CONTROL OF POLYMER ARCHITECTURE AND MOLECULAR WEIGHT DISTRIBUTION VIA MULTI-CENTERED SHUTTLING AGENT

Cross Reference Statement

This application claims the benefit of U.S. Provisional Application No. 60/717,543, filed September 15, 2005.

Background of the Invention

The present invention relates to a process for polymerizing a monomer or mixtures of two or more monomers such as mixtures of ethylene and one or more comonomers, to form an interpolymer product having unique physical properties, to a process for preparing such interpolymers, and to the resulting polymer products. In another aspect, the invention relates to the articles prepared from these polymers. The inventive polymer products include blends of generally uniform chemical composition and relatively broad molecular weight distribution, including a blend of two or more polymers of uniform monomer composition but differing in that at least one component has substantially higher in molecular weight than at least one other component. Also included are mixtures of two or more polymers comprising regions or segments (blocks) of differing chemical composition, characterized by the foregoing molecular weight distribution characteristics. In addition, at least one of the constituents of the polymer mixture contains a linking group which is the remnant of a multi-centered shuttling agent, causing the polymer to possess unique physical properties. These polymeric products and blends comprising the same are usefully employed in the preparation of solid articles such as moldings, films, sheets, and foamed objects by molding, extruding, or other processes, and are useful as components or ingredients in adhesives, laminates, polymeric blends, and other end uses. The resulting products are used in the manufacture of components for automobiles, such as profiles, bumpers and trim parts; packaging materials; electric cable insulation, and other applications.

The use of certain metal alkyl compounds and other compounds, such as hydrogen, as chain transfer agents to interrupt chain growth in olefin polymerizations is well known in the art. In addition, it is known to employ such compounds, especially aluminum alkyl compounds, as scavengers or as cocatalysts in olefin polymerizations. In Macromolecules, 33, 9192-9199 (2000) the use of certain aluminum trialkyl compounds as chain transfer agents in combination with certain paired zirconocene catalyst compositions resulted in polypropylene mixtures containing small quantities of polymer fractions containing both isotactic and atactic chain segments. In Liu and Rytter, Macromolecular Rapid Comm., 22, 952-956 (2001) and Bruaseth and Rytter, Macromolecules, 36, 3026-3034 (2003) mixtures of ethylene and 1-hexene were polymerized by a similar catalyst composition containing trimethylaluminum chain transfer agent. In the latter

reference, the authors summarized the prior art studies in the following manner (some citations omitted):

"Mixing of two metallocenes with known polymerization behavior can be used to control polymer microstructure. Several studies have been performed of ethene polymerization by mixing two metallocenes. Common observations were that, by combining catalysts which separately give polyethene with different *M*w, polyethene with broader and in some cases bimodal MWD can be obtained. [S]oares and Kim (J. Polym. Sci., Part A: Polym. Chem., 38, 1408-1432 (2000)) developed a criterion in order to test the MWD bimodality of polymers made by dual single-site catalysts, as exemplified by ethene/1-hexene copolymerization of the mixtures $Et(Ind)_2ZrCl_2/Cp_2HfCl_2$ and $Et(Ind)_2ZrCl_2$/ CGC (constrained geometry catalyst) supported on silica. Heiland and Kaminsky (Makromol. Chem., 193, 601-610 (1992)) studied a mixture of $Et\text{-}(Ind)_2ZrCl_2$ and the hafnium analogue in copolymerization of ethene and 1-butene.

These studies do not contain any indication of interaction between the two different sites, for example, by readsorption of a terminated chain at the alternative site. Such reports have been issued, however, for polymerization of propene. Chien et al. (J. Polym. Sci., Part A: Polym. Chem., 37, 2439-2445 (1999), Makromol., 30, 3447-3458 (1997)) studied propene polymerization by homogeneous binary zirconocene catalysts. A blend of isotactic polypropylene (i-PP), atactic polypropylene (a-PP), and a stereoblock fraction (i-PP-*b*-a-PP) was obtained with a binary system comprising an isospecific and an aspecific precursor with a borate and TIBA as cocatalyst. By using a binary mixture of isospecific and syndiospecific zirconocenes, a blend of isotactic polypropylene (i-PP), syndiotactic polypropylene (s-PP), and a stereoblock fraction (i-PP-*b*-s-PP) was obtained. The mechanism for formation of the stereoblock fraction was proposed to involve the exchange of propagating chains between the two different catalytic sites. Przybyla and Fink (Acta Polym., 50, 77-83 (1999)) used two different types of metallocenes (isospecific and syndiospecific) supported on the same silica for propene polymerization. They reported that, with a certain type of silica support, chain transfer between the active species in the catalyst system occurred, and stereoblock PP was obtained. Lieber and Brintzinger (Macromol. 3, 9192-9199 (2000)) have proposed a more detailed explanation of how the transfer of a growing polymer chain from one type of metallocene to another occurs. They studied propene polymerization by catalyst mixtures of two different *ansa*-zirconocenes. The different catalysts were first studied individually with regard to their tendency toward alkyl-polymeryl exchange with the

alkylaluminum activator and then pairwise with respect to their capability to produce polymers with a stereoblock structure. They reported that formation of stereoblock polymers by a mixture of zirconocene catalysts with different stereoselectivities is contingent upon an efficient polymeryl exchange between the Zr catalyst centers and the Al centers of the cocatalyst."

Brusath and Rytter then disclosed their own observations using paired zirconocene catalysts to polymerize mixtures of ethylene/1-hexene and reported the effects of the influence of the dual site catalyst on polymerization activity, incorporation of comonomer, and polymer microstructure using methylalumoxane cocatalyst.

Analysis of the foregoing results indicate that Rytter and coworkers likely failed to utilize combinations of catalyst, cocatalyst, and third components that were capable of readsorption of the polymer chain from the chain transfer agent onto both of the active catalytic sites, that is they failed to obtain two-way readsorption. While indicating that chain termination due to the presence of trimethylaluminum likely occurred with respect to polymer formed from the catalyst incorporating minimal comonomer, and thereafter that polymeryl exchange with the more open catalytic site followed by continued polymerization likely occurred, evidence of the reverse flow of polymer ligands appeared to be lacking in the reference. In fact, in a later communication, Rytter, et. al., Polymer, 45, 7853-7861 (2004), it was reported that no chain transfer between the catalyst sites actually took place in the earlier experiments. Similar polymerizations were reported in WO98/34970.

In USP's 6,380,341 and 6,169,151, use of a "fluxional" metallocene catalyst, that is a metallocene capable of relatively facile conversion between two stereoisomeric forms having differing polymerization characteristics such as differing reactivity ratios was said to result in production of olefin copolymers having a "blocky" structure. Disadvantageously, the respective stereoisomers of such metallocenes generally fail to possess significant difference in polymer formation properties and are incapable of forming both highly crystalline and amorphous block copolymer segments, for example, from a given monomer mixture under fixed reaction conditions. Moreover, because the relative ratio of the two "fluxional" forms of the catalyst cannot be varied, there is no ability, using "fluxional" catalysts, to vary polymer block composition or to vary the ratio of the respective blocks.

In JACS, 2004, 126, 10701-10712, Gibson, *et al* discuss the effects of "catalyzed living polymerization" on molecular weight distribution. The authors define catalyzed living polymerization in this manner:

"...if chain transfer to aluminum constitutes the sole transfer mechanism and the exchange of the growing polymer chain between the transition metal and the aluminum

centers is very fast and reversible, the polymer chains will appear to be growing on the aluminum centers. This can then reasonably be described as a catalyzed chain growth reaction on aluminum....An attractive manifestation of this type of chain growth reaction is a Poisson distribution of product molecular weights, as opposed to the Schulz-Flory distribution that arises when β-H transfer accompanies propagation."

The authors reported the results for the catalyzed living homopolymerization of ethylene using an iron containing catalyst in combination with $ZnEt_2$, $ZnMe_2$, or $Zn(i\text{-}Pr)_2$. Homoleptic alkyls of aluminum, boron, tin, lithium, magnesium and lead did not induce catalyzed chain growth. Using $GaMe_3$ as cocatalyst resulted in production of a polymer having a narrow molecular weight distribution. However, after analysis of time-dependent product distribution, the authors concluded this reaction was, "not a simple catalyzed chain growth reaction." Similar processes employing similar catalysts have been described in USP's 5,210,338, 5, 276,220, and 6,444,867.

It is known in the art that the presence of long chain branching (LCB) may improve certain polymer characteristics, especially processability and melt strength. The presence of LCB in a polymer is characterized by the occurrence of polymer moieties of a length greater than that of any $C_{3\text{-}8}$ olefin comonomer remnant attached to the main, backbone polymer chain. In prior art techniques, long chain branching may be generated in a polymer by incorporation of a vinyl-terminated macromer (either deliberately added or formed in situ during a polymerization such as through β-hydride elimination) either by action of the polymerization catalyst itself or by the use of a linking agent. These methods generally suffer from incomplete incorporation of the vinyl-terminated macromer or linking moiety into the polymer, and/or a lack of control over the extent of LCB for given process conditions.

There remains a need in the art for a polymerization process that is capable of preparing copolymers having unique properties in a high yield process adapted for commercial utilization. Moreover, it would be desirable if there were provided an improved process for preparing polymers, including copolymers of two or more comonomers such as ethylene and one or more comonomers, by the use of a multi-centered shuttling agent (MSA) to introduce coupled or branched properties, including long chain branching, in the resulting pseudo-block copolymers, in a controlled manner. More specifically, it would be desirable to provide a method for generating long chain branching in olefin polymers that does not require incorporation of a polymerizable functional group, such as a vinyl group into the polymer chain. In addition it would be desirable to provide such an improved process for preparing the foregoing coupled or branched pseudo-block copolymer products in a continuous process.

Summary of the Invention

According to the present invention there is now provided an olefin polymer composition uniquely characterized by a broad, especially a multimodal molecular weight distribution and a process for the preparation thereof. In particular, the present composition comprises two or more olefin polymers differing in molecular weights, wherein the weight average molecular weights of at least two such polymers differ by approximately an integer multiple. The polymer mixture is prepared *in situ* by the polymerization of one or more addition polymerizable monomers, preferably of two or more addition polymerizable monomers, especially ethylene and at least one copolymerizable comonomer, propylene and at least one copolymerizable comonomer having 4 or more carbons, or 4-methyl-1-pentene and at least one different copolymerizable comonomer having 4 or more carbons, optionally comprising multiple blocks or segments of differentiated polymer composition or properties, especially blocks or segments comprising differing comonomer incorporation levels. The process comprises contacting an addition polymerizable monomer or mixture of monomers under addition polymerization conditions with a composition comprising at least one addition polymerization catalyst, a cocatalyst and a multi-centered shuttling agent.

Because the polymer is comprised of at least some polymer joined by means of one or more remnants of a multi-centered shuttling agent, the resulting polymeric composition possesses unique physical and chemical properties compared to random mixtures of polymers of the same gross chemical composition and compared to pseudo-block copolymers prepared with a chain shuttling agent lacking in multiple shuttling centers. Depending on the number of active centers in the multi-centered shuttling agent, that is, whether each shuttling agent molecule has two, three or more active shuttling sites, and the number of separate additions of such agent, the resulting polymer may be distinctly multi-modal or form a more uniform, broad distribution of molecular weight polymers and/or branched or multiply branched. In general, the resulting polymers contain reduced incidence of crosslinked polymer formation evidenced by reduced gel fraction. Preferably, the polymers of the invention comprise less than 2 percent of a crosslinked gel fraction, more preferably less than 1 percent crosslinked gel fraction, and most preferably less than 0.5 percent of crosslinked gel fraction.

In another embodiment of the invention there is provided a copolymer, especially such a copolymer comprising in polymerized form ethylene and a copolymerizable comonomer, propylene and at least one copolymerizable comonomer having from 4 to 20 carbons, or 4-methyl-1-pentene and at least one different copolymerizable comonomer having from 4 to 20 carbons, said copolymer comprising two or more, preferably two or three intramolecular regions comprising differing chemical or physical properties, especially regions of differentiated comonomer incorporation, joined in a dimeric, linear, branched or polybranched polymer structure. Such polymers may be

prepared by altering the polymerization conditions during a polymerization that includes a multi-centered shuttling agent, for example by using two reactors with differing comonomer ratios, multiple catalysts with differing comonomer incorporation abilities, or a combination of such process conditions, and optionally a polyfunctional coupling agent.

In another embodiment of the invention there is provided a process and the resulting polymer, said process comprising:

polymerizing one or more olefin monomers in the presence of an olefin polymerization catalyst and a multi-centered shuttling agent (MSA) in a polymerization reactor or zone thereby causing the formation of at least some quantity of a polymer joined with the remnant of the multi-centered shuttling agent.

In yet another embodiment of the invention there is provided a process and the resulting polymer, said process comprising:

polymerizing one or more olefin monomers in the presence of an olefin polymerization catalyst and a multi-centered shuttling agent (MSA) in a polymerization reactor or zone thereby causing the formation of at least some quantity of an initial polymer joined with the remnant of the multi-centered shuttling agent within the reactor or zone;

discharging the reaction product from the first reactor or zone to a second polymerization reactor or zone operating under polymerization conditions that are distinguishable from those of the first polymerization reactor or zone;

transferring at least some of the initial polymer joined with the remnant of the multi-centered shuttling agent to an active catalyst site in the second polymerization reactor or zone by means of at least one remaining shuttling site of the multi-centered shuttling agent; and

conducting polymerization in the second polymerization reactor or zone so as to form a second polymer segment bonded to some or all of the initial polymer by means of a remnant of the multi-centered shuttling agent, said second polymer segment having distinguishable polymer properties from the initial polymer segment.

Highly desirably, the polymer products herein comprise at least some quantity of a polymer containing two or more blocks or segments joined by means of a remnant of a multi-centered shuttling agent. Generally the product comprises distinct polymer species having different molecular weights, ideally the larger molecular weights being integer multiples of the smallest. As a general rule, the product comprises a first polymer having a first molecular weight and at least some quantity of a second polymer having a molecular weight that is approximately an integer multiple of the molecular weight of the first polymer, wherein the integer is equal to the number of shuttling centers in the shuttling agent. The polymer recovered from the present process may be terminated to form conventional type polymers, coupled through use of a polyfunctional coupling

agent to form multiblock copolymers, including hyper-branched or dendrimeric copolymers, or functionalized by conversion of remnants of the multi-centered shuttling agents into vinyl-, hydroxyl-, amine-, silane, carboxylic acid-, carboxylic acid ester, ionomeric, or other functional groups, according to known techniques.

