenyl)methylene. In some embodiments, each X is, independently, hydrocarbyl or halo, such as methyl, benzyl, fluoro or chloro. In some embodiments, M is preferably zirconium. In alternative embodiments, M is hafnium.

[0068] A subset of the metallocene compounds (pre-catalysts) represented by formula (1) having C_s or pseudo- C_s symmetry that may be used are represented by formula (1a):

(1a)



Wherein

M, G and X are defined as in formula (1);

each R^a and R^b is, independently, selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl, germlycarbyl or polar radicals, and optionally two or more adjacent substituents may join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent, with the proviso that each R^a is the same and each R^b is the same allowing the compound to be C_s -symmetric or pseudo C_s -symmetric;

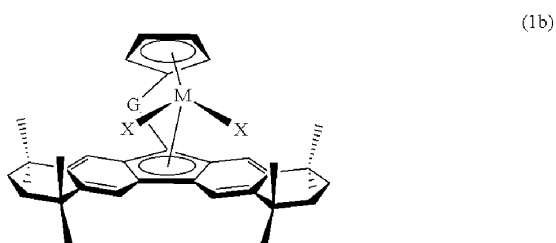
each R^c is, independently, a symmetric or pseudo symmetric substituent with respect to the other and is selected from hydrogen or a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl radicals;

each R^d is a symmetric or pseudo symmetric substituent with respect to the other and is, independently, selected from hydrogen or a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl radicals.

[0069] In some embodiments of formula (1a), each R^d , R^a and R^c are hydrogen, and each R^b is a hydrogen, hydrocarbyl, halogen, silylcarbyl, or polar radical; such as hydrogen, methyl, ethyl, propyl, butyl, phenyl, mesityl, fluoro, chloro, bromo, dimethylamido, diethylamido or methoxy; such as hydrogen or butyl; such as hydrogen or tert-butyl; such as tert-butyl.

[0070] In other embodiments of formula (1a), each R^d , R^b and R^c is hydrogen, and each R^a is, independently, a hydrogen, hydrocarbyl, halogen, or silylcarbyl; such as hydrogen, methyl, ethyl, propyl, butyl, fluoro, chloro, or bromo; such as hydrogen or butyl; such as hydrogen or tert-butyl; such as hydrogen.

[0071] Still, in other embodiments of formula (1a), each R^d and R^c is hydrogen, and each R^a and R^b are joined together to form a fused partially saturated six-membered carbon ring, each such fused ring may be substituted with four methyl substituents. Such ligand structure is illustrated in formula (1b):



[0072] Still in other embodiments of formula (1a) R^c and R^d are hydrogen; each R^a and R^b are independently hydrogen, bromine, chlorine, methyl, ethyl, propyl, butyl or phenyl, such as R^a is hydrogen and R^b is hydrogen, methyl, ethyl, propyl, or butyl, or R^b is hydrogen and R^a is hydrogen, methyl, ethyl, propyl, or butyl. In some embodiments, R^a is hydrogen and R^b is tert-butyl or hydrogen. G can be methylene, dimethylmethylene, diphenylmethylene, dimethylsilylene, diphenylsilylene, di(4-triethylsilylphenyl)silylene, ethylene, di(para-triethylsilylphenyl)methylene such as diphenylmethylene, dimethylmethylene, diphenylsilylene, and dimethylsilylene; such as diphenylmethylene. Each X is independently

hydrocarbyl or halo, such as methyl, benzyl, fluoro or chloro, such as methyl or chloro. In some embodiments, M is zirconium. In other embodiments, M is hafnium.

[0073] In some preferred embodiments of the invention, for the metallocene compounds of formula (1), (1a) and/or (1b), M is zirconium.

[0074] In some preferred embodiments of the invention, for the metallocene compounds of formula (1), (1a) and/or (1b), X is methyl.

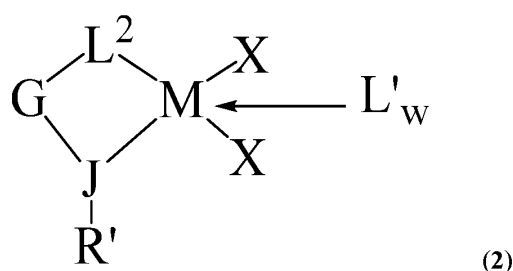
[0075] In some embodiments of formula (1a), each R^d, R^a and R^c are hydrogen, and each R^b is a methyl, ethyl, propyl, butyl, with tert-butyl being most preferred.

[0076] In some preferred embodiments of the invention, for the metallocene compounds of formula (1a) and/or (1b) G is di(para-triethylsilylphenyl)methylene.

[0077] Examples of pre-catalysts represented by formula (1) may include: diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride, methylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride, dimethylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride, dimethylsilylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride, diphenylsilylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride, ethylene(cyclopentadienyl)(9-fluorenyl)zirconium dichloride, diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dimethyl, methylene(cyclopentadienyl)(9-fluorenyl)zirconium dimethyl, dimethylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dimethyl, dimethylsilylene(cyclopentadienyl)(9-fluorenyl)zirconium dimethyl, diphenylsilylene(cyclopentadienyl)(9-fluorenyl)zirconium dimethyl, ethylene(cyclopentadienyl)(9-fluorenyl)zirconium dimethyl, di(para-triethylsilylphenyl)methylene(2,7-di-tertbutyl fluorenyl)(cyclopentadienyl)zirconium dimethyl, diphenylmethylene(cyclopentadienyl)(9-fluorenyl)hafnium dichloride, methylene(cyclopentadienyl)(9-fluorenyl)hafnium dichloride, dimethylmethylene(cyclopentadienyl)(9-fluorenyl)hafnium dichloride, dimethylsilylene(cyclopentadienyl)(9-fluorenyl)hafnium dichloride, diphenylsilylene(cyclopentadienyl)(9-fluorenyl)hafnium dichloride, ethylene(cyclopentadienyl)(9-fluorenyl)hafnium dichloride, diphenylmethylene(cyclopentadienyl)(9-fluorenyl)hafnium dimethyl, methylene(cyclopentadienyl)(9-fluorenyl)hafnium dimethyl, dimethylmethylene(cyclopentadienyl)(9-fluorenyl)hafnium dimethyl, dimethylsilylene(cyclopentadienyl)(9-fluorenyl)hafnium dimethyl, diphenylsilylene(cyclopentadienyl)(9-fluorenyl)hafnium dimethyl, ethylene(cyclopentadienyl)(9-fluorenyl)hafnium dimethyl, and di(para-triethylsilylphenyl)methylene(2,7-di-tertbutyl fluorenyl)(cyclopentadienyl)hafnium dimethyl. In some embodiments, pre-catalysts

represented by formula (1) can be diphenylmethylene(cyclopentadienyl)(9-fluorenyl)hafnium dimethyl, diphenylmethylene(cyclopentadienyl)(9-fluorenyl)hafnium dimethyl, di(para-triethylsilylphenyl)methylene(2,7-di-tertbutylfluorenyl)(cyclopentadienyl)hafnium dimethyl, diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dimethyl, diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dimethyl, or di(para-triethylsilylphenyl)methylene(2,7-di-tertbutylfluorenyl)(cyclopentadienyl)zirconium dimethyl. In some embodiments, zirconium based catalysts of formula 1, 1a and 1b are preferred such as, for example diphenylmethylene(cyclopentadienyl)(9-fluorenyl)zirconium dimethyl, or di(para-triethylsilylphenyl)methylene(2,7-di-tertbutylfluorenyl)(cyclopentadienyl)zirconium dimethyl

[0078] Catalysts capable of making the syndiotactic polypropylene homopolymers and syndiotactic propylene-rich ethylene-propylene copolymers can also include metallocene compounds (pre-catalysts) having the structure represented by formula (2) having C_s or pseudo- C_s symmetry:



wherein:

M is hafnium, zirconium or titanium;

L^1 is a unsubstituted fluorenyl, heterocyclopentapentalenyl, or heterofluorenyl, or a substituted fluorenyl, heterocyclopentapentalenyl, or heterofluorenyl ligand with one or more symmetric or pseudo symmetric substituents, each substituent group being, independently, a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germlycarbyl, and optionally two or more adjacent substituents may join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent;

G is a bridging group;

J is a heteroatom from group 15, such as N or P, such as N;

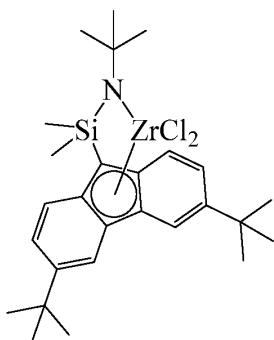
R' is a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, or substituted halocarbyl;

L' is a neutral Lewis base and w represents the number of L' bonded to M where w is 0, 1, or 2, and optionally any L' and any X may be bonded to one another;

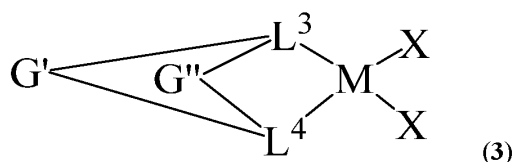
each X is independently hydride radicals, hydrocarbyl radicals, substituted hydrocarbyl radicals, halocarbyl radicals, substituted halocarbyl radicals, silylcarbyl radicals, substituted silylcarbyl radicals, germylcarbyl radicals, or substituted germylcarbyl radicals; or both X are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand; both X may, independently, be a halogen, alkoxide, aryloxy, amide, phosphide or other univalent anionic ligand or both X can also be joined to form a dianionic chelating ligand.

[0079] In some embodiments of formula (2), L¹ is fluorenyl or substituted fluorenyl, such as fluorenyl, 2,7-dimethylfluorenyl, 2,7-diethylfluorenyl, 2,7-dipropylfluorenyl, 2,7-dibutylfluorenyl, 2,7-diphenylfluorenyl, 2,7-dichlorofluorenyl, 2,7-dibromofluorenyl, 3,6-dimethylfluorenyl, 3,6-diethylfluorenyl, 3,6-dipropylfluorenyl, 3,6-dibutylfluorenyl, 3,6-diphenylfluorenyl, 3,6-dichlorofluorenyl, 3,6-dibromofluorenyl or 1,1,4,4,7,7,10,10-octamethyl-octahydrodibenzofluorenyl. In some embodiments, G is methylene, dimethylmethylene, diphenylmethylene, dimethylsilylene, methylphenylsilylene, diphenylsilylene, di(4-triethylsilylphenyl)silylene, ethylene, such as diphenylmethylene, diphenylsilylene, methylphenylsilylene, and dimethylsilylene; such as dimethylsilylene. In some embodiments, J is nitrogen. In some embodiments, R' is hydrocarbyl or halocarbyl, such as C₃-C₂₀ hydrocarbyl, such as all isomers (including cyclics and polycyclics) of propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, benzyl, phenyl and substituted phenyl, such as tert-butyl, neopentyl, benzyl, phenyl, diisopropylphenyl, adamantyl, norbornyl, cyclohexyl, cyclooctyl, cyclodecyl, and cyclododecyl, such as tert-butyl, adamant-1-yl, norborn-2-yl, cyclohexyl, cyclooctyl, and cyclododecyl. In some embodiments, X is hydrocarbyl or halo, such as methyl, benzyl, fluoro or chloro, such as methyl or chloro. In some embodiments, w is zero (L' being absent) and M is zirconium or titanium.

[0080] In some embodiments, a catalyst of Formula (2) is:



[0081] Catalysts useful for making the syndiotactic polypropylene homopolymers and syndiotactic propylene-rich ethylene-propylene copolymers can also include metallocene compounds (pre-catalysts) having a structure represented by formula (3) having C_s or pseudo- C_s symmetry:



wherein:

M is hafnium or zirconium;

L^3 is a cyclopentadienyl ring optionally substituted in the 4 position of the ring, the substituent group being chosen from a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl;

L^4 is a substituted cyclopentadienyl ring with symmetric or pseudo symmetric substituents in the 3 and 5 positions of the ring, each substituent group being, independently, a radical group which is a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl;

G' and G'' are bridging groups;

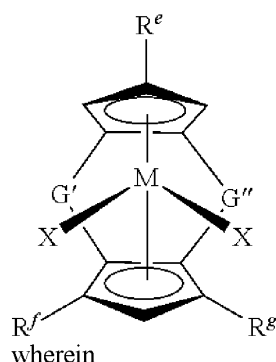
[0082] each X is independently a hydride radical, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl; or both X are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand; both X may, independently, be a halogen, alkoxide, aryloxy, amide, phosphide or other univalent anionic ligand or both X can also be joined to form a dianionic chelating ligand.

