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(54) Title: SOLUTION PROCESS TO MAKE ETHYLENE COPOLYMERS

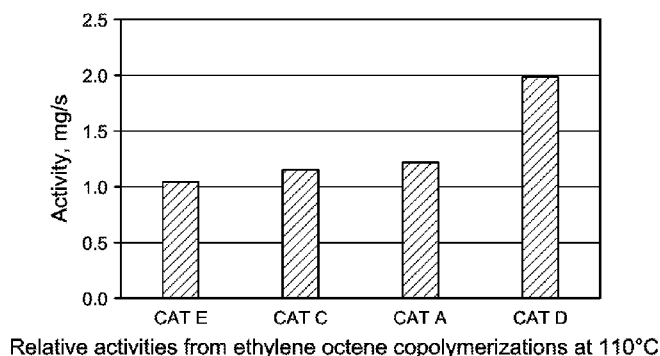
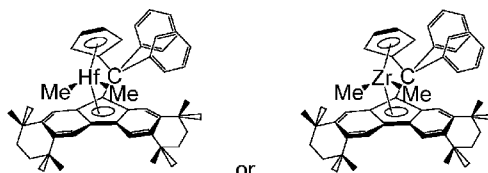


FIG. 1

(57) Abstract: This invention relates to a process to polymerize olefins comprising contacting, in solution phase at a temperature of 60°C to 200°C, ethylene, and at least one olefin comonomer with a catalyst system comprising a non-coordinating anion activator and a metallocene catalyst compound, preferably represented by the formula: and 2) obtaining ethylene polymer having an Mw greater than 100,000 g/mol, preferably greater than 400,000 g/mol.



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- *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

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Title: Solution Process to Make Ethylene Copolymers5 **PRIORITY CLAIM**

This application claims priority to and the benefit of USSN 62/477,094, filed March 27, 2017 and EP 17173988.1, filed June 1, 2017 and are incorporated by reference in their entirety.

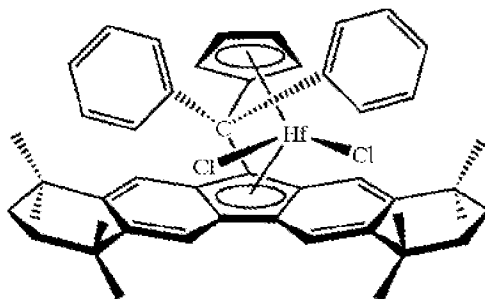
FIELD OF THE INVENTION

10 This invention relates to process to make ethylene copolymers using cyclopentadienyl-fluorenyl transition metal compounds.

BACKGROUND OF THE INVENTION

Olefin polymers are of great use in industry. Hence there is interest in finding new processes that increase the commercial usefulness of catalysts to make olefin polymers and
15 enhance the production of polymers having improved properties.

US 6,693,153, at column 47, discloses the production of syndiotactic polypropylene at zero and 20°C using methylalumoxane and the compound of the formula:



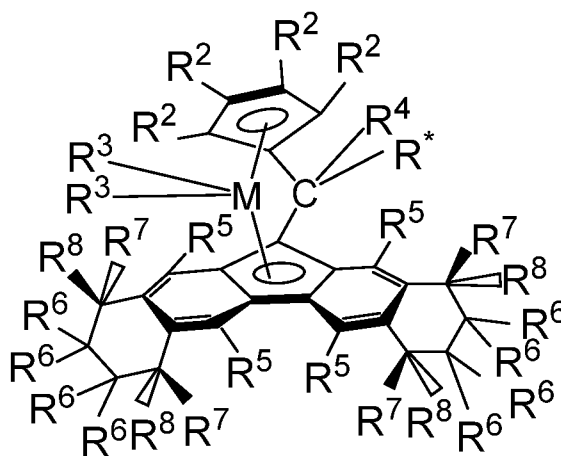
Other references of interest include: EP 1 052 263 A2; US 2005/131171; US 2003/162651;
20 US 2002/086958; US 2005/148460; US 2004/192866; US 2007/255021; US 2005/288178;
US 5,756,607; EP 1 086 146 A1; US 8,129,473; US 2002/103313; US 6,914,027; US
6,559,089; US 6,897,273; EP 1 727 841 B1; US 7,393,907; US 6,383,969; US 2003/162651
A1; J. Am. Chem. Soc. 2004, 126, 16716-16717; US 2006/251835 and US 9,150,676.

There is still a need in the art for new and improved processes for the polymerization
25 of olefins, particularly ethylene, in order to achieve specific polymer properties, such as high
molecular weights in combination with excellent comonomer incorporation.

SUMMARY OF THE INVENTION

This invention relates to a method to polymerize olefins comprising contacting, in

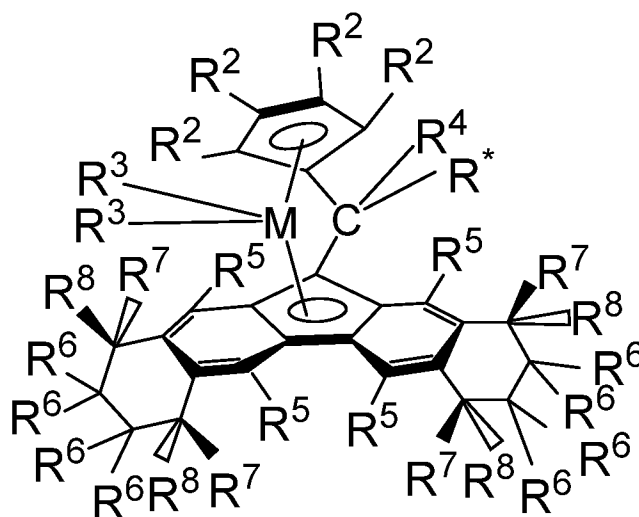
solution phase at a temperature of 60°C to 200°C, ethylene and at least one olefin comonomer with a catalyst system comprising a non-coordinating anion activator and a metallocene catalyst compound represented by the formula:



- 5 wherein M is Hf or Zr;
 each R³ is independently an anionic group;
 each R² is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl;
 R⁴ is a hydrocarbyl radical having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof;
- 10 R* is phenyl or a substituted phenyl;
 each R⁵, R⁶, R⁷, and R⁸ is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl;
 where at least one of each adjacent pair of R⁷ and R⁸ is not H; and
- 2) obtaining ethylene polymer having an Mw greater than 100,000 g/mol, and optionally
- 15 a) the % comonomer incorporated is X% or more, where $X = (Z - 858,441) / (-26,760)$, where Z is the Mn in g/mol of the polymer; and/or
- b) the polymer comprises ethylene, diene, and optional C₃ to C₂₀ olefin comonomer.

This invention relates to a method to polymerize olefins comprising contacting, in solution phase at a temperature of 60°C to 200°C, ethylene, at least one diene comonomer, and optionally a C₃ to C₂₀ alpha olefin with a catalyst system comprising a non-coordinating anion activator and a metallocene catalyst compound represented by the formula:

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wherein M is Hf or Zr;

each R³ is independently an anionic group;

each R² is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl;

5 R⁴ is a hydrocarbyl radical having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof;

R^{*} is phenyl or a substituted phenyl;

each R⁵, R⁶, R⁷, and R⁸ is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl;

10 where at least one of each adjacent pair of R⁷ and R⁸ is not H; and

2) obtaining ethylene polymer having an Mw of 400,000 g/mol or more.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a graph showing relative activities from ethylene octene copolymerizations at 110°C.

15 Figure 2 is a graph showing a comparison of Mn (g/mol) to comonomer content (wt%) at 65°C.

Figure 3 is a graph showing a comparison of Mn (g/mol) to comonomer content (wt%) at 85°C.

20 Figure 4 is a graph showing a comparison of Mn (g/mol) to comonomer content (wt%) at 115°C.

Figure 5 is graph showing relative activities from ethylene octene copolymers at 65°C, 85°C, and 115°C.

Figure 6 is a graph showing melting point of ethylene norbornene copolymers.

Figure 7 is a graph showing activities of ethylene norbornene copolymerizations.

Figure 8 is a graph showing melting point of ethylene norbornene copolymers.

Figure 9 is a graph showing activities of ethylene norbornene copolymerizations.

DETAILED DESCRIPTION OF THE INVENTION

5 For the purposes of this invention and the claims thereto, the new numbering scheme for the Periodic Table Groups is used as described in CHEMICAL AND ENGINEERING NEWS, 63(5), pg. 27 (1985). Therefore, a “group 4 metal” is an element from group 4 of the Periodic Table, e.g. Hf, Ti, or Zr.

10 Unless otherwise indicated, “catalyst productivity” unless otherwise indicated, is a measure of how many grams of polymer (P) are produced using a polymerization catalyst comprising W g of catalyst (cat), over a period of time of T hours; and may be expressed by the following formula: $P/(T \times W)$ and expressed in units of $\text{gPgcat}^{-1}\text{hr}^{-1}$. Conversion is the amount of monomer that is converted to polymer product, and is reported as mol% and is calculated based on the polymer yield and the amount of monomer fed into the reactor.

15 Unless otherwise indicated, catalyst activity is a measure of how active the catalyst is and is reported as the mass of product polymer (P) produced per mole of catalyst (cat) used (kgP/molcat).

20 An “olefin,” alternatively referred to as “alkene,” is a linear, branched, or cyclic compound of carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an “ethylene” content of 35 wt% to 55 wt%, it is understood that the mer unit in the copolymer is derived from ethylene in the polymerization reaction and said derived units are present at 35 wt% to 55 wt%, based upon the weight of the copolymer. A “polymer” has two or more of the same or different mer units. A “homopolymer” is a polymer having mer units that are the same. A “copolymer” is a polymer having two or more mer units that are different from each other. A “terpolymer” is a polymer having three mer units that are different from each other. “Different” as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. An “ethylene polymer” or “ethylene copolymer” is a polymer or copolymer comprising at least 50 mol% ethylene derived units, a

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“propylene polymer” or “propylene copolymer” is a polymer or copolymer comprising at least 50 mol% propylene derived units, and so on.

For the purposes of this invention, ethylene shall be considered an α -olefin.

For purposes of this invention and claims thereto, unless otherwise indicated, the term
5 “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. However, in relation to catalyst compounds, the term “substituted” means that a hydrogen group has been replaced with a hydrocarbyl group, a heteroatom, or a
10 heteroatom containing group. For example, methyl cyclopentadiene (Cp) is a Cp group substituted with a methyl group.

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, is
15 defined to be Mw divided by Mn. Unless otherwise noted, all molecular weight units (e.g., Mw, Mn, Mz) are g/mol. The following abbreviations may be used herein: Me is methyl, Et is ethyl, Pr is propyl, cPr is cyclopropyl, nPr is n-propyl, iPr is isopropyl, Bu is butyl, nBu is normal butyl, iBu is isobutyl, sBu is sec-butyl, tBu is tert-butyl, Oct is octyl, Ph is phenyl, Bn or Bz is benzyl, TMS is trimethylsilyl, TIBAL is triisobutylaluminum, TNOAL is tri(n-
20 octyl)aluminum, THF (also referred to as thf) is tetrahydrofuran, RT is room temperature (and is 23°C unless otherwise indicated), tol is toluene, EtOAc is ethyl acetate, and Cy is cyclohexyl, MAO is methylalumoxane.

A “catalyst system” is combination of at least one catalyst compound, at least one activator, an optional co-activator, and an optional support material. For the purposes of this
25 invention and the claims thereto, when catalyst systems are described as comprising neutral stable forms of the components, it is well understood by one of ordinary skill in the art, that the ionic form of the component is the form that reacts with the monomers to produce polymers.

In the description herein, the catalyst may be described as a catalyst precursor, a pre-
30 catalyst compound, catalyst compound or a transition metal compound, and these terms are used interchangeably. A polymerization catalyst system is a catalyst system that can polymerize monomers to polymer. An “anionic ligand” is a negatively charged ligand which donates one or more pairs of electrons to a metal ion.