In one embodiment of the invention a two-centered shuttling agent is used, resulting in polymers containing at least some quantity of a polymer containing the remnant of the two-centered chain shuttling agent and further step growth polymers based thereon. The resulting product is a polydisperse, in situ prepared, polymer blend, typically having a bimodal molecular weight distribution with one peak approximately twice the molecular weight of the other. If both a multi-centered shuttling agent and a monocenter chain shuttling agent are employed, either simultaneously or sequentially in the same polymerization, the result is a mixture of polymer products having polydisperse molecular weight distribution and pseudo-block copolymer properties.

In yet another embodiment of the invention, the multi-centered shuttling agent employed in the foregoing processes is a two-centered shuttling agent, which uniquely causes the formation of a product comprising distinct polymer segments after undergoing sequential polymerization in two reactors or zones connected in series. In a further preferred embodiment, the two-centered shuttling agent's active sites are located near or at both termini of a linear shuttling agent (or form such a shuttling agent by ring opening of a cyclic MSA) and result in the formation of terminally functionalized polymers, including those polymers converted into further functional groups as previously disclosed. The foregoing two-centered shuttling agents are referred to here-in-after as α,ω-two-centered shuttling agents due to their usefulness in the formation of α,ω-di-functionalized polymers, particularly low molecular weight α,ω-dihydroxy- or α,ω-divinyl- substituted polyolefins having a molecular weights from 500 to 10,000, preferably from 1000 to 6000. Such products may be prepared by the reaction of oxygen or an oxygen – containing electrophile with the alpha-omega di-metallated polymer formed by incorporation of the present α,ω-two-centered shuttling agent into a growing polymer, or by displacement of the metal center with an olefin, such as ethylene, to make the α,ω-diene, which may then be converted to the diol by hydroformylation and hydrogenation if desired. Such polymers, especially low molecular weight versions thereof are useful for conversion to polyurethanes, polyesters, and other products used in coating, adhesive, sealant and elastomer production.

In the foregoing embodiments of the invention, the resulting polymer may be linear or contain one or more branching centers, depending on whether a two-centered-, three-centered-, or higher centered shuttling agent is employed. Highly desirably, the foregoing copolymers are characterized by terminal blocks or segments of polymer having higher tacticity or crystallinity from at least some remaining blocks or segments. Even more preferably, the polymer is a triblock

copolymer comprising a central polymer block or segment that is relatively amorphous or even elastomeric.

In yet another embodiment, the MSA is a three centered shuttling agent and the resulting polymers are characterized by the presence of long chain branching. In this embodiment, there is furthermore provided a method for generating long chain branching in olefin polymers without use of a polymerizable functional group, such as a vinyl group. Instead, the LCB branch point is the remnant of such a three-centered MSA. Because the extent of LCB in the polymer is easily controlled by addition of the three centered MSA to a polymerization reaction at the desired rate the resulting process is advantaged over prior art processes.

In a still further embodiment of the present invention, there is provided a polymer mixture comprising: (1) an organic or inorganic polymer, preferably a homopolymer of ethylene or of propylene and/or a copolymer of ethylene or propylene with one or more copolymerizable comonomers, and (2) a polymer or polymer mixture according to the present invention or prepared according to the process of the present invention.

Brief Description of the Drawings

Figure 1 is a schematic representation of one process for forming a polymer composition according to the present invention using a single catalyst.

Figure 2 is a schematic representation of an alternate process for forming a polymer composition according to the present invention using a single catalyst.

Figure 3 is a schematic representation of one process for forming a multi-modal polymer composition according to the present invention using two different catalysts.

Figure 4 is a schematic representation of one process for forming a diblock copolymer composition according to the present invention using two different catalysts.

Detailed Description of the Invention

All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Group or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight. For purposes of United States patent practice, the contents of any patent, patent application, or publication referenced herein are hereby incorporated by reference in their entirety (or the equivalent US version thereof is so incorporated by reference) especially with respect to the disclosure of synthetic techniques,

definitions (to the extent not inconsistent with any definitions provided herein) and general knowledge in the art.

The term "comprising" and derivatives thereof is not intended to exclude the presence of any additional portion, component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, "consisting essentially of" excludes from the scope of any succeeding recitation any other portion, component, step or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any portion, component, step or procedure not specifically delineated or listed. The term "or", unless stated otherwise, refers to the listed members individually as well as in any combination.

The term "polymer", includes both homopolymers, that is, homogeneous polymers prepared from a single monomer, and copolymers (interchangeably referred to herein as interpolymers), meaning polymers prepared by reaction of at least two monomers or otherwise containing chemically differentiated segments or blocks therein even if formed from a single monomer. More specifically, the term "polyethylene" includes homopolymers of ethylene and copolymers of ethylene and one or more C_{3-8} α-olefins. The term "crystalline" if employed, refers to a polymer that possesses a first order transition or crystalline melting point (Tm) as determined by differential scanning calorimetry (DSC) or equivalent technique. The term may be used interchangeably with the term "semicrystalline". The term "amorphous" refers to a polymer lacking a crystalline melting point. The term "elastomer" or "elastomeric" refers to a polymer or polymer segment having Tg less than 0°C, more preferably less than -15°C, most preferably less than -25°C, and a sample of which, when deformed by application of stress, is generally capable of recovering its size and shape when the deforming force is removed. Specifically, as used herein, elastic or elastomeric is meant to be that property of any material which upon application of a biasing force, permits that material to be stretchable to a length which is at least 25 percent greater than its unbiased length without rupture, and that will cause the material to recover at least 40 percent of its elongation upon release of the force. A hypothetical example which would satisfy this definition of an elastomeric material would be a 1 cm sample of a material which may be elongated to a length of at least 1.25 cm and which, upon being elongated to 1.25 cm and released, will recover to a length of not more than 1.15 cm. Many elastic materials may be stretched by much more than 25 percent of their relaxed length, and many of these will recover to substantially their original relaxed length upon release of the elongating force.

The term "pseudo-block copolymer" refers to a copolymer comprising two or more blocks or segments of differing chemical or physical properties, such as variable comonomer content,

crystallinity, density, tacticity, regio-error, or other property. Non-adjacent blocks are not necessarily of identical chemical composition, but may vary in one or more of the foregoing respects, from the composition of all other blocks or regions. Compared to random copolymers, pseudo-block copolymers possess sufficient differences in chemical properties, especially crystallinity, between blocks or segments, and sufficient block lengths to achieve one or more of the desired properties of true block copolymers, such as thermoplastic/ elastomeric properties, while at the same time being amenable to preparation in conventional olefin polymerization processes, especially continuous solution polymerization processes employing catalytic quantities of polymerization catalysts. The polymers and blocks thereof fit a broader distribution than conventional block copolymers, which in theory have molecular weight distributions of 1.0. Pseudo-block copolymers possess broader molecular weight distributions. In addition, the respective blocks of a pseudo-block copolymer desirably possess a PDI fitting a Schulz-Flory distribution rather than a Poisson distribution.

It may be readily appreciated by the skilled artisan that in one embodiment of the present invented process the MSA may be added once, more than once (intermittently) or added continuously to each polymerization reactor or zone employed in the polymerization. Highly desirably, the MSA is added to the reaction mixture prior to initiation of polymerization, at the same time as polymerization is initiated, or at least during a significant portion of the time in which polymerization is conducted, especially in the first reactor if multiple reactors are utilized. Thorough mixing of MSA and reaction mixture may be occasioned by active or static mixing devices or by use of any stirring or pumping device employed in mixing or transferring the reaction mixture.

As used herein with respect to a chemical compound, unless specifically indicated otherwise, the singular includes all isomeric forms and vice versa (for example, "hexane", includes all isomers of hexane individually or collectively). The terms "compound" and "complex" are used interchangeably herein to refer to organic-, inorganic- and organometal compounds. The term, "atom" refers to the smallest constituent of an element regardless of ionic state, that is, whether or not the same bears a charge or partial charge or is bonded to another atom. The term "heteroatom" refers to an atom other than carbon or hydrogen. Preferred heteroatoms include: F, Cl, Br, N, O, P, B, S, Si, Sb, Al, Sn, As, Se and Ge.

The term, "hydrocarbyl" refers to univalent substituents containing only hydrogen and carbon atoms, including branched or unbranched, saturated or unsaturated, cyclic or noncyclic species. Examples include alkyl-, cycloalkyl-, alkenyl-, alkadienyl-, cycloalkenyl-, cycloalkadienyl-, aryl-, and alkynyl- groups. "Substituted hydrocarbyl" refers to a hydrocarbyl group that is substituted with one or more nonhydrocarbyl substituent groups. The terms,

"heteroatom containing hydrocarbyl" or "heterohydrocarbyl" refer to univalent groups in which at least one atom other than hydrogen or carbon is present along with one or more carbon atom and one or more hydrogen atoms. The term "heterocarbyl" refers to groups containing one or more carbon atoms and one or more heteroatoms and no hydrogen atoms. The bond between the carbon atom and any heteroatom as well as the bonds between any two heteroatoms, may be saturated or unsaturated. Thus, an alkyl group substituted with a heterocycloalkyl-, substituted heterocycloalkyl-, heteroaryl-, substituted heteroaryl-, alkoxy-, aryloxy-, dihydrocarbylboryl-, dihydrocarbylphosphino-, dihydrocarbylamino-, trihydrocarbylsilyl-, hydrocarbylthio-, or hydrocarbylseleno- group is within the scope of the term heteroalkyl. Examples of suitable heteroalkyl groups include cyano-, benzoyl-, (2-pyridyl)methyl-, and trifluoromethyl- groups.

As used herein the term "aromatic" refers to a polyatomic, cyclic, conjugated ring system containing $(4\delta+2)$ π-electrons, wherein δ is an integer greater than or equal to 1. The term "fused" as used herein with respect to a ring system containing two or more polyatomic, cyclic rings means that with respect to at least two rings thereof, at least one pair of adjacent atoms is included in both rings. The term "aryl" refers to a monovalent aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The aromatic ring(s) may include phenyl, naphthyl, anthracenyl, and biphenyl, among others.

"Substituted aryl" refers to an aryl group in which one or more hydrogen atoms bound to any carbon is replaced by one or more functional groups such as alkyl, substituted alkyl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halogen, alkylhalos (e.g., CF_3), hydroxy, amino, phosphido, alkoxy, amino, thio, nitro, and both saturated and unsaturated cyclic hydrocarbons which are fused to the aromatic ring(s), linked covalently or linked to a common group such as a methylene or ethylene moiety. The common linking group may also be a carbonyl as in benzophenone or oxygen as in diphenylether or nitrogen in diphenylamine.

The term, "comonomer incorporation index", refers to the percent comonomer incorporated into a copolymer prepared by the catalyst under consideration. The selection of metal complexes or catalyst compositions having the greatest difference in comonomer incorporation indices under different polymerization conditions, in one embodiment of the present invention, results in copolymers from two or more monomers having the largest difference in block or segment properties, such as density, for the same comonomer composition distribution. Comonomer incorporation index is generally determined by the use of NMR spectroscopic techniques. It may also be estimated based on monomer reactivities and reactor kinetics according to known theoretical techniques.

In a polymer containing distinguishable segments each segment may be the same or chemically different or generally characterized by a distribution of properties. The latter result may be achieved if the polymer chain experiences different polymerization conditions in differing reactors or polymerization zones during formation. Different polymerization conditions in the respective reactors or zones include the use of different monomers, different comonomers, or different monomer/comonomer(s) ratios, different polymerization temperatures, pressures or partial pressures of various monomers, different catalysts, simultaneous use of mono-centered chain shuttling agents, differing monomer gradients, or any other difference leading to formation of a distinguishable polymer segment. In this manner, at least a portion of the polymer resulting from the present process may comprise two, three, or more, preferably two or three, differentiated polymer segment types arranged intramolecularly.

According to the present invention, by selecting highly active catalyst compositions capable of rapid transfer of polymer segments both to and from a suitable multi-centered shuttling agent, a polymer product having at least two different molecular weight fractions is formed. Due to the use of at least one multi-centered shuttling agent and catalysts capable of rapid and efficient exchange of growing polymer chains, the polymer experiences discontinuous polymer growth and transfer to a remnant of the multi-centered shuttling agent, thereby forming at least some polymer having approximately double, triple or other multiple of the molecular weight of a remaining component of the polymer blend, and optionally, chemically distinct polymer segments.

By the term, "approximately" as used with respect to the comparison of modes in a multi-modal molecular weight distribution of a polymer blend herein, is meant that the mean molecular weight of the higher molecular weight component of the multi-modal blend is within 15 percent, preferably within 10 percent of an integer multiple of the lower molecular weight component, said integer being 2 or higher.

Monomers

Suitable monomers for use in preparing the copolymers of the present invention include any addition polymerizable monomer, preferably any olefin or diolefin monomer, more preferably any α-olefin, and most preferably ethylene and at least one copolymerizable comonomer, propylene and at least one copolymerizable comonomer having from 4 to 20 carbons, or 4-methyl-1-pentene and at least one different copolymerizable comonomer having from 4 to 20 carbons. Examples of suitable monomers include straight-chain or branched α-olefins of 2 to 30, preferably 2 to 20 carbon atoms, such as ethylene, propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexane, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene; cycloolefins of 3 to 30, preferably 3 to 20 carbon atoms, such as cyclopentene,

cycloheptene, norbornene, 5-methyl-2-norbornene, tetracyclododecene, and 2-methyl-1,4,5,8-dimethano-1,2,3,4,4a,5,8,8a-octahydronaphthalene; di- and poly-olefins, such as butadiene, isoprene, 4-methyl-1,3-pentadiene, 1,3-pentadiene, 1,4-pentadiene, 1,5-hexadiene, 1,4-hexadiene, 1,3-hexadiene, 1,3-octadiene, 1,4-octadiene, 1,5-octadiene, 1,6-octadiene, 1,7-octadiene, ethylidene norbornene, vinyl norbornene, dicyclopentadiene, 7-methyl-1,6-octadiene, 4-ethylidene-8-methyl-1,7-nonadiene, and 5,9-dimethyl-1,4,8-decatriene; aromatic vinyl compounds such as mono- or poly-alkylstyrenes (including styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, o,p-dimethylstyrene, o-ethylstyrene, m-ethylstyrene and p-ethylstyrene), and functional group-containing derivatives, such as methoxystyrene, ethoxystyrene, vinylbenzoic acid, methyl vinylbenzoate, vinylbenzyl acetate, hydroxystyrene, o-chlorostyrene, p-chlorostyrene, divinylbenzene, 3-phenylpropene, 4-phenylpropene and α-methylstyrene, vinylchloride, 1,2-difluoroethylene, 1,2-dichloroethylene, tetrafluoroethylene, and 3,3,3-trifluoro-1-propene, provided the monomer is polymerizable under the conditions employed.