[0083] In formula (3), L^3 is cyclopentadienyl, or hydrocarbyl or silylcarbyl substituted cyclopentadienyl with the substitution on the 4-position of the cyclopentadienyl ring, such as

cyclopentadienyl, 4-methylcyclopentadienyl, 4-ethylcyclopentadienyl, 4-propylcyclopentadienyl, 4-butylcyclopentadienyl, 4-pentylcyclopentadienyl, 4-hexylcyclopentadienyl, 4-heptylcyclopentadienyl, 3-octylcyclopentadienyl, or 4-trimethylsilylcyclopentadienyl, such as cyclopentadienyl, 4-isopropylcyclopentadienyl, 4-tert-butylcyclopentadienyl, 4-(2,2-dimethylpent-3-yl)cyclopentadienyl, 4-(2,2-dimethylbut-3-yl)cyclopentadienyl or 4-trimethylsilylcyclopentadienyl, such as cyclopentadienyl, 4-isopropylcyclopentadienyl, or 4-trimethylsilylcyclopentadienyl. In some embodiments, L^4 is hydrocarbyl or silylcarbyl substituted cyclopentadienyl with the substitutions on the 3- and 5-positions of the cyclopentadienyl ring, such as 3,5-dimethylcyclopentadienyl, 3,5-diethylcyclopentadienyl, 3,5-dipropylcyclopentadienyl, 3,5-dibutylcyclopentadienyl, 3,5-dipentylcyclopentadienyl, 3,5-dihexylcyclopentadienyl, 3,5-dibenzylcyclopentadienyl, or 3,5-bis(trimethylsilyl)cyclopentadienyl, such as 3,5-dimethylcyclopentadienyl, 3,5-diisopropylcyclopentadienyl, 3,5-di-tert-butylcyclopentadienyl, 3,5-dicyclopentylcyclopentadienyl, 3,5-dipent-3-ylcyclopentadienyl, 3,5-dicyclohexylcyclopentadienyl, 3,5-dibenzylcyclopentadienyl, or 3,5-bis(trimethylsilyl)cyclopentadienyl, such as 3,5-dimethylcyclopentadienyl, 3,5-diisopropylcyclopentadienyl, 3,5-di-tert-butylcyclopentadienyl, 3,5-dibenzylcyclopentadienyl, or 3,5-bis(trimethylsilyl)cyclopentadienyl. In some embodiments, each G' and G'' are methylene, dimethylmethylene, dimethylsilylene, such as dimethylmethylene or dimethylsilylene; such as dimethylsilylene. In some embodiments, each X is hydrocarbyl or halo, such as methyl, benzyl, fluoro or chloro, such as methyl or chloro. In some embodiments, M is zirconium. In alternative embodiments, M is hafnium.

[0084] A subset of the metallocene compounds (pre-catalysts) represented by formula (3) that may be used include those having C_s or pseudo- C_s symmetry are represented by formula (3a):

(3a)



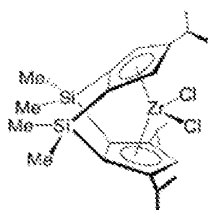
M, G', G'', and X are defined as in formula (3);

R^e is selected from hydrogen or a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl radicals;

each R^f and R^g are selected from hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl, or germylcarbyl, with the proviso that each R^f and R^g are chosen to allow the compound to be C_s-symmetric or pseudo C_s-symmetric.

[0085] In some embodiments of formula (3a), each R^f and R^g are independently hydrocarbyl or silylcarbyl, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, or trimethylsilyl, such as methyl, isopropyl, tert-butyl, cyclopentyl, pent-3-yl, cyclohexyl, benzyl, or trimethylsilyl, such as methyl, isopropyl, tert-butyl, benzyl or trimethylsilyl. In some embodiments, R^e is hydrogen, hydrocarbyl or silylcarbyl, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, or trimethylsilyl; such as hydrogen, isopropyl, tert-butyl, 2,2-dimethylpent-3-yl, 2,2-dimethylbut-3-yl, or trimethylsilyl, such as hydrogen, isopropyl or trimethylsilyl.

[0086] In some embodiments, a catalyst of formula (3) is:

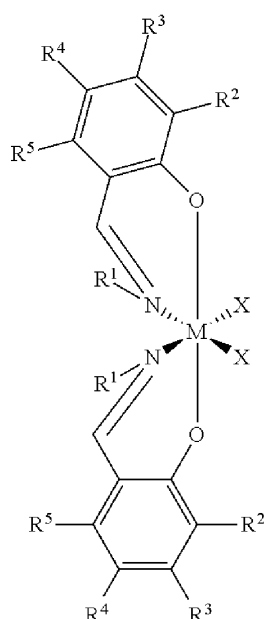


[0087] In some embodiments of formulas 1, 1a, 1b, 2, 3, or 3a, G, G' and G'' are selected from R^{*}₂C, R^{*}₂Si, R^{*}₂Ge, R^{*}₂CCR^{*}₂, R^{*}C=CR^{*}, R^{*}₂CSiR^{*}₂, R^{*}₂SiSiR^{*}₂, R^{*}B, R^{*}₂C—BR^{*}, R^{*}N, R^{*}P, O, S, and Se, where each R^{*} is independently selected from hydrogen, C₁-C₂₀ containing hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl substituent and optionally two or more adjacent R^{*} may join to form a substituted or unsubstituted, saturated, partially unsaturated, cyclic or polycyclic substituent. In some embodiments, G, G' and G'' are selected from R^{*}₂C, R^{*}₂Si, R^{*}₂Ge, R^{*}₂CCR^{*}₂, R^{*}B, R^{*}N, R^{*}P, O, S, and Se, where each R^{*} is independently selected from hydrogen, C₁-C₂₀ containing hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl substituent and optionally two or more adjacent R^{*} may join to form a substituted or unsubstituted, saturated, partially unsaturated, cyclic or polycyclic substituent. In some embodiments, G, G' and G'' are independently selected from R^{*}₂C, R^{*}₂Si,

and $R^*_2CCR^*_2$ where each R^* is independently selected from hydrogen, C_1 - C_{20} containing hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germlylcarbyl substituent and optionally two or more adjacent R^* may join to form a substituted or unsubstituted, saturated, partially unsaturated, cyclic or polycyclic substituent.

[0088] Catalysts capable of making the syndiotactic polypropylene polymers and syndiotactic propylene-based ethylene-propylene copolymers described herein may also include compounds (pre-catalysts) having a structure represented by formula (4) having C_2 symmetry:

(4)



wherein:

M is zirconium or titanium;

O is oxygen;

N is nitrogen;

R^1 is hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germlylcarbyl, such as R^1 is halocarbyl;

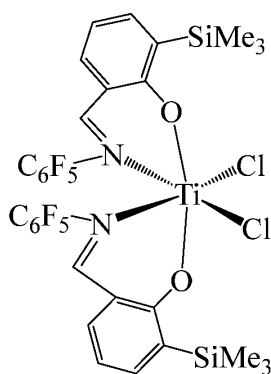
R^2 is hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germlylcarbyl, such as R^2 is hydrocarbyl having three or more carbon atoms or silylcarbyl having three or more carbon atoms;

each of R^3 , R^4 , and R^5 is independently hydrogen or a hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germlylcarbyl, such as R^3 , R^4 and R^5 are hydrogen;

each X is independently a hydride radical, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germlylcarbyl; or both X are joined and bound to the metal atom to form a metallacycle ring containing from about 3 to about 20 carbon atoms; or both together can be an olefin, diolefin or aryne ligand; both X may independently be a halogen, alkoxide, aryloxide, amide, phosphide or other univalent anionic ligand or both X can also be joined to form a dianionic chelating ligand.

[0089] In some embodiments of formula (4), R^1 is hydrocarbyl or halocarbyl radical, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, benzyl, phenyl, methylphenyl, dimethylphenyl, ethylphenyl, diethylphenyl, propylphenyl, dipropylphenyl, perfluorophenyl, trifluorophenyl, difluorophenyl, or fluorophenyl, such as phenyl, 2-methylphenyl, 2,6-dimethylphenyl, 2-isopropylphenyl, perfluorophenyl, 2,4,6-trifluorophenyl, 2,6-difluorophenyl, 3,5-difluorophenyl or 4-fluorophenyl, such as perfluorophenyl. In some embodiments, R^2 is hydrocarbyl or silylcarbyl radicals, such as C_3 - C_{12} hydrocarbyl or C_3 - C_{12} silylcarbyl, such as propyl, butyl, pentyl, hexyl, heptyl, octyl, cumyl, or trimethylsilyl, such as isopropyl, tert-butyl, cumyl, or trimethylsilyl, such as tert-butyl or trimethylsilyl. In some embodiments, R^3 , R^4 , and R^5 are independently hydrogen or hydrocarbyl radicals. In some embodiments, each X is hydrocarbyl or halo, such as methyl, benzyl, fluoro or chloro, such as methyl or chloro. In some embodiments, M is titanium.

[0090] In some embodiments, a catalyst compound of formula (4) is:



Activators and Catalyst Activation

[0091] The terms “cocatalyst” and “activator” are used herein interchangeably and are defined to be any compound which can activate any one of the pre-catalyst compounds described above by converting the neutral pre-catalyst compound to a catalytically active cationic compound. Non-limiting activators, for example, include alumoxanes, aluminum alkyls, ionizing activators, which may be neutral (Lewis acid activators) or ionic (ionic activators), and conventional-type cocatalysts. Activators may include alumoxane compounds, modified alumoxane compounds, or ionizing anion precursor compounds that abstract a reactive, σ -bound, metal ligand making the metal complex cationic and providing a charge-balancing noncoordinating or weakly coordinating anion.

[0092] Alumoxane activators are utilized as activators in the catalyst systems described herein. Alumoxanes are generally oligomeric compounds containing $-\text{Al}(\text{R}^1)-\text{O}-$ 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. A visually clear methylalumoxane can be used. 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 methylalumoxane (MMAO) cocatalyst type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A, covered under patent number U.S. Patent No. 5,041,584). Another useful alumoxane is solid polymethylaluminumoxane as described in US 9,340,630; US 8,404,880; and US 8,975,209.

[0093] When the activator is an alumoxane (modified or unmodified), at least one embodiment selects the maximum amount of activator typically at up to a 5000-fold molar excess Al/M over the catalyst compound (per metal catalytic site). The minimum activator-to-catalyst-compound is a 1:1 molar ratio. Alternative suitable ranges include from 1:1 to 500:1, alternatively from 1:1 to 200:1, alternatively from 1:1 to 100:1, or alternatively from 1:1 to 50:1.

[0094] In an alternative embodiment, little or no alumoxane is used in the polymerization processes described herein. For example, alumoxane is present at zero mole %, alternatively the alumoxane is present at a molar ratio of aluminum to catalyst compound transition metal less than 500:1, such as less than 300:1, such as less than 100:1, such as less than 1:1.

[0095] Lewis acid activators include triphenylboron, tris-perfluorophenylboron, tris-perfluorophenylaluminum, but exclude the class of activators referred to as alumoxanes. Ionic activators include dimethylanilinium tetrakis(perfluorophenyl)borate, triphenylcarbonium tetrakis(perfluorophenyl)borate, dimethylanilinium tetrakis(perfluorophenyl)aluminum. Lewis acid activators and ionic activators are referred to as stoichiometric activators since relatively low molar ratios of activator to transition metal compound are needed as compared to alumoxane activators that require large excess of activator relative to transition metal compound.

[0096] Neutral or ionic activators such as tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, trisperfluorophenylboron, trisperfluoronaphthylboron, polyhalogenated heteroborane anions, boric acid, or combinations thereof may also be used.

[0097] Stoichiometric activators (at times used in combination with a co-activator) may be used in producing the syndiotactic polypropylene homopolymers and syndiotactic propylene-based ethylene-propylene copolymers described herein.

[0098] For example, activators such as 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) are used.