For purposes of this invention and claims thereto, "alkoxides" include those where the alkyl group is a C₁ to C₁₀ hydrocarbyl. The alkyl group may be straight chain, branched, or cyclic. The alkyl group may be saturated or unsaturated. In some embodiments, the alkyl group may comprise at least one aromatic group.

5 The terms "hydrocarbyl radical," "hydrocarbyl," "hydrocarbyl group," "alkyl radical," and "alkyl" are used interchangeably throughout this document. Likewise, the terms "group," "radical," and "substituent" are also used interchangeably in this document. For purposes of this disclosure, unless otherwise indicated, "hydrocarbyl radical" is defined to be a C₁-C₁₀₀ radical, that may be linear, branched, or cyclic, and when cyclic, aromatic or non-aromatic.
10 Examples of such radicals include, but are not limited to, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, pentyl, iso-amyl, hexyl, octyl cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cyclooctyl, and the like including their substituted analogues. Substituted hydrocarbyl radicals are radicals in which at least one hydrogen atom of the hydrocarbyl radical has been substituted with a heteroatom or heteroatom containing group,
15 preferably the hydrocarbyl has been substituted with at least one halogen (such as Br, Cl, F or I) or at least one functional group such as NR^{*}₂, OR^{*}, SeR^{*}, TeR^{*}, PR^{*}₂, AsR^{*}₂, SbR^{*}₂, SR^{*}, BR^{*}₂, SiR^{*}₃, GeR^{*}₃, SnR^{*}₃, PbR^{*}₃, where R^{*} is a C₁ to C₂₀ hydrocarbyl and the like, or where at least one heteroatom has been inserted within a hydrocarbyl ring.

20 The term "alkenyl" means a straight-chain, branched-chain, or cyclic hydrocarbon radical having one or more double bonds. These alkenyl radicals may be optionally substituted. Examples of suitable alkenyl radicals include, but are not limited to, ethenyl, propenyl, allyl, 1,4-butadienyl cyclopropenyl, cyclobutenyl, cyclopentenyl, cyclohexenyl, cyclooctenyl and the like including their substituted analogues.

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

Where isomers of a named alkyl, alkenyl, alkoxide, or aryl group exist (e.g., n-butyl, iso-butyl, sec-butyl, and tert-butyl) reference to one member of the group (e.g., n-butyl) shall

expressly disclose the remaining isomers (e.g., iso-butyl, sec-butyl, and tert-butyl) in the family. Likewise, reference to an alkyl, alkenyl, alkoxide, or aryl group without specifying a particular isomer (e.g., butyl) expressly discloses all isomers (e.g., n-butyl, iso-butyl, sec-butyl, and tert-butyl).

5 “Complex” as used herein, is also often referred to as catalyst precursor, precatalyst, catalyst, catalyst compound, transition metal compound, or transition metal complex. These words are used interchangeably. Activator and cocatalyst are also used interchangeably.

 A scavenger is a compound that is typically added to facilitate polymerization by scavenging impurities. Some scavengers may also act as activators and may be referred to as
10 co-activators. A co-activator, that is not a scavenger, may also be used in conjunction with an activator in order to form an active catalyst. In some embodiments a co-activator can be pre-mixed with the transition metal compound to form an alkylated transition metal compound.

 In the description herein, the catalyst may be described as a catalyst precursor, a pre-catalyst compound, catalyst compound or a transition metal compound, and these terms are
15 used interchangeably. A polymerization catalyst system is a catalyst system that can polymerize monomers to polymer.

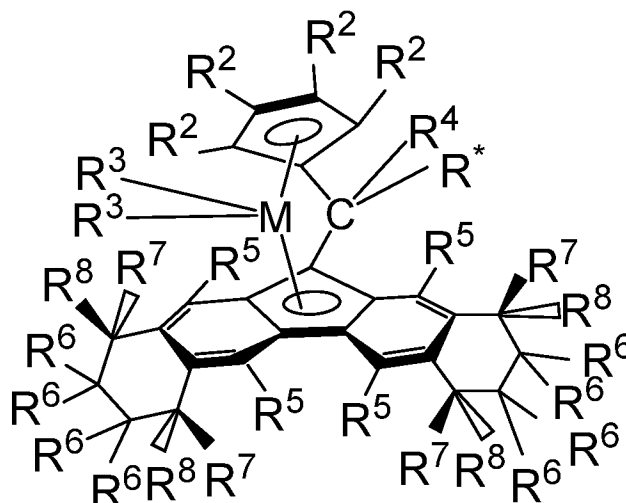
 The term “continuous” means a system that operates without interruption or cessation. For example, a continuous process to produce a polymer would be one where the reactants are continually introduced into one or more reactors and polymer product is continually
20 withdrawn.

Process

 This invention relates to a method to polymerize olefins comprising contacting, in solution phase at a temperature of 60°C to 200°C, ethylene and at least olefin comonomer (preferably C₃ to C₂₀ olefin, preferably propylene, hexene, octene, norbornene or diene) with
25 a catalyst system comprising a non-coordinating anion activator, preferably a bulky activator as defined below, and a metallocene catalyst compound described herein.

 This invention also relates to a method to polymerize olefins comprising contacting, in solution phase at a temperature of 60°C to 200°C, ethylene and at least one diene comonomer and, optionally, an olefin comonomer (preferably C₃ to C₂₀ olefin, preferably
30 propylene, hexene, octene, or norbornene) with a catalyst system comprising a non-coordinating anion activator, preferably a bulky activator as defined below and a metallocene catalyst compound represented by the catalyst compounds described herein.

This invention relates to a method to polymerize olefins comprising contacting, in solution phase at a temperature of 60°C to 200°C, ethylene and at least one olefin comonomer with a catalyst system comprising a non-coordinating anion activator and a metallocene catalyst compound represented by the formula:



5

wherein M is Hf or Zr;

each R³ is independently an anionic group;

each R² is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl;

R⁴ is a hydrocarbyl radical having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, preferably R⁴ is H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl, preferably R⁴ is a C₁ to C₂₀ alkyl, such as butyl, t-butyl, phenyl, or substituted phenyl);

R* is phenyl or a substituted phenyl (such as an alkoxy substituted phenyl, where the alkyl in the alkoxy is a C₁ to C₂₀ alkyl);

15 each R⁵ is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl);

each R⁶ is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl);

20 each R⁷ is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl);

each R⁸ is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl

(preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, or docecyl);

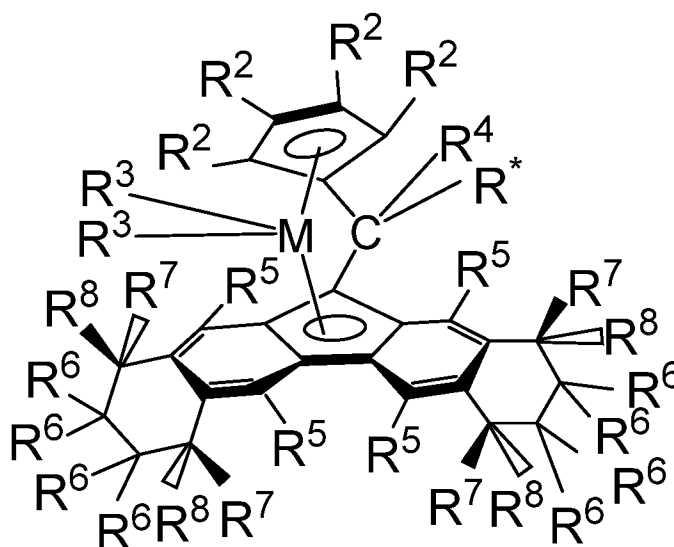
where at least one of each adjacent pair of R^7 and R^8 is not H; and

2) obtaining ethylene polymer having an M_w greater than 100,000 g/mol and, optionally:

- 5 a) the % comonomer incorporated is X% or more, where $X = (Z - 858,441) / (-26,760)$, where Z is the M_n in g/mol of the polymer (alternately $X = (Z - 875,000) / (-26,760)$, preferably $X = (Z - 890,000) / (-26,760)$); and/or

b) the polymer comprises ethylene, diene, and optional C_3 to C_{20} olefin comonomer.

10 This invention relates to a method to polymerize olefins comprising contacting, in solution phase at a temperature of 60°C to 200°C, ethylene, at least one diene comonomer, and optionally a C_3 to C_{20} alpha olefin with a catalyst system comprising a non-coordinating anion activator and a metallocene catalyst compound represented by the formula:



wherein M is Hf or Zr;

- 15 each R^3 is independently an anionic group;
 each R^2 is independently H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl;
 R^4 is H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl (preferably a C_1 to C_{20} alkyl, such as butyl, t-butyl, phenyl, or substituted phenyl);
 R^* is phenyl or a substituted phenyl (such as an alkoxy substituted phenyl, where the alkyl in
 20 the alkoxy is a C_1 to C_{20} alkyl);
 each R^5 is independently H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, or docecyl);

each R^6 is independently H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl);

each R^7 is independently H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl);

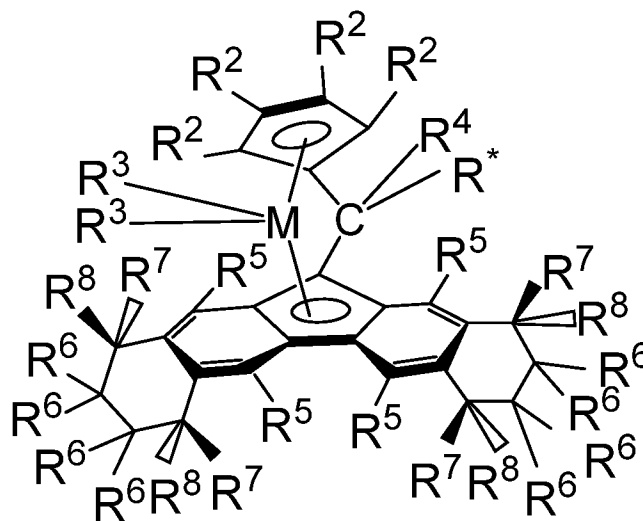
each R^8 is independently H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl);

10 where at least one of each adjacent pair of R^7 and R^8 is not H; and

2) obtaining ethylene polymer having an Mw of 100,000 g/mol or more.

Catalyst Compounds

In a preferred embodiment, this invention relates to catalyst compounds, and catalyst systems comprising such compounds, represented by the formula:



15

wherein M is Hf or Zr;

each R^3 is independently an anionic group;

each R^2 is independently H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl;

16 R^4 is H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl (preferably a C_1 to C_{20} alkyl, such as butyl, t-butyl, phenyl, or substituted phenyl);

R^* is phenyl or a substituted phenyl (such as an alkoxy substituted phenyl, where the alkyl of the alkoxy is a C_1 to C_{20} alkyl);

each R^5 is independently H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl

(preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, or an isomer thereof);

each R^6 is independently H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, or an isomer thereof);

5

each R^7 is independently H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, or an isomer thereof);

each R^8 is independently H or a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl (preferably methyl, ethyl, propyl, butyl, including t-butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, or an isomer thereof); and

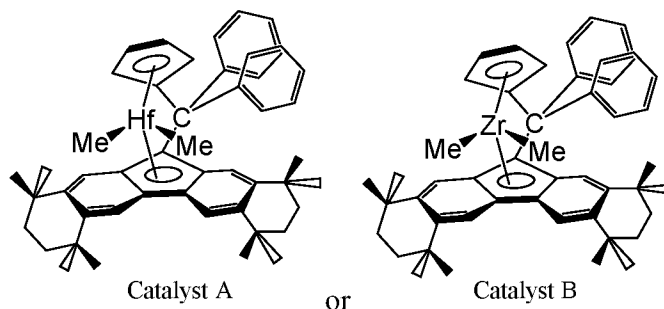
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where at least one of each adjacent pair of R^7 and R^8 is not H.

In any embodiment of the invention, R^2 , R^5 , R^6 , R^7 and/or R^8 is independently methyl, ethyl, or propyl.