Preferred monomers or mixtures of monomers for use in combination with at least one MSA herein include ethylene; propylene; mixtures of ethylene with one or more monomers selected from the group consisting of propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, and styrene; and mixtures of ethylene, propylene and a conjugated or non-conjugated diene.

Chain Shuttling Agents

The term, "shuttling agent" or "chain shuttling agent", refers to a compound or mixture of compounds that is capable of causing polymeryl transfer between the various active catalyst sites under the conditions of the polymerization. That is, transfer of a polymer fragment occurs both to and from an active catalyst site in a facile manner. In contrast to a shuttling agent, a "chain transfer agent" causes termination of polymer chain growth and amounts to a one-time transfer of growing polymer from the catalyst to the transfer agent. Desirably, the intermediate formed between the chain shuttling agent and the polymeryl chain is sufficiently stable that chain termination is relatively rare.

The term, "multi-centered shuttling agent" refers to a compound or molecule containing more than one, preferably 2 or 3, chain shuttling moieties joined by a polyvalent linking group. In practice, suitable chain shuttling moieties preferably include metal centers derived from a metal selected from Groups 2-14 of the Periodic Table of the Elements and having one or more available valencies able to reversibly bind to a growing polymer chain prepared by a coordination polymerization catalyst. At the same time that the chain shuttling moiety binds to the growing polymer chain, the remnant of the polyvalent linking group remaining after loss of the chain shuttling moiety or moieties incorporates or otherwise bonds to one or more active catalyst sites,

thereby forming a catalyst composition containing an active coordination polymerization site capable of polymer insertion at at least one terminus of what was originally the polyvalent linking group. Desirably, at least 0.5 percent, preferably at least 1 percent, more preferably at least 2 percent and most preferably at least 3 percent and up to 99 percent, preferably up to 98 percent, and more preferably up to 95 percent of the total polymer comprises a higher molecular weight polymer component. Particularly desirable compositions are blends of two polymers prepared according to the invention in which 25, 50 or 75 percent of the total blend is the higher molecular weight component.

While attached to the growing polymer chain, the shuttling agent desirably does not alter the polymer structure or incorporate additional monomer. That is, the shuttling agent does not also possess significant catalytic properties for polymerization. Rather, the shuttling agent forms a metal-alkyl or other type interaction with the polymer moiety until transfer of the polymer moiety to an active polymerization catalyst site again occurs. Transfer of the same shuttling agent site back to the original catalyst merely results in an increase in polymer molecular weight. Transfer to a different catalyst (if more than one catalyst type is employed) results in formation of a distinguishable polymer type, due for example, to a difference in monomer incorporation properties, tacticity, or other property of the subsequent catalyst. Transfer by means of one of the remaining shuttling sites results in step growth from a different point in the polymer molecule. With a two-centered shuttling agent, at least some of the resulting polymer is approximately double the molecular weight of remaining polymer segments. Under certain circumstances, the subsequently formed polymer region also possesses a distinguishable physical or chemical property, such as a different monomer or comonomer identity, a difference in comonomer composition distribution, crystallinity, density, tacticity, regio-error, or other property, compared to the polymer formed at other times during the polymerization. Subsequent repetitions of the foregoing process can result in formation of segments or blocks having a multiplicity of differing properties, or a repetition of a previously formed polymer composition, depending on the rates of polymeryl exchange, number of reactors or zones within a reactor, transport between the reactors or zones, number of different catalysts, monomer gradient in the reactor(s), and so forth. The polymers of the invention may be characterized by either a narrow or a broad molecular weight distribution. Polymers having a narrow molecular weight distribution typically have a PDI (Mw/Mn) from 2.0 to 2.8. Polymers having a broad PDI are those with PDI from 2.8 to 20, more preferably from 3.0 to 10.

The process of the invention employing a two-centered chain shuttling agent and single catalyst may be further elucidated by reference to Figure 1, where there is illustrated an activated catalyst, 10, and a multi-centered shuttling agent, 14, containing two separate chain shuttling sites, M. Under chain growth polymerization conditions the activated catalyst forms a polymer chain, 12.

In step 1, the shuttling agent exchanges one chain shuttling moiety with a catalyst/polymer combination, thereby binding the polymer chain, 12, to a chain shuttling moiety, M. Simultaneously, the remnant of the chain shuttling agent, 14, resulting from loss of a moiety, M, attaches to an active catalyst site, forming a new species, 11, capable of continued polymerization. In step 2, new polymer segment, 12a is produced by the catalyst site, thereby forming a polymer segment joined to chain shuttling remnant, 14. No chain growth occurs at the other species of the reaction, the polymer chain, 12 terminated with chain shuttling agent remnant, M. In step 3, chain transfer followed by polymerization occurs thereby forming a new polymer segment, 12b, attached to original polymer segment 12, and regeneration of a two centered chain shuttling MSA including polymer extension 12a attached to moiety 14 and two M moieties. In step 4, a final transfer of this two centered chain shuttling MSA via the second shuttling center results in formation of active catalyst attached to the combined MSA moiety, 14 and polymer segment 12a and separate polymer segment 12 joined to polymer segment 12b. Although depicted as separate polymer regions, it is to be understood that the two polymers 12 and 12b formed under nearly identical polymerization conditions by the same catalyst species are substantially identical, and under homogeneous polymerization conditions, the combination of polymer 12 and 12b is essentially indistinguishable from polymer 12 itself. In step 5, new polymer segment, 12c is formed at the active catalyst site attached to MSA remnant 14. Termination in step 6 results in formation of two polymer products, 18 and 19, which are distinguishable based on molecular weight as well as the presence of the residue of the two-centered chain shuttling agent, 14, in polymer product 18.

Transfer of the growing polymer may occur multiple times with continued growth of the polymer segment each time it is attached to an active catalyst. Under uniform polymerization conditions, the growing polymer blocks are substantially homogeneous, though their size conforms to a distribution of sizes, desirably a most probable distribution. If differing polymerization conditions such as the presence of different monomers or monomer gradients in a reactor, multiple reactors operating under differing process conditions, and so forth, the respective polymer segments may also be distinguished based on differences in chemical or physical properties. Chain shuttling and further growth may continue in the foregoing manner for any number of cycles. However, the resulting product mixture contains at least two separate species distinguishable primarily based on molecular weight difference, with polymer species 18, containing the remnant of the multi-centered shuttling agent, 14, being approximately double the size of polymer product, 19. Accordingly, in this instance a product of substantially homogeneous composition and having a bimodal molecular weight distribution is formed.

In Figure 2 a similar, but less prevalent process is illustrated wherein simultaneous growth at both centers of a two centered MSA takes place. In particular, an activated catalyst, 20, and a

multi-centered shuttling agent, 24 containing two separate chain shuttling sites, M are present in a reactor operating under polymerization conditions. The catalyst forms a polymer segment 22. In step 1, the shuttling agent exchanges one of the two active sites with the catalyst/polymer combination, thereby forming a species comprising the polymer chain, 22 attached to M. Simultaneously, the remnant of the chain shuttling agent, 24-M attaches to an active catalyst site, forming a new species, 21, capable of continued polymerization. In step 2, new polymer segment, 22a is produced by the catalyst site, thereby forming a polymer segment joined to chain shuttling remnant, 24. In step 3, chain transfer and growth involving the remaining site of the two centered MSA occurs while still attached to the original catalyst, thereby forming a polymer species, 26 having two active catalyst sites separated by polymer segment 22a and shuttling agent remnant, 24. In step 4, continued polymerization from both active sites forms a polymeric species, 27 containing two regions of polymer growth, 22a and 22b joined by the remnant of the two-centered shuttling agent, 24 with active catalyst sites on each end. Termination of chain growth in step 5 results in formation of two polymer products, 28 and 29, which are distinguishable based on molecular weight as well as the presence of the residue of the two-centered chain shuttling agent, 24, in polymer product 28.

The process of the invention employing a two-centered chain shuttling agent and two different catalysts, C' and C", is illustrated in Figure 3, where a first activated catalyst, C', forms a polymer chain, 32. The second activated catalyst, C", also forms a polymer segment which is not depicted. In step 1, the shuttling agent exchanges one chain shuttling moiety with a catalyst/polymer combination, thereby binding the polymer chain, 32, to a chain shuttling moiety, M. Simultaneously, the remnant of the chain shuttling agent, 34 resulting from loss of a moiety, M, attaches to an active catalyst site, forming a new species, 31, capable of continued polymerization. In step 2, new polymer segment, 32a is produced by the catalyst site, thereby forming a polymer segment joined to the remnant of multi-centered shuttling remnant, 34. No chain growth occurs at the shuttling agent terminated polymer chain, 32. In step 3, chain transfer occurs involving the second catalyst, C", followed by polymerization to form a polymeric species, 35, comprising polymer segment, 36 attached to originally formed polymer chain 32. Polymer segment, 36 has different polymer properties such as comonomer incorporation or tacticity from polymer segment 32 or 32a. In step 4, chain transfer occurs once again, involving both catalyst C' and C". Continued polymerization from both catalyst sites in step 5 forms new polymer segments, 32b and 36a, also having different polymer properties such as comonomer incorporation or tacticity. These polymer segments are each joined by the remnant of the two-centered shuttling agent, 34 to polymer segment 32a. Termination in step 6 results in formation of three polymer products, 38 and 39, and 40, which are distinguishable based on molecular weight as well as the presence of the residue of

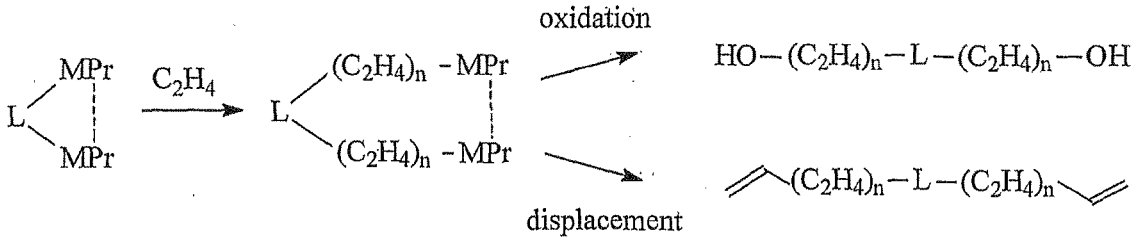
the two-centered chain shuttling agent, 34, in polymer products 38 and 40. In addition, products 38 and 39 are pseudo-block copolymers due to the presence of differing polymer regions formed by the respective catalysts C' and C". Additional polymer formed solely from catalyst C' or C" (not illustrated) may be present in the product mixture as well.

In figure 4, a variation of the foregoing process employing two catalysts C and C' in the polymerization of ethylene, 1 and a C_{3-20} α-olefin (T = C_{1-18} hydrocarbyl), 2 in the presence of a dicentered shuttling agent, 3, having a divalent linking group, L, joining two chain shuttling moieties, M^1 and M^2 is illustrated. The shuttling moieties, M^1 and M^2 have differing affinities with respect to the catalysts, C and C'. In particular, M^1 is more inclined to engage in polymer transfer with catalyst C whereas M^2 has a higher reactivity (increased shuttling index) with catalyst C'. In the various chain shuttling steps 1) and 3) shuttling between M^1 and catalyst C as well as between M^2 and catalyst C' are illustrated. The skilled artisan will appreciate that the various steps illustrated may occur in any order. By also selecting the catalysts C and C' with respect to their ability or inability to incorporate comonomer (or otherwise produce distinguishable polymers), the polymer segments formed by the respective catalysts. 4 and 5, will possess distinct physical properties and the resulting product will be a diblock copolymer. In particular, a diblock copolymer having one block of a highly crystalline ethylene or propylene polymer (little or no comonomer incorporation) and the other of an amorphous ethylene or propylene copolymer (greater quantity of comonomer incorporation) may be readily prepared in this manner.

The skilled artisan will appreciate that by employing multiple catalysts, multiple monomers, multiple shuttling agents (including both CSA and MSA types) and/or multiple reactors or variable reactor conditions, multitudinous combinations of reaction products are attainable.

The polymer product may be recovered by termination, such as by reaction with water or other proton source, or functionalized, if desired, forming vinyl, hydroxyl, silane, carboxylic acid, carboxylic acid ester, ionomeric, or other functional terminal groups, especially to replace the chain shuttling agent. Alternatively, the polymer segments may be coupled with a polyfunctional coupling agent, especially a difunctional coupling agent such as tolylene diisocyanate, dichlorodimethylsilane or ethylenedichloride, and recovered.

Application of the foregoing techniques to the preparation of low molecular weight α,ω-terminally functionalized polymers, especially α,ω-diols or α,ω-dienes, is disclosed in the following schematic illustration:



where an α,ω-two centered MSA, (PrM'LMPr) containing two metal sites, M', such a Zn, joined by a divalent ligand group, L (such as a hydrocarbylene group) and substituted with protecting groups Pr, such as trimethylsilyl groups, which optionally may be joined together as indicated by dotted lines, is added to an ethylene polymerization process. A metal di-terminated polymer is formed in the reaction which may be converted by known techniques (such as oxidation or displacement) to the corresponding dihydroxyl- or divinyl- functionalized polymer products using conventional processes. Suitable techniques for conversion of metallated polymers via displacement reactions are disclosed in J. Am. Chem. Soc., 126, 10701-10712 (2004), J. Am. Chem. Soc., 127, 10166-10167 (2005), and references cited therein.

The skilled artisan will readily appreciate that the foregoing process may employ a multi-centered shuttling agent initially containing 2, 3, 4 or even more active centers, resulting in the formation of polymer mixtures containing some quantity of a polymer that has approximately double, triple, quadruple, or other multiple of the molecular weight of the remaining polymer and a star or branched morphology.

