

HALOGEN SUBSTITUTED HETEROCYCLIC HETEROATOM CONTAINING LIGANDS-ALUMOXANE ACTIVATION OF METALLOCENES

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PRIORITY

5 [0001] This invention claims priority to USSN 11/937,043, filed November 8, 2007 and EP Application No. 08154608.7, filed April 16, 2008.

FIELD OF THE INVENTION

10 [0002] The present invention relates to polymerization catalyst activator compounds, to methods of making these activator compounds, to polymerization catalyst systems containing these activator compounds, and to polymerization processes utilizing the same. More specifically, the activators of the invention are the reaction product of a halogen substituted indole and an alkyl alumoxane.

BACKGROUND OF THE INVENTION

15 [0003] Polymerization catalyst compounds are typically combined with an activator (or co-catalyst) to yield compositions having a vacant coordination site that will coordinate, insert, and polymerize olefins. Metallocene polymerization catalysts, for example, are typically activated with alumoxanes which are generally oligomeric compounds containing —Al(R)—O— subunits, where R is an alkyl group. A common alumoxane activator is methylalumoxane (MAO), typically produced by the hydrolysis of trimethylaluminum (TMA). MAO, however, is expensive to utilize because it generally must be added in great excess relative to the metallocene and because of the high cost of TMA. Additionally, MAO tends to be unstable as it precipitates out of solution over time.

25 [0004] As a result, alternative activators for metallocenes and other single-site polymerization catalysts have been discovered in recent years. For example, perfluorophenyl aluminum and borane complexes containing one anionic nitrogen-containing group have recently gained much attention.

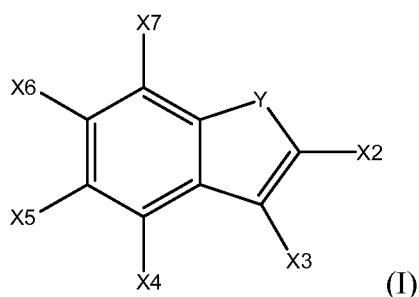
30 [0005] Activator complexes having a Group 13 atom have also been suggested as a viable alternative to the expensive alumoxane activators. For example, U.S. Pat. Nos. 6,147,173 and 6,211,105 disclose a polymerization process and polymerization catalyst where the catalyst includes an activator complex having a Group 13 element and at least one halogenated, nitrogen-containing aromatic group ligand.

[0006] Each of these alternatives, including the formation of alumoxane, requires multi-step, complicated syntheses. There is a need, therefore, to provide a simpler method of cocatalyst synthesis and catalyst activation. There is also a need to improve catalyst economics by providing a highly active co-catalyst, particularly in propylene polymerizations.

[0007] US 6,703,338 discloses heterocyclic compounds (such as indole) combined with alkyl aluminum or alkyl alumoxane and a support material as an activator. Examples 5 and 16 of US 6,703,338 disclose the use of "tetraethylaluminumoxane" and 4,5,6,7-tetrafluoroindole with (1,3-Me,BuCp)₂ZrMe₂ to make polyethylene at, among other things, high Mw's and activities below 1500 gpolymer/gcatalyst•hr. US 6,989,341 discloses certain halogenated indoles combined with alkyl aluminum or alumoxane to increase activity. US 6,930,070 discloses compositions having two or more heterocyclic compounds (such as indole/indolyl) combined with an alkyl aluminum or alumoxane as an activator. US 2007/0055028 discloses a process to make higher Mw isotactic polypropylene using a bis-indenyl Group 4 metallocene compound supported on silica where the silica has been treated with an organoaluminum compound (such as triethylaluminum) and a heterocyclic compound (such as 4,5,6,7-tetrafluoroindole). In contrast, the instant invention provides a method to polymerize propylene with certain bis-indenyl Group 4 metallocene catalysts using an isoalkyl alumoxane at certain ratios that provides, among other things, lower Mw combined with a melting temperature of 140°C or more.

BRIEF SUMMARY OF THE INVENTION

[0008] Embodiments of the invention include an activator and a catalyst system comprising one or more polymerization catalysts (preferably a bridged bisindenyl Group 4 metallocene) and at least one activator. In one aspect, the activator includes heteroatom containing ligands coordinated to an alkyl alumoxane, wherein the activator is a reaction product of one or more alkyl alumoxanes and one or more heterocyclic heteroatom containing compounds, wherein the heterocyclic heteroatom containing ligands are represented by Formula (I):



wherein Y is O, S, PH or, in particular, NH;

wherein each substituent X2, X3, X4, X5, X6 and X7 is independently a hydrogen, chlorine, fluorine, iodine or bromine, provided at least one of X2, X3, X4, X5, X6 and X7 is not hydrogen when Y is NH; and

wherein the ratio of the heterocyclic heteroatom containing ligand to aluminum is between about 0.01:1 and about 10:1 molar equivalents, more particularly between about 0.1:1 to about 5:1, even more particularly between about 0.2:1 to about 5:1, e.g. 0.3:1 to about 4:1 molar equivalents.

10 [0009] Surprisingly, altering of the ratio of heteroatom containing ligand to aluminum provides the ability to control the molecular weight of the polymer produced from a polymerization reaction.

[0010] The catalyst system may be supported or, preferably, non-supported.

[0011] In one aspect, the alumoxane is isobutylalumoxane.

15 [0012] In another aspect, the heterocyclic heteroatom containing ligand is a mono-substituted indole or a di-substituted indole. The substituents are halogens and in particular can be bromine or chlorine. In one aspect, the indole is mono-substituted or di-substituted with bromine and in particular is 5-bromoindole or 5-chloroindole. In another aspect, the halogen is not fluorine.

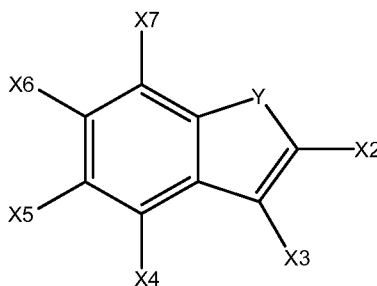
20 [0013] In yet another aspect, the catalyst system provides a method to prepare isotactic low molecular weight polymers, such as isotactic polypropylene with molecular weights, for example, between about 10,000 and about 200,000 g/mol. Unless otherwise stated all molecular weights are weight average molecular weights in units of g/mol.

[0014] In one particular aspect, the catalyst system includes 5-bromoindole in
25 combination with a metallocene, such as $\text{rac-Me}_2\text{Si}-(2\text{-methyl-indenyl})_2\text{Zr}(\text{CH}_3)_2$, $\text{rac-Me}_2\text{Si}-(2\text{-methyl-4- } 3', 5' \text{ di tert-butyl phenyl-indenyl})_2\text{Zr}(\text{CH}_3)_2$ or $\text{rac-Me}_2\text{Si}-(2\text{-methyl-4-phenyl-indenyl})_2\text{Zr}(\text{CH}_3)_2$, and isobutylalumoxane. Polymerization of propylene with this system provides an isotactic polypropylene having a weight average molecular weight range of

between about 10,000 and about 200,000, more particularly between about 15,000 and about 150,000 and more particularly between about 20,000 and about 100,000, more particularly from 10,000 to 50,000 g/mol.

[0015] In another aspect, this invention relates to a process to polymerize propylene comprising:

1) contacting propylene and from 0 to 50 wt% comonomer with a catalyst system comprising: a) a metallocene represented by the formula ACp_2MX_2 where M is Ti, Hf or Zr and M is bound to each Cp group, A is a bridging group connecting the two Cp groups, each Cp is, independently, an indenyl group or a substituted indenyl group, each X is an anionic leaving group, (preferably the metallocene represented by the formula *rac*- ACp_2MX_2 where "rac" indicates that the metallocene is partially or completely racemized, preferably the metallocene is completely racemized, i.e. racemic, and A, Cp, M, and X are as defined above); b) an activator comprising one or more heterocyclic heteroatom containing ligands coordinated to an isoalkyl alumoxane, wherein the activator is a reaction product of a solution of one or more isoalkyl alumoxanes and one or more heterocyclic heteroatom containing compounds, wherein the heterocyclic heteroatom containing ligand is represented by:



wherein Y is NH or N-R where R is a C_1 to C_{12} alkyl group; each of X2 and X3 is hydrogen, halogen or X2 and X3 may form a six membered aromatic ring; X4, X5, X6 and X7 are hydrogen or a halogen; and wherein the ratio of the heterocyclic heteroatom containing ligand to aluminum is between 0.01:1 and 10:1 molar equivalents, (and optionally the ratio of water to aluminum in the alumoxane solution is 0.7:1 or less); and 2) obtaining polymer having at least 50 wt% propylene, an Mw of 5,000 to 200,000 g/mol (preferably 10,000 to 120,000) and a melting point of 140°C or more (preferably 145°C or more, preferably 150°C or more, preferably 155°C or more, preferably 160°C or more, preferably 165°C or more, preferably 160°C or more, preferably 165°C or more, preferably 160°C or more, preferably 165°C or more, as measured by the DSC procedure described in US 7,271,209 column 9, lines 1-30), provided that the melting point is also greater than or equal to $0.000143x(Mw \text{ in g/mol})+133$, and optionally, an Mw/Mn of 4 or less, preferably 2.5 or less, preferably from greater than 1 to 2.

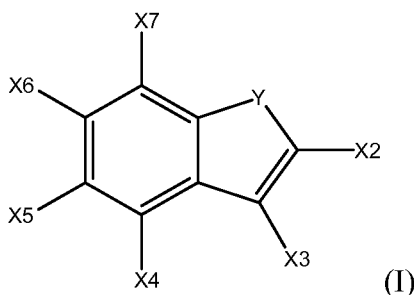
Preferably if the Mw is 40,000 g/mol or more then the melting point is 145°C or more, or alternately if the Mw is 50,000 g/mol or more then the melting point is 150°C or more.

[0016] Alternately other polypropylene produced herein may have an Mn of 1) more than 100,000 g/mol when the activity of the catalyst system is 1500 g polymer/g catalyst-hour or more, or 2) between 100,000 and 200,000 g/mol when the activity of the catalyst system is 400 g polymer/g catalyst-hour or more.

DETAILED DESCRIPTION

[0017] A catalyst system for olefin polymerization is provided. The catalyst system may be supported or non-supported and includes one or more catalysts and at least one activator.

10 The activator is a reaction product of one or more alkyl alumoxanes (preferably isoalkyl alumoxanes) and one or more heterocyclic heteroatom containing compounds having the general formula (I):



wherein Y is O, S, PH or NH;

15 wherein each substituent X2, X3, X4, X5, X6 and X7 is independently a hydrogen, chlorine, fluorine, iodine or bromine, provided at least one of X2, X3, X4, X5, X6 and X7 is not hydrogen when Y is NH.

[0018] Preferably, the ring of the heterocyclic compound includes at least one nitrogen, oxygen, and/or sulfur atom, and more preferably includes at least one nitrogen atom. A non-limiting example of a heterocyclic compound includes indole. In a specific embodiment, the activator includes a mono-halogen substituted indole or a bi-halogen substituted indole. The halogen may be chlorine, iodine, bromine, fluorine, or any combination thereof. Preferably, the halogen is chlorine, bromine, fluorine, or any combination thereof.

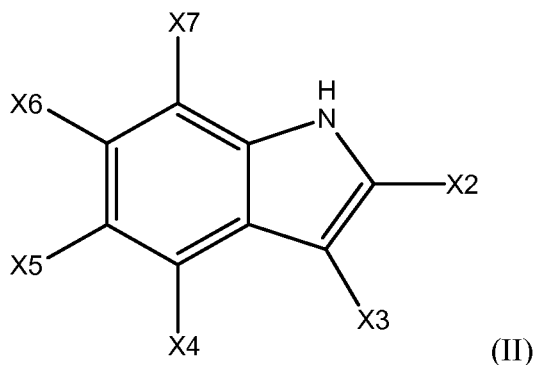
25 [0019] The alkyl alumoxane is preferably a C₁ to C₁₂ alumoxane, such as methyl alumoxane, ethyl alumoxane, tri-isobutyl alumoxane or modified alumoxane. A useful alumoxane is modified methyl alumoxane (MMAO) cocatalyst type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type 3A, covered under patent number US 5,041,584. It may be preferable to use a visually clear

methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from the cloudy solution. Alternately the alumoxane is an isoalkyl alumoxane, preferably the isoalkyl is a C₃ to C₁₂ isoalkyl, preferably isopropyl, isobutyl, isohexyl, isopentyl or isooctyl.

5 [0020] The term “activator” as used herein refers to any compound or component, or combination of compounds or components, capable of enhancing the ability of a catalyst to polymerize olefin monomers to form polyolefins. The term “catalyst” is used interchangeably with the terms “catalyst component” and “catalyst compound”, and includes
10 any compound or component, or combination of compounds or components, that is capable of increasing the rate of a chemical reaction, such as the polymerization or oligomerization of one or more olefins. The term “catalyst system” as used herein includes at least one “catalyst” and at least one “activator”. The “catalyst system” may also include other components, such as a support for example. The catalyst system may include any number of catalysts in any combination as described herein, as well as any activator in any combination
15 as described herein. The use of the term “reaction product” with respect to two or more elements means the result of combining the elements, regardless of whether the elements chemically react.

[0021] As used herein, in reference to Periodic Table “Groups” of Elements, the “new” numbering scheme for the Periodic Table Groups as used as in the CRC HANDBOOK OF
20 CHEMISTRY AND PHYSICS (David R. Lide ed., CRC Press 81st ed. 2000). Me is methyl, Et is ethyl, iPr is isopropyl, Pr is propyl, iBu is isobutyl, Bu is butyl, and tBu is tertiary butyl.

[0022] In a preferred embodiment, the activator includes one or more heterocyclic nitrogen-containing ligands coordinated to an alumoxane. The heterocyclic nitrogen-containing ligand is an indole represented by Formula (II).

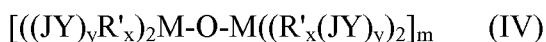


[0023] The indole includes substituents X2, X3, X4, X5, X6, and X7 located about the heterocyclic ring, as shown in Formula (II). Each substituent X2 to X7 is independently selected from hydrogen, halogens, alkyl groups, aryl groups, alkoxide groups, aryloxy groups, cyano groups, nitrous groups, sulfonyl groups, nitrile groups, phosphonyl groups, and alkyl substituted aryl groups wherein each group may be halogenated or partially halogenated. In an alternate embodiment, X2 and X3 are hydrogen and X4, X5, X6 and X7 are hydrogen or halogen, provided that at least one of X4, X5, X6 and X7 is halogen.

[0024] In preferred embodiments, (in either formula I or II), X4 is a halogen and X2, X3, X5, and X7 are each hydrogen. In another aspect, X5 is a halogen and X2, X4, X6, and X7 are each hydrogen. In yet another aspect, X6 is a halogen and X2, X5 and X7 are each hydrogen. In still yet another aspect, both X5 and X6 are a halogen. The halogen may be chlorine, iodine, bromine, fluorine, or any combination thereof. Preferably, the halogen is chlorine, bromine, fluorine, or any combination thereof.

[0025] Useful alumoxanes are oligomeric compounds containing —Al(R)—O— or —Al(R)₂—O— subunits, where R is an alkyl group, typically a C₁ to C₁₂ alkyl group. Examples of useful alumoxanes include methylalumoxane (MAO), modified methylalumoxane (MMAO), ethylalumoxane, triethylalumoxane, triisobutylalumoxane, tetraethyldialumoxane and di-isobutylalumoxane. There are a variety of methods for preparing alumoxane and modified alumoxanes, such as the methods described in U.S. Pat. No. 4,542,199 and Chen and Marks, 100 Chem. Rev. 1391 (2000).