[0099] In at least one embodiment, the activator 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, triphenylcarbonium tetrakis(perfluorophenyl)borate, triphenylcarbonium tetrakis(perfluoronaphthyl)borate, triphenylcarbonium tetrakis(perfluorobiphenyl)borate, triphenylcarbonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbonium 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, tropillium tetrakis(perfluoronaphthyl)borate,
 di(hydrogenated tallow)methylammonium tetrakis(perfluorophenyl)borate, di(hydrogenated
 tallow)methylammonium tetrakis(perfluoronaphthyl)borate, dioctadecylmethylammonium
 tetrakis(perfluorophenyl)borate, and dioctadecylmethylammonium
 tetrakis(perfluoronaphthyl)borate. Additional useful activators include:

N-methyl-4-nonadecyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-hexadecyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-tetradecyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-dodecyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-decyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-octyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-hexyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-butyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-octadecyl-*N*-decylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-nonadecyl-*N*-dodecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-nonadecyl-*N*-tetradecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-4-nonadecyl-*N*-hexadecylanilinium [tetrakis(perfluorophenyl)borate],
N-ethyl-4-nonadecyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-*N,N*-dioctadecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-*N,N*-dihexadecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-*N,N*-ditetradecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-*N,N*-didodecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-*N,N*-didecylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-*N,N*-dioctylammonium [tetrakis(perfluorophenyl)borate],
N-ethyl-*N,N*-dioctadecylammonium [tetrakis(perfluorophenyl)borate],
N,N-di(octadecyl)tolylammonium [tetrakis(perfluorophenyl)borate],
N,N-di(hexadecyl)tolylammonium [tetrakis(perfluorophenyl)borate],
N,N-di(tetradecyl)tolylammonium [tetrakis(perfluorophenyl)borate],
N,N-di(dodecyl)tolylammonium [tetrakis(perfluorophenyl)borate],

N-octadecyl-*N*-hexadecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-octadecyl-*N*-hexadecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-octadecyl-*N*-tetradecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-octadecyl-*N*-dodecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-octadecyl-*N*-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-hexadecyl-*N*-tetradecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-hexadecyl-*N*-dodecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-hexadecyl-*N*-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-tetradecyl-*N*-dodecyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-tetradecyl-*N*-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-dodecyl-*N*-decyl-tolylammonium [tetrakis(perfluorophenyl)borate],
N-methyl-*N*-octadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-*N*-hexadecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-*N*-tetradecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-*N*-dodecylanilinium [tetrakis(perfluorophenyl)borate],
N-methyl-*N*-decylanilinium [tetrakis(perfluorophenyl)borate], and *N*-methyl-*N*-octylanilinium [tetrakis(perfluorophenyl)borate]

[00100] Examples of neutral stoichiometric activators include tri-substituted boron, tellurium, aluminum, gallium and indium or mixtures thereof. The three substituent groups are each independently selected from alkyls, alkenyls, halogen, substituted alkyls, aryls, arylhalides, alkoxy and halides. For example, the three substituent groups are independently selected from halogen, mono or multicyclic (including halosubstituted) aryls, alkyls, and alkenyl compounds and mixtures thereof, for example can be alkenyl groups having 1 to 20 carbon atoms, alkyl groups having 1 to 20 carbon atoms, alkoxy groups having 1 to 20 carbon atoms and aryl groups having 3 to 20 carbon atoms (including substituted aryls). In some embodiments, the three substituent groups are alkyls having 1 to 4 carbon groups, phenyl, naphthyl or mixtures thereof. In some embodiments, the three substituent groups are halogenated, such as fluorinated aryl groups. In some embodiments, the neutral stoichiometric activator is tris(perfluorophenyl)boron or tris(perfluoronaphthyl)boron.

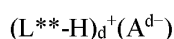
[00101] Ionic stoichiometric activator compounds may contain an active proton, or some other cation associated with, but not coordinated to, or only loosely coordinated to, the remaining ion of the ionizing compound. Such compounds are described in European publications EP-A-0 570 982, EP-A-0 520 732, EP-A-0 495 375, EP-B1-0 500 944, EP-A-0

277 003 and EP-A-0 277 004, and U.S. Pat. Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,384,299, 5,502,124, and 5,972,823, and publications US2021079537, WO2021/086467, US2019/0330169, US2019/0330392, all of which are herein incorporated by reference.

[00102] Ionic catalysts can be prepared by reacting a transition metal compound with an activator, such as $B(C_6F_5)_3$, which upon reaction with the hydrolyzable ligand (X') of the transition metal compound forms an anion, such as $[B(C_6F_5)_3(X')]^-$, which stabilizes the cationic transition metal species generated by the reaction. The catalysts can be prepared with activator components which are ionic compounds or compositions. However, preparation of activators utilizing neutral compounds is also contemplated.

[00103] Compounds useful as an activator component in the preparation of the ionic catalyst systems used in the process may comprise a cation, which can be a Brønsted acid capable of donating a proton, and a compatible non-coordinating anion which anion is relatively large (bulky), capable of stabilizing the active catalyst species which is formed when the two compounds are combined and said anion will be sufficiently labile to be displaced by olefinic diolefinic and acetylenically unsaturated substrates or other neutral Lewis bases such as ethers, nitriles and the like. Two classes of compatible non-coordinating anions have been disclosed in EPA 277,003 and EPA 277,004 published 1988: 1) anionic coordination complexes comprising a plurality of lipophilic radicals covalently coordinated to and shielding a central charge-bearing metal or metalloid core, and 2) anions comprising a plurality of boron atoms such as carboranes, metallacarboranes and boranes.

[00104] In at least one embodiment, the ionic stoichiometric activators include a cation and an anion component, and may be represented by the following formula:



wherein

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

[00105] The cation component $(L^{**}-H)_d^+$ 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 precatalyst after alkylation.

[00106] The activating cation $(L^{**}-H)_d^+$ may be a Brønsted acid, capable of donating a proton to the alkylated transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof, such as

ammoniums of methylamine, aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, trimethylamine, triethylamine, N,N-dimethylaniline, 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 and tetrahydrothiophene, and mixtures thereof. The activating cation $(L^{**}-H)_d^+$ may also be a moiety such as silver, tropylium, carbeniums, ferroceniums and mixtures, such as carboniums and ferroceniums; such as triphenyl carbonium. The anion component A^{d-} include those having the formula $[M^{k+} Q_n]^{d-}$ wherein k is an integer from 1 to 3; n is an integer from 2-6; $n-k=d$; M is an element selected from group 13 of the Periodic Table of the Elements, such as boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, aryloxy, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, and halosubstituted-hydrocarbyl radicals, said Q having up to 20 carbon atoms with the proviso that in not more than one occurrence is Q a halide. For example, each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, such as each Q is a fluorinated aryl group, such as each Q is a pentafluoryl aryl group. Examples of suitable A^{d-} also include diboron compounds as disclosed in U.S. Pat. No. 5,447,895, which is fully incorporated herein by reference.

[00107] In some embodiments, boron compounds which may be used as a non-coordinating anion activator in combination with a co-activator in the preparation of the catalysts of this disclosure are tri-substituted ammonium salts such as: trimethylammonium tetraphenylborate, triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-butyl)ammonium tetraphenylborate, tri(tert-butyl)ammonium tetraphenylborate, N,N-dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetraphenylborate, trimethylammonium tetrakis(pentafluorophenyl)borate, triethylammonium tetrakis(pentafluorophenyl)borate, tripropylammonium tetrakis(pentafluorophenyl)borate, tri(n-butyl)ammonium tetrakis(pentafluorophenyl)borate, tri(sec-butyl)ammonium tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, N,N-diethylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triethylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tripropylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tri(n-butyl)ammonium tetrakis-(2,3,4,6-

tetrafluorophenyl)borate, dimethyl(tert-butyl)ammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dimethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-diethylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trimethylammonium tetrakis(perfluoronaphthyl)borate, triethylammonium tetrakis(perfluoronaphthyl)borate, tripropylammonium tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate, tri(tert-butyl)ammonium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluoronaphthyl)borate, trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate, tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate, tri(tert-butyl)ammonium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(perfluorobiphenyl)borate, trimethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tripropylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tri(n-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, tri(tert-butyl)ammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-diethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, and dialkyl ammonium salts such as: di-(isopropyl) ammonium tetrakis(pentafluorophenyl)borate, and dicyclohexylammonium tetrakis(pentafluorophenyl)borate; and other salts such as tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl)borate, tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl)borate, tropillium tetraphenylborate, triphenylcarbenium tetraphenylborate, triphenylphosphonium tetraphenylborate, triethylsilylium tetraphenylborate, benzene(diazonium)tetraphenylborate, tropillium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylphosphonium tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate, benzene(diazonium) tetrakis(pentafluorophenyl)borate, tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-

tetrafluorophenyl)borate, triphenylphosphonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triethylsilylium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, benzene(diazonium) tetrakis-(2,3,4,6-tetrafluorophenyl)borate, tropillium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)borate, tropillium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate, tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylphosphonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylsilylium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, and benzene(diazonium) tetrakis(3,5-bis(trifluoromethyl)phenyl)borate.

[00108] In some embodiments, the non-coordinating anion activator, $(L^{**}-H)_d^+ (A^{d-})$, is 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, or triphenylcarbenium tetra(perfluorophenyl)borate.

[00109] The catalyst precursors can also be activated with cocatalysts or activators that comprise non-coordinating anions containing metalloid-free cyclopentadienide ions, as described in U.S. Patent Publication 2002/0058765 A1, and for the instant disclosure, require the addition of a co-activator to the catalyst pre-cursor. “Compatible” non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral transition metal compound and a neutral by-product from the anion. Example non-coordinating anions useful in accordance with this disclosure are those that are compatible, stabilize the transition metal complex cation in the sense of balancing its ionic charge at +1, and yet retain sufficient liability to permit displacement by an ethylenically or acetylenically unsaturated monomer during polymerization. These types of cocatalysts are

sometimes used with scavengers such as but not limited to tri-iso-butylaluminum, tri-n-octylaluminum, tri-n-hexylaluminum, triethylaluminum or trimethylaluminum.

[00110] Disclosure processes also can employ cocatalyst compounds or activator compounds that are initially neutral Lewis acids but form a cationic metal complex and a non-coordinating anion, or a zwitterionic complex upon reaction with the alkylated transition metal compounds. The alkylated metallocene compound is formed from the reaction of the catalyst precursor and the co-activator. For example, tris(pentafluorophenyl) boron or aluminum act to abstract a hydrocarbyl ligand to yield an disclosure cationic transition metal complex and stabilizing non-coordinating anion, see EP-A-0 427 697 and EP-A-0 520 732 for illustrations of analogous group-4 metallocene compounds. Also, see the methods and compounds of EP-A-0 495 375. For formation of zwitterionic complexes using analogous group 4 compounds, see U.S. Pat. Nos. 5,624,878; 5,486,632; and 5,527,929.

[00111] Additional neutral Lewis-acids are known in the art and are suitable for abstracting formal anionic ligands. See in particular the review article by E. Y.-X. Chen and T. J. Marks, "Cocatalysts for Metal-Catalyzed Olefin Polymerization: Activators, Activation Processes, and Structure-Activity Relationships", Chem. Rev., 100, 1391-1434 (2000).

[00112] When the cations of non-coordinating anion activators are Bronsted acids such as protons or protonated Lewis bases (excluding water), or reducible Lewis acids such as ferrocenium or silver cations, or alkali or alkaline earth metal cations such as those of sodium, magnesium or lithium, the catalyst-precursor-to-activator molar ratio may be any ratio. Combinations of the described activator compounds may also be used for activation.

[00113] When an ionic or neutral stoichiometric activator (such as an NCA) is used, the catalyst-precursor-to-activator molar ratio is from 1:10 to 1:1; 1:10 to 10:1; 1:10 to 2:1; 1:10 to 3:1; 1:10 to 5:1; 1:2 to 1.2:1; 1:2 to 10:1; 1:2 to 2:1; 1:2 to 3:1; 1:2 to 5:1; 1:3 to 1.2:1; 1:3 to 10:1; 1:3 to 2:1; 1:3 to 3:1; 1:3 to 5:1; 1:5 to 1:1; 1:5 to 10:1; 1:5 to 2:1; 1:5 to 3:1; 1:5 to 5:1; 1:1 to 1:1.2. The catalyst-precursor-to-co-activator molar ratio is from 1:500 to 1:1, 1:100 to 100:1; 1:75 to 75:1; 1:50 to 50:1; 1:25 to 25:1; 1:15 to 15:1; 1:10 to 10:1; 1:5 to 5:1, 1:2 to 2:1; 1:100 to 1:1; 1:75 to 1:1; 1:50 to 1:1; 1:25 to 1:1; 1:15 to 1:1; 1:10 to 1:1; 1:5 to 1:1; 1:2 to 1:1; 1:10 to 2:1.

[00114] In some embodiments, activators and activator/co-activator combinations include dimethylanilinium tetrakis(pentafluorophenyl)borate or tris(pentafluorophenyl)boron, or mixtures of trialkyl aluminum with dimethylanilinium tetrakis(pentafluorophenyl)borate or tris(pentafluorophenyl)boron. In some embodiments, scavenging compounds are used with

activators. Typical aluminum or boron alkyl components useful as scavengers are represented by the general formula $R^xJ'Z'_2$ where J' is aluminum or boron, R^x is as previously defined above, and each Z' is independently R^x or a different univalent anionic ligand such as halogen (Cl, Br, I), alkoxide (OR^x) and the like. Aluminum alkyls can include triethylaluminum, diethylaluminum chloride, tri-iso-butylaluminum, tri-n-octylaluminum, tri-n-hexylaluminum, trimethylaluminum and the like. Boron alkyls can include triethylboron. Scavenging compounds can be alumoxanes and modified alumoxanes including methylalumoxane and modified methylalumoxane.

[00115] In some embodiments, the precatalyst and or activator are combined with an alkylaluminum compound, such as a trialkylaluminum compound, prior to entering the reactor. For example, the alkylaluminum compound can be represented by the formula: R_3Al , where each R is independently a C_1 to C_{20} alkyl group; such as the R groups are independently selected from methyl, ethyl, propyl, isopropyl, butyl, isobutyl, n-butyl, pentyl, isopentyl, n-pentyl, hexyl, isohexyl, n-hexyl, heptyl, octyl, isooctyl, n-octyl, nonyl, isononyl, n-nonyl, decyl, isodecyl, n-decyl, undecyl, isoundecyl, n-undecyl, dodecyl, isododecyl, and n-dodecyl, such as isobutyl, n-octyl, n-hexyl, and n-dodecyl. In some embodiments, the alkylaluminum compound is selected from tri-isobutyl aluminum, tri n-octyl aluminum, tri-n-hexyl aluminum, and tri-n-dodecyl aluminum.