Ideally, the rate of chain shuttling is equivalent to or faster than the rate of polymer termination, even up to 10 or even 100 times faster than the rate of polymer termination and significant with respect to the rate of polymerization. This permits formation of significant quantities of polymer chains terminated with chain shuttling agents and capable of continued monomer insertion leading to significant quantities of the higher molecular weight polymer.

By selecting different shuttling agents or mixtures of agents with a catalyst, by altering the comonomer composition, temperature, pressure, optional chain terminating agent such as H_2, or other reaction conditions in separate reactors or zones of a reactor operating under plug flow conditions, polymer products having segments of varying density or comonomer concentration, monomer content, and/or other distinguishing property can be prepared, as well. For example, in a typical process employing two continuous solution polymerization reactors connected in series and operating under differing polymerization conditions, the resulting polymer segments will each have a relatively broad molecular weight distribution characteristic of typical olefin coordination polymerization catalysts, preferably a Mw/Mn from 1.2 to 10, more preferably from 1.5 to 5.0, but will reflect differing polymerization conditions of their formation. In addition, certain quantities of

a conventional random copolymer may also be formed coincident with formation of the present polymer composition, resulting in a resin blend. If a relatively fast shuttling agent is employed, a copolymer having shorter block lengths but more uniform composition is obtained, with little formation of random copolymer. By proper selection of both catalyst and multi-centered shuttling agent, relatively pure mixtures of two polymers differing in molecular weight by approximately an integer value, copolymers containing relatively large polymer segments or blocks approximating true block copolymers, or blends of the foregoing with more random copolymers can all be obtained.

Highly desired polymer compositions according to the present invention comprise a polyolefin, especially a copolymer of ethylene and a C_{3-8} comonomer alone or in admixture with a homopolymer of ethylene or a homopolymer of propylene, said composition having a distinct bimodal molecular weight distribution, the higher molecular weight component having a Mw approximately double or triple that of the lower molecular weigh component.

Suitable chain shuttling agents, if employed in addition to a multi-centered shuttling agent, include metal compounds or complexes of metals of Groups 1-13, preferably Group 1, 2, 12 or 13 of the Periodic Table of the Elements, containing at least one C_{1-20} hydrocarbyl group, preferably hydrocarbyl substituted aluminum, gallium or zinc compounds containing from 1 to 12 carbons in each hydrocarbyl group, and reaction products thereof with a proton source. Preferred hydrocarbyl groups are alkyl groups, preferably linear or branched, C_{2-8} alkyl groups. Most preferred shuttling agents for use in the present invention are trialkyl aluminum and dialkyl zinc compounds, especially triethylaluminum, tri(i-propyl) aluminum, tri(i-butyl)aluminum, tri(n-hexyl)aluminum, tri(n-octyl)aluminum, triethylgallium, or diethylzinc. Additional suitable shuttling agents include the reaction product or mixture formed by combining the foregoing organometal compound, preferably a tri(C_{1-8}) alkyl aluminum or di(C_{1-8}) alkyl zinc compound, especially triethylaluminum, tri(i-propyl) aluminum, tri(i-butyl)aluminum, tri(n-hexyl)aluminum, tri(n-octyl)aluminum, or diethylzinc, with less than a stoichiometric quantity (relative to the number of hydrocarbyl groups) of a secondary amine or a hydroxyl compound, especially bis(trimethylsilyl)amine, t-butyl(dimethyl)siloxane, 2-hydroxymethylpyridine, di(n-pentyl)amine, 2,6-di(t-butyl)phenol, ethyl(1-naphthyl)amine, bis(2,3,6,7-dibenzo-1-azacycloheptaneamine), or 2,6-diphenylphenol. Desirably, sufficient amine or hydroxyl reagent is used such that one hydrocarbyl group remains per metal atom. The primary reaction products of the foregoing combinations most desired for use in the present invention as shuttling agents are n-octylaluminum di(bis(trimethylsilyl)amide), i-propylaluminum bis(dimethyl(t-butyl)siloxide), and n-octylaluminum di(pyridinyl-2-methoxide), i-butylaluminum bis(dimethyl(t-butyl)siloxane), i-butylaluminum bis(di(trimethylsilyl)amide), n-octylaluminum di(pyridine-2-methoxide), i-butylaluminum bis(di(n-pentyl)amide), n-octylaluminum bis(2,6-di-t-

butylphenoxide), n-octylaluminum di(ethyl(1-naphthyl)amide), ethylaluminum bis(t-butyldimethylsiloxide), ethylaluminum di(bis(trimethylsilyl)amide), ethylaluminum bis(2,3,6,7-dibenzo-1-azacycloheptaneamide), n-octylaluminum bis(2,3,6,7-dibenzo-1-azacycloheptaneamide), n-octylaluminum bis(dimethyl(t-butyl)siloxide, ethylzinc (2,6-diphenylphenoxide), and ethylzinc (t-butoxide).

Preferred chain shuttling agents possess the highest transfer rates of polymer transfer as well as the highest transfer efficiencies (reduced incidences of chain termination). Such shuttling agents may be used in reduced concentrations and still achieve the desired degree of shuttling. Highly desirably, chain shuttling agents with a single exchange site are employed due to the fact that the effective molecular weight of the polymer in the reactor is lowered, thereby reducing viscosity of the reaction mixture and consequently reducing operating costs.

Suitable multi-centered shuttling agents for use herein are compounds or complexes containing two or more chain shuttling moieties per molecule which are capable of forming reversible electronic interactions with polymer chains prepared by a coordination polymerization catalyst. In addition, the remnant formed upon loss of the chain shuttling moieties must be capable of interaction with an active catalyst composition, ultimately resulting in polymer growth at two or more sites of the remnant. Preferred multi-centered shuttling agents are compounds corresponding to the formula: $(M')_mA$ wherein M' is a chain shuttling moiety, preferably a monovalent derivative of a chain shuttling agent formed by separation from a linking group, A, and m is an integer from 2 to 6, preferably 2 or 3. Preferred A groups are organic groups, especially hydrocarbon or inertly substituted hydrocarbon groups, most preferably alkadiyl or alkatriyl groups and inertly substituted derivatives thereof. A most preferred A group is C_{2-20} hydrocarbadiyl. Specific examples of suitable M' groups include monovalent Group 6-13 metal containing radicals, especially zinc or aluminum containing radicals. Preferred M' radicals are those of the formula $-M''(P^g)_p$, where M'' is the metal, P^g is an organic radical, and p is a number from 1 to 5 indicating the number of P^g groups. Suitable P^g groups are selected from hydrogen, halo, hydrocarbyl, dihydrocarbylamido, hydrocarbyloxy, dihydrocarbylphosphido, tri(hydrocarbyl)silyl, halo- substituted hydrocarbyl, halo-substituted tri(hydrocarbyl)silyl, Lewis base containing chelating derivatives of the foregoing, and neutral Lewis base chelating ligands, such as tetrahydrofuran or acetylacetonate.

Specific examples of the foregoing MSA's include: (1,2-ethylene)di(zincchloride), (1,2-ethylene)di(zincbromide), (1,2-ethylene)di(ethylzinc), (1,2-ethylene)bis((trimethyl)silylzinc), (1,4-butylene)di(zincchloride), (1,4-butylene)di(zincbromide), (1,4-butylene)di(ethylzinc), (1,4-butylene)bis((trimethyl)silylzinc), bis(1,2-ethylenedizinc), bis(1,3-propylenedizinc), bis(1,4-butylenedizinc), methyltri(1,2-ethylenezincbromide), (1,2-ethylene)bis(dichloroaluminum), and (1,2-ethylene)bis(diethylaluminum).

Catalysts

Suitable catalysts for use herein include any compound or combination of compounds that is adapted for preparing polymers of the desired composition or type. Both heterogeneous and homogeneous catalysts may be employed. Examples of heterogeneous catalysts include the well known Ziegler-Natta compositions, especially Group 4 metal halides supported on Group 2 metal halides or mixed halides and alkoxides and the well known chromium or vanadium based catalysts. Preferably however, for ease of use and for production of narrow molecular weight polymer segments in solution, the catalysts for use herein are homogeneous catalysts comprising a relatively pure organometallic compound or metal complex, especially compounds or complexes based on metals selected from Groups 3-15 or the Lanthanide series of the Periodic Table of the Elements.

Preferred metal complexes for use herein include complexes of metals selected from Groups 3 to 15 of the Periodic Table of the Elements containing one or more delocalized, π-bonded ligands or polyvalent Lewis base ligands. Examples include metallocene, half-metallocene, constrained geometry, and polyvalent pyridylamine, or other polychelating base complexes. The complexes are generically depicted by the formula: $MK_kX_xZ_z$, or a dimer thereof, wherein

M is a metal selected from Groups 3-15, preferably 3-10, more preferably 4-10, and most preferably Group 4 of the Periodic Table of the Elements;

K independently each occurrence is a group containing delocalized π-electrons or one or more electron pairs through which K is bound to M, said K group containing up to 50 atoms not counting hydrogen atoms, optionally two or more K groups may be joined together forming a bridged structure, and further optionally one or more K groups may be bound to Z, to X or to both Z and X;

X independently each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more X groups may be bonded together thereby forming a divalent or polyvalent anionic group, and, further optionally, one or more X groups and one or more Z groups may be bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto;

Z independently each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one unshared electron pair through which Z is coordinated to M;

k is an integer from 0 to 3;

x is an integer from 1 to 4;

z is a number from 0 to 3; and

the sum, k+x, is equal to the formal oxidation state of M.

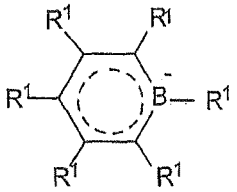
Suitable metal complexes include those containing from 1 to 3 π-bonded anionic or neutral ligand groups, which may be cyclic or non-cyclic delocalized π-bonded anionic ligand groups. Exemplary of such π-bonded groups are conjugated or nonconjugated, cyclic or non-cyclic diene and dienyl groups, allyl groups, boratabenzene groups, phosphole, and arene groups. By the term " π-bonded" is meant that the ligand group is bonded to the transition metal by a sharing of electrons from a partially delocalized π-bond.

Each atom in the delocalized π-bonded group may independently be substituted with a radical selected from the group consisting of hydrogen, halogen, hydrocarbyl, halohydrocarbyl, hydrocarbyl-substituted heteroatoms wherein the heteroatom is selected from Group 14-16 of the Periodic Table of the Elements, and such hydrocarbyl- substituted heteroatom radicals further substituted with a Group 15 or 16 hetero atom containing moiety. In addition two or more such radicals may together form a fused ring system, including partially or fully hydrogenated fused ring systems, or they may form a metallocycle with the metal. Included within the term "hydrocarbyl" are C_{1-20} straight, branched and cyclic alkyl radicals, C_{6-20} aromatic radicals, C_{7-20} alkyl-substituted aromatic radicals, and C_{7-20} aryl-substituted alkyl radicals. Suitable hydrocarbyl-substituted heteroatom radicals include mono-, di- and tri-substituted radicals of boron, silicon, germanium, nitrogen, phosphorus or oxygen wherein each of the hydrocarbyl groups contains from 1 to 20 carbon atoms. Examples include N,N-dimethylamino, pyrrolidinyl, trimethylsilyl, triethylsilyl, t-butyldimethylsilyl, methyldi(t-butyl)silyl, triphenylgermyl, and trimethylgermyl groups. Examples of Group 15 or 16 hetero atom containing moieties include amino, phosphino, alkoxy, or alkylthio moieties or divalent derivatives thereof, for example, amide, phosphide, alkyleneoxy or alkylenethio groups bonded to the transition metal or Lanthanide metal, and bonded to the hydrocarbyl group, π-bonded group, or hydrocarbyl- substituted heteroatom.

Examples of suitable anionic, delocalized π-bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, decahydroanthracenyl groups, phosphole, and boratabenzyl groups, as well as inertly substituted derivatives thereof, especially C_{1-10} hydrocarbyl- substituted or tris(C_{1-10} hydrocarbyl)silyl- substituted derivatives thereof. Preferred anionic delocalized π-bonded groups are cyclopentadienyl, pentamethylcyclopentadienyl, tetramethylcyclopentadienyl, tetramethylsilylcyclopentadienyl, indenyl, 2,3-dimethylindenyl, fluorenyl, 2-methylindenyl, 2-methyl-4-phenylindenyl, tetrahydrofluorenyl, octahydrofluorenyl, 1-indacenyl, 3-pyrrolidinoinden-1-yl, 3,4-(cyclopenta(*l*)phenanthren-1-yl, and tetrahydroindenyl.

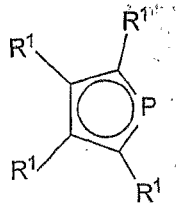
The boratabenzenyl ligands are anionic ligands which are boron containing analogues to benzene. They are previously known in the art having been described by G. Herberich, et al., in

Organometallics, 14,1, 471-480 (1995). Preferred boratabenzenyl ligands correspond to the formula:



wherein R^1 is an inert substituent, preferably selected from the group consisting of hydrogen, hydrocarbyl, silyl, halo or germyl, said R^1 having up to 20 atoms not counting hydrogen, and optionally two adjacent R^1 groups may be joined together. In complexes involving divalent derivatives of such delocalized π-bonded groups one atom thereof is bonded by means of a covalent bond or a covalently bonded divalent group to another atom of the complex thereby forming a bridged system.

Phospholes are anionic ligands that are phosphorus containing analogues to a cyclopentadienyl group. They are previously known in the art having been described by WO 98/50392, and elsewhere. Preferred phosphole ligands correspond to the formula:



wherein R^1 is as previously defined.