[0026] Preferably, the alumoxane and the halogen substituted heterocyclic compounds of Formula (I) yield an activator represented by the following Formulas (IV) or (V):



or



M is aluminum;

(JY) represents the heterocyclic group of Formula (I) or Formula (II) and is associated with M, and preferably coordinated to M;

z is a number from 1 to 1000 preferably 1 to 100, more preferably 5 to 50, and even more preferably 5 to 25;

m is a number from 1 to 10, preferably 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10;

x is 0, 1, 2, 3 or 4;

y is 1, 2, 3 or 4;

k is 0, 1, 2, 3 or 4;

q is 1, 2, 3 or 4;

provided that $x+y$ = the valence of M-1 and $k+q$ = valence of M-2, where the valence of M is preferably 2, 3, 4, or 5; and

each R' is, independently, a substituent group bonded to M. Non-limiting examples of substituent R' groups include hydrogen, linear or branched alkyl radicals, linear or branched alkenyl radicals, linear or branched alkynyl radicals, cycloalkyl radicals, aryl radicals, acyl radicals, aroyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxycarbonyl radicals, carbamoyl radicals, alkyl radicals, dialkyl radicals, carbamoyl radicals, acyloxy radicals, acylamino radicals, arylamino radicals, straight alkylene radicals, branched alkylene radicals, cyclic alkylene radicals, or any combination thereof.

[0027] More specific embodiments of R' include a methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl or phenyl group, including all their isomers, for example tertiary butyl, isopropyl, and the like. Other embodiments of R' include hydrocarbyl radicals such as fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl, chlorobenzyl; hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyldiethylsilyl and the like; halocarbyl-substituted organometalloid radicals including tris(trifluoromethyl)silyl, methyl-bis(difluoromethyl)silyl, bromoethyldimethylgermyl and the like; disubstituted boron radicals including dimethylboron for example; disubstituted Group 15 radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine; and Group 16 radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide.

[0028] Further, each R' may include carbon, silicon, boron, aluminum, nitrogen, phosphorous, oxygen, tin, sulfur, or germanium atoms and the like. Still further, each R' may include olefins such as olefinically unsaturated substituents including vinyl-terminated ligands, such as but-3-enyl, prop-2-enyl, hex-5-enyl and the like, for example. Also, at least two R' groups, preferably two adjacent R' groups, may be joined to form a ring structure having from 3 to 30 atoms selected from carbon, nitrogen, oxygen, phosphorous, silicon, germanium, aluminum, boron, or a combination thereof. Also, a substituent group R' such as 1-butanyl may form a carbon sigma bond to the metal M. In a preferred embodiment each R'

is an isoalkyl, preferably the isoalkyl is a C₃ to C₁₂ isoalkyl, preferably isopropyl, isobutyl, isohexyl, isopentyl or isooctyl.

[0029] The ratio of the heterocyclic heteroatom containing ligand to aluminum is preferably between about 0.01 and about 10: 1 molar equivalents, more particularly between about 0.1 to about 5:1, even more particularly between about 0.2 to about 5:1, e.g. 0.3 to about 4:1 molar equivalents. Alternately, the ratio of the heterocyclic heteroatom containing ligand to aluminum is preferably between about 0.01 and about 0.4: 1 molar equivalents, more particularly between about 0.1 to about 0.3:1 molar equivalents.

Catalyst Compositions

10 [0030] The activators described above may be utilized in conjunction with any suitable polymerization catalyst to form an active polymerization catalyst system. Typically, the mole ratio of the metal of the activator to the metal of the catalyst composition is in the range of between 0.3:1 to 10,000:1, preferably 100:1 to 5000:1, and most preferably 500:1 to 2000:1. Exemplary polymerization catalysts include metallocene catalyst compositions, Group 15-
15 containing metal catalyst compositions, and phenoxide transition metal catalyst compositions, which are discussed in more detail below.

Metallocene Catalyst Compositions

[0031] Metallocene catalyst compounds are generally described throughout in, for example, 1 & 2 METALLOCENE-BASED POLYOLEFINS (John Scheirs & W. Kaminsky
20 eds., John Wiley & Sons, Ltd. 2000); G. G. Hlatky in 181 COORDINATION CHEM. REV. 243 296 (1999) and in particular, for use in the synthesis of polyethylene in 1 METALLOCENE-BASED POLYOLEFINS 261 377 (2000). The metallocene catalyst compounds as described herein include “half sandwich” and “full sandwich” compounds having one or more Cp ligands (cyclopentadienyl and ligands isolobal to cyclopentadienyl)
25 bound to at least one Group 3 to Group 12 metal atom (preferably a group 4 atom, preferably Hf, Ti or Zr), and one or more leaving group(s) bound to the at least one metal atom. Hereinafter, these compounds will be referred to as “metallocenes” or “metallocene catalyst components”. The metallocene catalyst component may be supported on a support material, and may be supported with or without another catalyst component.

30 [0032] The Cp ligands are one or more rings or ring system(s), at least a portion of which includes π -bonded systems, such as cycloalkadienyl ligands and heterocyclic analogues. The ring(s) or ring system(s) typically comprise atoms selected from the group consisting of

Groups 13 to 16 atoms, and more particularly, the atoms that make up the Cp ligands are selected from the group consisting of carbon, nitrogen, oxygen, silicon, sulfur, phosphorous, germanium, boron and aluminum and combinations thereof, wherein carbon makes up at least 50% of the ring members. Even more particularly, the Cp ligand(s) are selected from the group consisting of substituted and unsubstituted cyclopentadienyl ligands and ligands isolobal to cyclopentadienyl, non-limiting examples of which include cyclopentadienyl, indenyl, fluorenyl and other structures. Further non-limiting examples of such ligands include cyclopentadienyl, cyclopentaphenanthrenyl, indenyl, benzindenyl, fluorenyl, octahydrofluorenyl, cyclooctatetraenyl, cyclopentacyclododecene, phenanthrindenyl, 3,4-benzofluorenyl, 9-phenylfluorenyl, 8-H-cyclopent[a]acenaphthylenyl, 7H-dibenzofluorenyl, indeno[1,2-9]anthrene, thiophenoindenyl, thiophenofluorenyl, hydrogenated versions thereof (e.g., 4,5,6,7-tetrahydroindenyl, or "H₄Ind"), substituted versions thereof (as described in more detail below), and heterocyclic versions thereof. Preferred Cp ligands include substituted and unsubstituted cyclopentadienyl, indenyl and fluorenyl groups. (By substituted is meant that at least one hydrogen on the cyclopentadienyl, indenyl or fluorenyl group is replaced with a non-hydrogen atom containing group, preferably a hydrocarbyl group (such as methyl, ethyl, propyl, butyl, isobutyl, hexyl, octyl, and the like) or a heteroatom containing group (preferred heteroatoms include N, P, Br, Cl, and the like).

[0033] The metal atom "M" of the metallocene catalyst compound, as described throughout the specification and claims, may be selected from the group consisting of Groups 3 through 12 atoms and lanthanide Group atoms in one embodiment; and selected from the group consisting of Groups 3 through 10 atoms in a more particular embodiment, and selected from the group consisting of Sc, Ti, Zr, Hf, V, Nb, Ta, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, and Ni in yet a more particular embodiment; and selected from the group consisting of Groups 4, 5 and 6 atoms in yet a more particular embodiment, and a Ti, Zr, Hf atoms in yet a more particular embodiment, and Zr in yet a more particular embodiment. The oxidation state of the metal atom "M" may range from 0 to +7 in one embodiment; and in a more particular embodiment, is +1, +2, +3, +4 or +5; and in yet a more particular embodiment is +2, +3 or +4. The groups bound to the metal atom "M" are such that the compounds described below in the formulas and structures are neutral, unless otherwise indicated. The Cp ligand(s) form at least one chemical bond with the metal atom M to form the "metallocene

catalyst compound". The Cp ligands are distinct from the leaving groups bound to the catalyst compound in that they are not highly susceptible to substitution/abstraction reactions.

[0034] In one aspect, the one or more metallocene catalyst components are represented formula (VI):



wherein M is as described above; each X is chemically bonded to M; each Cp group is chemically bonded to M; and n is 0 or an integer from 1 to 4, and either 1 or 2 in a particular embodiment.

[0035] The ligands represented by Cp^{A} and Cp^{B} in formula (VI) may be the same or different cyclopentadienyl ligands or ligands isolobal to cyclopentadienyl, either or both of which may contain heteroatoms and either or both of which may be substituted by a group R. In one embodiment, Cp^{A} and Cp^{B} are independently selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, and substituted derivatives of each.

[0036] Independently, each Cp^{A} and Cp^{B} of formula (VI) may be unsubstituted or substituted with any one or combination of substituent groups R. Non-limiting examples of substituent groups R as used in structure (VI) include hydrogen radicals, alkyls, alkenyls, alkynyls, cycloalkyls, aryls, acyls, aroyls, alkoxys, aryloxys, alkylthiols, dialkylamines, alkylamidols, alkoxycarbonyls, aryloxycarbonyls, carbamoyls, alkyl- and dialkyl-carbamoyls, acyloxys, acylaminos, arylaminos, and combinations thereof.

[0037] More particular non-limiting examples of alkyl substituents R associated with formula (VI) through (V) include methyl, ethyl, propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl, phenyl, methylphenyl, and tert-butylphenyl groups and the like, including all their isomers, for example tertiary-butyl, isopropyl, and the like. Other possible radicals include substituted alkyls and aryls such as, for example, fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl, chlorobenzyl and hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyldiethylsilyl and the like; and halocarbyl-substituted organometalloid radicals including tris(trifluoromethyl)silyl, methylbis(difluoromethyl)silyl, bromomethyldimethylgermyl and the like; and disubstituted boron radicals including dimethylboron for example; and disubstituted Group 15 radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, Group 16 radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide. Other substituents R include olefins such as but not limited to olefinically

unsaturated substituents including vinyl-terminated ligands, for example 3-butenyl, 2-propenyl, 5-hexenyl and the like. In one embodiment, at least two R groups, two adjacent R groups in one embodiment, are joined to form a ring structure having from 3 to 30 atoms selected from the group consisting of carbon, nitrogen, oxygen, phosphorous, silicon,
 5 germanium, aluminum, boron and combinations thereof. Also, a substituent group R group such as 1-butenyl may form a bonding association to the element M.

[0038] Each X in the formula (VI) above and for the formulas/structures (II) through (V) below is independently selected from the group consisting of: any leaving group in one embodiment; halogen ions, hydrides, C₁ to C₁₂ alkyls, C₂ to C₁₂ alkenyls, C₆ to C₁₂ aryls, C₇
 10 to C₂₀ alkylaryls, C₁ to C₁₂ alkoxys, C₆ to C₁₆ aryloxys, C₇ to C₁₈ alkylaryloxys, C₁ to C₁₂ fluoroalkyls, C₆ to C₁₂ fluoroaryls, and C₁ to C₁₂ heteroatom-containing hydrocarbons and substituted derivatives thereof in a more particular embodiment; hydride, halogen ions, C₁ to C₆ alkyls, C₂ to C₆ alkenyls, C₇ to C₁₈ alkylaryls, C₁ to C₆ alkoxys, C₆ to C₁₄ aryloxys, C₇ to C₁₆ alkylaryloxys, C₁ to C₆ alkylcarboxylates, C₁ to C₆ fluorinated alkylcarboxylates, C₆ to
 15 C₁₂ arylcarboxylates, C₇ to C₁₈ alkylarylcboxylates, C₁ to C₆ fluoroalkyls, C₂ to C₆ fluoroalkenyls, and C₇ to C₁₈ fluoroalkylaryls in yet a more particular embodiment; hydride, chloride, fluoride, methyl, phenyl, phenoxy, benzoxy, tosyl, fluoromethyls and fluorophenyls in yet a more particular embodiment; C₁ to C₁₂ alkyls, C₂ to C₁₂ alkenyls, C₆ to C₁₂ aryls, C₇ to C₂₀ alkylaryls, substituted C₁ to C₁₂ alkyls, substituted C₆ to C₁₂ aryls, substituted C₇ to C₂₀
 20 alkylaryls and C₁ to C₁₂ heteroatom-containing alkyls, C₁ to C₁₂ heteroatom-containing aryls and C₁ to C₁₂ heteroatom-containing alkylaryls in yet a more particular embodiment; chloride, fluoride, C₁ to C₆ alkyls, C₂ to C₆ alkenyls, C₇ to C₁₈ alkylaryls, halogenated C₁ to C₆ alkyls, halogenated C₂ to C₆ alkenyls, and halogenated C₇ to C₁₈ alkylaryls in yet a more particular embodiment; fluoride, methyl, ethyl, propyl, phenyl, methylphenyl,
 25 dimethylphenyl, trimethylphenyl, fluoromethyls (mono-, di- and trifluoromethyls) and fluorophenyls (mono-, di-, tri-, tetra- and pentafluorophenyls) in yet a more particular embodiment.

[0039] Other non-limiting examples of X groups in formula (VI) include amines, phosphines, ethers, carboxylates, dienes, hydrocarbon radicals having from 1 to 20 carbon
 30 atoms, fluorinated hydrocarbon radicals (e.g., —C₆F₅ (pentafluorophenyl)), fluorinated alkylcarboxylates (e.g., CF₃C(O)O⁻), hydrides and halogen ions and combinations thereof. Other examples of X ligands include alkyl groups such as cyclobutyl, cyclohexyl, methyl,

heptyl, tolyl, trifluoromethyl, tetramethylene, pentamethylene, methyldiene, methoxy, ethoxy, propoxy, phenoxy, bis(N-methylanilide), dimethylamide, dimethylphosphide radicals and the like. In one embodiment, two or more X's form a part of a fused ring or ring system.

- 5 [0040] In another aspect, the metallocene catalyst component includes those of formula (VI) where Cp^{A} and Cp^{B} are bridged to each other by at least one bridging group, (A), such that the structure is represented by formula (VII):



- 10 [0041] These bridged compounds represented by formula (VII) are known as "bridged metallocenes". Cp^{A} , Cp^{B} , M, X and n in structure (VII) are as defined above for formula (VI); and wherein each Cp ligand is chemically bonded to M, and (A) is chemically bonded to each Cp. Non-limiting examples of bridging group (A) include divalent hydrocarbon groups containing at least one Group 13 to 16 atom, such as but not limited to at least one of a carbon, oxygen, nitrogen, silicon, aluminum, boron, germanium and tin atom and
15 combinations thereof; wherein the heteroatom may also be C_1 to C_{12} alkyl or aryl substituted to satisfy neutral valency. The bridging group (A) may also contain substituent groups R as defined above (for formula (VI)) including halogen radicals and iron. More particular non-limiting examples of bridging group (A) are represented by C_1 to C_6 alkenes, substituted C_1 to C_6 alkenes, oxygen, sulfur, $\text{R}'_2\text{C}=\text{}$, $\text{R}'_2\text{Si}=\text{}$, $\text{—Si(R}')}_2\text{Si(R}')_2\text{—}$, $\text{R}'_2\text{Ge}=\text{}$, $\text{R}'\text{P}=\text{}$ (wherein
20 "—" represents two chemical bonds), where R' is independently selected from the group consisting of hydride, hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, hydrocarbyl-substituted organometalloid, halocarbyl-substituted organometalloid, disubstituted boron, disubstituted Group 15 atoms, substituted Group 16 atoms, and halogen radical; and wherein two or more R' may be joined to form a ring or ring system. In one
25 embodiment, the bridged metallocene catalyst component of formula (VII) has two or more bridging groups (A).