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In a preferred embodiment, the catalyst compound is represented by the formula:



The catalyst compounds described herein may be prepared according to the general procedures described in US 6,693,153. Synthesis of Catalysts A and B is described below in the Experimental section.

20

In a preferred embodiment, in any of the processes described herein one catalyst compound is used, e.g., the catalyst compounds are not different. For purposes of this invention, one catalyst compound is considered different from another if they differ by at least one atom. For example, “bisindenyl zirconium dichloride” is different from “(indenyl)(2-methylindenyl) zirconium dichloride” which is different from “(indenyl)(2-methylindenyl) hafnium dichloride.”

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In some embodiments, two or more different catalyst compounds are present in the catalyst system used herein. In some embodiments, two or more different catalyst compounds are present in the reaction zone where the process(es) described herein occur. When two

transition metal compound based catalysts are used in one reactor as a mixed catalyst system, the two transition metal compounds are preferably chosen such that the two are compatible. A simple screening method such as by ^1H or ^{13}C NMR, known to those of ordinary skill in the art, can be used to determine which transition metal compounds are compatible. It is
5 preferable to use the same activator for the transition metal compounds, however, two different activators, such as a non-coordinating anion activator and an alumoxane, can be used in combination. If one or more transition metal compounds contain an R^4 or R^* ligand which is not a hydride, hydrocarbyl, or substituted hydrocarbyl, then the alumoxane is typically contacted with the transition metal compounds prior to addition of the non-
10 coordinating anion activator.

The two transition metal compounds (pre-catalysts) may be used in any ratio. Preferred molar ratios of (A) transition metal compound to (B) transition metal compound fall within the range of (A:B) 1:1000 to 1000:1, alternatively 1:100 to 500:1, alternatively 1:10 to 200:1, alternatively 1:1 to 100:1, alternatively 1:1 to 75:1, and alternatively 5:1 to 50:1. The
15 particular ratio chosen will depend on the exact pre-catalysts chosen, the method of activation, and the end product desired. In a particular embodiment, when using the two pre-catalysts, where both are activated with the same activator, useful mole percents, based upon the molecular weight of the pre-catalysts, are 10% to 99.9% A to 0.1% to 90% B, alternatively 25% to 99% A to 0.5% to 50% B, alternatively 50% to 99% A to 1% to 25% B,
20 and alternatively 75% to 99% A to 1% to 10% B.

Activators

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

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

Non-limiting activators, for example, include ionizing activators, which may be neutral or ionic. Preferred activators typically include 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.

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),
5 modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane.

In an embodiment, little or no alumoxane is used in the polymerization processes described herein. Preferably, alumoxane is present at zero mol%, alternately the alumoxane is present at a molar ratio of aluminum to catalyst compound transition metal less than 500:1, preferably less than 300:1, preferably less than 100:1, preferably less than 1:1.

10 Noncoordinating Anion Activators

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

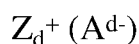
25 “Compatible” non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral transition metal compound and a neutral by-product from the anion. Non-coordinating anions useful in accordance with this invention are those that are compatible, stabilize the transition metal
30 cation in the sense of balancing its ionic charge at +1, and yet retain sufficient lability to permit displacement during polymerization.

It is within the scope of this invention to use an ionizing or stoichiometric activator, neutral or ionic, such as tri (n-butyl) ammonium tetrakis(pentafluorophenyl)borate, a tris

perfluorophenyl boron metalloid precursor or a tris perfluoronaphthyl boron metalloid precursor, polyhalogenated heteroborane anions (WO 98/43983), boric acid (US 5,942,459), or combination thereof. It is also within the scope of this invention to use neutral or ionic activators alone or in combination with alumoxane or modified alumoxane activators.

5 The catalyst systems of this invention can include at least one non-coordinating anion (NCA) activator.

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



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

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

The activating cation Z_d^+ may also be a moiety such as silver, tropylium, carboniums, ferroceniums and mixtures, preferably carboniums and ferroceniums. Most preferably Z_d^+ is triphenyl carbonium. Preferred reducible Lewis acids can be any triaryl carbonium (where
 20 the aryl can be substituted or unsubstituted, such as those represented by the formula: (Ar_3C^+) , where Ar is aryl or aryl substituted with a heteroatom, a C_1 to C_{40} hydrocarbyl, or a substituted C_1 to C_{40} hydrocarbyl), preferably the reducible Lewis acids in formula (14) above as "Z" include those represented by the formula: (Ph_3C) , where Ph is a substituted or
 25 unsubstituted phenyl, preferably substituted with C_1 to C_{40} hydrocarbyls or substituted a C_1 to C_{40} hydrocarbyls, preferably C_1 to C_{20} alkyls or aromatics or substituted C_1 to C_{20} alkyls or aromatics, preferably Z is a triphenylcarbonium.

When Z_d^+ is the activating cation $(L-H)_d^+$, it is preferably a Bronsted acid, capable of donating a proton to the transition metal catalytic precursor resulting in a transition metal cation, including ammoniums, oxoniums, phosphoniums, silyliums, and mixtures thereof,
 30 preferably 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,

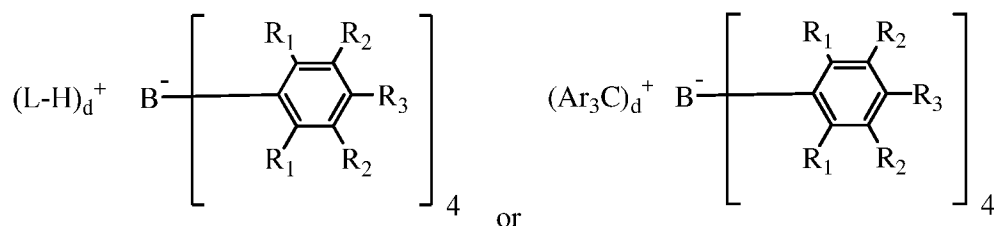
oxoniums from ethers such as dimethyl ether diethyl ether, tetrahydrofuran and dioxane, sulfoniums from thioethers, such as diethyl thioethers, tetrahydrothiophene, and mixtures thereof.

The anion component A^{d-} includes those having the formula $[M^{k+}Q_n]^{d-}$ wherein k is 1, 2, or 3; n is 1, 2, 3, 4, 5, or 6 (preferably 1, 2, 3, or 4); n - k = d; M is an element selected from Group 13 of the Periodic Table of the Elements, preferably boron or aluminum, and Q is independently a hydride, bridged or unbridged dialkylamido, halide, alkoxide, 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 1 occurrence is Q a halide. Preferably, each Q is a fluorinated hydrocarbyl group having 1 to 20 carbon atoms, more preferably each Q is a fluorinated aryl group, and most preferably each Q is a pentafluoryl aryl group. Examples of suitable A^{d-} also include diboron compounds as disclosed in US 5,447,895, which is fully incorporated herein by reference.

Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst are the compounds described as (and particularly those specifically listed as) activators in US 8,658,556, which is incorporated by reference herein.

Most preferably, the ionic stoichiometric activator Z_d^+ (A^{d-}) is one or more of N,N-dimethylanilinium tetra(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.

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



wherein:

each R_1 is, independently, a halide, preferably a fluoride;

Ar is substituted or unsubstituted aryl group (preferably a substituted or unsubstituted phenyl), preferably substituted with C₁ to C₄₀ hydrocarbyls, preferably C₁ to C₂₀ alkyls or aromatics;

each R₂ is, independently, a halide, a C₆ to C₂₀ substituted aromatic hydrocarbyl group or a siloxy group of the formula -O-Si-R_a, where R_a is a C₁ to C₂₀ hydrocarbyl or hydrocarbylsilyl group (preferably R₂ is a fluoride or a perfluorinated phenyl group);

each R₃ is a halide, C₆ to C₂₀ substituted aromatic hydrocarbyl group or a siloxy group of the formula -O-Si-R_a, where R_a is a C₁ to C₂₀ hydrocarbyl or hydrocarbylsilyl group (preferably R₃ is a fluoride or a C₆ perfluorinated aromatic hydrocarbyl group); wherein R₂ and R₃ can form one or more saturated or unsaturated, substituted or unsubstituted rings (preferably R₂ and R₃ form a perfluorinated phenyl ring);

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

wherein the anion has a molecular weight of greater than 1020 g/mol; and

wherein at least three of the substituents on the B atom each have a molecular volume of greater than 250 cubic Å, alternately greater than 300 cubic Å, or alternately greater than 500 cubic Å.

Preferably (Ar₃C)_d⁺ is (Ph₃C)_d⁺, where Ph is a substituted or unsubstituted phenyl, preferably substituted with C₁ to C₄₀ hydrocarbyls or substituted C₁ to C₄₀ hydrocarbyls, preferably C₁ to C₂₀ alkyls or aromatics or substituted C₁ to C₂₀ alkyls or aromatics and d is 1, 2, or 3.

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

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

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

For a list of particularly useful Bulky activators please see US 8,658,556, which is incorporated by reference herein.

In another embodiment, one or more of the NCA activators is chosen from the
5 activators described in US 6,211,105.

Preferred activators include N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorophenyl)borate, N,N-dimethylanilinium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
10 triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, [Ph₃C⁺][B(C₆F₅)₄⁻], [Me₃NH⁺][B(C₆F₅)₄⁻]; 1-(4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium; and tetrakis(pentafluorophenyl)borate, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine.

15 In a preferred embodiment, the activator comprises a triaryl carbonium (such as triphenylcarbenium tetraphenylborate, triphenylcarbenium tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate).

20 In another embodiment, the activator comprises one or more of trialkylammonium tetrakis(pentafluorophenyl)borate, N,N-dialkylanilinium tetrakis(pentafluorophenyl)borate, N,N-dimethyl-(2,4,6-trimethylanilinium) tetrakis(pentafluorophenyl)borate, trialkylammonium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, N,N-dialkylanilinium tetrakis-(2,3,4,6-tetrafluorophenyl)borate, trialkylammonium tetrakis(perfluoronaphthyl)borate, N,N-
25 dialkylanilinium tetrakis(perfluoronaphthyl)borate, trialkylammonium tetrakis(perfluorobiphenyl)borate, N,N-dialkylanilinium tetrakis(perfluorobiphenyl)borate, trialkylammonium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkylanilinium

tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, N,N-dialkyl-(2,4,6-trimethylanilinium)
 tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, di-(i-propyl)ammonium
 tetrakis(pentafluorophenyl)borate, (where alkyl is methyl, ethyl, propyl, n-butyl, sec-butyl, or
 t-butyl).