Preferred transition metal complexes for use herein correspond to the formula: $MK_kX_xZ_z$, or a dimer thereof, wherein:

M is a Group 4 metal;

K is a group containing delocalized π-electrons through which K is bound to M, said K group containing up to 50 atoms not counting hydrogen atoms, optionally two K groups may be joined together forming a bridged structure, and further optionally one K may be bound to X or Z;

X each occurrence is a monovalent, anionic moiety having up to 40 non-hydrogen atoms, optionally one or more X and one or more K groups are bonded together to form a metallocycle, and further optionally one or more X and one or more Z groups are bonded together thereby forming a moiety that is both covalently bound to M and coordinated thereto;

Z independently each occurrence is a neutral, Lewis base donor ligand of up to 50 non-hydrogen atoms containing at least one unshared electron pair through which Z is coordinated to M;

k is an integer from 0 to 3;

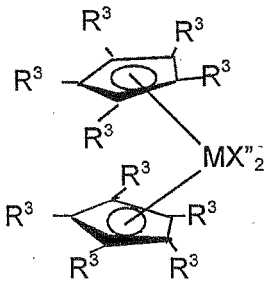
x is an integer from 1 to 4;

z is a number from 0 to 3; and

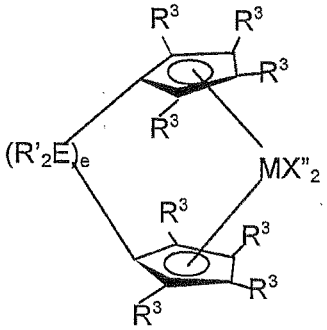
the sum, k+x, is equal to the formal oxidation state of M.

Preferred complexes include those containing either one or two K groups. The latter complexes include those containing a bridging group linking the two K groups. Preferred bridging groups are those corresponding to the formula $(ER'_2)_e$ wherein E is silicon, germanium, tin, or carbon, R' independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R' having up to 30 carbon or silicon atoms, and e is 1 to 8. Preferably, R' independently each occurrence is methyl, ethyl, propyl, benzyl, tert-butyl, phenyl, methoxy, ethoxy or phenoxy.

Examples of the complexes containing two K groups are compounds corresponding to the formula:



or



wherein:

M is titanium, zirconium or hafnium, preferably zirconium or hafnium, in the +2 or +4 formal oxidation state;

R^3 in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R^3 having up to 20 non-hydrogen atoms, or adjacent R^3 groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system, and

X" independently each occurrence is an anionic ligand group of up to 40 non-hydrogen atoms, or two X" groups together form a divalent anionic ligand group of up to 40 non-hydrogen atoms or together are a conjugated diene having from 4 to 30 non-hydrogen atoms bound by means of delocalized π-electrons to M, whereupon M is in the +2 formal oxidation state, and

R', E and e are as previously defined.

Exemplary bridged ligands containing two π-bonded groups are: dimethylbis(cyclopentadienyl)silane, dimethylbis(tetramethylcyclopentadienyl)silane, dimethylbis(2-ethylcyclopentadien-1-yl)silane, dimethylbis(2-t-butylcyclopentadien-1-yl)silane,

2,2-bis(tetramethylcyclopentadienyl)propane, dimethylbis(inden-1-yl)silane, dimethylbis(tetrahydroinden-1-yl)silane, dimethylbis(fluoren-1-yl)silane, dimethylbis(tetrahydrofluoren-1-yl)silane, dimethylbis(2-methyl-4-phenylinden-1-yl)-silane, dimethylbis(2-methylinden-1-yl)silane, dimethyl(cyclopentadienyl)(fluoren-1-yl)silane, dimethyl(cyclopentadienyl)(octahydrofluoren-1-yl)silane, dimethyl(cyclopentadienyl)(tetrahydrofluoren-1-yl)silane, (1, 1, 2, 2-tetramethy)-1, 2-bis(cyclopentadienyl)disilane, (1, 2-bis(cyclopentadienyl)ethane, and dimethyl(cyclopentadienyl)-1-(fluoren-1-yl)methane.

Preferred X" groups are selected from hydride, hydrocarbyl, silyl, germyl, halohydrocarbyl, halosilyl, silylhydrocarbyl and aminohydrocarbyl groups, or two X" groups together form a divalent derivative of a conjugated diene or else together they form a neutral, π-bonded, conjugated diene. Most preferred X" groups are C_{1-20} hydrocarbyl groups.

Examples of metal complexes of the foregoing formula suitable for use in the present invention include:

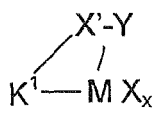
bis(cyclopentadienyl)zirconiumdimethyl,
bis(cyclopentadienyl)zirconium dibenzyl,
bis(cyclopentadienyl)zirconium methyl benzyl,
bis(cyclopentadienyl)zirconium methyl phenyl,
bis(cyclopentadienyl)zirconiumdiphenyl,
bis(cyclopentadienyl)titanium-allyl,
bis(cyclopentadienyl)zirconiummethylmethoxide,
bis(cyclopentadienyl)zirconiummethylchloride,
bis(pentamethylcyclopentadienyl)zirconiumdimethyl,
bis(pentamethylcyclopentadienyl)titaniumdimethyl,
bis(indenyl)zirconiumdimethyl,
indenylfluorenylzirconiumdimethyl,
bis(indenyl)zirconiummethyl(2-(dimethylamino)benzyl),
bis(indenyl)zirconiummethyltrimethylsilyl,
bis(tetrahydroindenyl)zirconiummethyltrimethylsilyl,
bis(pentamethylcyclopentadienyl)zirconiummethylbenzyl,
bis(pentamethylcyclopentadienyl)zirconiumdibenzyl,
bis(pentamethylcyclopentadienyl)zirconiummethylmethoxide,
bis(pentamethylcyclopentadienyl)zirconiummethylchloride,
bis(methylethylcyclopentadienyl)zirconiumdimethyl,
bis(butylcyclopentadienyl)zirconiumdibenzyl,

bis(t-butylcyclopentadienyl)zirconiumdimethyl,
bis(ethyltetramethylcyclopentadienyl)zirconiumdimethyl,
bis(methylpropylcyclopentadienyl)zirconiumdibenzyl,
bis(trimethylsilylcyclopentadienyl)zirconiumdibenzyl,
dimethylsilylbis(cyclopentadienyl)zirconiumdimethyl,
dimethylsilylbis(tetramethylcyclopentadienyl)titanium (III) allyl
dimethylsilylbis(t-butylcyclopentadienyl)zirconiumdichloride,
dimethylsilylbis(n-butylcyclopentadienyl)zirconiumdichloride,
(methylenebis(tetramethylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,
(methylenebis(n-butylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,
dimethylsilylbis(indenyl)zirconiumbenzylchloride,
dimethylsilylbis(2-methylindenyl)zirconiumdimethyl,
dimethylsilylbis(2-methyl-4-phenylindenyl)zirconiumdimethyl,
dimethylsilylbis(2-methylindenyl)zirconium-1,4-diphenyl-1,3-butadiene,
dimethylsilylbis(2-methyl-4-phenylindenyl)zirconium (II) 1,4-diphenyl-1,3-butadiene,
dimethylsilylbis(tetrahydroindenyl)zirconium(II) 1,4-diphenyl-1,3-butadiene,
dimethylsilylbis(tetramethylcyclopentadienyl)zirconium dimethyl
dimethylsilylbis(fluorenyl)zirconiumdimethyl,
dimethylsilyl-bis(tetrahydrofluorenyl)zirconium bis(trimethylsilyl),
(isopropylidene)(cyclopentadienyl)(fluorenyl)zirconiumdibenzyl, and
dimethylsilyl(tetramethylcyclopentadienyl)(fluorenyl)zirconium dimethyl.

A further class of metal complexes utilized in the present invention corresponds to the preceding formula: MKZ_zX_x, or a dimer thereof, wherein M, K, X, x and z are as previously defined, and Z is a substituent of up to 50 non-hydrogen atoms that together with K forms a metallocycle with M.

Preferred Z substituents include groups containing up to 30 non-hydrogen atoms comprising at least one atom that is oxygen, sulfur, boron or a member of Group 14 of the Periodic Table of the Elements directly attached to K, and a different atom, selected from the group consisting of nitrogen, phosphorus, oxygen or sulfur that is covalently bonded to M.

More specifically this class of Group 4 metal complexes used according to the present invention includes "constrained geometry catalysts" corresponding to the formula:



wherein:

M is titanium or zirconium, preferably titanium in the +2, +3, or +4 formal oxidation state;

K^1 is a delocalized, π-bonded ligand group optionally substituted with from 1 to 5 R^2 groups,

R^2 in each occurrence independently is selected from the group consisting of hydrogen, hydrocarbyl, silyl, germyl, cyano, halo and combinations thereof, said R^2 having up to 20 non-hydrogen atoms, or adjacent R^2 groups together form a divalent derivative (that is, a hydrocarbadiyl, siladiyl or germadiyl group) thereby forming a fused ring system,

each X is a halo, hydrocarbyl, hydrocarbyloxy or silyl group, said group having up to 20 non-hydrogen atoms, or two X groups together form a neutral C_{5-30} conjugated diene or a divalent derivative thereof;

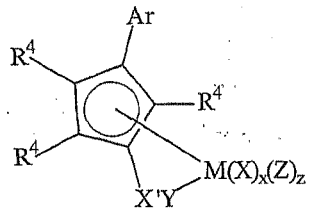
x is 1 or 2;

Y is -O-, -S-, -NR'-, -PR'-; and

X' is SiR'_2, CR'_2, $SiR'_2SiR'_2$, $CR'_2CR'_2$, CR'=CR', $CR'_2SiR'_2$, or GeR'_2, wherein

R' independently each occurrence is hydrogen or a group selected from silyl, hydrocarbyl, hydrocarbyloxy and combinations thereof, said R' having up to 30 carbon or silicon atoms.

Specific examples of the foregoing constrained geometry metal complexes include compounds corresponding to the formula:



,

wherein,

Ar is an aryl group of from 6 to 30 atoms not counting hydrogen;

R^4 independently each occurrence is hydrogen, Ar, or a group other than Ar selected from hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylgermyl, halide, hydrocarbyloxy, trihydrocarbylsiloxy, bis(trihydrocarbylsilyl)amino, di(hydrocarbyl)amino, hydrocarbadiylamino, hydrocarbylimino, di(hydrocarbyl)phosphino, hydrocarbadiylphosphino, hydrocarbylsulfido, halo-substituted hydrocarbyl, hydrocarbyloxy- substituted hydrocarbyl, trihydrocarbylsilyl- substituted hydrocarbyl, trihydrocarbylsiloxy- substituted hydrocarbyl, bis(trihydrocarbylsilyl)amino-substituted hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylenephosphino- substituted hydrocarbyl, or hydrocarbylsulfido- substituted hydrocarbyl,

said R group having up to 40 atoms not counting hydrogen atoms, and optionally two adjacent R^4 groups may be joined together forming a polycyclic fused ring group;

M is titanium;

X' is SiR^6_2, CR^6_2, $SiR^6_2SiR^6_2$, $CR^6_2CR^6_2$, $CR^6{=}CR^6$, $CR^6_2SiR^6_2$, BR^6, BR^6L'', or GeR^6_2;

Y is -O-, -S-, $-NR^5-$, $-PR^5-$; $-NR^5_2$, or $-PR^5_2$;

R^5, independently each occurrence, is hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl, said R^5 having up to 20 atoms other than hydrogen, and optionally two R^5 groups or R^5 together with Y or Z form a ring system;

R^6, independently each occurrence, is hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, $-NR^5_2$, and combinations thereof, said R^6 having up to 20 non-hydrogen atoms, and optionally, two R^6 groups or R^6 together with Z forms a ring system;

Z is a neutral diene or a monodentate or polydentate Lewis base optionally bonded to R^5, R^6, or X;

X is hydrogen, a monovalent anionic ligand group having up to 60 atoms not counting hydrogen, or two X groups are joined together thereby forming a divalent ligand group;

x is 1 or 2; and

z is 0, 1 or 2.

Preferred examples of the foregoing metal complexes are substituted at both the 3- and 4-positions of a cyclopentadienyl or indenyl group with an Ar group.

Examples of the foregoing metal complexes include:

(3-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,3-diphenyl-1,3-butadiene;

(3-(pyrrol-1-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-(pyrrol-1-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3-(pyrrol-1-yl)cyclopentadien-1-yl))dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

(3-(1-methylpyrrol-3-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-(1-methylpyrrol-3-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3-(1-methylpyrrol-3-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

(3,4-diphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3,4-diphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3,4-diphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,3-pentadiene;

(3-(3-N,N-dimethylamino)phenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-(3-N,N-dimethylamino)phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3-(3-N,N-dimethylamino)phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

(3-(4-methoxyphenyl)-4-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-(4-methoxyphenyl)-4-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3-4-methoxyphenyl)-4-phenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

(3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

(3-phenyl-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

(3-phenyl-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

(3-phenyl-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

2-methyl-(3,4-di(4-methylphenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,

2-methyl-(3,4-di(4-methylphenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,

2-methyl-(3,4-di(4-methylphenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

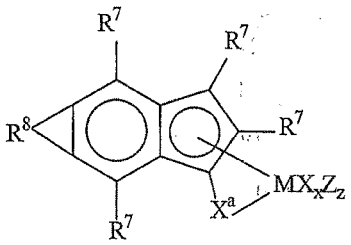
((2,3-diphenyl)-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silane titanium dichloride,

((2,3-diphenyl)-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silane titanium dimethyl,

((2,3-diphenyl)-4-(N,N-dimethylamino)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

(2,3,4-triphenyl-5-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(2,3,4-triphenyl-5-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
(2,3,4-triphenyl-5-methylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;
(3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
(3-phenyl-4-methoxycyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;
(2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl,
(2,3-diphenyl-4-(n-butyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;
(2,3,4,5-tetraphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dichloride,
(2,3,4,5-tetraphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium dimethyl, and
(2,3,4,5-tetraphenylcyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene.