- [0042] Other non-limiting examples of bridging group (A) include methylene, ethylene, ethylidene, propylidene, isopropylidene, diphenylmethylene, 1,2-dimethylethylene, 1,2-diphenylethylene, 1,1,2,2-tetramethylethylene, dimethylsilyl, diethylsilyl, methyl-ethylsilyl,
30 trifluoromethylbutylsilyl, bis(trifluoromethyl)silyl, di(n-butyl)silyl, di(n-propyl)silyl, di(i-propyl)silyl, di(n-hexyl)silyl, dicyclohexylsilyl, diphenylsilyl, cyclohexylphenylsilyl, t-butylcyclohexylsilyl, di(t-butylphenyl)silyl, di(p-tolyl)silyl and the corresponding moieties

wherein the Si atom is replaced by a Ge or a C atom; dimethylsilyl, diethylsilyl, dimethylgermyl and diethylgermyl.

[0043] In another embodiment, bridging group (A) may also be cyclic, comprising, for example 4 to 10, 5 to 7 ring members in a more particular embodiment. The ring members
5 may be selected from the elements mentioned above, from one or more of B, C, Si, Ge, N and O in a particular embodiment. Non-limiting examples of ring structures which may be present as or part of the bridging moiety are cyclobutylidene, cyclopentylidene, cyclohexylidene, cycloheptylidene, cyclooctylidene and the corresponding rings where one or two carbon atoms are replaced by at least one of Si, Ge, N and O, in particular, Si and Ge. The bonding
10 arrangement between the ring and the Cp groups may be either cis-, trans-, or a combination.

[0044] The cyclic bridging groups (A) may be saturated or unsaturated and/or carry one or more substituents and/or be fused to one or more other ring structures. If present, the one or more substituents are selected from the group consisting of hydrocarbyl (e.g., alkyl such as methyl) and halogen (e.g., F, Cl) in one embodiment. The one or more Cp groups which the
15 above cyclic bridging moieties may optionally be fused to may be saturated or unsaturated and are selected from the group consisting of those having 4 to 10, more particularly 5, 6 or 7 ring members (selected from the group consisting of C, N, O and S in a particular embodiment) such as, for example, cyclopentyl, cyclohexyl and phenyl. Moreover, these ring structures may themselves be fused such as, for example, in the case of a naphthyl group.
20 Moreover, these (optionally fused) ring structures may carry one or more substituents. Illustrative, non-limiting examples of these substituents are hydrocarbyl (particularly alkyl) groups and halogen atoms.

[0045] The ligands Cp^{A} and Cp^{B} of formulae (VI) and (VII) are different from each other in one embodiment, and the same in another embodiment.

[0046] In another embodiment, the metallocene catalyst component is a bridged bisindenyl Group 4 metallocene represented by the formula: ACp_2MX_2 where M is a Group 4 metal, (preferably Ti, Hf or Zr, preferably Hf or Zr); A is a bridging group connecting the two Cp groups; each Cp is, independently, a substituted indenyl group or an indenyl group bound to M; each X is an anionic leaving group (preferably the metallocene is represented by the
25 formula *rac*- ACp_2MX_2 where "*rac*" indicates that the metallocene is partially or completely racemized, preferably the metallocene is completely racemized, i.e. racemic, and A, Cp, M, and X are as defined above). In some embodiments, A is as described for Formula (VII). In
30

other embodiments, A is represented by the formula $-\text{CR}^{**}_2-(\text{CR}^{**}_2)_n-$ or $-\text{SiR}^{**}_2-$, where n is 0, 1 or 2, and each R^{**} is, independently, H or a C_1 to C_{12} alkyl group, and any two R^{**} may form a cyclic group. Preferably R^{**} is H, methyl, or ethyl. In another embodiment, A is a dialkylsilyl group (preferably the alkyl is methyl, ethyl, propyl or butyl, preferably A is dimethylsilyl). Preferably each X is independently a C_1 to C_{20} alkyl group or a halogen, preferably methyl, ethyl, propyl, butyl, chlorine or bromine. By "substituted indenyl group" is meant that at least one hydrogen on the indenyl group is replaced with a hydrocarbyl group (such as methyl, ethyl, propyl, butyl, hexyl, octyl, or isomers thereof) or a heteroatom containing group (preferred heteroatoms include N, P, Br, Cl, and the like). The bridging group A is not counted as a substitution. Further, in a preferred embodiment, the substituted indenyl group is not a fluorenyl group. In a preferred embodiment, the indenyl group is substituted at the 2 or at the 2 and 4 positions with a hydrocarbyl group (numbering begins at the bridge). Preferred hydrocarbyl groups include C_1 to C_{30} linear, cyclic, or branched, saturated or unsaturated hydrocarbyl groups, such as methyl, ethyl, propyl, butyl, phenyl, benzyl, substituted phenyl, substituted benzyl, and the like. In a preferred embodiment the indenyl group is substituted with from 1, 2, 3, 4, 5, or 6 hydrocarbyl or substituted hydrocarbyl group(s) (preferably C_1 to C_{20} alkyl group(s)).

[0047] In a preferred embodiment the activity of the catalyst system is 1500 g polymer/g catalyst-hour or more, preferably 1700 g polymer/g catalyst-hour or more, preferably 1900 g polymer/g catalyst-hour or more, preferably 2500 g polymer/g catalyst-hour or more.

[0048] In yet another aspect, the metallocene catalyst components include mono-ligand metallocene compounds (e.g., mono cyclopentadienyl catalyst components) such as described in WO 93/08221 for example. In this embodiment, the at least one metallocene catalyst component is a bridged "half-sandwich" metallocene represented by the formula (VIII):



wherein Cp^{A} is defined above and is bound to M; (A) is a bridging group bonded to Q and Cp^{A} ; and wherein an atom from the Q group is bonded to M; and n is 0 or an integer from 1 to 3; 1 or 2 in a particular embodiment. In formula (VIII) above, Cp^{A} , (A) and Q may form a fused ring system. The X groups and n of formula (VIII) are as defined above in formula (VI) and (VII). In one embodiment, Cp^{A} is selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, substituted versions thereof, and combinations thereof.

[0049] In formula (VIII), Q is a heteroatom-containing ligand in which the bonding atom (the atom that is bonded with the metal M) is selected from the group consisting of Group 15 atoms and Group 16 atoms in one embodiment, and selected from the group consisting of nitrogen, phosphorus, oxygen or sulfur atom in a more particular embodiment, and nitrogen and oxygen in yet a more particular embodiment. Non-limiting examples of Q groups include alkylamines, arylamines, mercapto compounds, ethoxy compounds, carboxylates (e.g., pivalate), carbamates, azenyl, azulene, pentalene, phosphoyl, phosphinimine, pyrrolyl, pyrolyl, carbazoyl, borabenzene other compounds comprising Group 15 and Group 16 atoms capable of bonding with M.

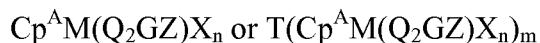
[0050] In yet another aspect, the at least one metallocene catalyst component is an unbridged "half sandwich" metallocene represented by the formula (IX):



wherein Cp^{A} is defined as for the Cp groups in (VI) and is a ligand that is bonded to M; each Q is independently bonded to M; Q is also bound to Cp^{A} in one embodiment; X is a leaving group as described above in (VI); n ranges from 0 to 3, and is 1 or 2 in one embodiment; q ranges from 0 to 3, and is 1 or 2 in one embodiment. In one embodiment, Cp^{A} is selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, substituted version thereof, and combinations thereof.

[0051] In formula (IX), Q is selected from the group consisting of ROO^- , $\text{RO}-$, $\text{R(O)}-$, $-\text{NR}-$, $-\text{CR}_2-$, $-\text{S}-$, $-\text{NR}_2$, $-\text{CR}_3$, $-\text{SR}$, $-\text{SiR}_3$, $-\text{PR}_2$, $-\text{H}$, and substituted and unsubstituted aryl groups, wherein R is selected from the group consisting of C_1 to C_6 alkyls, C_6 to C_{12} aryls, C_1 to C_6 alkylamines, C_6 to C_{12} alkylarylamines, C_1 to C_6 alkoxys, C_6 to C_{12} aryloxys, and the like. Non-limiting examples of Q include C_1 to C_{12} carbamates, C_1 to C_{12} carboxylates (e.g., pivalate), C_2 to C_{20} allyls, and C_2 to C_{20} heteroallyl moieties.

[0052] Described another way, the "half sandwich" metallocenes above can be described as in formula (X), such as described in, for example, U.S. Pat. No. 6,069,213:



wherein M, Cp^{A} , X and n are as defined above;

Q_2GZ forms a polydentate ligand unit (e.g., pivalate), wherein at least one of the Q groups form a bond with M, and is defined such that each Q is independently selected from the group consisting of $-\text{O}-$, $-\text{NR}-$, $-\text{CR}_2-$ and $-\text{S}-$; G is either carbon or silicon; and Z is

selected from the group consisting of R, —OR, —NR₂, —CR₃, —SR, —SiR₃, —PR₂, and hydride, providing that when Q is —NR—, then Z is selected from the group consisting of —OR, —NR₂, —SR, —SiR₃, —PR₂; and provided that neutral valency for Q is satisfied by Z; and wherein each R is independently selected from the group consisting of C₁ to C₁₀ heteroatom containing groups, C₁ to C₁₀ alkyls, C₆ to C₁₂ aryls, C₆ to C₁₂ alkylaryls, C₁ to C₁₀ alkoxy, and C₆ to C₁₂ aryloxy;

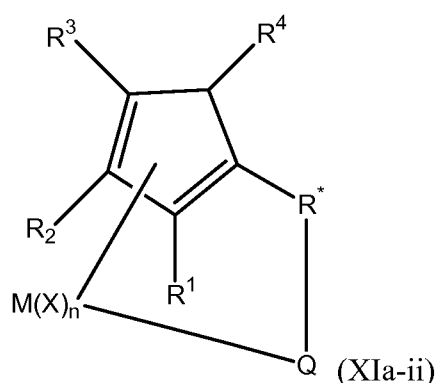
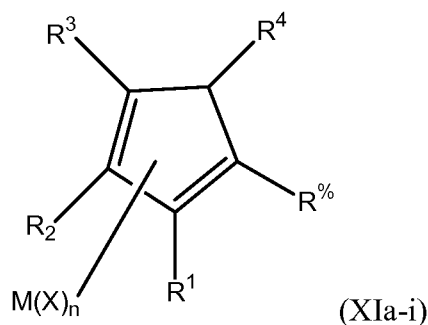
n is 1 or 2 in a particular embodiment; and

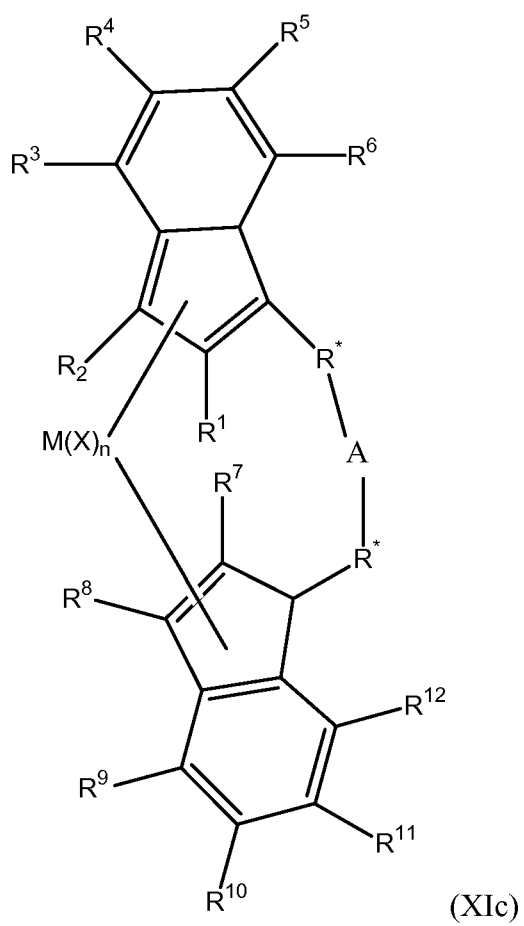
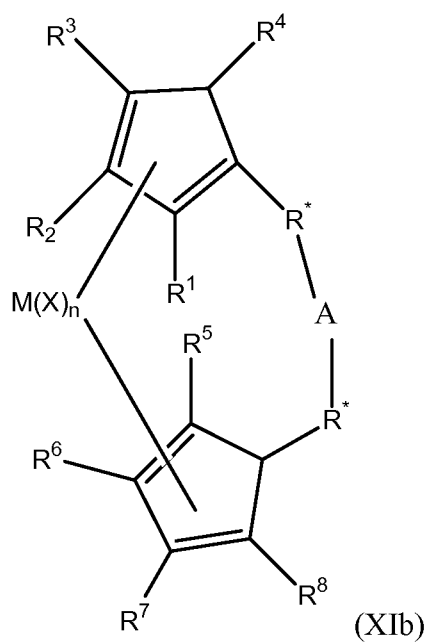
T is a bridging group selected from the group consisting of C₁ to C₁₀ alkenes, C₆ to C₁₂ aryls and C₁ to C₁₀ heteroatom containing groups, and C₆ to C₁₂ heterocyclic groups;

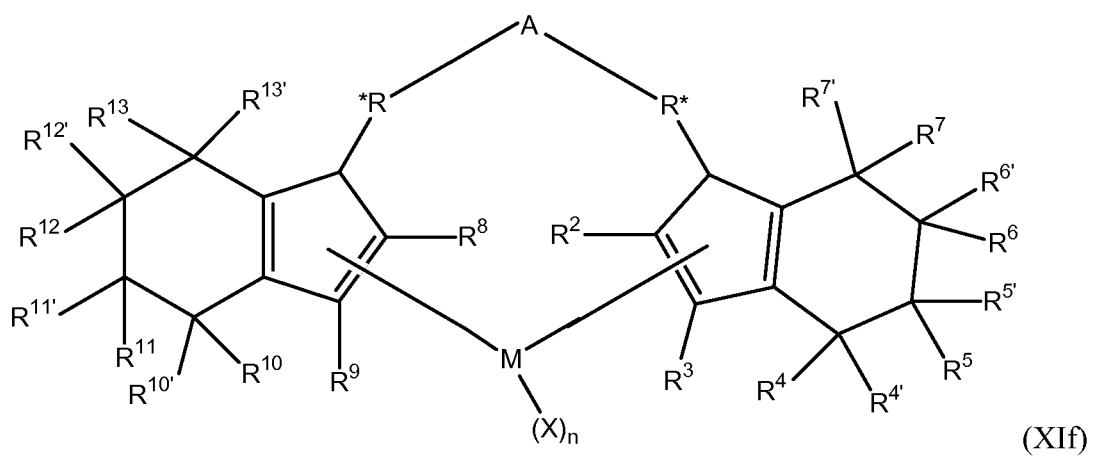
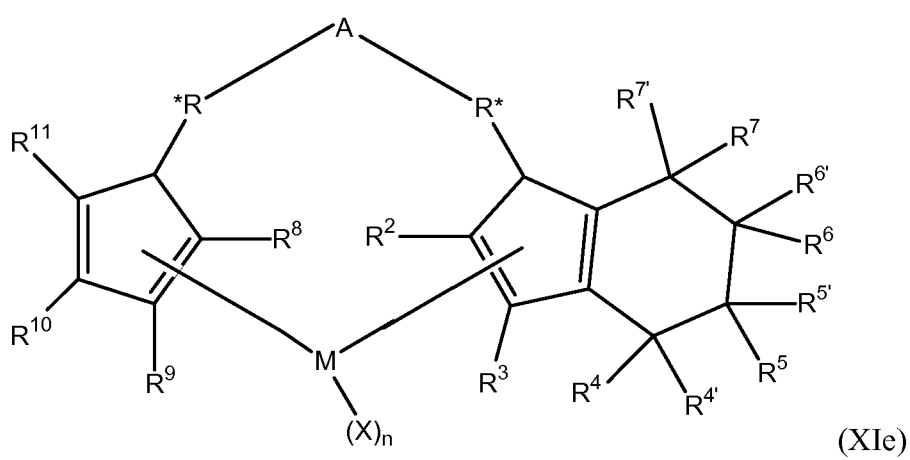
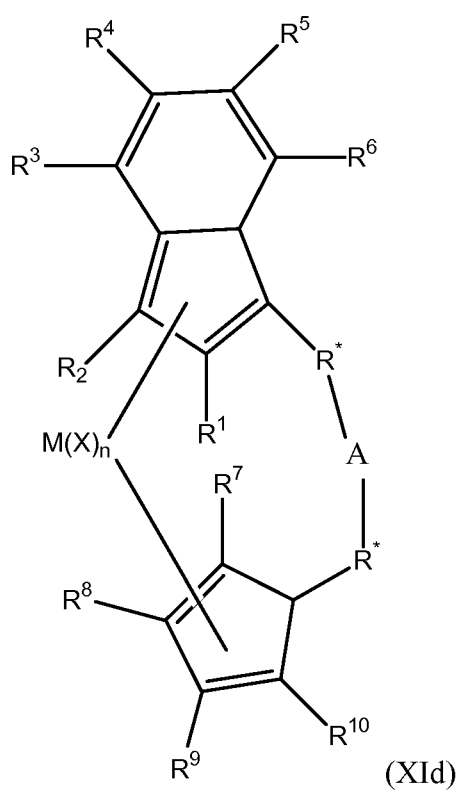
wherein each T group bridges adjacent “Cp^AM(Q₂GZ)X_n” groups, and is chemically bonded to the Cp^A groups.