- 5 In useful embodiments of the invention described herein, the activator is one or more
 of: N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, triphenylcarbenium
 tetrakis(pentafluorophenyl)borate, trimethylammonium tetrakis(perfluoronaphthyl)borate,
 triethylammonium tetrakis(perfluoronaphthyl)borate, tripropylammonium
 tetrakis(perfluoronaphthyl)borate, tri(n-butyl)ammonium tetrakis(perfluoronaphthyl)borate,
 10 tri(t-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, tropillium
 tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
 triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium
 15 tetrakis(perfluoronaphthyl)borate, benzene(diazonium) tetrakis(perfluoronaphthyl)borate,
 trimethylammonium tetrakis(perfluorobiphenyl)borate, triethylammonium
 tetrakis(perfluorobiphenyl)borate, tripropylammonium tetrakis(perfluorobiphenyl)borate,
 tri(n-butyl)ammonium tetrakis(perfluorobiphenyl)borate, tri(t-butyl)ammonium
 tetrakis(perfluorobiphenyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,
 20 N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-
 trimethylanilinium) tetrakis(perfluorobiphenyl)borate, tropillium
 tetrakis(perfluorobiphenyl)borate, triphenylcarbenium tetrakis(perfluorobiphenyl)borate,
 triphenylphosphonium tetrakis(perfluorobiphenyl)borate, triethylsilylium
 tetrakis(perfluorobiphenyl)borate, benzene(diazonium) tetrakis(perfluorobiphenyl)borate, [4-
 25 t-butyl-PhNMe₂H][(C₆F₃(C₆F₅)₂)₄B], trimethylammonium tetraphenylborate,
 triethylammonium tetraphenylborate, tripropylammonium tetraphenylborate, tri(n-
 butyl)ammonium tetraphenylborate, tri(t-butyl)ammonium tetraphenylborate, N,N-
 dimethylanilinium tetraphenylborate, N,N-diethylanilinium tetraphenylborate, N,N-dimethyl-
 (2,4,6-trimethylanilinium) tetraphenylborate, tropillium tetraphenylborate,
 30 triphenylcarbenium tetraphenylborate, triphenylphosphonium tetraphenylborate,
 triethylsilylium tetraphenylborate, benzene(diazonium)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, tropillium
5 tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(pentafluorophenyl)borate,
triphenylphosphonium tetrakis(pentafluorophenyl)borate, triethylsilylium
tetrakis(pentafluorophenyl)borate, benzene(diazonium) 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-
10 tetrafluorophenyl)borate, tri(n-butyl)ammonium tetrakis-(2,3,4,6-tetrafluoro-phenyl)borate,
dimethyl(t-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, tropillium tetrakis-(2,3,4,6-tetrafluorophenyl)borate,
15 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, trimethylammonium
tetrakis(3,5-bis(trifluoromethyl)phenyl)borate, triethylammonium tetrakis(3,5-
bis(trifluoromethyl)phenyl)borate, tripropylammonium tetrakis(3,5-
20 bis(trifluoromethyl)phenyl)borate, tri(n-butyl)ammonium tetrakis(3,5-
bis(trifluoromethyl)phenyl)borate, tri(t-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-
25 bis(trifluoromethyl)phenyl)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, benzene(diazonium) tetrakis(3,5-
bis(trifluoromethyl)phenyl)borate, di-(i-propyl)ammonium tetrakis(pentafluorophenyl)borate,
30 dicyclohexylammonium tetrakis(pentafluorophenyl)borate, tri(o-tolyl)phosphonium
tetrakis(pentafluorophenyl)borate, tri(2,6-dimethylphenyl)phosphonium
tetrakis(pentafluorophenyl)borate, triphenylcarbenium tetrakis(perfluorophenyl)borate, 1-(4-
(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluorophenyl)pyrrolidinium,

tetrakis(pentafluorophenyl)borate, 4-(tris(pentafluorophenyl)borate)-2,3,5,6-tetrafluoropyridine, triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate) or a combination thereof.

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

It is also within the scope of this invention that the catalyst compounds can be combined with combinations of alumoxanes and NCA's (see for example, US 5,153,157; US 5,453,410; EP 0 573 120 B1; WO 94/07928; and WO 95/14044 which discuss the use of an alumoxane in combination with an ionizing activator).

Chain transfer agents may also be used in the polymerizations described herein. Useful chain transfer agents are typically alkylalumoxanes, a compound represented by the formula AlR_3 , ZnR_2 (where each R is, independently, a C_1 - C_8 aliphatic radical, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, methylalumoxane, trimethylaluminum, triisobutylaluminum, trioctylaluminum, or a combination thereof.

Optional Scavengers or Co-Activators

In addition to these activator compounds, scavengers or co-activators may be used. Aluminum alkyl or organoaluminum compounds which may be utilized as scavengers or co-activators include, for example, trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, and diethyl zinc.

Polymerization Processes

In embodiments herein, the invention relates to polymerization processes where monomer (such as ethylene), and optionally comonomer, are contacted with a catalyst system comprising an activator and at least one catalyst compound, as described above. The catalyst compound and activator may be combined in any order, and are combined typically prior to contacting with the monomer.

Monomers useful herein include substituted or unsubstituted C_2 to C_{40} alpha olefins, preferably C_2 to C_{20} alpha olefins, preferably C_2 to C_{12} alpha olefins, preferably ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene, norbornene, and isomers thereof. In a preferred embodiment of the invention, the monomer comprises propylene and an optional comonomers comprising one or more ethylene or C_4 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. In another preferred embodiment, the monomer comprises ethylene and an optional comonomers comprising one or more C₃ to C₄₀ olefins, preferably C₄ to C₂₀ olefins, or preferably C₆ to C₁₂ olefins. The C₃ to C₄₀ olefin monomers may be linear, branched, or cyclic. The C₃ 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 ethylene, propylene, 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.

In a preferred embodiment, one or more dienes are present in the polymer produced herein at up to 10 wt%, preferably at 0.00001 to 1.0 wt%, preferably 0.002 to 0.5 wt%, even more preferably 0.003 to 0.2 wt%, based upon the total weight of the composition. In some embodiments, 500 ppm or less of diene is added to the polymerization, preferably 400 ppm or less, preferably or 300 ppm or less. In other embodiments, at least 50 ppm of diene is added to the polymerization, or 100 ppm or more, or 150 ppm or more.

Preferred diolefin monomers useful in this invention include any hydrocarbon structure, preferably C₄ to C₃₀, having at least two unsaturated bonds, wherein at least two of the unsaturated bonds are readily incorporated into a polymer by either a stereospecific or a non-stereospecific catalyst(s). It is further preferred that the diolefin monomers be selected from alpha, omega-diene monomers (i.e., di-vinyl monomers). More preferably, the diolefin monomers are linear di-vinyl monomers, most preferably those containing from 4 to 30 carbon atoms. Examples of preferred dienes include butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene, tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene,

pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene, triacontadiene, particularly preferred dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, and low molecular weight polybutadienes (Mw less than 1000 g/mol).

5 Preferred cyclic dienes include cyclopentadiene, vinylnorbornene, norbornadiene, ethylidene norbornene, divinylbenzene, dicyclopentadiene or higher ring containing diolefins with or without substituents at various ring positions.

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

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

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Polymerization processes of this invention can be carried out in any manner known in the art. Any suspension, homogeneous, bulk, or solution, polymerization process known in the art can be used. Such processes can be run in a batch, semi-batch, or continuous mode. Homogeneous polymerization processes are preferred. (Preferred homogeneous polymerization processes are those where at least 90 wt% of the product is soluble in the reaction media.) A bulk homogeneous process is particularly preferred, especially one 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). In another preferred embodiment, the process is a solution process.

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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;

cyclic and alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof, such as can be found commercially (Isopar™); perhalogenated hydrocarbons, such as perfluorinated C₄₋₁₀ alkanes, chlorobenzene, and aromatic and alkylsubstituted aromatic compounds, such as benzene, toluene, mesitylene, and xylene. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, 1-butene, 1-hexene, 1-pentene, 3-methyl-1-pentene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. In 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.

In a preferred embodiment, the feed concentration of the monomers and comonomers for the polymerization is 60 vol% solvent or less, preferably 40 vol% or less, or preferably 20 vol% or less, based on the total volume of the feedstream. Preferably the polymerization is run in a bulk process.

Preferred polymerizations can be run at any temperature and/or pressure suitable to obtain the desired ethylene polymers. Typical temperatures and/or pressures include a temperature in the range of from about 60°C to about 200°C, preferably about 70°C to about 200°C, preferably about 80°C to about 175°C, preferably from about 85°C to about 160°C; and optionally at a pressure in the range of from about 0.35 MPa to about 10 MPa, preferably from about 0.45 MPa to about 6 MPa, or preferably from about 0.5 MPa to about 4 MPa.

In a typical polymerization, the run time of the reaction is up to 300 minutes, preferably in the range of from about 5 to 250 minutes, or preferably from about 10 to 120 minutes.

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 0.1 to 10 psig (0.7 to 70 kPa).

In a preferred embodiment, little or no alumoxane is used in the process to produce the polymers. Preferably, alumoxane is present at zero mol%, alternately the alumoxane is

present at a molar ratio of aluminum to transition metal less than 500:1, preferably less than 300:1, preferably less than 100:1, preferably less than 1:1.

In a preferred embodiment, little or no scavenger is used in the process to produce the ethylene polymer. Preferably, scavenger (such as tri-alkyl aluminum) is present at zero
5 mol%, alternately the scavenger is present at a molar ratio of scavenger metal to transition metal of less than 100:1, preferably less than 50:1, preferably less than 15:1, preferably less than 10:1.

In a preferred embodiment, the polymerization:

- 1) is conducted at temperatures of 60°C to 300°C (preferably 70°C to 200°C, preferably 80°C
10 to 160°C);
- 2) is conducted at a pressure of atmospheric pressure to 10 MPa (preferably 0.35 to 10 MPa, preferably from 0.45 to 6 MPa, preferably from 0.5 to 4 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
15 alicyclic hydrocarbons, such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; preferably where aromatics are 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) wherein the catalyst system used in the polymerization comprises less than 0.5 mol%,
20 preferably 0 mol% alumoxane, alternately the alumoxane is present at a molar ratio of aluminum to transition metal less than 500:1, preferably less than 300:1, preferably less than 100:1, preferably less than 1:1;
- 5) the polymerization preferably occurs in one reaction zone;
- 6) the productivity of the catalyst compound is at least 80,000 g/mmol/hr (preferably at least
25 150,000 g/mmol/hr, preferably at least 200,000 g/mmol/hr, preferably at least 250,000 g/mmol/hr, preferably at least 300,000 g/mmol/hr);
- 7) optionally, scavengers (such as trialkyl aluminum compounds) are absent (e.g., present at zero mol%, alternately the scavenger is present at a molar ratio of scavenger metal to transition metal of less than 100:1, preferably less than 50:1, preferably less than 15:1,
30 preferably less than 10:1); and
- 8) optionally, 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 0.1 to 10 psig (0.7 to 70 kPa)). In a preferred embodiment, the catalyst system

used in the polymerization comprises no more than one catalyst compound. A “reaction zone” also referred to as a “polymerization zone” is a vessel where polymerization takes place, for example a batch reactor. When multiple reactors are used in either series or parallel configuration, each reactor is considered as a separate polymerization zone. For a multi-stage
5 polymerization in both a batch reactor and a continuous reactor, each polymerization stage is considered as a separate polymerization zone.

In a preferred embodiment, the polymerization occurs in one reaction zone.

Other additives may also be used in the polymerization, as desired, such as one or more scavengers, promoters, modifiers, chain transfer agents (such as diethyl zinc), reducing
10 agents, oxidizing agents, hydrogen, aluminum alkyls, or silanes.

Useful chain transfer agents are typically alkylaluminumoxanes, a compound represented by the formula AlR_3 , ZnR_2 (where each R is, independently, a C_1 - C_8 aliphatic radical, preferably methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl or an isomer thereof) or a combination thereof, such as diethyl zinc, methylaluminumoxane, trimethylaluminum,
15 triisobutylaluminum, trioctylaluminum, or a combination thereof.

Polyolefin Products

This invention also relates to compositions of matter produced by the methods described herein.

In a preferred embodiment, the process described herein produces olefin polymers,
20 preferably polyethylene and polypropylene homopolymers and copolymers.

In a preferred embodiment, the polymers produced herein are homopolymers of ethylene or propylene, are copolymers of ethylene preferably having from 0 to 45 mol% (alternately from 0.5 to 35 mol%, alternately from 1 to 25 mol%, preferably from 3 to 10 mol%) of one or more C_3 to C_{20} olefin comonomer (preferably norbornene and or C_3 to C_{12}
25 alpha-olefin, preferably propylene, butene, hexene, octene, decene, dodecene, norbornene preferably propylene, butene, hexene, octene, norbornene), or are copolymers of propylene preferably having from 0 to 45 mol% (alternately from 0.1 to 25 mol%, alternately from 0.5 to 20 mol%, alternately from 1 to 15 mol%, alternately from 3 to 10 mol%) of one or more of C_2 or C_4 to C_{20} olefin comonomer (preferably ethylene or C_4 to C_{12} alpha-olefin, preferably
30 ethylene, butene, hexene, octene, decene, dodecene, norbornene, preferably ethylene, butene, hexene, octene, norbornene).

In a preferred embodiment, the monomer is ethylene and the comonomer is hexene, preferably from 1 to 15 mol% hexene, alternately 1 to 10 mol%.