Chain Transfer Agent

[00116] Polymerization processes of the present disclosure may include polymerization in the presence of a chain transfer agent or chain shuttling agent.

[00117] Chain transfer agents include alkylaluminum compounds represented by the formula: R_3Al , where each R is, independently, a C_1 to C_{18} alkyl group, such as each R is, independently, selected from methyl, ethyl, n-propyl, isopropyl, iso-butyl, n-butyl, t-butyl, n-pentyl, iso-pentyl, neopentyl, n-hexyl, iso-hexyl, n-heptyl, iso-heptyl, n-octyl, iso-octyl, n-nonyl, n-decyl, n-undecyl, n-dodecyl, n-tridecyl, n-tetradecyl, n-pentadecyl, n-hexadecyl, n-heptadecyl, n-octadecyl, and their iso-analogs.

[00118] In the process, hydrogen can also be used as a useful chain transfer agent in the reaction. In some embodiments, alternative chain transfer agents can be used in the processes described herein, reducing the need for hydrogen wherein hydrogen is absent or used in limited amounts. In some embodiments, chain transfer agents include diethylzinc, and trialkylaluminums such as triisobutylaluminum, tri-n-octylaluminum, triethylaluminum and the like, or mixtures thereof.

[00119] In some embodiment, the chain transfer agent can be used at a molar ratio of the chain transfer agent to the transition metal compound of from 1:1 to 150:1. In at least one embodiment, the molar ratio of chain transfer agent to the transition metal compound can be greater than 5:1, or greater than 10:1, or greater than 20. Likewise, the molar ratio of chain transfer agent to the transition metal compound can be less than 120:1, or less than 100:1, or less than 80:1.

Polymerization process

[00120] The syndiotactic propylene-based ethylene-propylene copolymers can be produced by contacting ethylene and propylene with at least one catalyst in any manner known in the art. Any homogeneous, bulk, solution (including supercritical) phase, slurry- and gas-phase polymerization processes known in the art can be used. Such processes can be run in a batch, semi-batch, or continuous mode. Such processes can also be run in systems with single reactor or multiple reactors in series and/or parallel configuration. Homogeneous polymerization processes are preferred. A homogeneous polymerization process is defined to be a process where at least 90 wt% of the product is soluble in the reaction media at polymerization condition. The monomer itself can be also used as a solvent/diluent in a bulk polymerization process. A bulk process is typically a process where monomer concentration in all feeds to the reactor is 70 vol% or more. Alternately, no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the carrier for the catalyst system or other additives, or amounts typically found with the monomer; e.g., propane in propylene).

[00121] Suitable diluents/solvents for polymerization include non-coordinating, inert liquids. Examples include straight and branched-chain hydrocarbons, such as isobutane, butane, pentane, isopentane, hexanes, isohexane, heptane, octane, dodecane, and mixtures thereof; normal paraffins (such as Norpar solvents available for ExxonMobil Chemical Company, Houston, Texas), or isoparaffin solvents (such as Isopar solvents available for ExxonMobil Chemical Company, Houston, Texas) (Isopar™); cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; aromatic and alkyl substituted aromatic compounds such as toluene and or xylenes and or ethylbenzene; perhalogenated hydrocarbons, such as perfluorinated C₄₋₁₀ alkanes, chlorobenzene. Mixtures of any of the foregoing hydrocarbon solvents may also be used. 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 a preferred embodiment, 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 another embodiment, the solvent is not aromatic, preferably aromatics are present in the solvent at less than 1 wt%, preferably less than 0.5 wt%, preferably less than 0 wt% based upon the weight of the solvents.

[00122] Preferred polymerizations 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 50°C to about 200°C, from about 55°C to about 150°C, from about 58°C to about 120°C, preferably from about 60°C to about 110°C, preferably from about 60°C to about 90°C; and at a pressure in the range of from about 0.35 MPa to about 14 MPa, preferably from about 2 MPa to about 13 MPa, preferably from about 4 MPa to about 13 MPa, preferably from about 7 MPa to about 12 MPa, preferably from about 9 MPa to about 11.5 MPa, preferably from about 9 MPa to about 11 MPa. In some catalyst systems, the syndiotacticity of the ethylene-propylene copolymer varies with polymerization temperature, selection of temperature can be determined by the desirable level of the syndiotacticity of the ethylene-propylene copolymer. In one embodiment, the polymerization is conducted at a temperature of 60 °C or higher with an upper temperature limit of 120 °C, and at a pressure of 9.5 MPa or higher.

[00123] In one embodiment, the polymerization occurs at a polymerization temperature of $TP1$ or higher, wherein $TP1 = 0.9 * \text{EXP}(-0.005 * rr)$. Preferably, the polymerization temperature is at least of $TP2$, wherein $TP2 = 1.15 * \text{EXP}(-0.006 * rr)$. The unit of $TP1$ and $TP2$ is in °C, rr is triad tacticity index of the syndiotactic ethylene-propylene copolymers measured using ^{13}C NMR.

[00124] In some embodiments, hydrogen is present in the polymerization reactor at a partial pressure of 0.001 to 50 psig (0.007 to 345 kPa), preferably from 0.01 to 25 psig (0.07 to 172 kPa), more preferably from 0.1 to 10 psig (0.7 to 70 kPa). In some embodiments, hydrogen is not added the polymerization reactor, i.e., hydrogen may be present from other sources, such as a hydrogen generating catalyst, but none is added to the reactor. Alternatively, the hydrogen concentration is 10000 ppm or less in the feed, preferably 5000 ppm or less.

[00125] The catalysts typically have catalyst activity higher than 10,000 kg of polymer per kg of catalyst or more, 20,000 kg of polymer per kg of catalyst or more, 50,000 kg of polymer per kg of catalyst or more, 100,000 kg of polymer per kg of catalyst or more when

polymerization occurs in a continuous process. Likewise, the conversion of olefin monomer is at least 10%, based upon polymer yield and the weight of the monomer entering the reaction zone, preferably 20% or more, preferably 30% or more, preferably 50% or more, preferably 80% or more.

[00126] The catalyst and activator may be delivered as a solution, neat liquid, suspension 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. In one embodiment, the catalyst and the activator can be fed into the polymerization reactor in form of dry powder or slurry without the need of preparing a homogenous catalyst solution by dissolving the catalyst into a carrying solvent.

[00127] The syndiotactic propylene-based ethylene-propylene copolymers can also include at least one other monomer and can be prepared by contacting ethylene, propylene and at least one other monomer with at least one catalyst in any manner known in the art. Suitable other monomers include substituted or unsubstituted C2 to C40 alpha olefins, preferably C2 to C20 alpha olefins, preferably C2 to C12 alpha olefins, preferably butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene and isomers thereof. In a preferred embodiment of the invention, the monomer comprises propylene and an optional comonomers comprising one or more of ethylene or C4 to C40 olefins, preferably C4 to C20 olefins, or preferably C6 to C12 olefins. The C4 to C40 olefin monomers may be linear, branched, or cyclic. The C4 to C40 cyclic olefins may be strained or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and/or one or more functional groups. Exemplary C2 to C40 olefin monomers and optional comonomers include butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, norbornadiene, dicyclopentadiene, cyclopentene, cycloheptene, cyclooctene, cyclooctadiene, cyclododecene, 7-oxanorbornene, 7-oxanorbornadiene, substituted derivatives thereof, and isomers thereof, preferably hexene, heptene, octene, nonene, decene, dodecene, cyclooctene, 1,5-cyclooctadiene, 1-hydroxy-4-cyclooctene, 1-acetoxy-4-cyclooctene, 5-methylcyclopentene, cyclopentene, dicyclopentadiene, norbornene, norbornadiene, and their respective homologs and derivatives, preferably norbornene, norbornadiene, and dicyclopentadiene. Preferably, the polymer is a syndiotactic-rich ethylene-propylene-hexene terpolymers or syndiotactic-rich ethylene-propylene-octene terpolymers.

[00128] The polymerization can be carried out in multiple reactors in series and parallel configurations. In one embodiment, the copolymer is a reactor blend of a first polymer

component and a second polymer component. Thus, the comonomer content of the copolymer can be adjusted by adjusting the comonomer content of the first polymer component, adjusting the comonomer content of second polymer component, and/or adjusting the ratio of the first polymer component to the second polymer component present in the copolymer.

[00129] The syndiotactic propylene-based ethylene-propylene copolymers according to various embodiments can be a blend of at least two syndiotactic propylene-based ethylene-propylene copolymers. The blend can be prepared using two or more reactors in series or parallel. Preferably, the blend has a bimodal molecular weight distribution or wide molecular weight distribution with $MWD > 3.0$. The blend can also have a bimodal composition distribution or wide composition distribution. Preferably one component has ethylene content in the range of 0.2 to 5 wt%, and one component has ethylene content in the range of 2 to 15 wt%. Each of the blending component can be prepared in a different reactor when multiple reactors are used. This is accomplished by operating the reactor at different polymerization conditions and/or use different catalysts in each reactor. The syndiotactic propylene-based ethylene-propylene copolymer blend can also be made in a single reactor with multiple catalysts. In one embodiment, one component has Mw in the range of 10,000 to 30,000 g/mol and ethylene content in the range of 0.2 to 3 wt%, and one component has Mw in the range of 30,000 to 200,000 g/mol and ethylene content in the range of 2 to 10 wt%.

[00130] In one embodiment, solution polymerization process is preferred. Solution polymerization processes may be used to carry out the polymerization reactions disclosed herein in any suitable manner known to one having ordinary skill in the art. In particular embodiments, the polymerization processes may be carried out in continuous polymerization processes. The term “batch” refers to processes in which the complete reaction mixture is withdrawn from the polymerization reactor vessel at the conclusion of the polymerization reaction. In contrast, in a continuous polymerization process, one or more reactants are introduced continuously to the reactor vessel and a solution comprising the polymer product is withdrawn concurrently or near concurrently. A solution polymerization means a polymerization process in which the polymer produced is soluble in a liquid polymerization medium, such as an inert solvent or monomer(s) or their blends. A solution polymerization is typically homogeneous. 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.

[00131] In a typical solution process, catalyst components, solvent, monomers and hydrogen (when used) are fed under pressure to one or more reactors. 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 monomers are dissolved/dispersed in the solvent either prior to being fed to the first reactor or dissolve in the reaction mixture. The solvent and monomers are generally purified to remove potential catalyst poisons prior entering the reactor. The feedstock may be heated or cooled prior to feeding to the first reactor. Additional monomers and solvent may be added to the second reactor, and it may be heated or cooled. The catalysts/activators can be fed in the first reactor or split between two reactors. In solution polymerization, polymer produced is molten and remains dissolved in the solvent under reactor conditions, forming a polymer solution (also referred as to effluent).

[00132] The solution polymerization process of this invention uses stirred tank reactor system comprising one or more stirred polymerization reactors. Generally, the reactors should be operated under conditions to achieve a thorough mixing of the reactants. In a multiple reactor system, the first polymerization reactor preferably operates at lower temperature. The residence time in each reactor will depend on the design and the capacity of the reactor. The catalysts/activators can be fed into the first reactor only or split between two reactors. In an alternative embodiment, a loop reactor and plug flow reactors can be employed for current invention.

[00133] The polymer solution is then discharged from the reactor as an effluent stream and the polymerization reaction is quenched, typically with coordinating polar compounds, to prevent further polymerization. On leaving the reactor system the polymer solution is passed through a heat exchanger system on route to a devolatilization system and polymer finishing process. The lean phase and volatiles removed downstream of the liquid phase separation can be recycled to be part of the polymerization feed.

[00134] A polymer can be recovered from the effluent of either reactor or the combined effluent, by separating the polymer from other constituents of the effluent. Conventional separation means may be employed. For example, polymer can be recovered from effluent by coagulation with a non-solvent such as isopropyl alcohol, acetone, or n-butyl alcohol, or the polymer can be recovered by heat and vacuum stripping the solvent or other media with heat or steam. One or more conventional additives such as antioxidants can be incorporated in the

polymer during the recovery procedure. Other methods of recovery such as by the use of lower critical solution temperature (LCST) followed by devolatilization are also envisioned.

[00135] In an embodiment, the polymerization: 1) is conducted in a solution process at temperatures of 50°C or higher (preferably 60°C or higher, preferably 65°C or higher) with an upper temperature limit of 120°C or lower, alternatively 110°C or lower, alternatively 100°C or lower; 2) is conducted at a pressure of atmospheric pressure to 15 MPa (preferably from 1 to 15 MPa, preferably from 2 to 14 MPa, preferably from 4 to 13 MPa); 3) is conducted in an aliphatic hydrocarbon 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; preferably where aromatics (such as toluene) are preferably present in the solvent at less than 1 wt%, preferably less than 0.5 wt%, preferably at 0 wt% based upon the weight of the solvents); 4) ethylene is present in the polymerization reactor at a concentration of 2 mole/liter or less); 5) the polymerization preferably occurs in one reaction zone; 6) the productivity of the catalyst compound is 5,000 kg of polymer per kg of catalyst or more (preferably 10,000 kg of polymer per kg of catalyst or more, such as 20,000 kg of polymer per kg of catalyst or more, such as 40,000 kg of polymer per kg of catalyst or more, such as 50,000 kg of polymer per kg of catalyst or more, such as the catalyst efficiency can be of from about 10,000 kg of polymer per kg of catalyst to about 500,000 kg of polymer per kg of catalyst).