[0053] m is an integer from 1 to 7; m is an integer from 2 to 6 in a more particular embodiment.

[0054] In another aspect, the at least one metallocene catalyst component can be described more particularly in structures (XIa), (XIb), (XIc), (XIId) (XIe) and (XIf):







wherein in structures (XIa) to (XIf) M is selected from the group consisting of Group 3 to Group 12 atoms, and selected from the group consisting of Group 3 to Group 10 atoms in a more particular embodiment, and selected from the group consisting of Group 3 to Group 6 atoms in yet a more particular embodiment, and selected from the group consisting of Group 4 atoms in yet a more particular embodiment, and selected from the group consisting of Zr and Hf in yet a more particular embodiment; and is Zr in yet a more particular embodiment;

wherein Q in (XIa) to (XIf) is selected from the group consisting of alkylenes, aryls, arylenes, alkoxys, aryloxys, amines, arylamines (e.g., pyridyl) alkylamines, phosphines, alkylphosphines, substituted alkyls, substituted aryls, substituted alkoxys, substituted aryloxys, substituted amines, substituted alkylamines, substituted phosphines, substituted alkylphosphines, carbamates, heteroalkyls, carboxylates (non-limiting examples of suitable carbamates and carboxylates include trimethylacetate, trimethylacetate, methylacetate, p-toluolate, benzoate, diethylcarbamate, and dimethylcarbamate), fluorinated alkyls, fluorinated aryls, and fluorinated alkylcarboxylates; wherein the saturated groups defining Q comprise from 1 to 20 carbon atoms in one embodiment; and wherein the aromatic groups comprise from 5 to 20 carbon atoms in one embodiment;

wherein each R* is independently: selected from the group consisting of hydrocarbylenes and heteroatom-containing hydrocarbylenes in one embodiment; and selected from the group consisting of alkylenes, substituted alkylenes and heteroatom-containing hydrocarbylenes in another embodiment; and selected from the group consisting of C₁ to C₁₂ alkylenes, C₁ to C₁₂ substituted alkylenes, and C₁ to C₁₂ heteroatom-containing hydrocarbylenes in a more particular embodiment; and selected from the group consisting of C₁ to C₄ alkylenes in yet a more particular embodiment; and wherein both R* groups are identical in another embodiment in structures (XI f);

A is as described above for (A) in structure (VII), and more particularly, selected from the group consisting of a chemical bond, —O—, —S—, —SO₂—, —NR—, =SiR₂, =GeR₂, =SnR₂, —R₂SiSiR₂—, RP=, C₁ to C₁₂ alkylenes, substituted C₁ to C₁₂ alkylenes, divalent C₄ to C₁₂ cyclic hydrocarbons and substituted and unsubstituted aryl groups in one embodiment; and selected from the group consisting of C₅ to C₈ cyclic hydrocarbons, —CH₂CH₂—, =CR₂ and =SiR₂ in a more particular embodiment; wherein and R is selected from the group consisting of alkyls, cycloalkyls, aryls, alkoxys, fluoroalkyls and heteroatom-containing hydrocarbons in one embodiment; and R is selected from the group

consisting of C₁ to C₆ alkyls, substituted phenyls, phenyl, and C₁ to C₆ alkoxys in a more particular embodiment; and R is selected from the group consisting of methoxy, methyl, phenoxy, and phenyl in yet a more particular embodiment;

wherein A may be absent in yet another embodiment, in which case each R* is defined as for R¹ R¹³;

each X is as described above in (VI);

n is an integer from 0 to 4, and from 1 to 3 in another embodiment, and 1 or 2 in yet another embodiment; and

R¹ through R¹³ are independently: selected from the group consisting of hydrogen radical, halogen radicals, C₁ to C₁₂ alkyls, C₂ to C₁₂ alkenyls, C₆ to C₁₂ aryls, C₇ to C₂₀ alkylaryls, C₁ to C₁₂ alkoxys, C₁ to C₁₂ fluoroalkyls, C₆ to C₁₂ fluoroaryls, and C₁ to C₁₂ heteroatom-containing hydrocarbons and substituted derivatives thereof in one embodiment; selected from the group consisting of hydrogen radical, fluorine radical, chlorine radical, bromine radical, C₁ to C₆ alkyls, C₂ to C₆ alkenyls, C₇ to C₁₈ alkylaryls, C₁ to C₆ fluoroalkyls, C₂ to C₆ fluoroalkenyls, C₇ to C₁₈ fluoroalkylaryls in a more particular embodiment; and hydrogen radical, fluorine radical, chlorine radical, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tertiary butyl, hexyl, phenyl, 2,6-di-methylpheyl, and 4-tertiarbutylpheyl groups in yet a more particular embodiment; wherein adjacent R groups may form a ring, either saturated, partially saturated, or completely saturated.

[0055] The structure of the metallocene catalyst component represented by (XIa) may take on many forms such as disclosed in, for example, U.S. Pat. Nos. 5,026,798, 5,703,187, and 5,747,406, including a dimer or oligomeric structure, such as disclosed in, for example, U.S. Pat. Nos. 5,026,798 and 6,069,213.

[0056] In a particular embodiment of the metallocene represented in (XIId), R¹ and R² form a conjugated 6-membered carbon ring system that may or may not be substituted.

[0057] Non-limiting examples of metallocene catalyst components consistent with the description herein include:

cyclopentadienylzirconium X_n, indenylzirconium X_n, (1-methylindenyl)zirconium X_n, (2-methylindenyl)zirconium X_n, (1-propylindenyl)zirconium X_n, (2-propylindenyl)zirconium X_n, (1-butylindenyl)zirconium X_n, (2-butylindenyl)zirconium X_n, (methylcyclopentadienyl)zirconium X_n, tetrahydroindenylzirconium X_n, (pentamethylcyclopentadienyl)zirconium X_n, cyclopentadienylzirconium X_n,

- pentamethylcyclopentadienyltitanium X_n , tetramethylcyclopentyltitanium X_n , 1,2,4-trimethylcyclopentadienylzirconium X_n , dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(cyclopentadienyl)zirconium X_n , dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(1,2,3-trimethylcyclopentadienyl)zirconium X_n ,
- 5 dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(1,2-dimethylcyclopentadienyl)zirconium X_n , dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(2-methylcyclopentadienyl)zirconium X_n , dimethylsilyl(cyclopentadienyl)(indenyl)zirconium X_n , dimethylsilyl(2-methylindenyl)(fluorenyl)zirconium X_n , diphenylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(3-propylcyclopentadienyl)zirconium X_n , dimethylsilyl (1,2,3,4-
- 10 tetramethylcyclopentadienyl)(3-t-butylcyclopentadienyl)zirconium X_n , dimethylgermyl(1,2,3,4-dimethylcyclopentadienyl)(3-isopropylcyclopentadienyl)zirconium X_n , dimethylsilyl(1,2,3,4-tetramethylcyclopentadienyl)(3-methylcyclopentadienyl)zirconium X_n , diphenylmethylenecyclopentadienyl(9-fluorenyl)zirconium X_n , diphenylmethylenecyclopentadienyl(indenyl)zirconium X_n , iso-
- 15 propylidenebis(cyclopentadienyl)zirconium X_n , iso-propylidene(cyclopentadienyl)(9-fluorenyl)zirconium X_n , iso-propylidene(3-methylcyclopentadienyl)(9-fluorenyl)zirconium X_n , ethylenebis(9-fluorenyl)zirconium X_n , meso-ethylenebis(1-indenyl)zirconium X_n , ethylenebis(1-indenyl)zirconium X_n , ethylenebis(2-methyl-1-indenyl)zirconium X_n , ethylenebis(2-methyl-4,5,6,7-tetrahydro-1-indenyl)zirconium X_n , ethylenebis(2-propyl-
- 20 4,5,6,7-tetrahydro-1-indenyl)zirconium X_n , ethylenebis(2-isopropyl-4,5,6,7-tetrahydro-1-indenyl)zirconium X_n , ethylenebis(2-butyl-4,5,6,7-tetrahydro-1-indenyl)zirconium X_n , ethylenebis(2-isobutyl-4,5,6,7-tetrahydro-1-indenyl)zirconium X_n , dimethylsilyl(4,5,6,7-tetrahydro-1-indenyl)zirconium X_n , diphenyl(4,5,6,7-tetrahydro-1-indenyl)zirconium X_n , ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium X_n ,
- 25 dimethylsilylbis(cyclopentadienyl)zirconium X_n , dimethylsilylbis(9-fluorenyl)zirconium X_n , dimethylsilylbis(1-indenyl)zirconium X_n , dimethylsilylbis(2-methylindenyl)zirconium X_n , dimethylsilylbis(2-propylindenyl)zirconium X_n , dimethylsilylbis(2-butylindenyl)zirconium X_n , diphenylsilylbis(2-methylindenyl)zirconium X_n , diphenylsilylbis(2-propylindenyl)zirconium X_n , diphenylsilylbis(2-butylindenyl)zirconium X_n ,
- 30 dimethylgermylbis(2-methylindenyl)zirconium X_n , dimethylsilylbis(tetrahydroindenyl)zirconium X_n , dimethylsilylbis(tetramethylcyclopentadienyl) zirconium X_n ,

- dimethylsilyl(cyclopentadienyl)(9-fluorenyl)zirconium X_n , diphenylsilyl (cyclopentadienyl)(9-fluorenyl)zirconium X_n , diphenylsilylbis(indenyl)zirconium X_n ,
 cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(cyclopentadienyl)zirconium X_n ,
 cyclotetramethylenesilyl(tetramethylcyclopentadienyl)(cyclopentadienyl)zirconium X_n ,
 5 cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(2-methylindenyl)zirconium X_n ,
 cyclotrimethylenesilyl(tetramethylcyclopentadienyl)(3-methylcyclopentadienyl)zirconium X_n ,
 cyclotrimethylenesilylbis(2-methylindenyl)zirconium X_n , cyclotrimethylenesilyl
 (tetramethylcyclopentadienyl)(2,3,5-trimethylcyclopentadienyl)zirconium X_n ,
 cyclotrimethylenesilylbis(tetramethylcyclopentadienyl)zirconium X_n ,
 10 dimethylsilyl(tetramethylcyclopentadienyl)(N-tert-butylamido)titanium X_n ,
 bis(cyclopentadienyl)chromium X_n , bis(cyclopentadienyl)zirconium X_n , bis(n-butylcyclopentadienyl)zirconium X_n , bis(n-dodecylcyclopentadienyl)zirconium X_n ,
 bis(ethylcyclopentadienyl)zirconium X_n , bis(iso-butylcyclopentadienyl)zirconium X_n , bis(iso-propylcyclopentadienyl)zirconium X_n , bis(methylcyclopentadienyl)zirconium X_n , bis(n-oxylcyclopentadienyl)zirconium X_n , bis(n-pentylcyclopentadienyl)zirconium X_n , bis(n-propylcyclopentadienyl)zirconium X_n , bis(trimethylsilylcyclopentadienyl)zirconium X_n ,
 15 bis(1,3-bis(trimethylsilyl)cyclopentadienyl)zirconium X_n , bis(1-ethyl-2-methylcyclopentadienyl)zirconium X_n , bis(1-ethyl-3-methylcyclopentadienyl)zirconium X_n ,
 bis(pentamethylcyclopentadienyl) zirconium X_n , bis(pentamethylcyclopentadienyl)zirconium
 20 X_n , bis(1-propyl-3-methylcyclopentadienyl) zirconium X_n , bis(1-n-butyl-3-methylcyclopentadienyl)zirconium X_n , bis(1-isobutyl-3-methylcyclopentadienyl)zirconium X_n ,
 bis(1-propyl-3-butylcyclopentadienyl) zirconium X_n , bis(1,3-n-butylcyclopentadienyl)zirconium X_n , bis(4,7-dimethylindenyl)zirconium X_n ,
 bis(indenyl)zirconium X_n , bis(2-methylindenyl)zirconium X_n ,
 25 cyclopentadienylindenylzirconium X_n , bis(n-propylcyclopentadienyl)hafnium X_n , bis(n-butylcyclopentadienyl)hafnium X_n , bis(n-pentylcyclopentadienyl) hafnium X_n , (n-propyl
 cyclopentadienyl)(n-butyl cyclopentadienyl)hafnium X_n , bis[(2-trimethylsilylethyl)cyclopentadienyl]hafnium X_n , bis(trimethylsilyl cyclopentadienyl)
 hafnium X_n , bis(2-n-propylindenyl)hafnium X_n , bis(2-n-butylindenyl)hafnium X_n ,
 30 dimethylsilylbis(n-propylcyclopentadienyl)hafnium X_n , dimethylsilylbis(n-butylcyclopentadienyl) hafnium X_n , bis(9-n-propylfluorenyl)hafnium X_n , bis(9-n-butylfluorenyl)hafnium X_n , (9-n-propylfluorenyl) (2-n-propylindenyl)hafnium X_n , bis(1-n-

propyl-2-methylcyclopentadienyl)hafnium X_n , (n-propylcyclopentadienyl)(1-n-propyl-3-n-butylcyclopentadienyl)hafnium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl)(cyclopropylamido)titanium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl) (cyclobutylamido)titanium X_n ,

5 dimethylsilyl(tetramethylcyclopentadienyl) (cyclopentylamido)titanium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl) (cyclohexylamido)titanium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl) (cycloheptylamido)titanium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl)(cyclooctylamido)titanium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl)(cyclononylamido)titanium X_n ,

10 dimethylsilyl(tetramethylcyclopentadienyl)(cyclodecylamido)titanium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl)(cycloundecylamido)titanium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl)(sec-butylamido)titanium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl)(n-octylamido)titanium X_n ,

15 dimethylsilyl(tetramethylcyclopentadienyl)(n-decylamido)titanium X_n ,

dimethylsilyl(tetramethylcyclopentadienyl)(n-octadecylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(cyclopropylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(cyclobutylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(cyclopentylamido)titanium X_n ,

20 methylphenylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(cycloheptylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(cyclooctylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(cyclononylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(cyclodecylamido)titanium, X_n ,

25 methylphenylsilyl(tetramethylcyclopentadienyl)(cycloundecylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(sec-butylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(n-octylamido)titanium X_n ,

methylphenylsilyl(tetramethylcyclopentadienyl)(n-decylamido)titanium X_n ,

30 methylphenylsilyl(tetramethylcyclopentadienyl)(n-octadecylamido)titanium X_n ,

diphenylsilyl(tetramethylcyclopentadienyl)(cyclopropylamido)titanium X_n ,

diphenylsilyl(tetramethylcyclopentadienyl)(cyclobutylamido)titanium X_n ,

- diphenylsilyl(tetramethylcyclopentadienyl)(cyclopentylamido)titanium X_n ,
 diphenylsilyl(tetramethylcyclopentadienyl)(cyclohexylamido)titanium X_n ,
 diphenylsilyl(tetramethylcyclopentadienyl)(cycloheptylamido)titanium X_n ,
 diphenylsilyl(tetramethylcyclopentadienyl)(cyclooctylamido)titanium X_n ,
 5 diphenylsilyl(tetramethylcyclopentadienyl)(cyclononylamido)titanium X_n ,
 diphenylsilyl(tetramethylcyclopentadienyl)(cyclodecylamido)titanium X_n ,
 diphenylsilyl(tetramethylcyclopentadienyl)(cycloundecylamido)titanium X_n ,
 diphenylsilyl(tetramethylcyclopentadienyl)(cyclododecylamido)titanium X_n ,
 diphenylsilyl(tetramethylcyclopentadienyl)(sec-butylamido)titanium X_n ,
 10 diphenylsilyl(tetramethylcyclopentadienyl)(n-octylamido)titanium X_n ,
 diphenylsilyl(tetramethylcyclopentadienyl)(n-decylamido)titanium X_n ,
 diphenylsilyl(tetramethylcyclopentadienyl)(n-octadecylamido)titanium X_n , and derivatives thereof.