In a preferred embodiment, the monomer is ethylene and the comonomer is octene, preferably from 1 to 15 mol% octene, alternately 1 to 10 mol%.

In a preferred embodiment, the monomer is ethylene and the comonomer is norbornene, preferably from 1 to 40 mol% norbornene, alternately 1 to 10 mol%.

5 In a preferred embodiment, the polymers produced herein are copolymers of ethylene preferably having from 0 to 25 mol% (alternately from 0.5 to 20 mol%, alternately from 1 to 15 mol%, preferably from 3 to 10 mol%) of one or more C₃ to C₂₀ olefin comonomers (preferably C₃ to C₁₂ alpha-olefin, preferably propylene, butene, hexene, octene, decene, dodecene, norbornene, preferably propylene, butene, hexene, octene), and from 0.1 to 25
10 mol% of a diene (alternately from 0.5 to 20 mol%, alternately from 1 to 15 mol%, preferably from 3 to 10 mol%), preferably the diene comprises one or more of butadiene, pentadiene, hexadiene, heptadiene, octadiene, nonadiene, decadiene, undecadiene, dodecadiene, tridecadiene, tetradecadiene, pentadecadiene, hexadecadiene, heptadecadiene, octadecadiene, nonadecadiene, icosadiene, heneicosadiene, docosadiene, tricosadiene, tetracosadiene, pentacosadiene, hexacosadiene, heptacosadiene, octacosadiene, nonacosadiene,
15 triacontadiene, particularly preferred dienes include 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, 1,13-tetradecadiene, low molecular weight polybutadienes (Mw less than 1000 g/mol) and cyclic dienes such as cyclopentadiene, vinylnorbornene, norbornadiene, ethylidene norbornene,
20 norbornene, divinylbenzene, and dicyclopentadiene.

In a preferred embodiment, the polymers produced herein are copolymers of ethylene preferably having from 0 to 25 mol% (alternately from 0.5 to 20 mol%, alternately from 1 to 15 mol%, preferably from 3 to 10 mol%) of one or more C₃ to C₂₀ olefin comonomers (preferably C₃ to C₁₂ alpha-olefin, preferably propylene, butene, hexene, octene, decene,
25 dodecene, norbornene, preferably propylene, butene, hexene, octene, norbornene), and from 0.1 to 25 wt% of a diene (alternately from 0.5 to 20 mol%, alternately from 1 to 15 mol%, preferably from 3 to 10 mol%), preferably vinylnorbornene, norbornadiene, ethylidene norbornene, or a mixture thereof (such as vinylnorbornene and ethylidene norbornene).

Typically, the polymers produced herein have an Mw of 100,000 to 1,000,000 g/mol
30 (preferably 125,000 to 850,000 g/mol, preferably 150,000 to 750,000 g/mol), and/or an Mw/Mn of greater than 1 to 40 (alternately 1.2 to 20, alternately 1.3 to 10, alternately 1.4 to 5, 1.5 to 4, alternately 1.5 to 3).

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

Unless otherwise indicated Mw, Mn, MWD are determined by GPC as described in US 2006/0173123, pages 24-25, paragraphs [0334] to [0341].

In a preferred embodiment, the polymer produced herein has a composition distribution breadth index (CDBI) of 50% or more, preferably 60% or more, preferably 70% or more. CDBI is a measure of the composition distribution of monomer within the polymer chains and is measured by the procedure described in PCT publication WO 93/03093, published February 18, 1993, specifically columns 7 and 8 as well as in Wild et al, J. Poly. Sci., Poly. Phys. Ed., Vol. 20, p. 441 (1982) and US 5,008,204, including that fractions having a weight average molecular weight (Mw) below 15,000 are ignored when determining CDBI.

Blends

In another embodiment, the polymer (preferably the polyethylene, polypropylene or ethylene propylene diene monomer polymer) produced herein is combined with one or more additional polymers prior to being formed into a film, molded part or other article. Other useful polymers include polyethylene, isotactic polypropylene, highly isotactic polypropylene, syndiotactic polypropylene, random copolymer of propylene and ethylene, and/or butene, and/or hexene, polybutene, ethylene vinyl acetate, LDPE, LLDPE, HDPE, ethylene vinyl acetate, ethylene methyl acrylate, copolymers of acrylic acid, polymethylmethacrylate or any other polymers polymerizable by a high-pressure free radical process, polyvinylchloride, polybutene-1, isotactic polybutene, ABS resins, ethylene-propylene rubber (EPR), vulcanized EPR, EPDM, block copolymer, styrenic block copolymers, polyamides, polycarbonates, PET resins, cross linked polyethylene, copolymers of ethylene and vinyl alcohol (EVOH), polymers of aromatic monomers such as polystyrene, poly-1 esters, polyacetal, polyvinylidene fluoride, polyethylene glycols, and/or polyisobutylene.

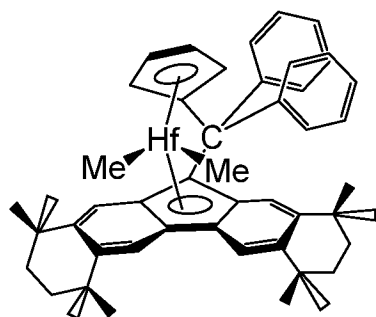
In a preferred embodiment, the polymer (preferably the polyethylene, polypropylene or EPDM) is present in the above blends, at from 10 to 99 wt%, based upon the weight of the polymers in the blend, preferably 20 to 95 wt%, even more preferably at least 30 to 90 wt%,

even more preferably at least 40 to 90 wt%, even more preferably at least 50 to 90 wt%, even more preferably at least 60 to 90 wt%, even more preferably at least 70 to 90 wt%.

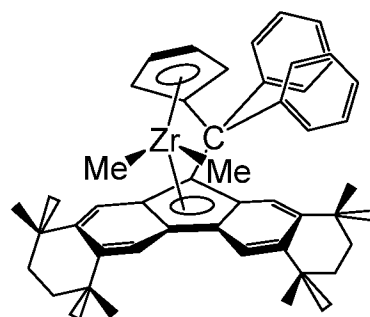
The blends described above may be produced by mixing the polymers of the invention with one or more polymers (as described above), by connecting reactors together in series to
 5 make reactor blends or by using more than one catalyst in the same reactor to produce multiple species of polymer. The polymers can be mixed together prior to being put into the extruder or may be mixed in an extruder.

The blends may be formed using conventional equipment and methods, such as by dry blending the individual components and subsequently melt mixing in a mixer, or by mixing
 10 the components together directly in a mixer, such as, for example, a Banbury mixer, a Haake mixer, a Brabender internal mixer, or a single or twin-screw extruder, which may include a compounding extruder and a side-arm extruder used directly downstream of a polymerization process, which may include blending powders or pellets of the resins at the hopper of the film extruder. Additionally, additives may be included in the blend, in one or more components of
 15 the blend, and/or in a product formed from the blend, such as a film, as desired. Such additives are well known in the art, and can include, for example: fillers; antioxidants (e.g., hindered phenolics such as IRGANOX™ 1010 or IRGANOX™ 1076 available from Ciba-Geigy); phosphites (e.g., IRGAFOS™ 168 available from Ciba-Geigy); anti-cling additives; tackifiers, such as polybutenes, terpene resins, aliphatic and aromatic hydrocarbon resins,
 20 alkali metal and glycerol stearates, and hydrogenated rosins; UV stabilizers; heat stabilizers; anti-blocking agents; release agents; anti-static agents; pigments; colorants; dyes; waxes; silica; fillers; talc; and the like.

Experimental



Catalyst A



Catalyst B

25 Catalysts A and B were made according to the procedures described below.

Catalyst C is $(o\text{-SiEt}_3\text{-Ph})_2\text{C}(\text{Cp})(3,7\text{ di-}t\text{-Bu-Flu})\text{HfMe}_2$.

Catalyst D is $\text{Ph}_2\text{C}(\text{Cp})(3,7\text{ di-Ph-Flu})\text{HfMe}_2$.

Catalyst E is $\text{Ph}_2\text{C}(\text{Cp})(3,7 \text{ di-}t\text{-Bu-Flu})\text{HfMe}_2$.

Test Methods

Crystallization temperature (T_c) and melting temperature (or melting point, T_m) are measured using Differential Scanning Calorimetry (DSC) on a commercially available instrument (e.g., TA Instruments 2920 DSC). Typically, 6 to 10 mg of molded polymer or plasticized polymer are sealed in an aluminum pan and loaded into the instrument at room temperature. Melting data (first heat) is acquired by heating the sample to at least 30°C above its melting temperature, typically 220°C for polypropylene, at a heating rate of $10^\circ\text{C}/\text{min}$. The sample is held for at least 5 minutes at this temperature to destroy its thermal history. Crystallization data are acquired by cooling the sample from the melt to at least 50°C below the crystallization temperature, typically -50°C for polypropylene, at a cooling rate of $20^\circ\text{C}/\text{min}$. The sample is held at this temperature for at least 5 minutes, and finally heated at $10^\circ\text{C}/\text{min}$ to acquire additional melting data (second heat). The endothermic melting transition (first and second heat) and exothermic crystallization transition are analyzed according to standard procedures. The melting temperatures reported are the peak melting temperatures from the second heat unless otherwise specified.

For polymers displaying multiple peaks, the melting temperature is defined to be the peak melting temperature from the melting trace associated with the largest endothermic calorimetric response (as opposed to the peak occurring at the highest temperature). Likewise, the crystallization temperature is defined to be the peak crystallization temperature from the crystallization trace associated with the largest exothermic calorimetric response (as opposed to the peak occurring at the highest temperature).

Areas under the DSC curve are used to determine the heat of transition (heat of fusion, H_f , upon melting or heat of crystallization, H_c , upon crystallization), which can be used to calculate the degree of crystallinity (also called the percent crystallinity). The percent crystallinity ($X\%$) is calculated using the formula: $[\text{area under the curve (in J/g)} / H^\circ \text{ (in J/g)}] * 100$, where H° is the ideal heat of fusion for a perfect crystal of the homopolymer of the major monomer component. These values for H° are to be obtained from the *Polymer Handbook, Fourth Edition*, published by John Wiley and Sons, New York, 1999, except that a value of 290 J/g is used for H° (polyethylene), a value of 140 J/g is used for H° (polybutene), and a value of 207 J/g is used for H° (polypropylene).

Catalyst Compounds

Synthesis of Catalyst B, C₄₉H₅₆Zr

(C₂Me₄(CH₂)₂)₂Fl (5.0 g, 12.9 mmol) was dissolved into Et₂O(100 ml) and 10M nBuli (1.5 ml, 15 mmol) was then slowly added. The reaction was stirred overnight at room temperature. Crude ¹H NMR showed that the reaction was complete. After the amount of Et₂O was reduced, the product (6.0 g) was isolated by filtration. The fluorenyl lithium (1.4 g, 3.0 mmol) was then slurried into toluene and reacted with diphenyl fulvene (0.69 g, 3.0 mmol) overnight. All volatiles were removed under vacuo and the crude product was reslurried in hexane. Ph₂CCp(C₂Me₄(CH₂)₂)₂FILi (1.6 g, 2.6 mmol) was isolated by filtration and washed by hexane. It was then dissolved in THF (50 ml) and KH (0.4g, 10.4 mmol) was added in one portion. The reaction was stirred at room temperature for 3 days. Crude ¹H NMR showed that the reaction was complete. Excess KH was removed by filtration. All volatiles were removed under vacuo. The product (1.25 g) was isolated as a dark purple solid. The solid Li/K salt (1.25 g, 1.78 mmol) was slurried in Et₂O (10 ml) and toluene (20 ml) mixture and reacted with ZrCl₄ (0.415 g, 1.78 mmol). The reaction was stirred at room temperature for 6 hours. Crude ¹H NMR showed that the reaction was complete. MeMgI (1.4 ml, 3 M in Et₂O) was then added and the reaction was stirred at 48°C for 16 hours. Crude ¹H NMR showed that reaction is complete. The reaction was cooled to room temperature and 1, 4 dioxane (0.6 ml) was added. The mixture was stirred for 15 min and solids were removed by filtration on celite and the crude product was redissolved into pentane. Leftover solids were removed by filtration on celite. All volatiles were then removed under vacuo. Final product (C₄₉H₅₆Zr) was isolated as a solid (0.6 g), which was analyzed by ¹H NMR (CD₂Cl₂, 400 MHz): δ 8.17 (s, 2H), 7.94 (ddd, *J* = 8.0, 2.0, 1.2 Hz, 2H), 7.87 – 7.79 (m, 2H), 7.42 (td, *J* = 7.6, 1.7 Hz, 2H), 7.32 – 7.20 (m, 4H), 6.24 (t, *J* = 2.6 Hz, 2H), 6.09 (s, 2H), 5.40 (d, *J* = 0.7 Hz, 2H), 1.76 – 1.54 (m, 8H), 1.45 (s, 6H), 1.42 (s, 6H), 0.96 (s, 6H), 0.81 (s, 6H), -1.73 (s, 6H).