[00136] The composition of the syndiotactic propylene-based ethylene-propylene copolymers according to various embodiments varies with feed compositions and concentrations of monomers in the polymerization reactor. In one embodiment, the molar ratio of ethylene to propylene in the feed is of 0.29 or less, preferably 0.25 or less, preferably 0.20 or less, preferably 0.15 or less preferably 0.10 or less. In another embodiment, the molar ratio of ethylene to propylene in the feed is of 0.03 or above, preferable 0.035 or above.

[00137] In a preferred embodiment, the polymerization is conducted in a solution process at a pressure of 9 MPa or higher and a temperature of 60 °C or above with an upper temperature limit of 120 °C, and with catalyst efficiency 50,000 kg of polymer per kg of catalyst to about 600,000 kg of polymer per kg of catalyst.

[00138] Preferably, the polymerization is conducted in a solution process at a pressure of 9 MPa or higher and with a feed molar ratio of ethylene to propylene of 0.03 or above and with catalyst efficiency 50,000 kg of polymer per kg of catalyst to about 600,000 kg of polymer per kg of catalyst.

Gel Permeation Chromatography with Three Detectors (GPC-3D)

[00139] Molecular weights (number average molecular weight (Mn), weight average molecular weight (Mw), and z-average molecular weight (Mz)) are determined using an Agilent PL220 high temperature GPC (gel permeation chromatograph) equipped with on-line differential refractive index (DRI), light scattering (LS), and viscometer (VIS) detectors. It uses three Polymer Laboratories PLgel 10 μ m Mixed-B columns for separation with a nominal flow rate of 0.5 ml/min and a nominal injection volume of 300 microliter. The detectors and columns were contained in an oven maintained at 145°C. The details of these detectors as well as their calibrations have been described by, for example, T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, in *Macromolecules*, Volume 34, Number 19, pp. 6812-6820, (2001), incorporated herein by reference.

[00140] Solvent for the GPC tests was prepared by dissolving 6 grams of butylated hydroxy toluene as an antioxidant in 4 liters of Aldrich reagent grade 1, 2, 4-trichlorobenzene (TCB). The TCB mixture was then filtered through a 0.1 micrometer Teflon filter. The TCB was then degassed with an online degasser before entering the GPC. Polymer solutions were prepared by placing dry polymer in a glass container, adding the desired amount of TCB, then heating the mixture at 160 °C with continuous agitation for about 2 hours. All quantities were measured gravimetrically. The injection concentration was from 1.0 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 DRI signal, I_{DRI} , using the following equation:

$$c = K_{DRI} I_{DRI} / (dn/dc)$$

where K_{DRI} is a constant determined by calibrating the DRI with a series of mono-dispersed polystyrene standards with molecular weight ranging from around 600 to 11M, and (dn/dc) is the refractive index increment for the system. For purposes of this invention and the claims thereto $(dn/dc) = 0.1048$ for all ethylene-propylene copolymers and homopolymers. Units of parameters used throughout this description of the GPC method are: concentration is expressed in g/cm³, molecular weight is expressed in g/mol, and intrinsic viscosity is expressed in dL/g.

[00141] The light scattering detector was a high temperature 18-angle Dawn Heleos (Wyatt Technology, Inc.). The molecular weight, M , at each point in the chromatogram was determined by analyzing the LS output using the Zimm model for static light scattering (M.B. Huglin, *LIGHT SCATTERING FROM POLYMER SOLUTIONS*, Academic Press, 1971):

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

Here, $\Delta R(\theta)$ is the measured excess Rayleigh scattering intensity at scattering angle θ , c is the polymer concentration determined from the DRI analysis, A_2 is the second virial coefficient. $P(\theta)$ is the form factor for a mono-disperse 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 $\lambda = 657\text{ nm}$. A high temperature Agilent 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, $[\eta]$, at each point in the chromatogram is calculated from the following equation:

$$\eta_s = c[\eta] + 0.3(c[\eta])^2$$

where c is concentration and was determined from the DRI output.

[00142] g'_{vis} is defined as the ratio of the intrinsic viscosity of the syndiotactic ethylene-propylene copolymer to the intrinsic viscosity of an isotactic-rich propylene-ethylene copolymer of equal molecular weight and composition and was calculated using the output of the SEC-DRI-LS-VIS method as follows. The average intrinsic viscosity, $[\eta]_{\text{avg}}$, of the sample was calculated by:

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

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

[00143] g'_{vis} is defined as:

$$g'_{\text{vis}} = \frac{[\eta]_{\text{avg}}}{KM_v^\alpha}$$

M_v is the viscosity-average molecular weight based on molecular weights determined by LS analysis, while α and K are calculated in the published literature (T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, pp. 6812-6820, (2001)), except that for purposes of this invention and claims thereto, $\alpha =$

$0.695 + \text{TRUNC}(10 * C3wt)/1000$ and $K = 0.000579 * (1 - 0.48601 * C3wt - 0.068989 * C3wt^2) * (200000)^{(-\text{TRUNC}(10 * C3wt)/1000)}$ for the ethylene-propylene copolymers. C3wt is propylene content of the copolymer in weight percent, concentrations are expressed in g/cm³, 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.

Differential Scanning Calorimetry (DSC)

[00144] 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 were determined using the following DSC procedure according to ASTM D3418-03. Differential scanning calorimetric (DSC) data were obtained using a TA Instruments model Q200 machine. Samples weighing approximately 5-10 mg were sealed in an aluminum hermetic sample pan. The DSC data were recorded by first gradually heating the sample to 200°C at a rate of 10°C/minute. The sample was 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 (J/g) / B (J/g)] * 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, that a value of 189 J/g (B) is used as the heat of fusion for 100% crystalline polypropylene, a value of 290 J/g is used for the heat of fusion for 100% crystalline polyethylene. The melting and crystallization temperatures reported here were obtained during the second heating/cooling cycle unless otherwise noted.

Carbon NMR

[00145] The comonomer content and sequence distribution of the polymers can be measured using ¹³C nuclear magnetic resonance (NMR) by methods well known to those skilled in the art. Unless otherwise indicated the polymer samples for ¹³C NMR spectroscopy were dissolved in 1,1,2,2-tetrachloroethane-d₂ at 140°C with a concentration of 67 mg/mL and the samples were recorded at 120°C using a Bruker NMR spectrometer with a ¹³C NMR frequency of 125 MHz or greater with a 10mm cryoprobe using a 90° pulse and gated decoupling with at least 512 scans. Chemical shift of solvent- 1,1,2,2-tetrachloroethane-d₂ was referenced to 74.24ppm so that main isotactic peak of the methyl would be at 21.83ppm. Calculations involved in the

characterization of polymers by NMR follow the work of Bovey, F. A. (1969) in Polymer Conformation and Configuration, Academic Press, New York and Randall, J. (1977) in Polymer Sequence Determination, Carbon-13 NMR Method, Academic Press, New York.

Region Intensity	Chemical Shift Range (ppm)	Assignments	Contributing Sequences
A	45-48.0	$\alpha\alpha$ (CH ₂)	[PPP] + 0.5*[PPE]
B	36-39.5	$\alpha\gamma$, $\alpha\delta^+$	[EPE] + 0.5*[PPE] + [PEP] + 0.5*[EEP]
C	32.9-33.4	CH (EPE)	[EPE]
D	30.4-31.5	CH (EPP), $\gamma\gamma$	[EPP] + [PEEP]
E	30.2-30.4	$\gamma\delta^+$	[PEEE]
F	29.8-30	$\delta^+\delta^+$	[EEE]n
G	27.9-29.0	CH (PPP)	[PPP]
H	24.2-24.9	$\beta\beta$	[PEP]
I1	21.2-22.30	CH ₃ (PPP)	[PPP]
I2	20.51-21.19	CH ₃ (PPE)	[PPP]+[PPE]
I3	19.77-20.19	CH ₃ (EPE)	[PPP] + [EPE]

[00146] The system of equations is solved using the linest function in excel with outputs being the triad area, assuming the constant is 0. Y is defined as the area of the chemical shift regions and X being the triad contribution for each region. This can then be converted to mole fraction of triads by taking the individual area divided by the total, eg. PPP (area) from linest/(PPP+PPE+EPE+PEP+EEP+EEE).

[00147] %rr (PP+EP) is calculated as follows using the CH₃ region of the propylene.

Assignment	Chemical Shift (ppm)	Calculations
%mm (PP+EP)	21.2 - 22.3	mm*100/total
%mr (PP+EP)	20.4 - 21.2	mr*100/total
%rr (PP+EP)	19.6 - 20.4	rr*100/total
Total	mm+mr+rr	

[00148] Chemical shift assignments for the ethylene-propylene copolymers are described by Randall in "A Review Of High Resolution Liquid Carbon Nuclear Magnetic Resonance Characterization of Ethylene-Based Polymers", Polymer Reviews, 29:2,201-5 317 (1989). The

copolymer content, mole and weight %, triad sequencing, and diad calculations are also calculated and described in the method established by Randall in this paper.

[00149] Unless stated otherwise, ethylene content of ethylene-propylene copolymers was determined using FTIR according ASTM D3900. The composition of other polymers may be obtained using ^{13}C NMR by methods well known to those in the art. For the claim herein, ethylene content from FTIR is used.

[00150] The melt flow rate (MFR) is measured in accordance with ASTM D1238-13 at 230°C and 2.16 kg load. The high load melt flow rate (MFR HL) is measured in accordance with ASTM D1238 at 230°C and 21.6 kg load.

Lubricating Oil Compositions

[00151] The syndiotactic propylene-based ethylene-propylene copolymers disclosed herein are useful as additives in lubricating oil. The concentration of the copolymers in the lubricating oil composition may range from 0.01 to 20 wt. % (e.g., 0.5 to 10 wt. %, 0.1 to 5 wt. %, 3 to 15 wt%, 4-12 wt%, 5-9 wt% etc.), based on the total weight of the lubricating oil composition.

[00152] The oil of a lubricant, (sometimes referred to as “base stock” or “base oil”) is the primary liquid constituent of a lubricant, into which additives and possibly other oils are blended, for example to produce a final lubricant (or lubricant composition). A base oil, which is useful for making concentrates as well as for making lubricating oil compositions therefrom, may be selected from natural (vegetable, animal or mineral) and synthetic lubricating oils and mixtures thereof.

[00153] Definitions for the base stocks and base oils in this disclosure are the same as those found in American Petroleum Institute (API) Publication 1509 Annex E (“API Base Oil Interchangeability Guidelines for Passenger Car Motor Oils and Diesel Engine Oils,” December 2016). Group I base stocks contain less than 90% saturates and/or greater than 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in API Publication 1509 Annex E. Group II base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 80 and less than 120 using the test methods specified in API Publication 1509 Annex E. Group III base stocks contain greater than or equal to 90% saturates and less than or equal to 0.03% sulfur and have a viscosity index greater than or equal to 120 using the test methods specified in Table E-1. Group IV base stocks are polyalphaolefins (PAO). Group V base stocks include all other base stocks not included in Group I, II, III, or IV.

[00154] Natural oils include animal oils, vegetable oils (e.g., castor oil and lard oil), and mineral oils. Animal and vegetable oils possessing favorable thermal oxidative stability can be used. Of the natural oils, mineral oils are preferred. Mineral oils vary widely as to their crude source, for example, as to whether they are paraffinic, naphthenic, or mixed paraffinic-naphthenic. Oils derived from coal or shale are also useful. Natural oils vary also as to the method used for their production and purification, for example, their distillation range and whether they are straight run or cracked, hydrorefined, or solvent extracted.

[00155] Synthetic oils include hydrocarbon oil. Hydrocarbon oils include oils such as polymerized and interpolymers of olefins (e.g., polybutylenes, polypropylenes, propylene isobutylene copolymers, ethylene-olefin copolymers, and ethylene-alphaolefin copolymers). Polyalphaolefin (PAO) oil base stocks are commonly used synthetic hydrocarbon oil. By way of example, PAOs derived from C₈ to C₁₄ olefins, e.g., C₈, C₁₀, C₁₂, C₁₄ olefins or mixtures thereof, may be utilized.

[00156] Other useful fluids for use as base oils include non-conventional or unconventional base stocks that have been processed, preferably catalytically, or synthesized to provide high performance characteristics.

[00157] Non-conventional or unconventional base stocks/base oils include one or more admixture(s) of base stock(s) derived from one or more Gas-to-Liquids (GTL) materials, as well as isomate/isodewaxate base stock(s) derived from natural wax or waxy feeds, mineral and or non-mineral oil waxy feed stocks such as slack waxes, natural waxes, and waxy stocks such as gas oils, waxy fuels hydrocracker bottoms, waxy raffinate, hydrocrackate, thermal crackates, or other mineral, mineral oil, or even non-petroleum oil derived waxy materials such as waxy materials received from coal liquefaction or shale oil, and mixtures of such base stocks.