- [0058] By “derivatives thereof” or “derivatives of”, it is meant any substitution or ring
 15 formation as described above in one embodiment; and in particular, replacement of the metal
 “M” (Cr, Zr, Ti or Hf) with an atom selected from the group consisting of Cr, Zr, Hf and Ti;
 and replacement of the “X” group with any of C_1 to C_5 alkyls, C_6 aryls, C_6 to C_{10} alkylaryls,
 fluorine or chlorine; n is 1, 2 or 3.

- [0059] It is contemplated that the metallocene catalysts components described above
 20 include their structural or optical or enantiomeric isomers (racemic mixture), and may be a
 pure enantiomer in one embodiment.

[0060] As used herein, a single, bridged, asymmetrically substituted metallocene catalyst
 component having a racemic and/or meso isomer does not, itself, constitute at least two
 different bridged, metallocene catalyst components.

- 25 [0061] The “metallocene catalyst component” may comprise any combination of any
 “embodiment” described herein.

Supported Catalyst Systems

- [0062] The activator and/or the polymerization catalyst compound may be combined with
 one or more support materials or carriers using any one of the support methods known in the
 30 art or as described below. In one embodiment the activator is in a supported form, for
 example deposited on, contacted with, vaporized with, bonded to, or incorporated within,
 adsorbed or absorbed in, or on, a support or carrier. In another embodiment, the activator and

a catalyst compound may be deposited on, contacted with, vaporized with, bonded to, or incorporated within, adsorbed or absorbed in, or on, a support or carrier.

[0063] The terms “support” or “carrier” for purposes of this patent specification are used interchangeably and are any support material, preferably a porous support material, including
5 inorganic or organic support materials. Non-limiting examples of inorganic support materials include inorganic oxides and inorganic chlorides. Other carriers include resinous support materials such as polystyrene, functionalized or crosslinked organic supports, such as polystyrene, divinyl benzene, polyolefins, or polymeric compounds, zeolites, talc, clays, or any other organic or inorganic support material and the like, or mixtures thereof.

10 [0064] In one embodiment, the heterocyclic compounds and the alumoxanes described above are combined with one or more support materials or carriers. In another embodiment the heterocyclic compound is combined with a support material, preferably silica, treated with the alumoxane compound, such that the support has aluminum alkyl groups bonded thereto. The supported catalyst systems described herein may be prepared, generally, by the
15 reaction of the heterocyclic compound with an alumoxane, the addition of the catalyst precursor, followed by addition of a support material such as silica or alumina.

[0065] The support materials utilized may be any of the conventional support materials. Preferably the supported material is a porous support material, for example, talc, inorganic oxides and inorganic chlorides. Other support materials include resinous support materials
20 such as polystyrene, functionalized or crosslinked organic supports, such as polystyrene divinyl benzene polyolefins or polymeric compounds, zeolites, clays, or any other organic or inorganic support material and the like, or mixtures thereof.

[0066] The preferred support materials are inorganic oxides that include those Group 2, 3, 4, 5, 13 or 14 metal oxides. The preferred supports include silica, fumed silica, alumina,
25 silica-alumina and mixtures thereof. Other useful supports include magnesia, titania, zirconia, magnesium chloride, montmorillonite, phyllosilicate, zeolites, talc, clays and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania and the like. Additional support materials may include those porous acrylic polymers. Other support materials include nanocomposites,
30 aerogels, spherulites, and polymeric beads. Another support is fumed silica available under the trade name Cabosil™. TS-610, available from Cabot Corporation. Fumed silica is

typically a silica with particles 7 to 30 nanometers in size that has been treated with dimethylsilyldichloride such that a majority of the surface hydroxyl groups are capped.

[0067] In another embodiment, any of the conventionally known inorganic oxides, such as silica, support materials that retain hydroxyl groups after dehydration treatment methods
5 will be suitable in accordance with the invention. Because of availability, both of silica and silica containing metal oxide based supports, for example, silica-alumina, are preferred. Silica particles, gels and glass beads are most typical.

[0068] These metal oxide compositions may additionally contain oxides of other metals, such as those of Al, K, Mg, Na, Si, Ti and Zr and should preferably be treated by thermal
10 and/or chemical means to remove water and free oxygen. Typically such treatment is in a vacuum in a heated oven, in a heated fluidized bed or with dehydrating agents such as organo silanes, siloxanes, alkyl aluminum compounds, etc. The level of treatment should be such that as much retained moisture and oxygen as is possible is removed, but that a chemically significant amount of hydroxyl functionality is retained. Thus calcining at up to 800 °C or
15 more up to a point prior to decomposition of the support material, for several hours is permissible, and if higher loading of supported anionic activator is desired, lower calcining temperatures for lesser times will be suitable. Where the metal oxide is silica, loadings to achieve from less than 0.1 mmol to 3.0 mmol activator/g SiO₂ are typically suitable and can be achieved, for example, by varying the temperature of calcining from 200°C to 1,000°C,
20 such as from 300°C to 900°C, 400°C to 875°C, 500°C to 850°C, 600°C to 825°C, 700°C to 800°C, and any combination of any limit with any lower limit.

[0069] The tailoring of hydroxyl groups available as attachment sites in this invention can also be accomplished by the pre-treatment with a less than stoichiometric amount of a chemical dehydrating agent. If calcining temperatures below 400°C are employed,
25 difunctional coupling agents (e.g., (CH₃)₃SiCl₂) may be employed to cap hydrogen bonded pairs of silanol groups which are present under the less severe calcining conditions. Similarly, use of the Lewis acid in excess of the stoichiometric amount needed for reaction with the transition metal compounds will serve to neutralize excess silanol groups without significant detrimental effect for catalyst preparation or subsequent polymerization.

30 [0070] In another embodiment, the support is a polymeric support, including hydroxyl-functional-group-containing polymeric substrates, but functional groups may be any of the primary alkyl amines, secondary alkyl amines, and others, where the groups are structurally

incorporated in a polymeric chain and capable of a acid-base reaction with the Lewis acid such that a ligand filling one coordination site of the aluminum is protonated and replaced by the polymer incorporated functionality. See, for example, the functional group containing polymers of U.S. Pat. No. 5,288,677.

5 [0071] It is preferred that the support material, most preferably an inorganic oxide, has a surface area in the range of from about 10 to about 700 m²/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 5 to about 500 μm. More preferably, the surface area of the support material is in the range of from about 50 to about 500 m²/g, pore volume of from about 0.5 to about 3.5 cc/g and
10 average particle size of from about 10 to about 200 μm. The average pore size of the carrier is typically in the range of from 10 to 1000 angstroms., preferably 50 to about 500 angstroms., and most preferably 75 to about 350 angstroms.

[0072] The support materials may be treated chemically, for example with a fluoride compound as described in WO 00/12565. Other supported activators are described in for
15 example WO 00/13792 that refers to supported boron containing solid acid complex.

[0073] In one embodiment, the support material having an alumoxane compound bonded thereto may be prepared by combining the aluminum containing compound with the support material in a suitable solvent. In one embodiment, the combining is carried out at any suitable pressure and temperature under an inert atmosphere. Preferably the combining is at
20 atmospheric pressure, ambient temperature under nitrogen. More preferably the mixture is heated to less than about 200°C, more preferably less than 150°C. The reactants are contacted for a suitable amount of time for example, for at least about 1 minute, preferably about 1 minute to about 10 hours, more preferably for about 1 minute to about 3 hours.

[0074] In another embodiment, an antistatic agent or surface modifier that is used in the
25 preparation of the supported catalyst system as described in PCT publication WO 96/11960 may be used with catalyst systems including the activator compounds described herein. The catalyst systems may also be prepared in the presence of an olefin, for example 1-hexene.

[0075] In another embodiment, the activator and/or catalyst system may be combined with a carboxylic acid salt of a metal ester, for example aluminum carboxylates such as
30 aluminum mono, di- and tri- stearates, aluminum octoates, oleates and cyclohexylbutyrates, as described in U.S. Pat. Nos. 6,300,436 and 6,306,984.

[0076] In another embodiment there is a method for producing a supported metallocene-type catalyst system, which may be used to support the activator described herein. In this method, the catalyst compound is slurried in a liquid to form a catalyst solution or emulsion. A separate solution is formed containing the activator. The liquid may be any compatible solvent or other liquid capable of forming a solution or the like with the catalyst compounds and/or activator. In the most preferred embodiment the liquid is a cyclic aliphatic or aromatic hydrocarbon, most preferably toluene. The catalyst compound and activator solutions are mixed together heated and added to a heated porous support or a heated porous support is added to the solutions such that the total volume of the metallocene-type catalyst compound solution and the activator solution or the metallocene-type catalyst compound and activator solution is less than four times the pore volume of the porous support, more preferably less than three times, even more preferably less than two times; preferred ranges being from 1.1 times to 3.5 times range and most preferably in the 1.2 to 3 times range.

[0077] In one embodiment, a method of forming a supported catalyst system, the amount of liquid, in which the activator described herein and/or a catalyst compound is present, is in an amount that is less than four times the pore volume of the support material, more preferably less than three times, even more preferably less than two times; preferred ranges being from 1.1 times to 3.5 times range and most preferably in the 1.2 to 3 times range. In an alternative embodiment, the amount of liquid in which the activator is present is from one to less than one times the pore volume of the support material utilized in forming the supported activator.

[0078] In one embodiment, the amount of heterocyclic heteroatom containing compound ranges from 0.005 grams to 2.0 grams per gram of alumoxane treated silica. In another embodiment, the amount of heterocyclic heteroatom containing compound ranges from 0.05 grams to 1.0 grams per gram of alumoxane treated silica. In yet another embodiment, the amount of heterocyclic containing compound ranges from 0.075 grams to 0.8 grams per gram of alumoxane treated silica.

Polymerization Process

[0079] The activators and catalysts described above, whether supported or not, are suitable for use in any prepolymerization and/or polymerization process over a wide range of temperatures and pressures. The temperatures may be in the range of from -60°C to about 280°C, preferably from 50°C to about 200°C. In one embodiment, the polymerization

temperature is above 0°C, above 50°C, above 80°C, above 100°C, above 150°C, or above 200°C. In one embodiment, the pressures employed may be in the range from 1 atmosphere to about 500 atmospheres (approx 101 kPa to 50650 kPa) or higher.

[0080] Polymerization processes include solution, gas phase, slurry phase, and a high pressure process, or a combination thereof. Particularly preferred is a gas phase or slurry phase polymerization of one or more olefin(s) at least one of which is ethylene or propylene.

[0081] In one embodiment, the process is a solution, high pressure, slurry or gas phase polymerization process of one or more olefin monomers having from 2 to 30 carbon atoms, preferably 2 to 12 carbon atoms, and more preferably 2 to 8 carbon atoms. The invention is particularly well suited to the polymerization of two or more olefin monomers of ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene, 1-octene and 1-decene.

[0082] Other monomers useful in the process include ethylenically unsaturated monomers, diolefins having 4 to 18 carbon atoms, conjugated or nonconjugated dienes, polyenes, vinyl monomers and cyclic olefins. Non-limiting monomers useful in the invention may include norbornene, norbornadiene, isobutylene, isoprene, vinylbenzocyclobutane, styrenes, alkyl substituted styrene, ethylidene norbornene, dicyclopentadiene and cyclopentene.

[0083] In another embodiment, a copolymer of ethylene is produced, where with ethylene, a comonomer having at least one alpha-olefin having from 4 to 15 carbon atoms, preferably from 4 to 12 carbon atoms, and most preferably from 4 to 8 carbon atoms, is polymerized in a gas phase process.

[0084] In another embodiment, ethylene or propylene is polymerized with at least two different comonomers, optionally one of which may be a diene, to form a terpolymer.

[0085] In one embodiment, the invention is directed to a polymerization process, particularly a gas phase or slurry phase process, for polymerizing propylene alone or with one or more other monomers including ethylene, and/or other olefins having from 4 to 12 carbon atoms.

[0086] Typically in a gas phase polymerization process, a continuous cycle is employed where in one part of the cycle of a reactor system, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. This heat is removed from the recycle composition in another part of the cycle by a cooling system external to the reactor. Generally, in a gas fluidized bed process for producing

polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer.

[0087] The reactor pressure in a gas phase process may vary from about 100 psig (690 kPa) to about 500 psig (3448 kPa), preferably in the range of from about 200 psig (1379 kPa) to about 400 psig (2759 kPa), more preferably in the range of from about 250 psig (1724 kPa) to about 350 psig (2414 kPa).

[0088] The reactor temperature in a gas phase process may vary from about 30°C to about 120°C, preferably from about 60°C to about 115°C, more preferably in the range of from about 70°C to 110°C, and most preferably in the range of from about 70°C to about 95°C. In another embodiment, the reactor temperature in a gas phase process is above 60°C.

[0089] Other gas phase processes include series or multistage polymerization processes. Also gas phase processes contemplated by the invention include those described in U.S. Pat. Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A-0 794 200 EP-B1-0 649 992, EP-A-0 802 202 and EP-B-634 421.

[0090] In another embodiment, the process may produce greater than 500 lbs of polymer per hour (227 Kg/hr) to about 200,000 lbs/hr (90,900 Kg/hr) or higher of polymer, preferably greater than 1000 lbs/hr (455 Kg/hr), more preferably greater than 10,000 lbs/hr (4540 Kg/hr), even more preferably greater than 25,000 lbs/hr (11,300 Kg/hr), still more preferably greater than 35,000 lbs/hr (15,900 Kg/hr), still even more preferably greater than 50,000 lbs/hr (22,700 Kg/hr) and most preferably greater than 65,000 lbs/hr (29,000 Kg/hr) to greater than 100,000 lbs/hr (45,500 Kg/hr).