Synthesis of Catalyst A, C₄₉H₅₆Hf

The solid dilithio salt (1.0 g) was slurried in Et₂O (50 ml) and reacted with HfCl₄ (0.4 g). The reaction was stirred at room temperature for 30 min. Crude ¹H NMR showed that the reaction was complete. MeMgI (1.0 g, 3 M in Et₂O) was then added and the reaction was stirred at 70°C for 1 hours. Crude ¹H NMR showed that reaction is complete. The reaction was cooled to room temperature and 1, 4 dioxane (2 ml) was added. The mixture was stirred for 15 min and solids were removed by filtration on celite. All volatiles were then removed

under vacuo. Final product (C₄₉H₅₆Hf) was isolated as a solid (0.5 g), which was analyzed by ¹H NMR (CD₂Cl₂, 400 MHz): δ 8.16 (s, 2H), 7.99 – 7.90 (m, 2H), 7.86 – 7.79 (m, 2H), 7.46 – 7.38 (m, 2H), 7.35 – 7.09 (m, 4H), 6.16 (t, *J* = 2.7 Hz, 2H), 6.14 (s, 2H), 5.37 (t, *J* = 2.6 Hz, 2H), 1.78 – 1.53 (m, 8H), 1.44 (s, 6H), 1.43 (s, 6H), 0.96 (s, 6H), 0.82 (s, 6H), -1.93 (s, 6H).

5 High Throughput Experimentation (HTE) General Description

Typical solution polymerizations were carried out in using high throughput robotic system manufactured by Symyx Technologies (Santa Clara, CA). The experimental details were developed using Library Studio version 7.1.9. The reactions were carried out in parallel with robotic control and typically take less than 2 hrs for completion. Individual reaction wells were lined with disposable glass inserts and were equipped with Teflon stirring paddles. Stock solutions of metallocene and activator in toluene were added separately to an isohexane reaction solvent containing a specific amount of scavenger, Al(C₈H₁₇)₃. Monomers were then added and the reactions controlled either by time or in some cases by a pre-specified pressure drop. The total volume of monomers, solvent, metallocene, activator and scavenger was maintained at 5.4 ml. The reactions were quenched with CO₂ addition and the volatiles were removed under reduced pressure.

Ethylene-Octene Copolymerizations

The ethylene pressure was maintained at 125 psi and 50 microliters of octene was used per run. The reaction temperature was 110°C. The amount of activator (N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate) was 0.022 micromol and that of the catalyst compound (A, C, D, or E) was 0.020 micromol per experiment. The scavenger used was tri-n-octylaluminum in the amount of 0.45 micromol per experiment. The reaction was quenched after 20 psi ethylene was consumed. Relative activities are reported in Figure 1.

The procedure above was followed for additional ethylene-octene copolymerizations. Catalyst compounds A, C and D were run at 3 different temperatures (65°C, 85°C, and 115°C) using 60 microliters of octene. All other variables were the same as above. Figures 2, 3, and 4 show comparisons of molecular weight and octene comonomer content. Figure 5 shows the relative activities of Catalyst compounds A, C, and D at 65°C, 85°C, and 115°C. The data in the figures are the average of 4 runs each and show that catalyst compound A produces the highest Mn at any temperature but is superior at 115°C.

Ethylene-Propylene Copolymerizations

Catalyst compounds A, C, D, and E were run according to the procedure above with ethylene and propylene at 110°C. Ethylene pressure was 125 psi. Propylene was present at

75, 150, or 250 microliters. Propylene comonomer wt% incorporation Mw and Mn are listed in the table below. Note that Mw's are higher for inventive Catalyst A at same level of propylene incorporation as compared with benchmark Catalyst C.

Ethylene-propylene copolymerization

Propylene content (microliters)	Catalyst Compound	Propylene (wt%)	Mw (g/mol)
250	C	59.9	256,469
250	E	63.4	287,946
250	D	60.1	450,301
250	C	63.3	336,230
250	E	63.4	503,721
250	D	59.8	544,068
250	A	63.4	466,066
150	C	60.8	447,032
150	E	62.2	414,001
150	D	59.6	460,815
150	A	52.6	479,615
150	C	50.9	525,934
150	E	50	559,513
150	D	59.7	538,707
150	A	59.5	584,861
75	C	45.9	792,129
75	E	63.4	535,799
75	D	57	685,823
75	A	62.3	700,078
75	C	42.7	717,907
75	E	59.7	619,737
75	A	59.2	752,474

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Ethylene-Norbornene Copolymerizations

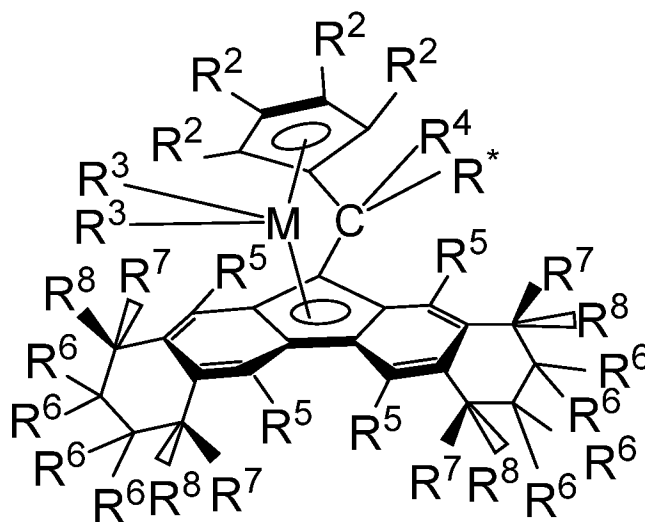
The procedure above was followed for ethylene-norbornene copolymerizations using activator N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate. Norbornene was added to the reactor as a solution of 85 wt% norbornene (NB) in toluene. To each cell, 42
 10 microliters of the NB solution was added. The ethylene pressure was maintained at 125 psi throughout the reaction. The reaction temperature was 110°C. The catalyst compound amount for each cell was 0.02 micromol and the amount of activator (N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate) was 0.022 micromol. Tri-n-octylaluminum was used as a scavenger in the amount of 0.450 micromol. The reaction was quenched when 40 psi of
 15 ethylene was consumed. The data are reported in Figures 6 and 7 (data points in figure 6 are average of at least 5 replicates and at least 6 replicates in Figure 7).

The procedure above was followed for additional ethylene-norbornene copolymerizations using activator N,N-dimethylanilinium tetrakis(pentafluoronaphthyl)borate. Norbornene was added as a solution of 85 wt% norbornene in toluene. To each cell, 42 microliters of the NB solution was added. The
5 ethylene pressure was maintained at 125 psi throughout the reaction. The reaction temperature was 110°C. The catalyst compound amount for each cell was 0.02 micromol and the amount of activator was 0.022 micromol. Tri-n-octylaluminum was used as a scavenger in the amount of 0.450 micromol. The reaction was quenched when 40 psi of ethylene was consumed. The data are reported in figures 8 and 9 (data points in figure 8 are average of at
10 least 4 replicates and at least 6 replicates in Figure 9).

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

Claims:

1. A process to polymerize olefins comprising contacting, in solution phase at a temperature of 60°C to 200°C, ethylene and at least one olefin comonomer with a catalyst system comprising a non-coordinating anion activator and a metallocene catalyst compound
- 5 represented by the formula:



wherein M is Hf or Zr;

each R³ is independently an anionic group;

each R² is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl;

- 10 R⁴ is a hydrocarbyl radical having from 1 to 20 carbon atoms, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof;

R^{*} is phenyl or a substituted phenyl;

each R⁵ is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl;

each R⁶ is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl;

- 15 each R⁷ is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl;

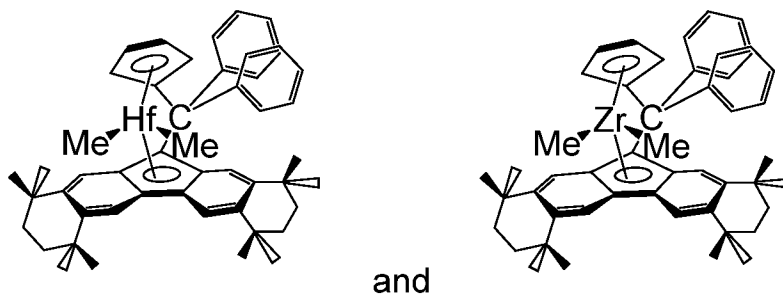
each R⁸ is independently H or a C₁ to C₂₀ hydrocarbyl or C₁ to C₂₀ substituted hydrocarbyl;

where at least one of each adjacent pair of R⁷ and R⁸ is not H; and

2) obtaining ethylene polymer having an Mw greater than 100,000 g/mol, and optionally

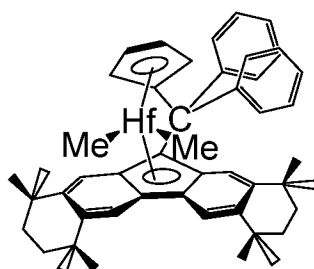
- a) the % comonomer incorporated is X% or more, where $X = (Z - 858,441) / (-26,760)$, where Z
- 20 is the Mn in g/mol of the polymer; and/or
- b) the polymer comprises ethylene, diene, and optional C₃ to C₂₀ olefin comonomer.

2. The process of claim 1, wherein R^4 is a C_1 to C_{20} hydrocarbyl or C_1 to C_{20} substituted hydrocarbyl.
3. The process of claim 1, wherein R^4 is a C_1 to C_{20} alkyl.
- 5
4. The process of claim 1, wherein R^4 and R^* are independently a phenyl or a substituted phenyl.
5. The process of any of claims 1 to 4, wherein R^* is alkoxy substituted phenyl, where
10 the alkyl in the alkoxy is a C_1 to C_{20} alkyl.
6. The process of any of claims 1 to 5, wherein M is Hf.
7. The process any of claims 1 to 6, wherein each R^5 , R^6 , R^7 and R^8 is independently
15 hydrogen, methyl, ethyl, propyl, butyl, pentyl, heptyl, octyl, nonyl, decyl, undecyl, docecyl, or an isomer thereof.
8. The process of claim 1, wherein the catalyst compound comprises one or more of:



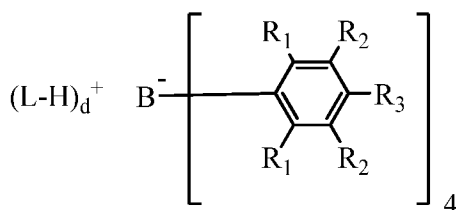
20

9. The process of claim 8, wherein the catalyst compound comprises:



10. The process of any of claims 1 to 9, wherein the activator comprises 0 mol% alumoxane.

11. The process of any of claims 1 to 10, wherein the activator is represented by the
5 formula:



where:

each R_1 is, independently, a halide;

each R_2 is, independently, a halide, a C_6 to C_{20} substituted aromatic hydrocarbyl group or a
10 siloxy group of the formula $-\text{O}-\text{Si}-\text{R}_a$, where R_a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl group;

each R_3 is a halide, C_6 to C_{20} substituted aromatic hydrocarbyl group or a siloxy group of the formula $-\text{O}-\text{Si}-\text{R}_a$, where R_a is a C_1 to C_{20} hydrocarbyl or hydrocarbylsilyl group;

L is an neutral Lewis base; $(\text{L-H})^+$ is a Bronsted acid; d is 1, 2, or 3, or $(\text{L-H})_d^+$ is $(\text{Ar}_3\text{C})_d^+$
15 where Ar is substituted or unsubstituted aryl group;

wherein the anion has a molecular weight of greater than 1020 g/mol; and

wherein at least three of the substituents on the B atom each have a molecular volume of greater than 250 cubic Å.