Additional examples of suitable metal complexes for use herein are polycyclic complexes corresponding to the formula:



where M is titanium in the +2, +3 or +4 formal oxidation state;

R^7 independently each occurrence is hydride, hydrocarbyl, silyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbylsulfido, halo-substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl-substituted hydrocarbyl, hydrocarbylsiloxy-substituted hydrocarbyl, hydrocarbylsilylamino-substituted hydrocarbyl, di(hydrocarbyl)amino-substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino-substituted hydrocarbyl, hydrocarbylene-phosphino-substituted hydrocarbyl, or hydrocarbylsulfido-substituted hydrocarbyl, said R^7 group having up to 40 atoms not counting hydrogen, and optionally two or more of the foregoing groups may together form a divalent derivative;

R^8 is a divalent hydrocarbylene- or substituted hydrocarbylene group forming a fused system with the remainder of the metal complex, said R^8 containing from 1 to 30 atoms not counting hydrogen;

X^a is a divalent moiety, or a moiety comprising one σ-bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said X^a comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

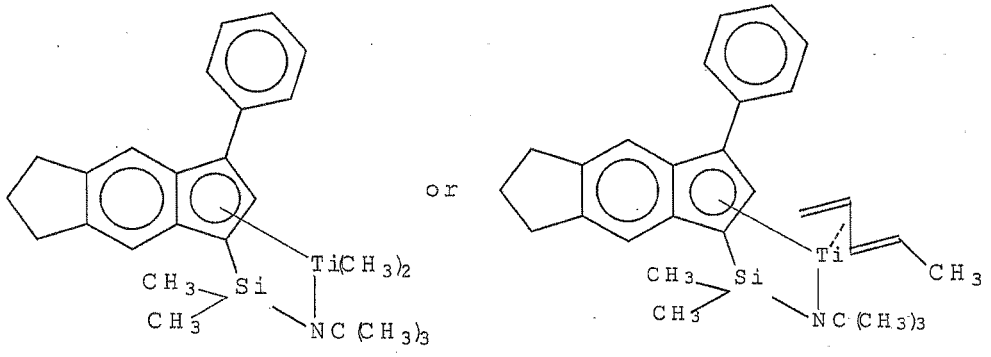
X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π-bound ligand groups and optionally two X groups together form a divalent ligand group;

Z independently each occurrence is a neutral ligating compound having up to 20 atoms;

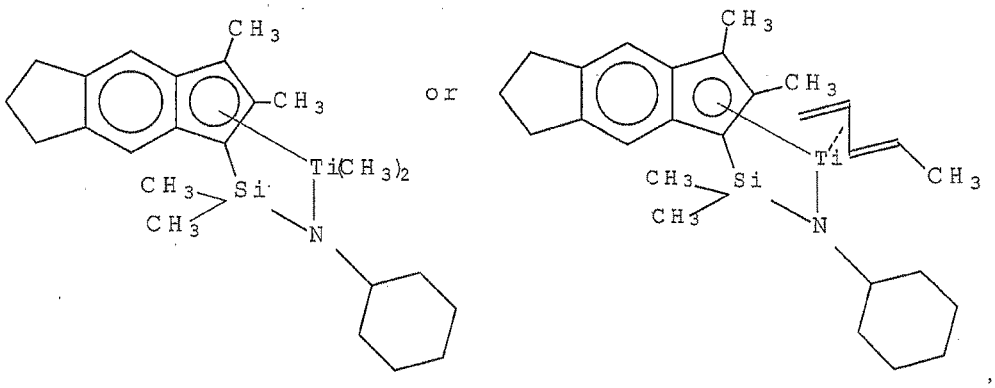
x is 0, 1 or 2; and

z is zero or 1.

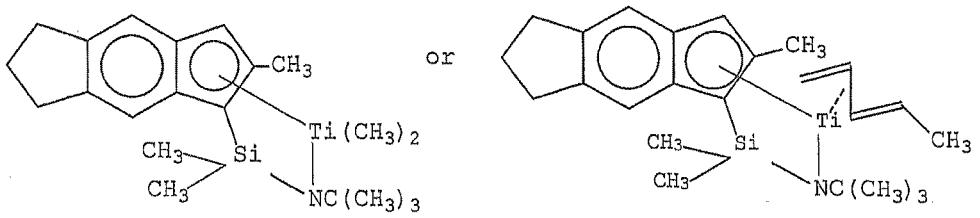
Preferred examples of such complexes are 3-phenyl-substituted s-indecenyl complexes corresponding to the formula:



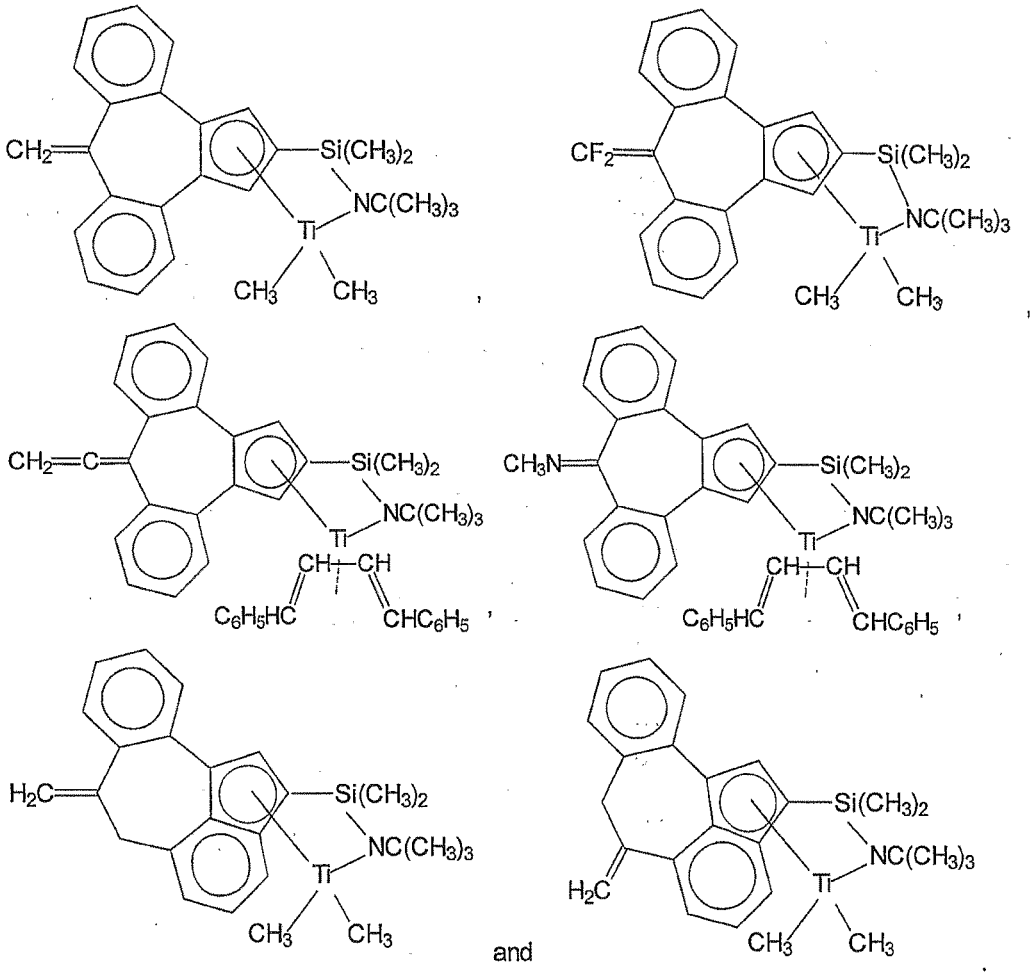
2,3-dimethyl-substituted s-indecenyl complexes corresponding to the formulas:



or 2-methyl-substituted s-indecenyl complexes corresponding to the formula:



Additional examples of metal complexes that are usefully employed according to the present invention include those of the formula:



Specific metal complexes include:

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,

(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,4-diphenyl-1,3-butadiene,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (II) 1,3-pentadiene,

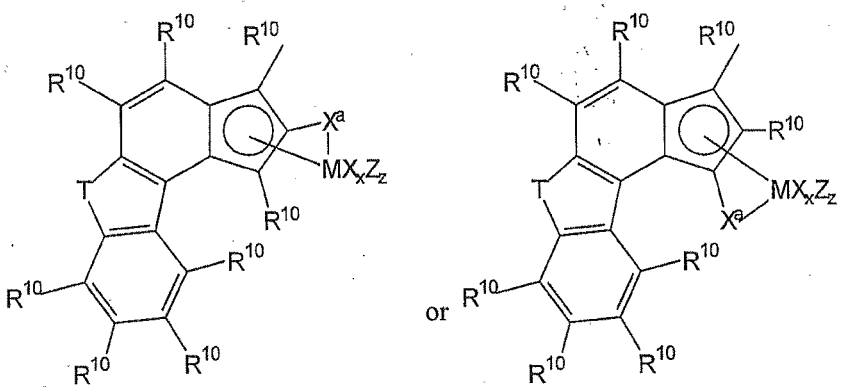
(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (III) 2-(N,N-dimethylamino)benzyl,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dichloride,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dimethyl,

(8-difluoromethylene-1,8-dihydrodibenzo[*e,h*]azulen-2-yl)-N-(1,1-dimethylethyl)dimethylsilanamide titanium (IV) dibenzyl, and mixtures thereof, especially mixtures of positional isomers.

Further illustrative examples of metal complexes for use according to the present invention correspond to the formula:



where M is titanium in the +2, +3 or +4 formal oxidation state;

T is $-NR^9-$ or -O-;

R^9 is hydrocarbyl, silyl, germyl, dihydrocarbylboryl, or halohydrocarbyl or up to 10 atoms not counting hydrogen;

R^{10} independently each occurrence is hydrogen, hydrocarbyl, trihydrocarbylsilyl, trihydrocarbylsilylhydrocarbyl, germyl, halide, hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino, hydrocarbyleneamino, di(hydrocarbyl)phosphino, hydrocarbylene-phosphino, hydrocarbylsulfido, halo- substituted hydrocarbyl, hydrocarbyloxy-substituted hydrocarbyl, silyl- substituted hydrocarbyl, hydrocarbylsiloxy- substituted hydrocarbyl, hydrocarbylsilylamino- substituted hydrocarbyl, di(hydrocarbyl)amino- substituted hydrocarbyl, hydrocarbyleneamino-substituted hydrocarbyl, di(hydrocarbyl)phosphino- substituted hydrocarbyl, hydrocarbylenephosphino- substituted hydrocarbyl, or hydrocarbylsulfido- substituted hydrocarbyl, said R^{10} group having up to 40 atoms not counting hydrogen atoms, and optionally two or more of

the foregoing adjacent R^{10} groups may together form a divalent derivative thereby forming a saturated or unsaturated fused ring;

X^n is a divalent moiety lacking in delocalized π-electrons, or such a moiety comprising one σ-bond and a neutral two electron pair able to form a coordinate-covalent bond to M, said X' comprising boron, or a member of Group 14 of the Periodic Table of the Elements, and also comprising nitrogen, phosphorus, sulfur or oxygen;

X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic ligand groups bound to M through delocalized π-electrons or two X groups together are a divalent anionic ligand group;

Z independently each occurrence is a neutral ligating compound having up to 20 atoms;

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

z is 0 or 1.

Highly preferably T is $=N(CH_3)$, X is halo or hydrocarbyl, x is 2, X' is dimethylsilane, z is 0, and R^{10} each occurrence is hydrogen, a hydrocarbyl, hydrocarbyloxy, dihydrocarbylamino, hydrocarbyleneamino, dihydrocarbylamino- substituted hydrocarbyl group, or hydrocarbyleneamino- substituted hydrocarbyl group of up to 20 atoms not counting hydrogen, and optionally two R^{10} groups may be joined together.

Illustrative metal complexes of the foregoing formula that may be employed in the practice of the present invention further include the following compounds:

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl,

(t-butylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl),

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl,

(cyclohexylamido)dimethyl-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl),

(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,

(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,

(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,

(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,

(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,

(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl,

(t-butylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl),

(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,4-diphenyl-1,3-butadiene,

(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (II) 1,3-pentadiene,

(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (III) 2-(N,N-dimethylamino)benzyl,

(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dichloride,

(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dimethyl,

(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) dibenzyl; and

(cyclohexylamido)di(p-methylphenyl)-[6,7]benzo-[4,5:2',3'](1-methylisoindol)-(3H)-indene-2-yl)silanetitanium (IV) bis(trimethylsilyl).

Illustrative Group 4 metal complexes that may be employed in the practice of the present invention further include:

(tert-butylamido)(1,1-dimethyl-2,3,4,9,10-η-1,4,5,6,7,8-hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,

(tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10-η-1,4,5,6,7,8-hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,

(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl) dimethylsilanetitanium dibenzyl,

(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethylsilanetitanium dimethyl,

(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)-1,2-ethanediyltitanium dimethyl,

(tert-butylamido)(tetramethyl-η^5-indenyl)dimethylsilanetitanium dimethyl,

(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethylsilane titanium (III) 2-(dimethylamino)benzyl;

(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethylsilanetitanium (III) allyl,

(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethylsilanetitanium (III) 2,4-dimethylpentadienyl,

(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-butadiene,

(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethylsilanetitanium (II) 1,3-pentadiene,

(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-butadiene,

(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,

(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 2,3-dimethyl-1,3-butadiene,

(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) isoprene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV)
2,3-dimethyl-1,3-butadiene,
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV)
isoprene
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dimethyl
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) dibenzyl
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,
(tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-
1,3-butadiene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dimethyl,
(tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) dibenzyl,
(tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II)
1,4-diphenyl-1,3-butadiene,
(tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 1,3-pentadiene,
(tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,
(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethyl- silanetitanium (IV)
1,3-butadiene,
(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethylsilanetitanium (IV)
2,3-dimethyl-1,3-butadiene,
(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethylsilanetitanium (IV)
isoprene,
(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethyl- silanetitanium (II)
1,4-dibenzyl-1,3-butadiene,
(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethylsilanetitanium (II)
2,4-hexadiene,
(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl)dimethyl- silanetitanium (II)
3-methyl-1,3-pentadiene,
(tert-butylamido)(2,4-dimethylpentadien-3-yl)dimethylsilanetitaniumdimethyl,
(tert-butylamido)(6,6-dimethylcyclohexadienyl)dimethylsilanetitaniumdimethyl,
(tert-butylamido)(1,1-dimethyl-2,3,4,9,10-η-1,4,5,6,7,8-hexahydronaphthalen-4-

yl)dimethylsilanetitaniumdimethyl,

(tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10-η-1,4,5,6,7,8-hexahydronaphthalen-4-yl)dimethylsilanetitaniumdimethyl

(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl methylphenylsilanetitanium (IV) dimethyl,