[00158] Base oils for use in the lubricating oil compositions of present disclosure are any of the variety of oils corresponding to API Group I, Group II, Group III, Group IV, and Group V oils, and mixtures thereof, preferably API Group II, Group III, Group IV, and Group V oils, and mixtures thereof, more preferably the Group III to Group V base oils due to their exceptional volatility, stability, viscometric and cleanliness features.

[00159] Typically, the base oil will have a kinematic viscosity at 100°C (ASTM D445) in a range of 1.4 to 20 mm²/s (e.g., 3 to 12 mm²/s, 4 to 10 mm²/s, or 4.5 to 8 mm²/s).

[00160] The present lubricating oil compositions may also contain conventional lubricant additives for imparting auxiliary functions to give a finished lubricating oil composition in which these additives are dispersed or dissolved. For example, the lubricating oil compositions

can be blended with antioxidants, dispersants such as ashless dispersants, anti-wear agents, detergents such as metal detergents, rust inhibitors, dehazing agents, demulsifying agents or demulsifiers, friction modifiers, metal deactivating agents, pour point depressants, viscosity modifiers, antifoaming agents or defoamers, co-solvents, package compatibilizers, corrosion-inhibitors, dyes, extreme pressure agents, and the like and mixtures thereof. A variety of the additives are known and commercially available. These additives, or their analogous compounds, can be employed for the preparation of the lubricating oil compositions of the disclosure by the usual blending procedures.

[00161] Each of the foregoing additives, when used, is used at a functionally effective amount to impart the desired properties to the lubricant. Thus, for example, if an additive is an ashless dispersant, a functionally effective amount of this ashless dispersant would be an amount sufficient to impart the desired dispersancy characteristics to the lubricant. Generally, the concentration of each of these additives, when used, may range, unless otherwise specified, from about 0.001 to about 20 wt. %, such as about 0.01 to about 10 wt. %, about 0.1 to about 5 wt. %, and about 1 to about 4 wt. %.

[00162] It may be desirable to store and transport the syndiotactic propylene-based ethylenebased ethylene-propylene copolymers of the present disclosure as concentrates. In concentrates, the copolymer is typically mixed with a diluent oil to facilitate further blending with other lubricant additives in preparation of a fully formulated lubricant. The diluent oil may comprise a Group I, Group II, Group III, Group IV or Group V oil or blends of the aforementioned oils. The diluent oil may also comprise a blend of a Group I oil and one or more Group II, Group III, Group IV or Group V oil. In some embodiments, the concentrate may include 0.5 wt. % to 50 wt. % of the syndiotactic propylene-based ethylene-propylene copolymer.

[00163] The lubricating oil comprising the copolymer composition can have a kinematic viscosity at 100°C, as measured by ASTM D445, of at least 2 mm²/s (e.g., at least 3 mm²/s, at least 4 mm²/s, at least 6 mm²/s, at least 8 mm²/s, at least 10 mm²/s, at least 12 mm²/s, or at least 15 mm²/s). Likewise, the lubricating oil comprising the copolymer composition can have a kinematic viscosity at 100°C, as measured by ASTM D445, of 200 mm²/s or less (e.g., 150 mm²/s or less, 100 mm²/s or less, 50 mm²/s or less, 40 mm²/s or less, 30 mm²/s or less, or even 20 mm²/s or less).

[00164] The following further embodiments are contemplated as within the scope of the present disclosure.

[00165] Embodiment A: A lubricant oil composition comprising: a major amount of a lubricant base oil; a minor amount of a viscosity index improver comprising a syndiotactic propylene-based ethylene-propylene copolymer comprising: a) 2 to 20 % by weight of ethylene and b). 80 to 98 % by weight of propylene; c) 50 to 99% rr triads; and d) Mw (DRI) of 10 to 250 kg/mol;

[00166] Embodiment B: The lubricant oil composition according to Embodiment A, wherein the copolymer has 4 to 18 wt. % by weight of ethylene.

[00167] Embodiment C: The lubricant oil composition according to Embodiment A, wherein the copolymer has 5 to 15 wt. % by weight of ethylene.

[00168] Embodiment D: The lubricant oil composition according to Embodiment A, wherein the copolymer has 6 to 12 wt. % by weight of ethylene.

[00169] Embodiment E: The lubricant oil composition according to Embodiment A, wherein the copolymer has 7 to 9 wt. % by weight of ethylene.

[00170] Embodiment F: The lubricant oil composition according to any one of Embodiments A to E, wherein the copolymer has 60 to 90% rr triads.

[00171] Embodiment G: The lubricant oil composition according to any one of Embodiments A to F, wherein the copolymer has 70 to 90% rr triads.

[00172] Embodiment H: The lubricant oil composition according to any one of Embodiments A to G, wherein the copolymer has 80 to 90% rr triads.

[00173] Embodiment I: The lubricant oil composition according to any one of Embodiments A to H wherein the syndiotactic propylene-based ethylene-propylene copolymer displays no substantial melting peak, wherein the heat of fusion of the peak is 5 J/g or less as determined by differential scanning calorimetry at a scan rate of 10 °C/min (ASTM D3418-03).

[00174] Embodiment J: The lubricant oil composition according to any one of Embodiments A to I, wherein the syndiotactic propylene-based ethylene-propylene copolymer is present in 0.01 wt. % to 20 wt. % in the lubricant oil composition.

[00175] Embodiment K: The lubricant oil composition according to any one of Embodiments A to J, wherein the lubricant base oil has a kinematic viscosity at 100°C of 1.4 to 20 mm²/s.

[00176] Embodiment L: The lubricant oil composition according to any one of Embodiments A to K, wherein the lubricant oil composition has a kinematic viscosity at 100°C of 3.0 to 30.0 mm²/s.

[00177] Embodiment M: The lubricant oil composition according to any one of

Embodiments A to L, wherein the lubricant base oil is a high-purity mineral base oil, a gas to liquid (GTL) base oil, an ester base oil or a synthetic lubricant base oil, as they have been grouped as Group I, Group II, Group III, Group IV or Group V oil or blend thereof.

[00178] Embodiment N: The lubricant composition according to any one of Embodiments A to M, further comprising at least one dispersant, a detergent, an antioxidant, a pour point depressant, a friction modifier, a wear modifier, an extreme pressure additive, a defoamer, a demulsifier, or a corrosion inhibitor.

[00179] Embodiment O: A method of manufacturing a lubricant oil composition comprising mixing a lubricant base oil and a viscosity index improver, wherein the viscosity index improver comprises: a syndiotactic propylene-based ethylene-propylene copolymer comprising: a) 2 to 20 % by weight of ethylene; b) 80 to 98 % by weight of propylene; c) 50 to 99% rr triads; d) Mw (DRI) of 10 to 250 kg/mol;

[00180] Embodiment P: The method of Embodiment O, wherein the copolymer has 5 to 15 wt. % by weight of ethylene.

[00181] Embodiment Q: The method of any one of Embodiments O or P wherein the copolymer has 60 to 90 wt. of rr triads.

[00182] Embodiment R: The method of any one of Embodiments O to Q wherein the syndiotactic propylene-based ethylene-propylene copolymer displays no substantial melting peak, wherein the heat of fusion of the peak is 5 J/g or less as determined by differential scanning calorimetry at a scan rate of 10 °C/min (ASTM D3418-03).

[00183] Embodiment S: The method of any one of Embodiments O to R, wherein the lubricant base oil further comprises at least one of: a dispersant, a detergent, an antioxidant, a pour point depressant, a friction modifier, a wear modifier, an extreme pressure additive, a defoamer, a demulsifier, or a corrosion inhibitor.

[00184] Embodiment T: The method of any one of Embodiments O to S wherein the lubricant base oil has a kinematic viscosity at 100°C of 1.4 to 20 mm²/s and is a high-purity mineral base oil, a gas to liquid (GTL) base oil, an ester base oil or a synthetic lubricant base oil, as they have been grouped as Group I, Group II, Group III, Group IV or Group V oil or blend thereof.

[00185] Embodiment U: A method of lubricating an engine, comprising: supplying to the engine a lubricating oil composition comprising: a major amount of a base oil of lubricating viscosity; and a syndiotactic propylene-based ethylene-propylene copolymer comprising: a) 2 to 20 % by weight of ethylene; b) 80 to 98 % by weight of propylene; c) 50 to 99% rr triads;

and d) Mw (DRI) of 10 to 250 kg/mol;

[00186] Embodiment V: The method of Embodiment U, wherein the copolymer has 5 to 15 wt. % by weight of ethylene.

[00187] Embodiment W: The method of any one of Embodiments V or U, wherein the copolymer has 60 to 90% rr triads.

[00188] Embodiment X: The method of any one of Embodiments U to W, wherein the syndiotactic propylene-based ethylene-propylene copolymer displays no substantial melting peak, wherein the heat of fusion of the peak is 5 J/g or less as determined by differential scanning calorimetry at a scan rate of 10 °C/min (ASTM D3418-03).

[00189] Embodiment Y: The method of any one of Embodiments U to X, wherein the lubricating oil composition further comprises at least one of: a dispersant, a detergent, an antioxidant, a pour point depressant, a friction modifier, a wear modifier, an extreme pressure additive, a defoamer, a demulsifier, or a corrosion inhibitor.

[00190] In one embodiment, the lubricating oil composition of this disclosure can be identified by viscosity standards of the Society of Automotive Engineers (SAE) for automotive lubricants. As one example, the lubricating composition is identified by the SAE J300 standard, a viscosity classification for engine oils. The J300-201501 viscosity grades are the latest guideline from SAE.

[00191] When lubricating oil compositions contain one or more of the components discussed above, the additive(s) are blended into the composition in an amount sufficient for it to perform its intended function. Typical amounts of such additives useful in the present invention are shown in Table A below.

TABLE A

Typical Amounts of Various Lubricating Oil Components	
Component	Approximate wt%
Detergents	0.01 – 8
Dispersants	0.1 – 20
Antiwear agents	0.01 – 6
Friction Modifiers	0.01 – 15
Antioxidants	0.01 – 5
Pour Point Depressants	0.01 – 5
Anti-foam Agents	0.001 – 1
Corrosion Inhibitors	0 – 5
Other Viscosity Improvers (solid polymer basis)	0.25 – 10

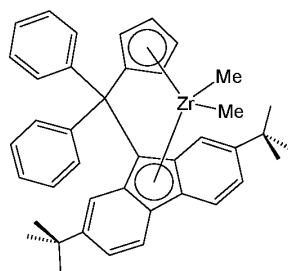
EXAMPLES

[00192] The syndiotactic ethylene-propylene copolymers were made in continuous solution polymerization processes. The polymerization for examples listed in Table 1 and Table 2 were carried out in a continuous stirred tank reactor system. A 1-liter Autoclave reactor was equipped with a stirrer, a pressure controller, and a water cooling/steam heating element with a temperature controller. The reactor was operated in liquid fill condition at a reactor pressure in excess of the bubbling point pressure of the reactant mixture, keeping the reactants in liquid phase. Isohexane and propylene were pumped into the reactors by Pulsafeed pumps. Ethylene and H₂ flowed as a gas under their own pressure through a Brooks flow controller. Ethylene, propylene and H₂ feeds were combined into one stream and then mixed with a pre-chilled isohexane stream that had been cooled to at least 0°C. The mixture was then fed to the reactor through a single line. Scavenger solution (an isohexane solution of tri-*n*-octylaluminum (TNOA) (25 wt % in hexane, Sigma Aldrich) was also added to the combined solvent and monomer stream just before it entered the reactor to further reduce any catalyst poisons. Catalyst solution was fed to the reactor using an ISCO syringe pump through a separated line. Isohexane (used as solvent), and monomers (e.g., ethylene and propylene) were purified over beds of alumina and molecular sieves. Toluene for preparing catalyst solutions was purified by the same technique.

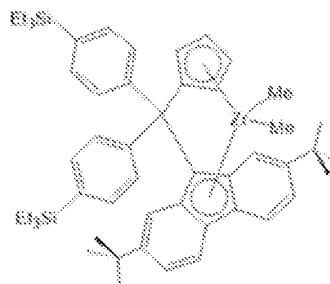
[00193] The polymer produced in the reactor exited through a back pressure control valve that reduced the pressure to atmospheric. This caused the unconverted monomers in the solution to flash into a vapor phase which was vented from the top of a vapor liquid separator. The liquid phase, comprising mainly polymer and solvent, was collected for polymer recovery. The collected samples were first air-dried in a hood to evaporate most of the solvent, and then dried in a vacuum oven at a temperature of about 90 °C for about 12 hours. The vacuum oven dried samples were weighed to obtain yields.