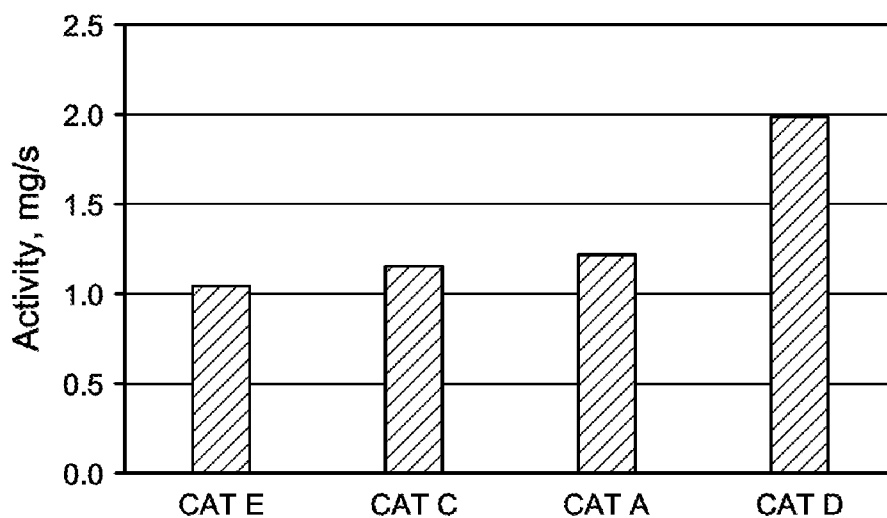
20 12. The process of claim 11, wherein $(\text{L-H})_d^+$ is $(\text{Ar}_3\text{C})_d^+$, where Ar is substituted or unsubstituted aryl group.

13. The process of any of claims 1 to 10, wherein the activator is one or more of:

N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate, triphenylcarbenium
25 tetrakis(pentafluorophenyl)borate, N,N-dimethylanilinium tetrakis(perfluoronaphthyl)borate,
N,N-diethylanilinium tetrakis(perfluoronaphthyl)borate, N,N-dimethyl-(2,4,6-
trimethylanilinium) tetrakis(perfluoronaphthyl)borate, tropillium
tetrakis(perfluoronaphthyl)borate, triphenylcarbenium tetrakis(perfluoronaphthyl)borate,
triphenylphosphonium tetrakis(perfluoronaphthyl)borate, triethylsilylium
30 tetrakis(perfluoronaphthyl)borate, N,N-dimethylanilinium tetrakis(perfluorobiphenyl)borate,

- N,N-diethylanilinium tetrakis(perfluorobiphenyl)borate, N,N-dimethyl-(2,4,6-
 trimethylanilinium) tetrakis(perfluorobiphenyl)borate, triphenylcarbenium
 tetrakis(perfluorobiphenyl)borate, triphenylphosphonium tetrakis(perfluorobiphenyl)borate,
 triethylsilylium tetrakis(perfluorobiphenyl)borate, [4-t-butyl-PhNMe₂H][(C₆F₃(C₆F₅)₂)₄B],
 5 triphenylcarbenium tetrakis-(2,3,4,6-tetrafluorophenyl)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, tropillium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate,
 and triphenylcarbenium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate.
- 10
14. The process of any of claims 1 to 13, wherein the process occurs at a temperature of
 from about 60°C to about 160°C, at a pressure in the range of from about 0.35 MPa to about
 10 MPa, and at a time up to 300 minutes.
- 15
15. The process of any of claims 1 to 14, wherein the comonomer comprises one or more
 of propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene,
 norbornene and isomers thereof.
16. The process of any of claims 1 to 14, wherein the comonomer comprises propylene.
- 20
17. The process of any of claims 1 to 14, wherein the comonomer comprises propylene
 and norbornene.
18. The process of any of claims 1 to 14, wherein the comonomer comprises octene.
- 25
19. The process of any of claims 1 to 14, wherein the comonomer comprises propylene
 and diene.
20. The process of claim 19, where the diene is ethylidene norbornene and/or vinyl
- 30 norbornene.

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Relative activities from ethylene octene copolymerizations at 110°C

FIG. 1

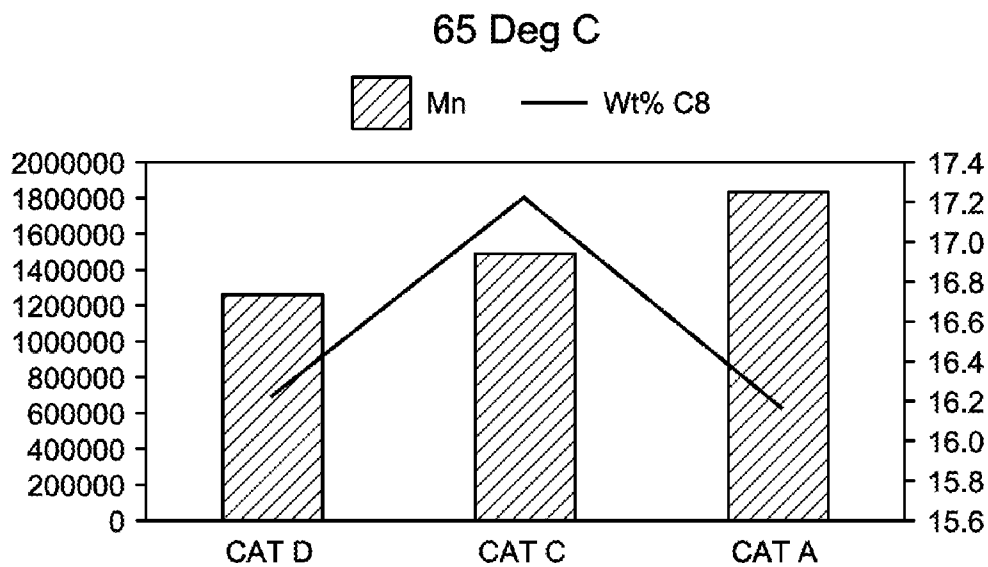


FIG. 2

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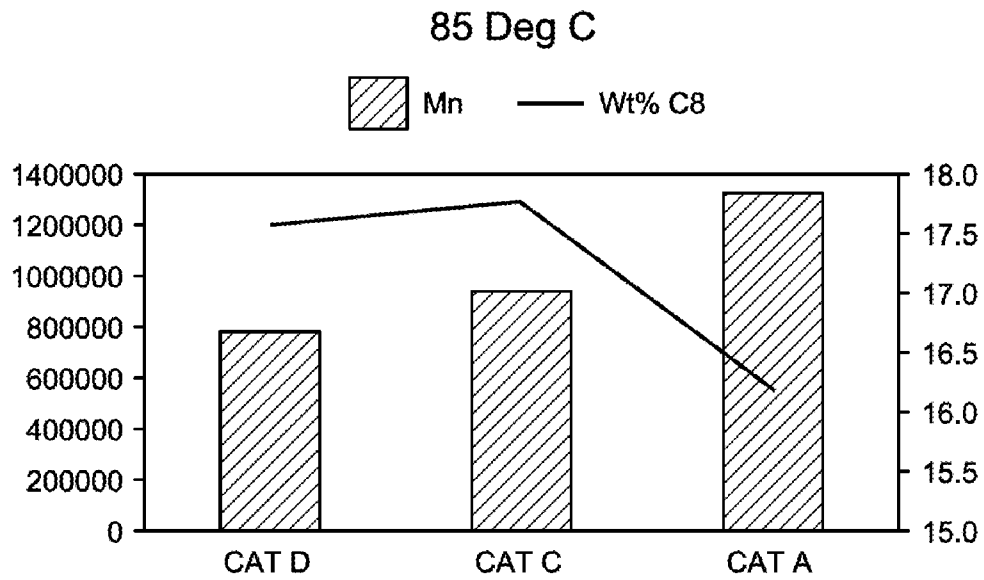


FIG. 3

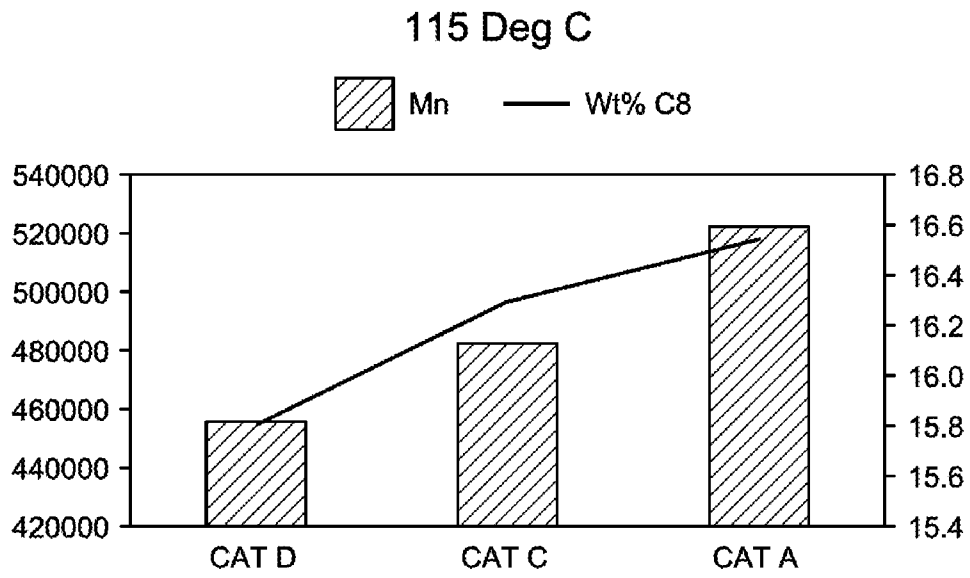


FIG. 4

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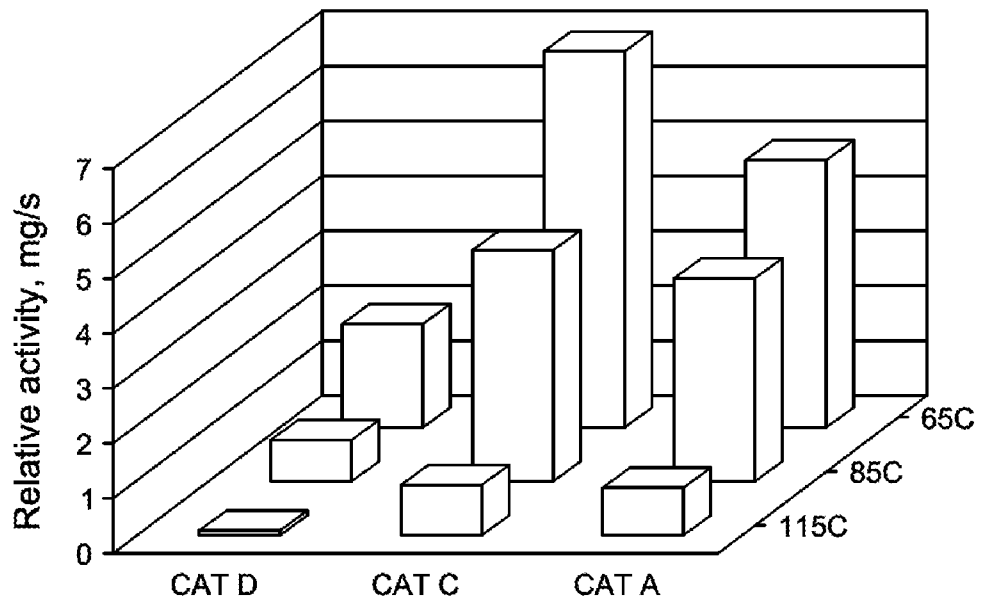