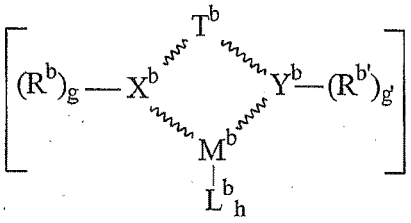
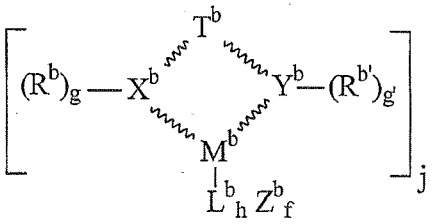
(tert-butylamido)(tetramethyl-η^5-cyclopentadienyl methylphenylsilanetitanium (II) 1,4-diphenyl-1,3-butadiene,

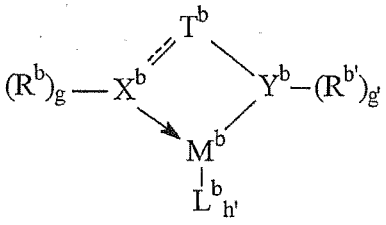
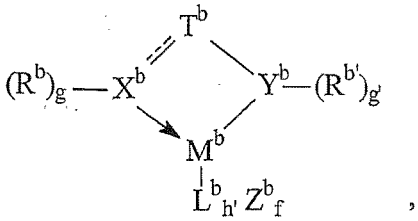
1-(tert-butylamido)-2-(tetramethyl-η^5-cyclopentadienyl)ethanediyltitanium (IV) dimethyl, and

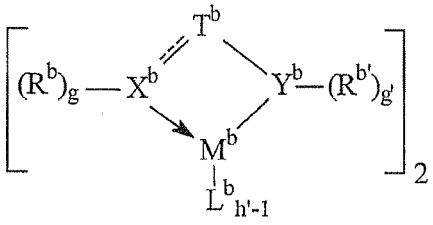
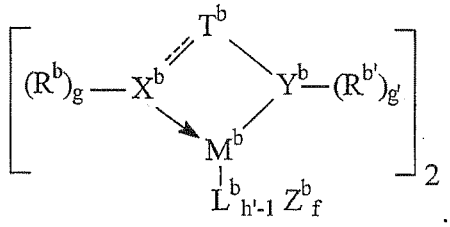
1-(tert-butylamido)-2-(tetramethyl-η^5-cyclopentadienyl)ethanediyl-titanium (II) 1,4-diphenyl-1,3-butadiene.

Other delocalized, π-bonded complexes, especially those containing other Group 4 metals, will, of course, be apparent to those skilled in the art, and are disclosed among other places in: WO 03/78480, WO 03/78483, WO 02/92610, WO 02/02577, US 2003/0004286 and US Patents 6,515,155, 6,555,634, 6,150,297, 6,034,022, 6,268,444, 6,015,868, 5,866,704, and 5,470,993.

Additional examples of metal complexes that are usefully employed herein include polyvalent Lewis base compounds corresponding to the formula:


, or

; preferably


,

,


, or

;

wherein T^b is a bridging group, preferably containing 2 or more atoms other than hydrogen,

X^b and Y^b are each independently selected from the group consisting of nitrogen, sulfur, oxygen and phosphorus; more preferably both X^b and Y^b are nitrogen,

R^b and $R^{b'}$ independently each occurrence are hydrogen or C_{1-50} hydrocarbyl groups optionally containing one or more heteroatoms or inertly substituted derivative thereof. Non-limiting examples of suitable R^b and $R^{b'}$ groups include alkyl, alkenyl, aryl, aralkyl, (poly)alkylaryl and cycloalkyl groups, as well as nitrogen, phosphorus, oxygen and halogen substituted derivatives thereof. Specific examples of suitable Rb and Rb' groups include methyl, ethyl, isopropyl, octyl, phenyl, 2,6-dimethylphenyl, 2,6-di(isopropyl)phenyl, 2,4,6-trimethylphenyl, pentafluorophenyl, 3,5-trifluoromethylphenyl, and benzyl;

g is 0 or 1;

M^b is a metallic element selected from Groups 3 to 15, or the Lanthanide series of the Periodic Table of the Elements. Preferably, M^b is a Group 3-13 metal, more preferably M^b is a Group 4-10 metal;

L^b is a monovalent, divalent, or trivalent anionic ligand containing from 1 to 50 atoms, not counting hydrogen. Examples of suitable L^b groups include halide; hydride; hydrocarbyl, hydrocarbyloxy; di(hydrocarbyl)amido, hydrocarbyleneamido, di(hydrocarbyl)phosphido; hydrocarbylsulfido; hydrocarbyloxy, tri(hydrocarbylsilyl)alkyl; and carboxylates. More preferred L^b groups are C_{1-20} alkyl, C_{7-20} aralkyl, and chloride;

h is an integer from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3, and j is 1 or 2, with the value h x j selected to provide charge balance;

Z^b is a neutral ligand group coordinated to M^b, and containing up to 50 atoms not counting hydrogen Preferred Z^b groups include aliphatic and aromatic amines, phosphines, and ethers, alkenes, alkadienes, and inertly substituted derivatives thereof. Suitable inert substituents include halogen, alkoxy, aryloxy, alkoxycarbonyl, aryloxycarbonyl, di(hydrocarbyl)amine, tri(hydrocarbyl)silyl, and nitrile groups. Preferred Z^b groups include triphenylphosphine, tetrahydrofuran, pyridine, and 1,4-diphenylbutadiene;

f is an integer from 1 to 3;

two or three of T^b, R^b and $R^{b'}$ may be joined together to form a single or multiple ring structure;

h is an integer from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3;

$\sim\sim$ indicates any form of electronic interaction comprising a net coulombic attraction, especially coordinate or covalent bonds, including multiple bonds;

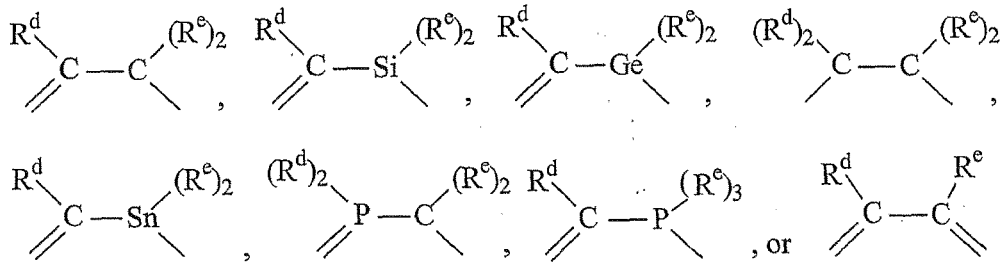
arrows signify coordinate bonds; and

dotted lines indicate optional double bonds.

In one embodiment, it is preferred that R^b have relatively low steric hindrance with respect to X^b. In this embodiment, most preferred R^b groups are straight chain alkyl groups, straight chain alkenyl groups, branched chain alkyl groups wherein the closest branching point is at least 3 atoms removed from X^b, and halo, dihydrocarbylamino, alkoxy or trihydrocarbylsilyl substituted derivatives thereof. Highly preferred R^b groups in this embodiment are C_{1-8} straight chain alkyl groups.

At the same time, in this embodiment $R^{b'}$ preferably has relatively high steric hindrance with respect to Y^b. Non-limiting examples of suitable $R^{b'}$ groups for this embodiment include alkyl or alkenyl groups containing one or more secondary or tertiary carbon centers, cycloalkyl, aryl, alkaryl, aliphatic or aromatic heterocyclic groups, organic or inorganic oligomeric, polymeric or cyclic groups, and halo, dihydrocarbylamino, alkoxy or trihydrocarbylsilyl substituted derivatives thereof. Preferred $R^{b'}$ groups in this embodiment contain from 3 to 40, more preferably from 3 to 30, and most preferably from 4 to 20 atoms not counting hydrogen and are branched or cyclic.

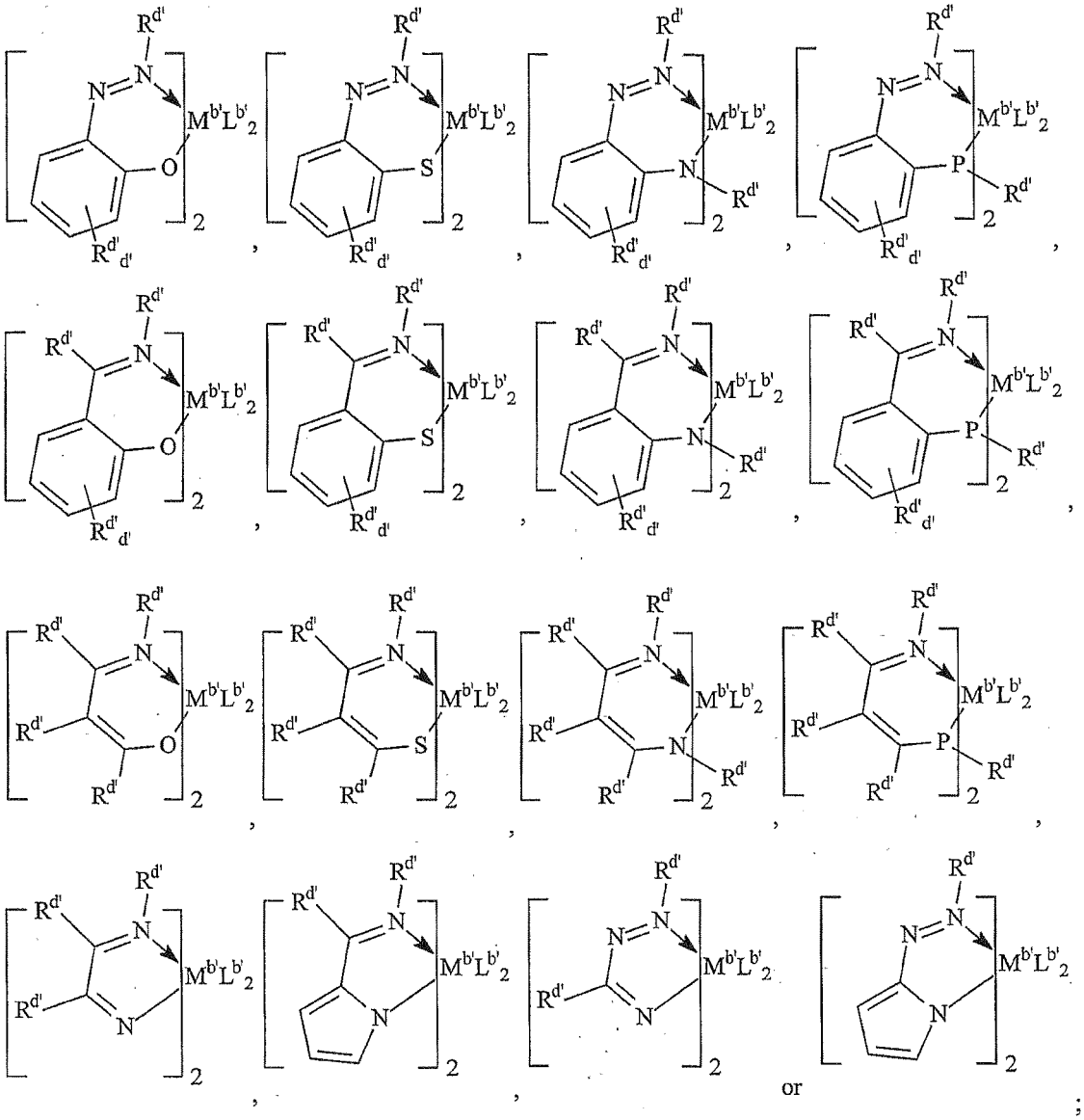
Examples of preferred T^b groups are structures corresponding to the following formulas:



, wherein

Each R^d is C_{1-10} hydrocarbyl group, preferably methyl, ethyl, n-propyl, i-propyl, t-butyl, phenyl, 2,6-dimethylphenyl, benzyl, or tolyl. Each R^e is C_{1-10} hydrocarbyl, preferably methyl, ethyl, n-propyl, i-propyl, t-butyl, phenyl, 2,6-dimethylphenyl, benzyl, or tolyl. In addition, two or more R^d or R^e groups, or mixtures of Rd and Re groups may together form a polyvalent derivative of a hydrocarbyl group, such as, 1,4-butylene, 1,5-pentylene, or a multicyclic, fused ring, polyvalent hydrocarbyl- or heterohydrocarbyl- group, such as naphthalene-1,8-diyl.

Preferred examples of the foregoing polyvalent Lewis base complexes include:



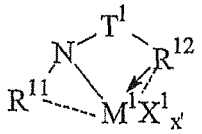
wherein $R^{d'}$ each occurrence is independently selected from the group consisting of hydrogen and C_{1-50} hydrocarbyl groups optionally containing one or more heteroatoms, or inertly substituted derivative thereof, or further optionally, two adjacent $R^{d'}$ groups may together form a divalent bridging group;

d' is 4;

$M^{b'}$ is a group 4 metal, preferably titanium or hafnium or a Group 10 metal, preferably Ni or Pd;

$L^{b'}$ is a monovalent ligand of up to 50 atoms not counting hydrogen, preferably halide or hydrocarbyl, or two $L^{b'}$ groups together are a divalent or neutral ligand group, preferably a C_{2-50} hydrocarbylene, hydrocarbadiyl or diene group.

The polyvalent Lewis base complexes for use in the present invention especially include Group 4 metal derivatives, especially hafnium derivatives of hydrocarbylamine substituted heteroaryl compounds corresponding to the formula:



wherein:

R^{11} is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen or a divalent derivative thereof;

T^1 is a divalent bridging group of from 1 to 41 atoms other than hydrogen, preferably 1 to 20 atoms other than hydrogen, and most preferably a mono- or di- C_{1-20} hydrocarbyl substituted methylene or silane group; and

R^{12} is a C_{5-20} heteroaryl group containing Lewis base functionality, especially a pyridin-2-yl- or substituted pyridin-2-yl group or a divalent derivative thereof;

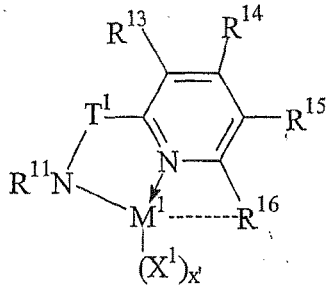
M^1 is a Group 4 metal, preferably hafnium;

X^1 is an anionic, neutral or dianionic ligand group;

x' is a number from 0 to 5 indicating the number of such X^1 groups; and

bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively.