[00194] For Example #1 to # 5 listed in Table 1, diphenylmethylene(2,7-di-*tert*-butylfluorenyl)(cyclopentadienyl) zirconium dimethyl (Catalyst #1) was used as the catalyst and *N,N*-dimethylanilinium tetrakis(pentafluorophenyl) borate was used as activator. Di(para-triethylsilylphenyl)methylene(2,7-di-*tert*-butylfluorenyl)(cyclopentadienyl) zirconium dimethyl (catalyst #2) was used as the catalyst in the Example # 13 to #22 (listed in Table 2). *N,N*-dimethylanilinium tetrakis(heptafluoro-2-naphthyl)borate was used as the activator for Example # 17 to #19 and #22. *N,N*-dimethylanilinium tetrakis(pentafluorophenyl) borate was

used as the activator for Example #13 to #16, and #20 to #21. All catalysts were preactivated with the activator at a molar ratio of 1:1 in toluene. The reactor pressure for all examples was 350 psig. The detailed process conditions and some characterization data are summarized in Tables 1 and 2. Catalyst # 1 and Catalyst # 2 have the following structures:



Catalyst #1



Catalyst # 2

Table 1

Example #	1	2	3	4	5
Polymerization temperature (°C)	77	74	70	70	70
Ethylene feed rate (g/min)	0.79	1.02	0.79	0.68	0.79
Propylene feed rate (g/min)	27	27	27	27	27
H ₂ feed rate (Scc/min)	0	0	0	2.41	2.41
Isohexane feed rate (g/min)	56.7	56.7	56.7	59.4	60
Catalyst #1 feed rate (mol/min)	1.379E-07	1.206E-07	1.206E-07	1.206E-07	4.308E-08
TNOA feed rate (mol/min)	7.385E-06	7.385E-06	7.385E-06	7.407E-06	8.230E-06
Polymer yield (g/min)	11.66	12.55	11.18	14.56	12.60
Conversion (%)	42.0%	44.8%	40.2%	52.6%	45.4%
Catalyst efficiency (kg polymer/kg catalyst)	163,975	201,677	179,794	234,076	567,246
MFR (g/10 min)	8.6	6.9	5.8	10.4	7.9
MFR HL (g/10 min)	191.7	176.7	134.9		201.4
Mn_DRI (g/mol)	73,161	81,772	97,189	64,482	76,688
Mw_DRI (g/mol)	164,273	156,347	184,545	153,917	148,219
Mz_DRI (g/mol)	278,705	248,168	294,914	220,852	230,870
MWD (-)	2.25	1.91	1.90	2.11	1.93
Mn_LS (g/mol)	72,188	75,117	90,218	55,095	68,297
Mw_LS (g/mol)	131,868	131,728	155,095	109,901	124,910
Mz_LS (g/mol)	196,305	197,958	232,005	166,145	195,933
Tg (°C)	-17.8	-18.8	-16.3	-	-
Ethylene content (wt %)	7.9%	9.6%	7.9%	4.8%	5.7%
Triad sequence distributions (¹³ C NMR)					
EEE	0.003	0.003	0.002	0.002	0.004
EEP	0.011	0.015	0.009	0.004	0.011
PEP	0.078	0.091	0.077	0.057	0.073
EPE	0.010	0.013	0.009	0.005	0.009
EPP	0.144	0.161	0.145	0.107	0.136
PPP	0.754	0.718	0.757	0.825	0.766
Tacticity triads (¹³ C NMR)					
mm(PP+EP)	3.80%	3.63%	3.31%	3.54%	4.11%
rr(EP+PP)	80.13%	79.80%	81.39%	80.60%	78.53%
Regio defect (mol%)	0.51	0.59	0.55	0.46	0.70
TE	2.36	2.23	2.45	2.75	2.1
SSI	35.7	39.9	41.7	48.9	32.2
TE/SSI	0.066	0.055	0.059	0.056	0.065

Table 2

Example #	13	14	15	16	17
Polymerization temperature (°C)	70	80	60	80	60
Ethylene feed rate (g/min)	1.13	0.23	1.36	2.38	1.36
Propylene feed rate (g/min)	27	27	27	27	27
Isohexane feed rate (g/min)	56.7	56.7	56.7	56.7	56.7
Catalyst #2 feed rate (mol/min)	1.712E-07	2.569E-07	1.168E-07	1.168E-07	1.168E-07
TNOA feed rate(mol/min)	3.703E-06	3.703E-06	3.703E-06	3.703E-06	3.703E-06
Polymer yield (g/min)	14.04	10.55	13.03	16.03	9.39
Conversion (%)	49.9%	38.8%	45.9%	54.6%	33.1%
Catalyst efficiency (kg polymer/kg catalyst)	95,715	47,958	130,199	160,262	93,838
MFR (g/10 min)	60.5	25.7	7.2	29.5	8.8
Mn_DRI (g/mol)	37,039	59,161	96,818	-	75,219
Mw_DRI (g/mol)	83,128	117,538	183,061	-	142,331
Mz_DRI (g/mol)	152,136	192,583	349,374	-	224,882
MWD (-)	2.24	1.99	1.89	-	1.89
Mn_LS (g/mol)	27,377	53,799	80,656	-	63,812
Mw_LS (g/mol)	62,873	90,007	123,401	-	115,595
Mz_LS (g/mol)	108,030	135,186	167,408	-	170,718
Tg (°C)	-	-7.0	-16.9	-22.1	-23.1
Ethylene content (wt %)	7.3%	2.1%	9.5%	12.6%	12.6%
Triad sequence distributions (¹³ C NMR)					
EEE	0.003	0.001	0.004	0.004	0.006
EEP	0.013	0.002	0.014	0.031	0.028
PEP	0.088	0.021	0.105	0.142	0.134
EPE	0.018	0.000	0.026	0.047	0.042
EPP	0.156	0.054	0.160	0.224	0.213
PPP	0.722	0.922	0.692	0.552	0.577
Tacticity triads (¹³ C NMR)					
mm(PP+EP)	2.86%	3.85%	3.28%	2.71%	2.56%
rr (EP+PP)	81.10%	75.68%	80.08%	78.17%	85.20%
Regio defect (mol%)	0.90	0.79	1.04	0.90	1.07
TE	2.04	1.76	2.32	n/a	2.21
SSI	31.95	22.37	38.22	n/a	36.95
TE/SSI	0.064	0.079	0.061	n/a	0.060

Table 2 (continued)

Example #	18	19	20	21	22
Polymerization temperature (°C)	80	60	90	100	90
Ethylene feed rate (g/min)	1.36	1.36	0.23	0.23	1.36
Propylene feed rate (g/min)	27	27	27	27	27
Isohexane feed rate (g/min)	56.7	56.7	56.7	56.7	56.7
Catalyst #2 feed rate (mol/min)	1.635E-07	1.297E-07	2.569E-07	2.569E-07	1.868E-07
TNOA feed rate (mol/min)	3.703E-06	3.703E-06	3.703E-06	3.703E-06	3.703E-06
Polymer yield (g/min)	5.31	10.67	10.17	9.30	5.46
Conversion (%)	18.7%	37.6%	37.4%	34.2%	19.2%
Catalyst efficiency (kg polymer/kg catalyst)	37,900	96,050	46,220	42,277	34,095
MFR (g/10 min)	29.6	6.8	103.1	769.3	54.9
Mn_DRI (g/mol)	53,990	78,764	44,967	28,213	45,278
Mw_DRI (g/mol)	99,916	153,718	85,040	58,032	83,535
Mz_DRI (g/mol)	155,001	245,016	132,577	94,585	130,098
MWD (-)	1.85	1.95	1.89	2.06	1.84
Mn_LS (g/mol)	54,333	74,135	37,614	25,040	42,601
Mw_LS (g/mol)	84,580	124,465	67,193	46,077	71,461
Mz_LS (g/mol)	122,999	181,435	102,815	69,246	104,403
Tg (°C)	-31.5	-21.4	-13.1	-11.4	-30.2
Ethylene content (wt %)	19.3%	11.6%	4.3%	6.8%	19.0%
Triad sequence distributions (¹³ C NMR)					
EEE	0.014	0.004	0.001	0.002	0.010
EEP	0.066	0.023	0.003	0.003	0.064
PEP	0.179	0.124	0.025	0.027	0.173
EPE	0.086	0.036	0.001	0.002	0.080
EPP	0.248	0.204	0.061	0.067	0.254
PPP	0.406	0.609	0.910	0.899	0.419
Tacticity triads (¹³ C NMR)					
mm(PP+EP)	3.17%	2.63%	4.71%	6.00%	3.30%
rr (EP+PP)	80.83%	86.30%	69.72%	63.19%	77.89%
Regio defect (mol%)	1.37	0.82	1.06	1.10	0.93
TE	1.7	2.31	-	-	1.5
SSI	22.47	39.23	-	-	17.43
TE/SSI	0.076	0.059	-	-	0.086

[00195] The polymerization for Examples #6 to #12 listed in Table 3 were carried out using a solution process in a 28-liter continuous stirred-tank reactor (autoclave reactor). The autoclave reactor was equipped with an agitator, a pressure controller, and insulation to prevent heat loss. The reactor temperature was controlled by controlling the catalyst feed rates and heat removal was provided by feed chilling. All solvents and monomers were purified over beds of alumina and molecular sieves. The reactor was operated liquid full and at a pressure of 1600 psig. Isohexane was used as a solvent. It was fed into the reactor using a turbine pump and its flow rate was controlled by a mass flow controller downstream. The compressed, liquefied propylene feed was controlled by a mass flow controller. Hydrogen (if used) was fed to the reactor through a thermal mass flow controller. Ethylene feed was also controlled by a mass flow controller. The ethylene, propylene and hydrogen (if used) were mixed into the isohexane steam at separate addition points via a manifold. A 3 wt% mixture of tri-n-octylaluminum in isohexane was also added to the manifold through a separate line (used as a scavenger) and the combined mixture of monomers, scavenger, and solvent was fed into the reactor through a single line.

[00196] The catalyst used for polymerization of Examples #6 to #12 was di(para-triethylsilylphenyl)methylene(2,7-di-tert-butylfluorenyl)(cyclopentadienyl) zirconium dimethyl (catalyst #2). This catalyst was preactivated with N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate at a molar ratio of about 1:1 in 4 liters of toluene. After the solids dissolved, with stirring, the solution was charged into an ISCO pump and metered into the reactor. The reactor product stream was treated with trace amounts of methanol to halt the polymerization. The mixture was then freed from solvent via a low-pressure flash separation, treated with Irganox™ 1076 then subjected to a devolatilizing extruder process. The dried polymer was then pelletized.

Table 3

Example #	6	7	8	9
Polymerization temperature (°C)	70	70	70	70
Ethylene feed rate (g/min)	6.67	6.67	6.67	6.67
Propylene feed rate (g/min)	291	291	291	278
Isohexane feed rate (g/min)	1598.3	1598.5	1598.2	1598.5
Catalyst #2 feed rate (mol/min)	3.79E-07	4.55E-07	6.30E-07	1.00E-06
Yield (g/min)	89.0	90.5	93.3	96.0
Catalyst efficiency (kg poly/kg	455,271	385,617	287,118	186,119
Ethylene conversion (%)	75.6	87.1	81.3	85.3

Example #	6	7	8	9
Propylene conversion (%)	28.7	28.9	30.1	29.4
MFR (g/10min)	227.5	141.2	61.8	30.8
Mn DRI (g/mol)	31,307	36,667	39,568	53,757
Mw DRI (g/mol)	59,616	69,497	85,693	101,809
Mz DRI (g/mol)	92,345	110,011	140,566	161,511
MWD (-)	1.90	1.90	2.17	1.89
Mn LS (g/mol)	28,656	32,451	31,704	48,581
Mw LS (g/mol)	47,277	53,203	63,265	80,131
Mz LS (g/mol)	69,853	74,744	91,950	117,057
g^*_{vis} (-)	1.303	1.305	1.323	1.334
Ethylene content (wt %)	7.7	7.5	7.3	6.8
Tg (°C)	-16.6	-15.6	-15.6	-14.5
Diad and triad sequence distributions (¹³ C NMR)				
[EEE]	0.004	0.003	0.007	0.010
[EEP]	0.012	0.012	0.013	0.012
[PEP]	0.095	0.091	0.091	0.086
[EPE]	0.020	0.018	0.019	0.013
[EPP]	0.170	0.163	0.169	0.157
[PPP]	0.700	0.713	0.701	0.723
[EE]	0.010	0.009	0.014	0.016
[PP]	0.785	0.795	0.786	0.802
[EP]	0.206	0.197	0.201	0.184
Tacticity diad and triads				
mm% (PP+EP)	2.7	2.7	2.2	3.3
rr% (PP+EP)	81.6	81.7	82.7	80.8
r% ^a (PP+EP)	89.5	89.5	90.3	88.8
TE	1.16	1.32	1.46	1.68
SSI	6.3	8.1	13.5	20.1
TE/SSI	0.185	0.163	0.108	0.084

Table 3 (continued)