FIG. 5

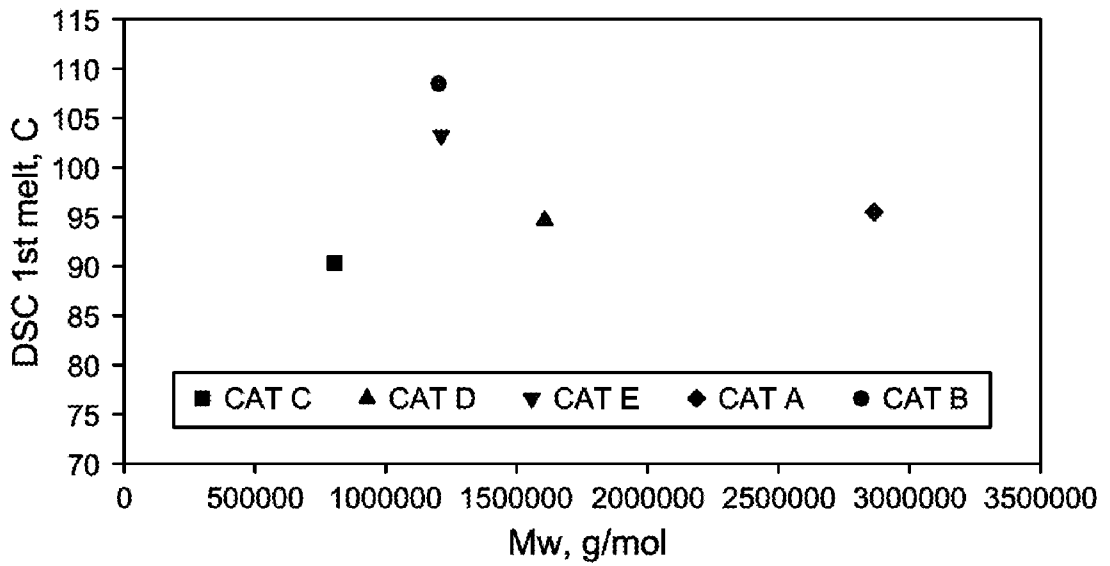


FIG. 6

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C2/NB Copolymerization

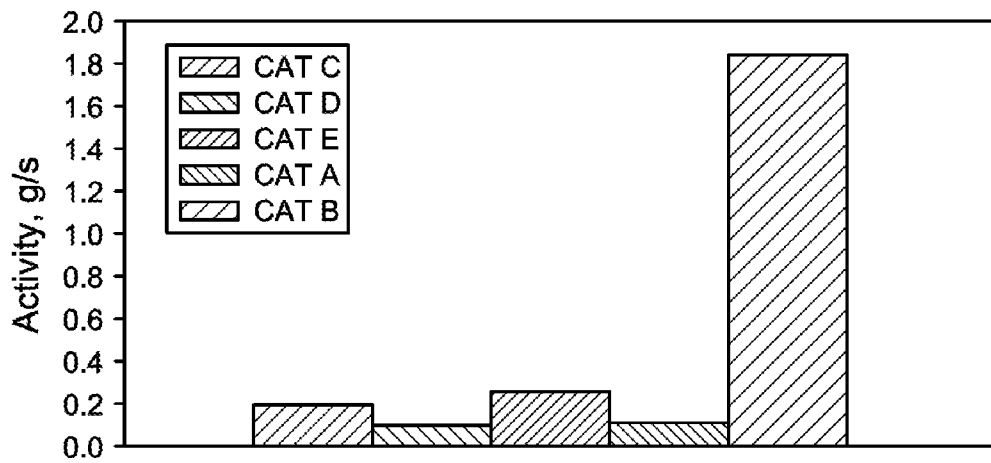


FIG. 7

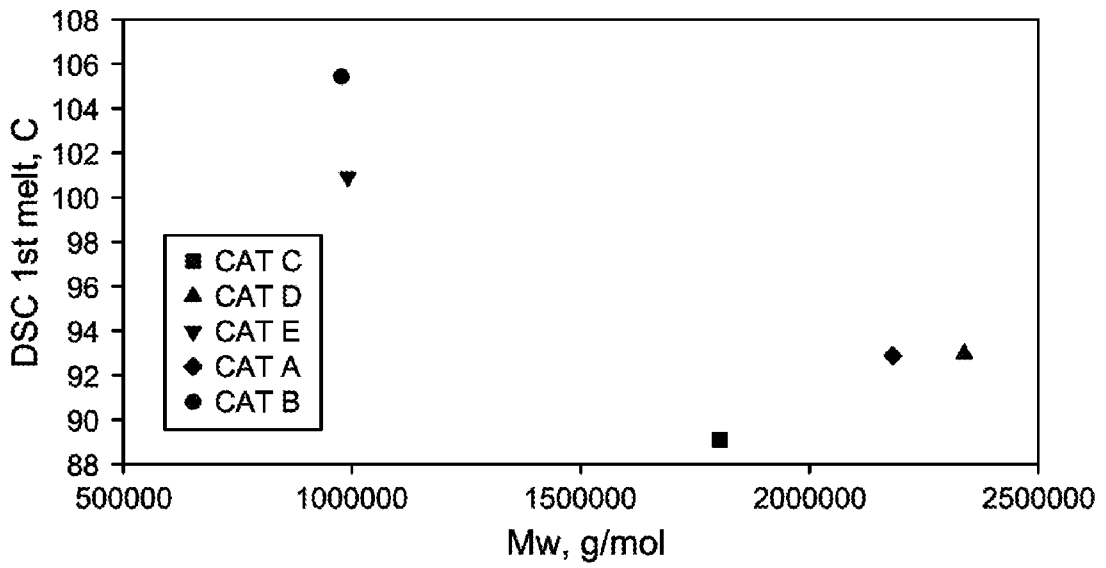


FIG. 8

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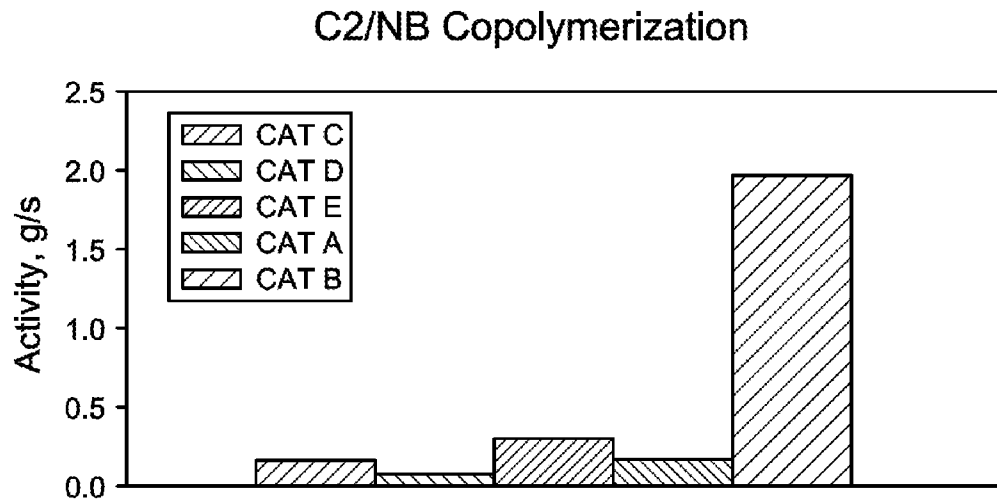


FIG. 9

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A. CLASSIFICATION OF SUBJECT MATTER

C08F 210/16(2006.01)i, C08F 4/6592(2006.01)i, C08F 4/52(2006.01)i, C08F 232/04(2006.01)i, C08F 2/38(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C08F 210/16; C08F 4/6592; B65G 15/32; C08F 210/18; C08F 4/44; C08F 10/00; C08F 4/643; C08F 4/52; C08F 232/04; C08F 2/38

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

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal), STN(Registry, Caplus), Google & keywords: olefin, ethylene, solution polymerization, metallocene catalyst, non-coordinating anion activator, Mw

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 3106481 A1 (MITSUI CHEMICALS, INC.) 21 December 2016 See claims 1-6; and paragraphs [0087]-[0116], [0136]-[0152], [0423], [0431]-[0434].	1-4, 8
Y		5, 9
X	WO 2015-122414 A1 (MITSUI CHEMICALS, INC.) 20 August 2015 See claims 1-8; and paragraphs [0164], [0232], [0237].	1-4
Y		5, 9
Y	US 2006-0270812 A1 (TOHI, YASUSHI et al.) 30 November 2006 See claim 1; and paragraphs [0084], [0085].	1-4, 8, 9
Y	WO 2013-161833 A1 (MITSUI CHEMICALS, INC.) 31 October 2013 See claims 1, 3; and paragraphs [0160], [0184].	1-4, 8, 9
Y	JP 2004-051676 A (MITSUI CHEMICALS INC.) 19 February 2004 See claims 1-8; and paragraphs [0029], [0030], [0117], [0124], [0125].	1-4, 8, 9

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

07 June 2018 (07.06.2018)

Date of mailing of the international search report

08 June 2018 (08.06.2018)

Name and mailing address of the ISA/KR

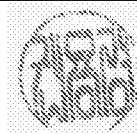
International Application Division
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Facsimile No. +82-42-481-8578

Authorized officer

KWON, Yong Kyong

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Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

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

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.: 12,20
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
Claims 12 and 20 are unclear because they refer to multiple dependent claims which do not comply with PCT Rule 6.4(a).

3. Claims Nos.: 6,7,10,11,13-19
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

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

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

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of any additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

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

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2018/017752

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 3106481 A1	21/12/2016	CN 106062019 A EP 3106481 A4 JP 6259842 B2 KR 10-1819847 B1 KR 10-2016-0114176 A TW 201538540 A US 2016-0355622 A1 WO 2015-122495 A1	26/10/2016 23/08/2017 10/01/2018 17/01/2018 04/10/2016 16/10/2015 08/12/2016 20/08/2015
WO 2015-122414 A1	20/08/2015	CA 2936511 A1 CN 105916888 A CN 105916888 B EP 3106475 A1 EP 3106475 A4 KR 10-2016-0101062 A SG 11201606561 A US 2017-0183432 A1 US 9969827 B2	20/08/2015 31/08/2016 16/03/2018 21/12/2016 20/09/2017 24/08/2016 29/09/2016 29/06/2017 15/05/2018
US 2006-0270812 A1	30/11/2006	CA 2514263 A1 CN 100523010 C CN 1771267 A EP 1731533 A1 EP 1731533 A4 JP 2005-314680 A JP 2011-153315 A JP 5166678 B2 JP 5476334 B2 KR 10-0738851 B1 KR 10-2006-0058670 A KR 10-2007-0061567 A US 7741419 B2 US RE42957 E1 WO 2005-100410 A1	30/09/2005 05/08/2009 10/05/2006 13/12/2006 18/05/2011 10/11/2005 11/08/2011 21/03/2013 23/04/2014 12/07/2007 30/05/2006 13/06/2007 22/06/2010 22/11/2011 27/10/2005
WO 2013-161833 A1	31/10/2013	BR 112014026599 A2 CN 104254546 A CN 104254546 B EP 2842972 A1 EP 2842972 A4 EP 2842972 B1 JP 5795119 B2 KR 10-1584027 B1 KR 10-2014-0138966 A SG 11201406929 A US 2015-0094434 A1 US 9340628 B2	18/07/2017 31/12/2014 02/11/2016 04/03/2015 24/06/2015 30/08/2017 14/10/2015 08/01/2016 04/12/2014 27/11/2014 02/04/2015 17/05/2016
JP 2004-051676 A	19/02/2004	None	