[0091] A slurry polymerization process generally uses pressures in the range of from about 1 to about 50 atmospheres (5065 kPa) and even greater and temperatures in the range of 0°C to about 120°C. In another embodiment, the slurry process temperature is above 100°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent

employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used the process must be operated above the reaction diluent critical temperature and pressure.

5 Preferably, a hexane or an isobutane medium is employed.

[0092] In another embodiment, the polymerization technique is referred to as a particle form polymerization, or a slurry process where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, and described in for instance U.S. Pat. No. 3,248,179 which is fully incorporated herein by
10 reference. Other slurry processes include those employing a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in U.S. Pat. No. 4,613,484, which is herein fully incorporated by reference.

15 [0093] In another embodiment, the process may produce greater than 2000 lbs of polymer per hour (907 Kg/hr), more preferably greater than 5000 lbs/hr (2268 Kg/hr), and most preferably greater than 10,000 lbs/hr (4540 Kg/hr). In another embodiment the slurry reactor may produce greater than 15,000 lbs of polymer per hour (6804 Kg/hr), preferably greater than 25,000 lbs/hr (11,340 Kg/hr) to about 100,000 lbs/hr (45,500 Kg/hr).

20 [0094] Examples of solution processes are described in U.S. Pat. Nos. 4,271,060, 5,001,205, 5,236,998 and 5,589,555 and PCT WO 99/32525.

[0095] In one embodiment the slurry or gas phase process is operated in the presence of the catalyst system described herein and in the absence of or essentially free of any scavengers, such as triethylaluminum, trimethylaluminum, tri-isobutylaluminum and tri-n-
25 hexylaluminum and diethyl aluminum chloride, dibutyl zinc and the like. This process is described in PCT publication WO 96/08520 and U.S. Pat. Nos. 5,712,352 and 5,763,543.

[0096] In another embodiment, the catalyst system may be injected into a reactor, particularly a gas phase reactor. In one embodiment the catalyst system is used in the unsupported form, preferably in a liquid form such as described in U.S. Pat. Nos. 5,317,036
30 and 5,693,727 and European publication EP-A-0 593 083. The polymerization catalyst in liquid form can be fed with an activator, and/or a support, and/or a supported activator

together or separately to a reactor. The injection methods described in PCT publication WO 97/46599 may be utilized.

[0097] Where an unsupported catalyst system is used the mole ratio of the metal of the activator component to the metal of the catalyst compound is in the range of between 0.3:1 to 10,000:1, preferably 100:1 to 5000:1, and most preferably 500:1 to 2000:1.

Polymer Products

[0098] The polymers produced can be used in a wide variety of products and end-use applications. The polymers produced include linear low density polyethylene, elastomers, plastomers, high density polyethylenes, medium density polyethylenes, low density polyethylenes, polypropylene and polypropylene copolymers.

[0099] The polymers, typically ethylene or propylene based polymers, have a density in the range of from 0.86 g/cc to 0.97 g/cc, preferably in the range of from 0.88 g/cc to 0.965 g/cc, more preferably in the range of from 0.900 g/cc to 0.96 g/cc, even more preferably in the range of from 0.905 g/cc to 0.95 g/cc, yet even more preferably in the range from 0.910 g/cc to 0.940 g/cc, and most preferably greater than 0.915 g/cc, preferably greater than 0.920 g/cc, and most preferably greater than 0.925 g/cc. Density is measured in accordance with ASTM-D-1238.

[00100] The polymers produced typically have a molecular weight distribution, a weight average molecular weight to number average molecular weight (M_w/M_n) of greater than 1.5 to about 15, particularly greater than 2 to about 10, more preferably greater than about 2.2 to less than about 8, and most preferably from 2.5 to 8. The polymers may have a narrow molecular weight distribution and a broad composition distribution or vice-versa, and may be those polymers described in U.S. Pat. No. 5,798,427.

[00101] Also, the polymers typically have a narrow composition distribution as measured by Composition Distribution Breadth Index (CDBI). Further details of determining the CDBI of a copolymer are known to those skilled in the art. See, for example, PCT Patent Application WO 93/03093, published Feb. 18, 1993. The polymers in one embodiment have CDBI's generally in the range of greater than 50% to 100%, preferably 99%, preferably in the range of 55% to 85%, and more preferably 60% to 80%, even more preferably greater than 60%, still even more preferably greater than 65%. In another embodiment, polymers produced using a catalyst system described herein have a CDBI less than 50%, more preferably less than 40%, and most preferably less than 30%.

[00102] The polymers in one embodiment have a melt index (MI) or (I_2) as measured by ASTM-D-1238-E (190/2.16) in the range from no measurable flow to 1000 dg/min, more preferably from about 0.01 dg/min to about 100 dg/min, even more preferably from about 0.1 dg/min to about 50 dg/min, and most preferably from about 0.1 dg/min to about 10 dg/min.

5 [00103] In one embodiment, the polymers have a melt index ratio (I_{21}/I_2) (I_{21} is measured by ASTM-D-1238-F) (190/21.6) of from 10 to less than 25, more preferably from about 15 to less than 25. The polymers, in a preferred embodiment, have a melt index ratio (I_{21}/I_2) of from greater than 25, more preferably greater than 30, even more preferably greater than 40, still even more preferably greater than 50 and most preferably greater than 65. For example,
10 melt index ratio (I_{21}/I_2) may be of from 5 to 300, 10 to 200, 20 to 180, 30 to 160, 40 to 120, 50 to 100, 60 to 90, and a combination of any upper limit with any lower limit.

[00104] In preferred embodiments, propylene based polymers are produced. These polymers include atactic polypropylene, isotactic polypropylene, hemi-isotactic and syndiotactic polypropylene. Other propylene polymers include propylene block or impact
15 copolymers. Propylene polymers of these types are well known in the art see for example U.S. Pat. Nos. 4,794,096, 3,248,455, 4,376,851, 5,036,034 and 5,459,117. In preferred embodiment, the propylene polymers have an Mw/Mn of more than 1 to 4, preferably less than 2, preferably from 1.2 to 2. Useful propylene polymers prepared herein may have an Mn of more than 100,000 g/mol, preferably more than 200,000 g/mol, preferably more than
20 350,000 g/mol, preferably more than 500,000 g/mol. Alternately the polypropylene may have an Mn of 100,000 to 200,000 g/mol. Alternately the polypropylene (preferably having at least 50 wt% propylene, preferably at least 80 wt% propylene, preferably at least 90 wt% propylene) may have an Mn of 10,000 to 50,000 g/mol (alternately from 15,000 to 45,000g/mol, alternately from 20,000 to 40,000 g/mol and a melting point of 140°C or more
25 (preferably 145°C or more, preferably 150°C or more, preferably 155°C or more, preferably 160°C or more, preferably 165°C or more).

[00105] In a preferred embodiment, the polypropylene produced herein has an Mw from 5,000 to 120,000 (preferably from 10,000 to 100,000 preferably from 12,000 to 75,000 preferably from 15,000 to 50,000 g/mol) and a melting point above 140°C (preferably 145°C
30 or more, preferably 150°C or more, preferably 155°C or more, preferably 160°C or more, preferably 165°C or more), provided that the melting point is also greater than or equal to $0.000143x(\text{Mw in g/mol})+133$, (preferably +134, preferably +135) and optionally, an

Mw/Mn of 4 or less, preferably 2.5 or less, preferably from greater than 1 to 2. Preferably if the Mw is 40,000 g/mol or more then the melting point is 145°C or more (preferably 150°C or more, preferably 155°C or more, preferably 160°C or more, preferably 165°C or more) or alternately if the Mw is 50,000 g/mol or more then the melting point is 150°C or more
5 (preferably 155°C or more, preferably 160°C or more, preferably 165°C or more).

[00106] In some embodiments the polypropylene may be isotactic, highly isotactic, syndiotactic, or highly syndiotactic. As used herein, "isotactic" is defined as having at least 10% isotactic pentads and "highly isotactic" is defined as having at least 60% isotactic pentads according to analysis by ¹³C-NMR where the samples are dissolved in d₂-1, 1, 2, 2-tetrachloroethane and the spectra are recorded at 125°C using a NMR spectrometer of 100
10 MHz. Polymer resonance peaks are referenced to mmmm = 21.8 ppm. Calculations involved in the characterization of polymers by NMR follow the work of F. A. Bovey in "Polymer Conformation and Configuration" Academic Press, New York 1969 and J. Randall in "Polymer Sequence Determination, ¹³C-NMR Method", Academic Press, New York, 1977.

15 The percent of methylene sequences of two in length, %(CH₂)₂, are calculated as follows: the integral of the methyl carbons between 14-18 ppm (which are equivalent in concentration to the number of methylenes in sequences of two in length) divided by the sum of the integral of the methylene sequences of one in length between 45-49 ppm and the integral of the methyl carbons between 14-18 ppm, times 100. This is a minimum calculation for the amount of
20 methylene groups contained in a sequence of two or more since methylene sequences of greater than two have been excluded. Assignments are based on H. N. Cheng and J. A. Ewen, Makromol. Chem. 1989, 190, 1931.

[00107] Comonomer is preferably present in the polymers (such as the propylene polymers) at 0 to 50 wt%, alternately from 1 to 20 wt%, alternately from 2 to 10 wt%.

25 [00108] The polymers may be blended and/or coextruded with any other polymer. Non-limiting examples of other polymers include linear low density polyethylenes, elastomers, plastomers, high pressure low density polyethylene, high density polyethylenes, polypropylenes and the like.

[00109] The polymers produced and blends thereof are useful in such forming operations
30 as film, sheet, and fiber extrusion and co-extrusion as well as blow molding, injection molding and rotary molding. Films include blown or cast films formed by coextrusion or by lamination useful as shrink film, cling film, stretch film, sealing films, oriented films, snack

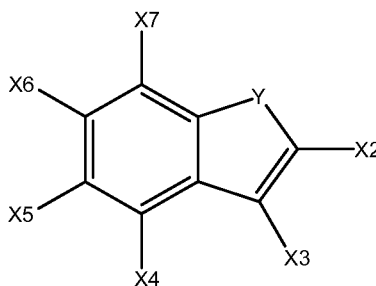
packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications. Fibers include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, medical garments,
 5 geotextiles, etc. Extruded articles include medical tubing, wire and cable coatings, pipe, geomembranes, and pond liners. Molded articles include single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

[00110] This invention further relates to:

10 1. A catalyst system comprising:

a metallocene;

an activator comprising one or more heterocyclic heteroatom containing ligands coordinated to an alkyl alumoxane, wherein the activator is a reaction product of one or more alkyl alumoxane and one or more heterocyclic heteroatom containing compounds, wherein the
 15 heterocyclic heteroatom containing ligand is represented by:



Y is O, S, PH or NH;

20 wherein each substituent X2, X3, X4, X5, X6 and X7 is independently a hydrogen, chlorine, fluorine, iodine or bromine, provided at least one of X2, X3, X4, X5, X6 and X7 is not hydrogen when Y is NH; and

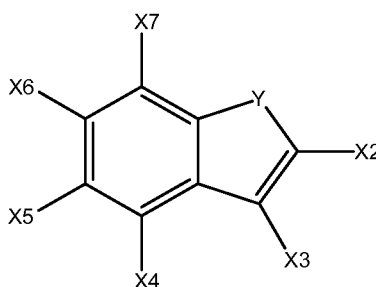
wherein the ratio of the heterocyclic heteroatom containing ligand to aluminum is between about 0.01 and about 10 molar equivalents.

25 2. The catalyst of paragraph 1, wherein the metallocene is $\text{rac-Me}_2\text{Si}-(2\text{-methyl-indenyl})_2\text{Zr}(\text{CH}_3)_2$ or $\text{rac-Me}_2\text{Si}-(2\text{-methyl-4-phenyl-indenyl})_2\text{Zr}(\text{CH}_3)_2$.

3. The catalyst of either of paragraphs 1 or 2, wherein the heterocyclic heteroatom containing ligand is mono-substituted.

4. The catalyst of paragraph 3, wherein the substituent is a bromine.
5. The catalyst of either of paragraphs 1 or 2, wherein the heterocyclic heteroatom containing ligand is di-substituted.
6. The catalyst of paragraph 5, wherein the substituents are chlorines.
- 5 7. The catalyst of any of paragraphs 1 through 6, wherein the ratio of heterocyclic heteroatom containing ligand to aluminum is between about 0.2 and about 5.
8. The catalyst of any of paragraphs 1 through 7, wherein Y is NH.
9. A process to polymerize one or more olefins comprising the step of contacting one or more olefins with a catalyst system of any of paragraphs 1 through 8.
- 10 10. The process of paragraph 9, wherein the one olefin is propylene.
11. The process of paragraph 10, wherein the molecular weight of the polymerized propylene is between about 5,000 and about 200,000.
12. The process of paragraph 11, wherein the molecular weight of the polymerized propylene is between about 10,000 and 15,000.
- 15 **[00111]** In another embodiment, this invention relates to:
 - 1A. A process to polymerize propylene comprising:
 - 1) contacting propylene and from 0 to 50 wt% comonomer (based upon the weight of all monomers present), alternately from 1 to 25 wt% comonomer, alternately 2 to 10 wt% comonomer with a (optionally supported) catalyst system comprising:
 - 20 a) a metallocene represented by the formula ACp_2MX_2 where M is Ti, Hf or Zr (preferably Hf or Zr) and is bound to each Cp group; A is a bridging group connecting the two Cp groups; each Cp is, independently, an indenyl group or a substituted indenyl group (preferably substituted with from 1, 2, 3, 4, 5, or 6 hydrocarbyl or substituted hydrocarbyl group(s) (preferably C_1 to C_{20} alkyl group(s))), preferably the indenyl group is substituted at
25 the 2 position or at the 2 and 4 positions; each X is an anionic leaving group; (preferably the metallocene represented by the formula $rac\text{-}ACp_2MX_2$ where "rac" indicates that the metallocene is partially or completely racemized, preferably the metallocene is completely racemized, i.e. racemic, and A, Cp, M, and X are as defined above);
 - b) an activator comprising one or more heterocyclic heteroatom containing ligands
30 coordinated to an isoalkyl alumoxane (preferably where the alkyl is a C_3 to C_{12} isoalkyl, preferably isopropyl, isobutyl, isohexyl, isopentyl, or isooctyl), wherein the activator is a reaction product of a solution of one or more isoalkyl alumoxanes (preferably where the

isoalkyl is a C₃ to C₁₂ isoalkyl, preferably isopropyl, isobutyl, isopentyl, isohexyl, or isooctyl), and one or more heterocyclic heteroatom containing compounds, wherein the heterocyclic heteroatom containing ligand is represented by:



5

Y is NH or N-R where R is a C₁ to C₁₂ alkyl group;

wherein each of X2 and X3 is hydrogen, halogen or X2 and X3 may form a six membered aromatic ring (preferably X2 and X3 are H);

10 X4, X5, X6 and X7 are, independently, hydrogen or a halogen, provided at least one of X2, X3, X4, X5, X6 and X7 is not hydrogen, (preferably X4, X5, X6 and X7 are all halogen, alternately one, two, or three of X4, X5, X6 and X7 is/are halogen (and optionally those of X4, X5, X6 and X7 that are not halogen are H), in a preferred embodiment, X5 is bromine and X4, X6 and X7 are H); and

15 preferably wherein the ratio of the heterocyclic heteroatom containing ligand to aluminum is between 0.01:1 and 10:1 molar equivalents; and

2) obtaining polymer having at least 50 wt% propylene, an Mw of 5,000 to 200,000 g/mol and a melting point of 140°C or more, provided that the melting point is also greater than or equal to 0.000143x(Mw in g/mol)+133, and optionally, an Mw/Mn of 4 or less, preferably

20 2.5 or less, preferably from greater than 1 to 2.