Example #	10	11	12
Polymerization temperature (°C)	70	65	65.8
Ethylene feed rate (g/min)	7.69	9.61	9.61
Propylene feed rate (g/min)	285	345	375
Isohexane feed rate (g/min)	1612.8	1286.5	1282.7
Catalyst #2 feed rate (mol/min)	3.19E-06	4.55E-07	1.62E-06
Yield (g/min)	97.0	115.0	127
Catalyst efficiency (kg poly/kg catalyst)	58,952	490,011	151,988
Ethylene conversion (%)	89.1	85.8	81.3
Propylene conversion (%)	30.7	30.7	30.1
MFR (g/10min)	16.0	17.9	12.0
Mn DRI (g/mol)	64,640	60,770	57,420
Mw DRI (g/mol)	123,513	118,448	187,020
Mz DRI (g/mol)	200,228	187,020	206,410

MWD (-)	1.91	1.95	3.26
Mn _{LS} (g/mol)	58,069	55,504	57,695
Mw _{LS} (g/mol)	95,668	92,556	102,288
Mz _{LS} (g/mol)	137,732	136,162	152,628
g _{vis} (-)	1.316	1.344	1.303
Ethylene content by FTIR (wt %)	7.4	8.0	7.56
Tg (°C)	-15.6	-16.5	-15.4
Diad and triad sequence distributions (¹³ C NMR)			
[EEE]	0.007	0.007	0.004
[EEP]	0.010	0.012	0.010
[PEP]	0.091	0.096	0.094
[EPE]	0.016	0.020	0.019
[EPP]	0.169	0.173	0.173
[PPP]	0.706	0.692	0.700
Tacticity diad and triads			
[EE]	0.012	0.013	0.009
[PP]	0.791	0.779	0.787
[EP]	0.197	0.209	0.205
mm% (PP+EP)	2.5	2.6	2.7
rr% (PP+EP)	81.5	82.1	83.2
r% (PP+EP)	89.5	89.8	90.3
TE	1.87	1.78	2.03
SSI	26.6	23.5	29.7
TE/SSI	0.070	0.076	0.068

[00197] In particular, Examples 1 to 15, 17 to 19 and 22 were tested as viscosity modifier for lubricating oil for TE, SSI, and TE/SSI ratio values. A discussion of TE including measurement method can be found in US Patent 8,105,992, which is hereby incorporated by reference. Specifically, Thickening efficiency (TE) is a relative measure of the thickening ability of the polymer in oil, and is defined as: $TE = 2/c \times \ln((kv(\text{polymer}+\text{oil}))/kv_{oil})/\ln(2)$, 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. TE and SSI of polymer samples herein are determined by dissolution in Group I diluent oil to a concentration that yields a viscosity at 100°C (ASTM D445) of approximately 15 cSt.

[00198] For comparison, Comparative Example A has an ethylene content of 48 wt. %, TE of 1.93, SSI of 29.2, Mw of 54,954 g/mol, Mw/Mn of 1.85 and TE/SSI of 0.066. It can be seen

clearly that the inventive materials have demonstrated wide range of TE and SSI suitable for use as viscosity modifiers with improved TE/SSI ratio over the Comparative Example A.

[00199] Table 4 summarizes low temperature performance of 5W-30 lubricating oils formulated with the syndiotactic propylene-based ethylene-propylene copolymers listed in Examples 1-12 and Comparative Example A. Formulation F1-F12 and comparative formulation (F13) are made by combining same baseline formulation with 9.5% polymer concentrates made with the inventive syndiotactic propylene-based ethylene-propylene copolymers listed in Examples 1-12 and Comparative Example A) to form a 5W-30 lubricating oil. The 5W30 oils all contain the same 7.65% of performance additive package including dispersant and inhibitors, pour point depressant and a balance 65/35 ratio of 4 and 6 cSt Group III diluent oil. The results show formulations containing the inventive syndiotactic propylene-based ethylene-propylene copolymers have better performance in the pour point test compared with the formulation containing the comparative example. Specifically, previous discussion had pointed out that high pour point of the lubricating engine oil can cause temporary disruption in the oil flow which can lead to an increase in bearing wear. For modern engine oil grade such as 5W-30, a pour point higher than -35°C should be avoided. The overall balanced performance meeting SAE J300 requirements makes the inventive examples great viscosity modifier candidates for lubricating oil applications. The tests were carried out according to the following protocols: Pour Point (ASTM D-97), CCS (ASTM D-5293), and MRV (ASTM D-4684).

Table 4

Formulation #	F1	F2	F3	F4	F5	F6
Copolymer, Example #	1	2	3	4	5	6
Ethylene content, wt%	7.9	9.6	7.9	4.8	5.7	7.7
Kinematic Viscosity (100°C), mm ² /s	10.34	10.34	10.27	10.69	10.34	10.4
CCS Viscosity (-30°C), mPa.s	3799	3863	3727	3628	3803	4688
MRV (-35°C) viscosity, mPa.s	16400	17300	16600	20100	20200	19900
MRV (-35°C) yield stress, Pa	<35	<35	<35	<35	<35	<35
Pour Point, °C	-39	-39	-42	-42	-42	-39

Table 4 (continued)

Formulation #	F7	F8	F9	F10	F11	F12	F13
Copolymer, Example #	7	8	9	10	11	12	Comp Ex A
Ethylene content, wt%	7.5	7.3	6.8	7.4	8.0	7.6	48
Kinematic Viscosity	10.32	10.48	10.39	10.43	10.41	10.46	10.32

(100°C), mm ² /s							
CCS Viscosity (-30°C), mPa.s	4504	4362	4172	3060	4133	3546	4104
MRV (-35°C) viscosity, mPa.s	19500	20000	18500	18800	19700	16700	14650
MRV (-35°C) yield stress, Pa	<35	<35	<35	<35	<35	<35	<35
Pour Point, °C	-36	-39	-36	-36	-36	-39	-30

[00200] For the sake of brevity, only certain ranges are explicitly disclosed herein. However, ranges from any lower limit may be combined with any upper limit to recite a range not explicitly recited, as well as, ranges from any lower limit may be combined with any other lower limit to recite a range not explicitly recited, in the same way, ranges from any upper limit may be combined with any other upper limit to recite a range not explicitly recited. Additionally, within a range includes every point or individual value between its end points even though not explicitly recited. Thus, every point or individual value may serve as its own lower or upper limit combined with any other point or individual value or any other lower or upper limit, to recite a range not explicitly recited.

[00201] As used herein, the term “major amount” refers to 50% or greater and the term “minor amount” refers to less than 50%. Also when amounts and percentages are given it is understood that such refers to weight unless stated otherwise.

[00202] The phrases, unless otherwise specified, “consists essentially of” and “consisting essentially of” do not exclude the presence of other steps, elements, or materials, whether or not, specifically mentioned in this specification, so long as such steps, elements, or materials, do not affect the basic and novel characteristics of the present disclosure, additionally, they do not exclude impurities and variances normally associated with the elements and materials used.

[00203] 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.

[00204] The terms “a” and “the” as used herein are understood to encompass the plural as well as the singular.

[00205] Room temperature is about 23°C unless otherwise noted.

[00206] 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.

[00207] Various terms have been defined above. To the extent a term used in a claim is not defined above, it should be given the broadest definition persons in the pertinent art have given that term as reflected in at least one printed publication or issued patent. Furthermore, all patents, test procedures, and other documents cited in this application are fully incorporated by reference to the extent such disclosure is not inconsistent with this application and for all jurisdictions in which such incorporation is permitted.

[00208] The foregoing description of the disclosure illustrates and describes the present disclosure. Additionally, the disclosure shows and describes only the preferred embodiments but, as mentioned above, it is to be understood that the disclosure is capable of use in various other combinations, modifications, and environments and is capable of changes or modifications within the scope of the concept as expressed herein, commensurate with the above teachings and/or the skill or knowledge of the relevant art. While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

[00209] The embodiments described hereinabove are further intended to explain best modes known of practicing it and to enable others skilled in the art to utilize the disclosure in such, or other, embodiments and with the various modifications required by the particular applications or uses. Accordingly, the description is not intended to limit it to the form disclosed herein. Also, it is intended that the appended claims be construed to include alternative embodiments.

CLAIMS

What is claimed is:

1. A lubricant oil composition comprising:
a major amount of a lubricant base oil; and
a minor amount of a viscosity index improver comprising a syndiotactic propylene-based ethylene-propylene copolymer comprising:
 - a) 2 to 20 % by weight of ethylene
 - b) 80 to 98 % by weight of propylene;
 - c) 50 to 99% rr triads; and
 - d) Mw (LS) of 10 to 250 kg/mol.
2. The lubricant oil composition according to claim 1, wherein the copolymer has 4 to 18 wt. % by weight of ethylene.
3. The lubricant oil composition according to claim 1, wherein the copolymer has 5 to 15 wt% by weight of ethylene.
4. The lubricant oil composition according to claim 1, wherein the copolymer has 6 to 12 wt. % by weight of ethylene.
5. The lubricant oil composition according to claim 1, wherein the copolymer has 7 to 9 wt. % by weight of ethylene.
6. The lubricant oil composition according to claim 1, wherein the copolymer has 60 to 90% rr triads.
7. The lubricant oil composition according to claim 1, wherein the copolymer has 70 to 90% rr triads.
8. The lubricant oil composition according to claim 1, wherein the copolymer has 80 to 90% rr triads.
9. The lubricant oil composition according to claim 1, wherein the syndiotactic propylene-based ethylene-propylene copolymer displays no substantial melting peak, wherein the heat of fusion of the peak is 5 J/g or less as determined by differential scanning calorimetry at a scan rate of 10 °C/min (ASTM D3418-03).
10. The lubricant oil composition according to claim 1, wherein the syndiotactic propylene-based ethylene-propylene copolymer is present in 0.01 wt. % to 20 wt. % in the lubricant oil composition.

11. The lubricant oil composition according to claim 1, wherein the lubricant base oil has a kinematic viscosity at 100°C of 1.4 to 20.0 mm²/s.
12. The lubricant oil composition according to claim 1, wherein the lubricant oil composition has a kinematic viscosity at 100°C of 3.0 to 30.0 mm²/s.
13. The lubricant oil composition according to claim 1, wherein the lubricant base oil is a high-purity mineral base oil, a gas to liquid (GTL) base oil, an ester base oil or a synthetic lubricant base oil, as they have been grouped as Group I, Group II, Group III, Group IV or Group V oil or blend thereof.
14. The lubricant composition according to claim 1, further comprising at least one dispersant, a detergent, an antioxidant, a pour point depressant, a friction modifier, a wear modifier, an extreme pressure additive, a defoamer, a demulsifier, or a corrosion inhibitor.
15. A method of manufacturing a lubricant oil composition comprising:
 - mixing a lubricant base oil and a viscosity index improver, wherein the viscosity index improver comprises:
 - a syndiotactic propylene-based ethylene-propylene copolymer comprising:
 - a) 2 to 20 % by weight of ethylene
 - b) 80 to 98 % by weight of propylene;
 - c) 50 to 99% rr triads; and
 - d) Mw (LS) of 10 to 250 kg/mol.
16. The method of claim 15, wherein the copolymer has 5 to 15 wt. % by weight of ethylene.
17. The method of claim 15, wherein the copolymer has 60 to 90 % rr triads.
18. The method of claim 15, wherein the syndiotactic propylene-based ethylene-propylene copolymer displays no substantial melting peak, wherein the heat of fusion of the peak is 5 J/g or less as determined by differential scanning calorimetry at a scan rate of 10 °C/min (ASTM D3418-03).
19. The method of claim 15, wherein the lubricant oil composition further comprises at least one of:
 - a dispersant, a detergent, an antioxidant, a pour point depressant, a friction modifier, a wear modifier, an extreme pressure additive, a defoamer, a demulsifier, or a corrosion inhibitor.
20. The method of claim 15, wherein the lubricant base oil has a kinematic viscosity at 100°C of 1.4 to 20 mm²/s and is a high-purity mineral base oil, a gas to liquid (GTL) base oil,

an ester base oil or a synthetic lubricant base oil, as they have been grouped as Group I, Group II, Group III, Group IV or Group V oil or blend thereof.

21. A method of lubricating an engine, comprising:

supplying to the engine a lubricating oil composition comprising:

a major amount of a base oil of lubricating viscosity; and

a syndiotactic propylene-based ethylene-propylene copolymer comprising:

a) 2 to 20 % by weight of ethylene

b) 80 to 98 % by weight of propylene;

c) 50 to 99% rr triads; and

d) Mw (LS) of 10 to 250 kg/mol.

22. The method of claim 21, wherein the copolymer has 5 to 15 wt. % by weight of ethylene.

23. The method of claim 21, wherein the copolymer has 60 to 90 % rr triads.

24. The method of claim 21, wherein the syndiotactic propylene-based ethylene-propylene copolymer displays no substantial melting peak, wherein the heat of fusion of the peak is 5 J/g or less as determined by differential scanning calorimetry at a scan rate of 10 °C/min (ASTM D3418-03).

25. The method of claim 21, wherein the lubricating oil composition further comprises at least one of:

a dispersant, a detergent, an antioxidant, a pour point depressant, a friction modifier, a wear modifier, an extreme pressure additive, a defoamer, a demulsifier, or a corrosion inhibitor.