2A. The process of paragraph 1A, wherein the metallocene is rac-(CH₃)₂Si-(2-methyl-indenyl)₂Zr(CH₃)₂ or rac-(CH₃)₂Si-(2-methyl-4-phenyl-indenyl)₂Zr(CH₃)₂.

3A. The process of paragraph 1A or 2A, wherein the ratio of heterocyclic heteroatom containing ligand to aluminum is from 0.1:1 to 5:1, (alternately 0.2:1 to 5:1, alternately 0.1 to 3).

25

4A. The process of paragraph 1A, 2A, or 3A wherein A is represented by the formula

-CR**₂-(CR**₂)_n- or -SiR**₂- (where n is 0, 1 or 2, each R** is, independently, H or a C₁ to C₁₂ alkyl group (and any two R** may form a cyclic group), preferably H, methyl, or ethyl); and/or each X is independently a C₁ to C₂₀ alkyl group or a halogen.

5A. The process of any of paragraphs 1A to 4A wherein the isoalkyl alumoxane comprises isobutyl alumoxane and or isohexyl alumoxane.

6A. The process of any of paragraphs 1A to 5A wherein the activity of the catalyst system is 1500 g polymer/g catalyst-hour or more.

7A. The process of any of paragraphs 1A to 6A, wherein the comonomer is selected from the group consisting of: ethylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene and dodecene.

8A. The process of any of paragraphs 1A to 7A wherein the polymer obtained has at least 80 wt% propylene (preferably at least 90 wt% propylene, preferably at least 95 wt% propylene, preferably 100 wt% propylene).

9A. The process of any of paragraphs 1A to 8A wherein if polymer obtained has an Mw of 40,000 g/mol or more then the melting point is 145°C or more, or if the Mw is 50,000 g/mol or more then the melting point is 150°C or more.

10A. The process of any of paragraphs 1A to 9A wherein if polymer obtained has an Mw of 10,000 to 120,000 g/mol.

11A. The catalyst system described in any of paragraphs 1A to 10A.

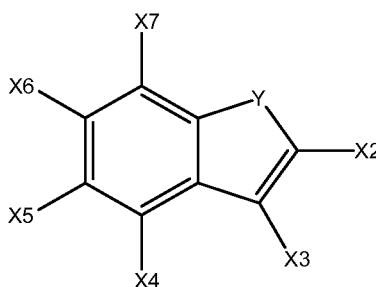
20 [00112] In another embodiment, this invention relates to:

1B. A catalyst system (optionally supported) comprising:

- a) a metallocene represented by the formula ACp₂MX₂ where M is Ti, Hf or Zr and is bound to each Cp group, A is a bridging group connecting the two Cp groups, each Cp is, independently, an indenyl group or a substituted indenyl group (preferably substituted with from 1 to 6 C₁ to C₂₀ alkyl groups, preferably the indenyl group is substituted at the 2 position or at the 2 and 4 positions), each X is an anionic leaving group, (preferably the metallocene represented by the formula *rac*-ACp₂MX₂ where "*rac*" indicates that the metallocene is partially or completely racemized, preferably the metallocene is completely racemized, i.e. racemic, and A, Cp, M, and X are as defined above);
- b) an activator comprising one or more heterocyclic heteroatom containing ligands coordinated to an isoalkyl alumoxane (preferably where the isoalkyl is a C₃ to C₁₂ isoalkyl, preferably isopropyl, isobutyl, isopentyl, isohexyl, or isooctyl), wherein the activator is a

reaction product of a solution of one or more isoalkyl alumoxanes (preferably where the alkyl is a C₃ to C₁₂ isoalkyl, preferably isopropyl, isobutyl, isopentyl, isohexyl, or isooctyl), and one or more heterocyclic heteroatom containing compounds, wherein the heterocyclic heteroatom containing ligand is represented by:

5



Y is NH or N-R where R is a C₁ to C₁₂ alkyl group;

wherein each of X2 and X3 is hydrogen, halogen or X2 and X3 may form a six membered aromatic ring (preferably X2 and X3 are H);

X4, X5, X6 and X7 are hydrogen or a halogen, provided that at least one of X⁵, X5, X6, or X7 is a halogen (preferably X5 is bromine and X4, X6 and X7 are H); and

wherein the ratio of the heterocyclic heteroatom containing ligand to aluminum is between 0.01:1 and 10:1 molar equivalents, and, optionally, the ratio of water to aluminum in the alumoxane solution is 0.7:1 or less.

2B. The catalyst system of paragraph 1B, wherein the metallocene is rac-Me₂Si-(2-methyl-indenyl)₂Zr(CH₃)₂ or rac-Me₂Si-(2-methyl-4-phenyl-indenyl)₂Zr(CH₃)₂.

3B. The catalyst system of paragraph 1B or 2B, wherein the ratio of heterocyclic heteroatom containing ligand to aluminum is from 0.1:1 to 5:1.

4B. The catalyst system of paragraph 1B, 2B, or 3B wherein A is a dialkylsilyl group and each X is independently a C₁ to C₂₀ alkyl group or a halogen.

5B. The catalyst system of any of paragraphs 1B to 5B wherein the alumoxane comprises isobutyl alumoxane or isohexyl alumoxane.

6B. The catalyst system of any of paragraphs 1B to 15B wherein the activity of the catalyst system is 1500 g polymer/g catalyst-hour or more.

In some embodiments, the catalyst system described above is supported, typically on silica.

EXAMPLES

[00113] Isobutylalumoxane was obtained commercially from Akzo Nobel Chemicals Inc. in two formulations: isobutylalumoxane (0.65 H₂O/Al), 3.5 wt% Al in hexanes and isobutylalumoxane (0.80 H₂O/Al), 3.5 wt% Al in heptane. The solvents used in both these formulations proved unsuitable for downstream reactions so, the solvents were replaced with the more polar solvent, toluene.

1. Synthesis of IBAO solutions: Replacement of solvent

Isobutylalumoxane (0.65 H₂O /Al):

[00114] Isobutylalumoxane (0.65 H₂O /Al), 3.5 wt% Al in hexanes was dried under vacuum to remove the hexanes and thereby yielded a viscous slurry. The slurry was weighed and then re-dissolved in an appropriate amount of toluene to give a 2.6 wt% solution.

[00115] In another embodiment, the slurry was weighed and re-dissolved in an appropriate amount of toluene to give a 10 wt% solution. These isobutylalumoxane solutions, IBAO (0.65, 2.6 wt% in toluene) and IBAO (0.65, 10 wt% in toluene), were used to prepare a series of liquid catalysts by reaction with selected organic ligands as shown below.

Isobutylalumoxane (0.80 H₂O/Al):

[00116] Similarly, isobutylalumoxane (0.80 H₂O/Al), 3.5 wt% Al in heptane was dried under vacuum to remove the heptane to yield a viscous slurry. The slurry was weighed and then re-dissolved in an appropriate amount of toluene to give a 10 wt% solution. This isobutylalumoxane solution, IBAO (0.80, 10 wt% in toluene), was used to prepare a series of liquid catalysts by reaction with selected organic ligands as shown below.

2. Reactions with IBAO (0.65):

[00117] Representative indoles were reacted with these IBAO solutions. The ratio of heterocycle to aluminum was shown to influence both the activity of the catalyst and the molecular weight of the resulting isotactic polypropylene.

I. Indole:

Synthesis of IBAO (0.65, 10 wt% in toluene)-INDO

[00118] 10.4g IBAO (0.65, 10 wt% in toluene) solution was weighed into a dry Wheaton glass bottle. A stir bar was added. 5.0g of indole was added to the solution. The indole dissolved readily to yield a yellow-orange solution. The solution was stirred overnight. The solution appeared to be fairly stable as no precipitation was observed even after storage at room temperature for a few months. [IBAO (0.65, 10 wt% in toluene)-5.0-INDO].

II. Halogenated Indoles:

5-Bromoindole:**Synthesis of IBAO (0.65, 2.6 wt% in toluene)–5-BrINDO**

[00119] 40 g IBAO (0.65, 2.6 wt% in toluene) solution was weighed into a dry Wheaton glass bottle. A stir bar was added. 0.25g of 5-bromoindole (Biosynth International) was added
5 to the solution. The 5-bromoindole dissolved readily to yield a very pale yellow solution. The solution was stirred overnight. [IBAO (0.65, 2.6 wt% in toluene)–0.25-5-BrINDO].

[00120] This reaction was conducted in various iterations by changing the amount of 5-bromoindole added. Solutions were made with 0.5g [IBAO (0.65, 2.6 wt% in toluene)–0.5-5-BrINDO], 1.0g [IBAO (0.65, 2.6 wt% in toluene)–1.0-5-BrINDO], and 5.0g [IBAO (0.65,
10 2.6 wt% in toluene)–5.0-5-BrINDO]. All solutions appeared to be fairly stable since no precipitation was observed even after storage at room temperature for a few months.

5,6-Dichloroindole:**Synthesis of IBAO (0.65, 10 wt% in toluene)-2,3-Cl₂INDO**

[00121] 40g IBAO (0.65, 10 wt% in toluene) solution was weighed into a dry Wheaton
15 glass bottle. A stir bar was added. 2.0g of 5,6-dichloroindole (Biosynth International) was added to the solution. The 5,6-dichloroindole dissolved readily to yield a yellow-orange solution. The solution was stirred overnight. The solution appeared to be fairly stable since no precipitation was observed even after storage at room temperature for a few months. [IBAO (0.65, 10 wt% in toluene)-0.5-2,3-Cl₂INDO]

3. Reactions with IBAO (0.80):

[00122] Representative members of the indole groups of organic ligands were reacted with these IBAO solutions. Reactivity of the individual ligands with the IBAO solutions varied depending on the substitutions on the ligand backbone. The effect of placing halogens or sterically bulky organic substituents on the ligand backbone on the resultant polypropylene
25 polymer was investigated.

I. Halogenated Indoles:**5-Bromoindole:****Synthesis of IBAO (0.80, 10 wt% in toluene)-5-BrINDO**

[00123] 10.4g IBAO (0.80, 10 wt% in toluene) solution was weighed into a dry Wheaton
30 glass bottle. A stir bar was added. 0.25g of 5-bromoindole (Biosynth International) was added to the solution. The 5-bromoindole dissolved readily to yield a yellow solution. The solution was stirred overnight. [IBAO (0.80, 10 wt% in toluene)-0.25-5-BrINDO].

[00124] This reaction was conducted in various iterations by changing the amount of 5-bromoindole added. Solutions were made with 0.5g [IBAO (0.80, 10 wt% in toluene)-0.5-5-BrINDO], 0.75g [IBAO (0.80, 10 wt% in toluene)-0.75-5-BrINDO], 1.0g [IBAO (0.80, 10 wt% in toluene)-1.0-5-BrINDO] and 5.0g [IBAO (0.80, 10 wt% in toluene)-5.0-5-BrINDO].

5 All solutions appeared to be fairly stable since no precipitation was observed even after storage at room temperature for a few months.

5-Chloroindole:

Synthesis of IBAO (0.80, 10 wt% in toluene)-5-chloroindole

10 [00125] 10.0g IBAO (0.80, 10 wt% in toluene) solution was weighed into a dry Wheaton glass bottle. A stir bar was added. 0.19g of 5-chloroindole (Biosynth International) was added to the solution. The 5-chloroindole dissolved readily to yield a yellow solution. The solution was stirred overnight. [IBAO (0.80, 10 wt% in toluene)-0.19-5-ClINDO].

[00126] This reaction was conducted in various iterations by changing the amount of 5-chloroindole added. Solutions were made with 0.4g [IBAO (0.80, 10 wt% in toluene)-0.40-5-ClINDO] and 0.65g [IBAO (0.80, 10 wt% in toluene)-0.65-5-ClINDO].

15 [00127] All the solutions appeared to be fairly stable as no precipitation was observed even after storage at room temperature for a few days.

II. Substituted Indoles

2-Phenylindole:

20 Synthesis of IBAO (0.80, 10 wt%)-2-phenylindole

[00128] 20.0g IBAO (0.80, 10 wt%) solution was weighed into a dry Wheaton glass bottle. A stir bar was added. 1.96g of 2-phenylindole was added to the solution. The 2-phenylindole dissolved readily to yield a yellow solution. The solution was stirred overnight. Yellow crystals were observed to fall out of solution on standing for a few days. [IBAO (0.80, 10 wt%)-0.83-2-phenylindole].

2,3-Dimethyl Indole:

Synthesis of IBAO (0.80, 10 wt%)-2,3-dimethylindole

[00129] 10.4g IBAO (0.80, 10 wt%) solution was weighed into a dry Wheaton glass bottle. A stir bar was added. 0.19g of 2,3-dimethylindole was added to the solution. The 2,3-dimethylindole dissolved readily to yield a yellow solution. The solution was stirred overnight. The solution appeared to be fairly stable as no precipitation was observed even after storage at room temperature for a few days. [IBAO (0.80, 10 wt%)-0.19-2,3-dimethyl-

indole]. This reaction was conducted in various iterations by changing the amount of 2,3-dimethylindole added: 0.38 grams and 0.76 grams [IBAO (0.80, 10 wt%)-0.38-2,3-dimethylindole][IBAO (0.80, 10 wt%)-0.76-2,3-dimethylindole].

3-Methylindole:

5 Synthesis of IBAO (0.80, 10 wt%)-3-Methylindole

[00130] 10.4g IBAO (0.80, 10 wt%) solution was weighed into a dry Wheaton glass bottle. A stir bar was added. 0.17g of 3-methylindole was added to the solution. The 3-methylindole dissolved readily to yield a yellow solution. The solution was stirred overnight. [IBAO (0.80, 10 wt%)-0.17-3-MeINDO].

10 [00131] This reaction was conducted in various iterations by changing the amount of 5-chloroindole added. Solutions were made of 0.34g [IBAO (0.80, 10 wt%)-0.34-3-MeINDO (24848-185)], and 0.8g [IBAO (0.80, 10 wt%)-0.80-3-MeINDO]. All solutions appeared to be fairly stable as no precipitation was observed even after storage at room temperature for a few days.

15 Experimental - Polymerizations:

[00132] In the following slurry phase experiments pressure is reported in atmospheres and pounds per square inch. The conversion factors to S.I. Units are; 1 psi equals 6.894757 kPa and 1 atm equals 101.325 kPa.

Feed

20 [00133] Polymerization grade propylene was used and further purified by passing it through a series of columns: 500 cc Oxyclear cylinder from Labclear (Oakland, CA) followed by a 500 cc column packed with dried 3Å mole sieves purchased from Aldrich Chemical Company, and a 500 cc column packed with dried 5Å mole sieves purchased from Aldrich Chemical Company.

25 Scavengers / Co-catalysts

[00134] Triisobutyl aluminum (TIBAL) was obtained from Akzo Chemicals, Inc. and used without further purification. Tri n-octyl aluminum (TNOAL) was obtained from Akzo Chemicals, Inc. and used without further purification.

30 [00135] Polymerization grade hexane was used and further purified by passing it through a series of columns: 500 cc Oxyclear cylinder from Labclear (Oakland, CA) followed by a 500 cc column packed with dried 3Å mole sieves purchased from Aldrich Chemical Company,

and a 500 cc column packed with dried 5Å mole sieves purchased from Aldrich Chemical Company.

Reactor Description and Preparation

[00136] Polymerizations were conducted in an inert atmosphere (N₂) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal volume of reactor = 22.5 mL), septum inlets, regulated supply of nitrogen, propylene, and equipped with disposable PEEK mechanical stirrers (400 RPM). The autoclaves were prepared by purging with dry nitrogen at 110°C or 115°C for 5 hours and then at 25°C for 5 hours.

Propylene polymerization:

[00137] The reactor was prepared as described above, and then purged with propylene. The reactors were heated to 40°C and propylene was first charged to the reactor.

[00138] A solution of scavenger / co-catalyst at room temperature and pressure was next added to the reactors via syringe. The reactors were then brought to process temperature (70°C) while stirring at 400 RPM.

[00139] In the nature that solutions are added via syringe, a hexanes solution is also injected via the same syringe following their addition to insure that minimal solution is remaining in the syringe. This procedure is applied after the addition of the scavenger/co-catalyst solution as well as the catalyst slurry.

[00140] Propylene was allowed to enter (through the use of computer controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure 450 psi(+/- 2 psig). Reactor temperature was monitored and typically maintained within +/- 1°C. Polymerizations were halted by addition of approximately 400 psig O₂/Ar (5 mole% O₂) gas mixture to the autoclaves for approximately 30 seconds. The polymerizations were quenched after 45 minutes polymerization time. The reactors were cooled and vented. The polymer was isolated after the remaining reaction components were removed in-vacuo.

Polymer characterization:

[00141] Polymer characterization results for polypropylene samples are reported in table 1. For analytical testing, polymer sample solutions were prepared by dissolving polymer in 1,2,4-trichlorobenzene (TCB, 99+% purity from Sigma-Aldrich) containing 2,6-di-*tert*-butyl-4-methylphenol (BHT, 99% from Aldrich) at 145°C in a shaker oven for approximately 3 hours. The typical final concentration of polymer in solution is between 0.4 to 0.9 mg/mL

with a BHT concentration of 1.25 mg BHT/mL of TCB. Samples are cooled to 135°C for testing

[00142] Molecular weights (weight average molecular weight (M_w) and number average molecular weight (M_n)) and molecular weight distribution ($MWD = M_w/M_n$), which is also sometimes referred to as the polydispersity (PDI) of the polymer, were measured by Gel Permeation Chromatography using a Symyx Technology GPC equipped with evaporative light scattering detector and calibrated using polystyrene standards from Polymer Mp (peak M_w) between 5000 and 3,390,000). Samples were run in TCB at (135°C sample temperatures, 165°C oven/columns) using three Polymer Laboratories: PLgel 10m Mixed-B 300 x 7.5mm columns in series. No column spreading corrections were employed. Numerical analyses were performed using Epoch® software available from Symyx Technologies.

Samples for DSC were performed on a TA Instruments Q100 DSC.

Sample preparation.

[00143] To prepare the samples, approximately 0.07 g of each polymer were weighed into tared glass vials. Each glass vial was then weighed by the Bohdan weigh station, and 2.8 ml of trichlorobenzene with BHT was added to each vial using the Rapid GPC prep station to obtain 25 mg/ml solutions. The polymers were then dissolved at 165°C with mixing bars and agitation. The Rapid GPC station then automatically dispensed approximately 0.4 ml of each polymer solution into DSC pans. The trichlorobenzene was evaporated at 165°C over approximately 15 minutes.

[00144] The DSC pans were then annealed in an oven purged with nitrogen to give them the same thermal history. The samples were annealed at 220°C for 15 minutes, and allowed to cool overnight to room temperature.

DSC measurements.

[00145] The following heating and cooling sequence were used to test samples in a high throughput mode. The first melt occurs when the pans are annealed in parallel in the purged oven.

1) Ramp 100°C/min to 220°C (second melt)

2) Hold 1 min at 220°C

3) Ramp 50°C/min to 40°C (crystallization)

Table 1. Catalyst: rac-Me₂Si(2-methyl-indenyl)₂Zr(CH₃)₂/IBAO(0.65)(5-BrINDO)

Activator	Average Mn	Average Mw	Average PDI	actual quench time	Yield (grams)	Activity (gPP/m moleZrsec)
MAO(comparative)	59958	86,497	1.44	340	0.0771	1.51
	57377	82,644	1.44	264	0.0565	1.42
	66141	95,024	1.43	379	0.0835	1.47
	68804	99,261	1.44	349	0.0849	1.62
	65679	94,400	1.43	376	0.086	1.52
	65497	94,212	1.43	363	0.0826	1.52
IBAO(0.65) (comparative)				900	0.0082	0.0607
				900	0.0063	0.0466
				900	0.0045	0.0333
				901	0.0061	0.0451
				900	0.0049	0.0363
				900	0.0054	0.04
IBAO(0.65)-0.5-5,6- dichloroindolyl-	9143	13,878	1.51	123	0.1322	7.14
	9737	14,683	1.50	131	0.1228	6.23
	9724	14,654	1.50	111	0.1035	6.21
	9281	14,077	1.51	138	0.1486	7.16
	10034	15,301	1.52	122	0.1233	6.73
	8977	13,596	1.51	148	0.1521	6.84
IBAO(0.65)-0.25-5- BrINDO	119434	175,855	1.47	900	0.0327	0.242
	119839	175,225	1.46	900	0.0299	0.221
	132647	193,977	1.46	901	0.033	0.244
	128962	188,859	1.46	900	0.0324	0.24
	131956	189,494	1.43	900	0.0311	0.23
	127470	185,011	1.45	659	0.0287	0.29
IBAO(0.65)-0.5-5- BrINDO	53418	79,319	1.48	900	0.045	0.333
	64681	93,723	1.44	900	0.0456	0.338
	63139	91,912	1.45	900	0.054	0.4
	61018	88,779	1.45	900	0.049	0.363
	59733	86,593	1.44	900	0.0481	0.356
	62484	90,644	1.45	900	0.0484	0.358
IBAO(0.65)-1.0-5- BrINDO	39682	58,704	1.47	665	0.0623	0.624
	38694	57,356	1.48	548	0.0607	0.738
	44832	66,142	1.47	630	0.0732	0.774
	38621	56,370	1.45	614	0.0668	0.725
	39743	58,470	1.47	758	0.0555	0.488
	38227	56301	1.47	616	0.0605	0.654

Activator	Average Mn	Average Mw	Average PDI	actual quench time	Yield (grams)	Activity (gPP/m moleZrsec)
IBAO(0.65)-5.0-5-BrINDO	7587	11755	1.54	92.9	0.1209	8.676
	7295	11286	1.54	94.2	0.1265	8.953
	4598	6843	1.48	186	0.0816	2.911
	7782	12196	1.56	104	0.136	8.651
	7600	11957	1.57	102	0.1312	8.575
	7933	12512	1.57	106	0.1337	8.393

30 umoles activator, 0.15umoles catalyst

Table 2. Catalyst: rac-Me₂Si(2-methyl-indenyl)₂Zr(CH₃)₂/IBAO(0.80)(5-BrINDO)

Activator	Average Mn	Average Mw	Average PDI	actual quench time	Yield (grams)	Activity	Tm
MAO(comparative)	64342	95,120	1.48	196	0.1134	3.85	139
	60805	87,069	1.43	183	0.0998	3.64	
	58688	84,690	1.44	163	0.0886	3.62	138
IBAO(0.80)-0.25-5-BrINDO	11363	18,765	1.65	351	0.0813	1.55	143
	10425	18,387	1.76	400	0.0826	1.38	141
	10829	18,500	1.71	438	0.0841	1.28	
IBAO(0.80)-0.5-5-BrINDO	7674.6	11,722	1.53	155	0.0603	2.59	
	8481.7	12,226	1.44	192	0.0747	2.59	145
	7867.5	11,959	1.52	209	0.0616	1.96	
	8291.6	12,483	1.51	193	0.0717	2.47	144
	8305.6	12,384	1.49	204	0.0613	2	
	8094.3	11,949	1.48	225	0.0526	1.56	145
IBAO(0.80)-1.0-5-BrINDO	10910	16,689	1.53	901	0.0118	0.087	
	12042	17,378	1.44	900	0.0117	0.087	
	11483	16,768	1.46	900	0.0113	0.084	
	11522	17,390	1.51	901	0.0128	0.095	
				900	0.0031	0.023	
				901	0.0091	0.067	
IBAO(0.80)-5.0-5-BrINDO				647	0.0111	0.114	
				901	0.0109	0.081	
				900	0.011	0.081	
				901	0.0114	0.084	
				901	0.0116	0.086	
				901	0.0114	0.084	

30 umoles activator, 0.15umoles catalyst

Table 3. Catalyst: rac-Me₂Si(2-methyl4-phenyl-indenyl)₂Zr(CH₃)₂/IBAO(0.80)(5-BrINDO)

Activator	Average Mn	Average Mw	Average PDI	actual quench time	Yield (grams)	Activity	Tm
IBAO(0.80)-0.25-5-BrINDO	66724	101,616	1.52	350	0.0517	0.985	158
	64749	102,254	1.58	438	0.1216	1.853	160
	65609	102,692	1.57	424	0.1174	1.846	159
	63056	98,622	1.56	348	0.126	2.415	159
	65205	98,728	1.51	390	0.0847	1.449	159
	60785	95,012	1.56	385	0.1001	1.733	159
IBAO(0.80)-0.5-5-BrINDO	35989	53,111	1.48	142	0.0992	4.654	157
	42897	62,850	1.47	160	0.0939	3.903	157
	42867	62,792	1.46	156	0.0822	3.522	158
	40746	59,229	1.45	145	0.1012	4.663	157
	39510	58,674	1.49	144	0.0877	4.057	156
	37159	56,596	1.52	150	0.0603	2.684	157
IBAO(0.80)-1.0-5-BrINDO	48756	69,713	1.43	109	0.0259	1.587	
	53216	79,628	1.5	92	0.0284	2.058	158
	58011	81,221	1.4	94.8	0.0265	1.864	157
	55280	80,676	1.46	85.8	0.0287	2.23	157
	53123	77,432	1.46	80.7	0.0311	2.569	156
	53174	76,605	1.44	112	0.0173	1.033	135
IBAO(0.80)-5.0-5-BrINDO				901	0.0113	0.084	
				901	0.0113	0.084	
				900	0.0115	0.085	
				900	0.0122	0.09	
				901	0.0124	0.092	
				900	0.0123	0.091	

30 umoles activator, 0.15umoles catalyst

[00146] 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 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" for purposes of Australian law.

CLAIMS

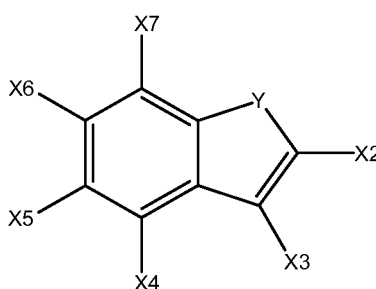
What is claimed is:

1. A process to polymerize propylene comprising:

1) contacting propylene and from 0 to 50 wt% comonomer with a catalyst system comprising:

a) a metallocene represented by the formula ACp_2MX_2 where M is Ti, Hf or Zr and M is bound to each Cp group, A is a bridging group connecting the two Cp groups, each Cp is, independently, an indenyl group or a substituted indenyl group, each X is an anionic leaving group;

b) an activator comprising one or more heterocyclic heteroatom containing ligands coordinated to an isoalkyl alumoxane, wherein the activator is a reaction product of a solution of one or more isoalkyl alumoxanes and one or more heterocyclic heteroatom containing compounds, wherein the heterocyclic heteroatom containing ligand is represented by:



Y is NH or N-R where R is a C_1 to C_{12} alkyl group;

wherein each of X2 and X3 is hydrogen, halogen or X2 and X3 may form a six membered aromatic ring;

X4, X5, X6 and X7 are hydrogen or a halogen (provided that at least one of X4, X5, X6 or X7 is a halogen); and

wherein the ratio of the heterocyclic heteroatom containing ligand to aluminum is between 0.01:1 and 10:1 molar equivalents; and

2) obtaining polymer having at least 50 wt% propylene, an Mw of 5,000 to 200,000 g/mol and a melting point of 140°C or more, provided that the melting point is also greater than or equal to $0.000143x(Mw \text{ in g/mol})+133$.

2. The process of claim 1, wherein the metallocene is $\text{rac-Me}_2\text{Si}-(2\text{-methyl-indenyl})_2\text{Zr}(\text{CH}_3)_2$ or $\text{rac-Me}_2\text{Si}-(2\text{-methyl-4-phenyl-indenyl})_2\text{Zr}(\text{CH}_3)_2$.

3. The process of claim 1 or 2, wherein the ratio of heterocyclic heteroatom containing ligand to aluminum is from 0.2:1 to 5:1.

5 4. The process of claim 1 or 3 wherein A is a dialkylsilyl group and each X is independently a C_1 to C_{20} alkyl group or a halogen.

5. The process of any of claims 1 to 4 wherein the isoalkyl alumoxane comprises isobutyl alumoxane and or isohexyl alumoxane.

6. The process of any of claim 1 to 5 wherein polymer produced has an Mw of 10,000 to 10 120,000 and wherein if polymer produced has an Mw of 40,000 g/mol or more then the melting point is 145°C or more.

7. The process of any of claims 1 to 6 wherein the activity of the catalyst system is 1500 g polymer/g catalyst-hour or more.

8. The process of any of claims 1 to 7, wherein the comonomer is selected from the 15 group consisting of: ethylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene and dodecene.

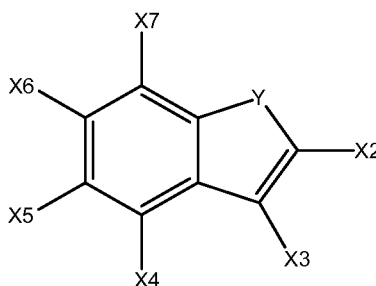
9. The process of any of claims 1 to 8 wherein the polymer obtained has at least 80 wt% propylene and wherein if polymer obtained has an Mw of 50,000 g/mol or more then the melting point is 150°C or more.

20 10. A catalyst system comprising:

a) a metallocene represented by the formula ACp_2MX_2 where M is Ti, Hf or Zr and M is bound to each Cp group, A is a bridging group connecting the two Cp groups, each Cp is, independently, an indenyl group or a substituted indenyl group, each X is an anionic leaving group;

25 b) an activator comprising one or more heterocyclic heteroatom containing ligands coordinated to an isoalkyl alumoxane, wherein the activator is a reaction product of a solution of one or more isoalkyl alumoxanes and one or more heterocyclic heteroatom containing compounds, wherein the heterocyclic heteroatom containing ligand is represented by:

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Y is NH or N-R where R is a C₁ to C₁₂ alkyl group;

wherein each of X2 and X3 is hydrogen, halogen or X2 and X3 may form a six membered aromatic ring;

X4, X5, X6 and X7 are hydrogen or a halogen (provided that at least one of X4, X5, X6 or X7 is a halogen); and

wherein the ratio of the heterocyclic heteroatom containing ligand to aluminum is between 0.01:1 and 10:1 molar equivalents.

11. The catalyst system of claim 10, wherein the metallocene is rac-Me₂Si-(2-methyl-indenyl)₂Zr(CH₃)₂ or rac-Me₂Si-(2-methyl-4-phenyl-indenyl)₂Zr(CH₃)₂.

12. The catalyst of claim 10 or 11, wherein the ratio of heterocyclic heteroatom containing ligand to aluminum is from 0.1:1 to 5:1.

13. The catalyst of claim 10 or 12 wherein A is a dialkylsilyl group and each X is independently a C₁ to C₂₀ alkyl group or a halogen.

14. The catalyst of any of claims 10 to 13 wherein the alumoxane comprises isobutyl alumoxane or isohexyl alumoxane.

15. The catalyst of any of claims 10 to 14 wherein the activity of the catalyst system is 1500 g polymer/g catalyst-hour or more.

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