Preferred complexes are those wherein ligand formation results from hydrogen elimination from the amine group and optionally from the loss of one or more additional groups, especially from R^{12}. In addition, electron donation from the Lewis base functionality, preferably an electron pair, provides additional stability to the metal center. Preferred metal complexes correspond to the formula:



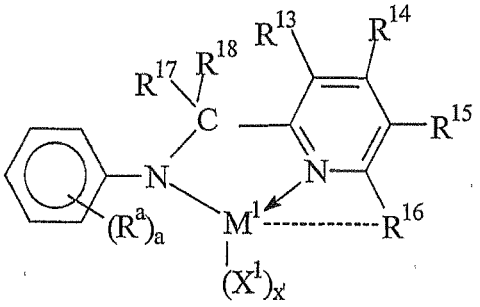
, wherein

M^1, X^1, x', R^{11} and T^1 are as previously defined,

R^{13}, R^{14}, R^{15} and R^{16} are hydrogen, halo, or an alkyl, cycloalkyl, heteroalkyl, heterocycloalkyl, aryl, or silyl group of up to 20 atoms not counting hydrogen, or adjacent R^{13}, R^{14}, R^{15} or R^{16} groups may be joined together thereby forming fused ring derivatives, and

bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.

More preferred examples of the foregoing metal complexes correspond to the formula:



, wherein

M^1, X^1, and x' are as previously defined,

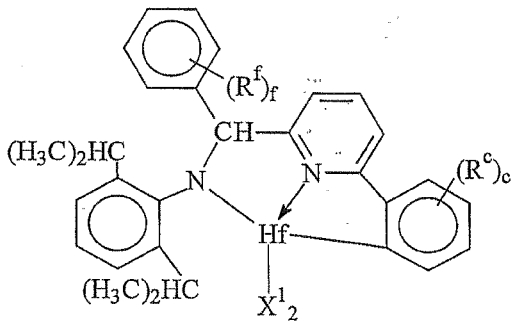
R^{13}, R^{14}, R^{15} and R^{16} are as previously defined, preferably R^{13}, R^{14}, and R^{15} are hydrogen, or C_{1-4} alkyl, and R^{16} is C_{6-20} aryl, most preferably naphthalenyl;

R^a independently each occurrence is C_{1-4} alkyl, and a is 1-5, most preferably R^a in two ortho- positions to the nitrogen is isopropyl or t-butyl;

R^{17} and R^{18} independently each occurrence are hydrogen, halogen, or a C_{1-20} alkyl or aryl group, most preferably one of R^{17} and R^{18} is hydrogen and the other is a C_{6-20} aryl group, especially 2-isopropyl, phenyl or a fused polycyclic aryl group, most preferably an anthracenyl group, and

bonds, optional bonds and electron pair donative interactions are represented by lines, dotted lines and arrows respectively.

Highly preferred metal complexes for use herein correspond to the formula:

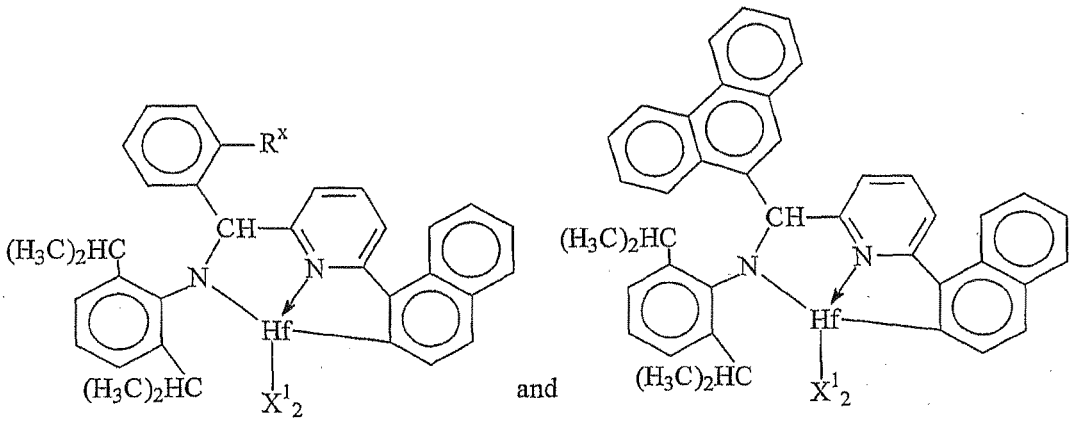


wherein X^1 each occurrence is halide, N,N-dimethylamido, or C_{1-4} alkyl, and preferably each occurrence X^1 is methyl;

R^f independently each occurrence is hydrogen, halogen, C_{1-20} alkyl, or C_{6-20} aryl, or two adjacent R^f groups are joined together thereby forming a ring, and f is 1-5; and

R^c independently each occurrence is hydrogen, halogen, C_{1-20} alkyl, or C_{6-20} aryl, or two adjacent R^c groups are joined together thereby forming a ring, and c is 1-5.

Most highly preferred examples of metal complexes for use according to the present invention are complexes of the following formulas:



wherein R^x is C_{1-4} alkyl or cycloalkyl, preferably methyl, isopropyl, t-butyl or cyclohexyl; and

X^1 each occurrence is halide, N,N-dimethylamido, or C_{1-4} alkyl, preferably methyl.

Examples of metal complexes usefully employed according to the present invention include:

[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);

[N-(2,6-di(1-methylethyl)phenyl)amido)(o-tolyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;

[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido);

[N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride;

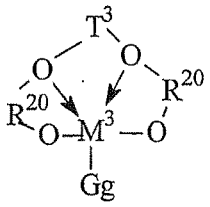
[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium di(N,N-dimethylamido); and

[N-(2,6-di(1-methylethyl)phenyl)amido)(phenanthren-5-yl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dichloride.

Under the reaction conditions used to prepare the metal complexes used in the present invention, the hydrogen of the 2-position of the α-naphthalene group substituted at the 6-position of the pyridin-2-yl group is subject to elimination, thereby uniquely forming metal complexes wherein the metal is covalently bonded to both the resulting amide group and to the 2-position of the α-naphthalenyl group, as well as stabilized by coordination to the pyridinyl nitrogen atom through the electron pair of the nitrogen atom.

Additional suitable metal complexes of polyvalent Lewis bases for use herein include compounds corresponding to the formula:



, where:

R^{20} is an aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen, or a polyvalent derivative thereof;

T^3 is a hydrocarbylene or silane group having from 1 to 20 atoms not counting hydrogen, or an inertly substituted derivative thereof;

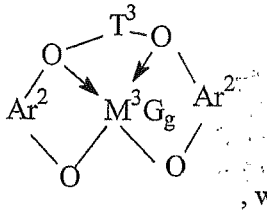
M^3 is a Group 4 metal, preferably zirconium or hafnium;

G is an anionic, neutral or dianionic ligand group; preferably a halide, hydrocarbyl or dihydrocarbylamide group having up to 20 atoms not counting hydrogen;

g is a number from 1 to 5 indicating the number of such G groups; and

bonds and electron donative interactions are represented by lines and arrows respectively.

Preferably, such complexes correspond to the formula:



, wherein:

T^3 is a divalent bridging group of from 2 to 20 atoms not counting hydrogen, preferably a substituted or unsubstituted, C_{3-6} alkylene group; and

Ar^2 independently each occurrence is an arylene or an alkyl- or aryl-substituted arylene group of from 6 to 20 atoms not counting hydrogen;

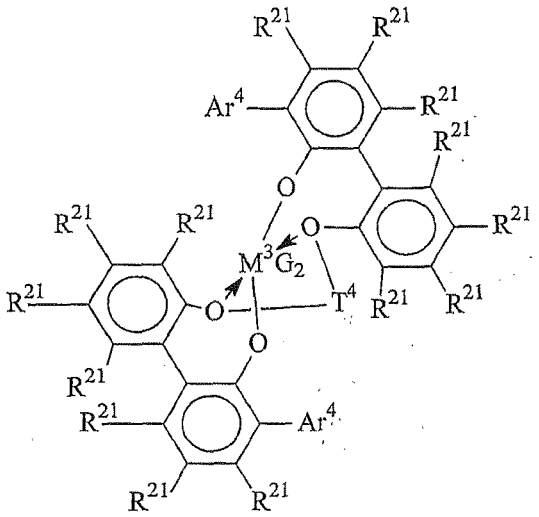
M^3 is a Group 4 metal, preferably hafnium or zirconium;

G independently each occurrence is an anionic, neutral or dianionic ligand group;

g is a number from 1 to 5 indicating the number of such X groups; and

electron donative interactions are represented by arrows.

Preferred examples of metal complexes of foregoing formula include the following compounds :



where M^3 is Hf or Zr;

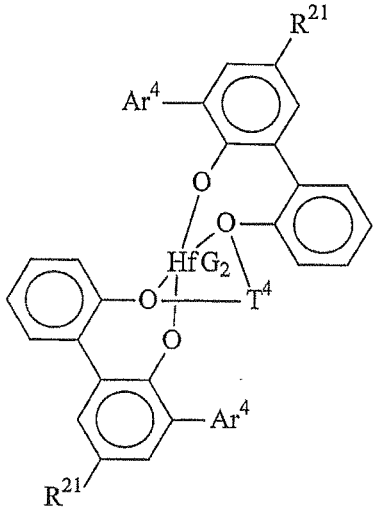
Ar^4 is C_{6-20} aryl or inertly substituted derivatives thereof, especially 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl, and

T^4 independently each occurrence comprises a C_{3-6} alkylene group, a C_{3-6} cycloalkylene group, or an inertly substituted derivative thereof;

R^{21} independently each occurrence is hydrogen, halo, hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl of up to 50 atoms not counting hydrogen; and

G, independently each occurrence is halo or a hydrocarbyl or trihydrocarbylsilyl group of up to 20 atoms not counting hydrogen, or 2 G groups together are a divalent derivative of the foregoing hydrocarbyl or trihydrocarbylsilyl groups.

Especially preferred are compounds of the formula:



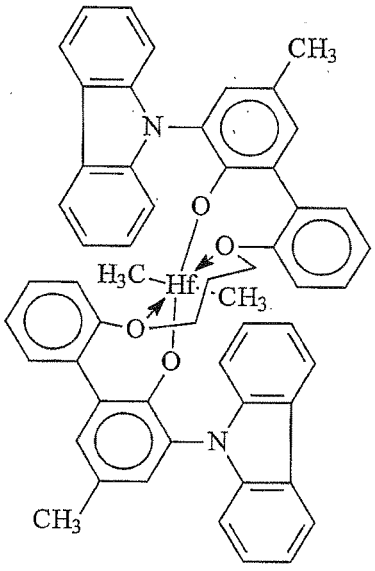
wherein Ar^4 is 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl,

R^{21} is hydrogen, halo, or C_{1-4} alkyl, especially methyl

T^4 is propan-1,3-diyl or butan-1,4-diyl, and

G is chloro, methyl or benzyl.

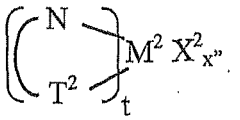
A most highly preferred metal complex of the foregoing formula is:



The foregoing polyvalent Lewis base complexes are conveniently prepared by standard metallation and ligand exchange procedures involving a source of the Group 4 metal and the neutral polyfunctional ligand source. In addition, the complexes may also be prepared by means of an amide elimination and hydrocarbylation process starting from the corresponding Group 4 metal tetraamide and a hydrocarbylating agent, such as trimethylaluminum. Other techniques may be

used as well. These complexes are known from the disclosures of, among others, US patents 6,320,005, 6,103,657, WO 02/38628, WO 03/40195, and US 04/0220050.

Additional suitable metal compounds for use herein include Group 4-10 metal derivatives corresponding to the formula:



wherein

M^2 is a metal of Groups 4-10 of the Periodic Table of the elements, preferably Group 4 metals, Ni(II) or Pd(II), most preferably zirconium;

T^2 is a nitrogen, oxygen or phosphorus containing group;

X^2 is halo, hydrocarbyl, or hydrocarbyloxy;

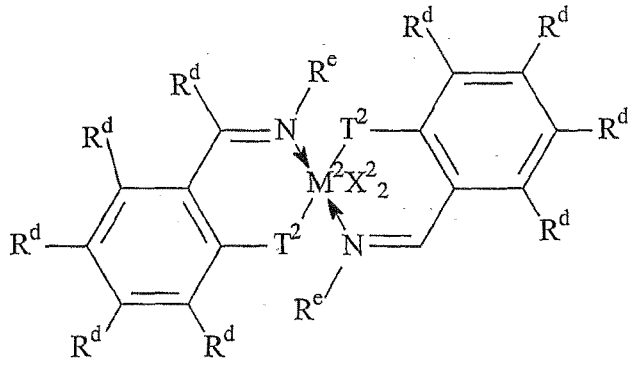
t is one or two;

x" is a number selected to provide charge balance;

and T^2 and N are linked by a bridging ligand.

Such catalysts have been previously disclosed in J. Am. Chem. Soc., 118, 267-268 (1996), J. Am. Chem. Soc., 117, 6414 -6415 (1995), and Organometallics, 16, 1514-1516, (1997), among other disclosures.

Preferred examples of the foregoing metal complexes are aromatic diimine or aromatic dioxyimine complexes of Group 4 metals, especially zirconium, corresponding to the formula:



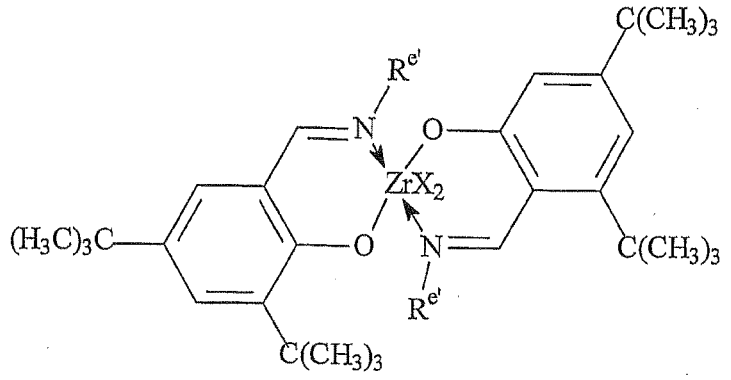
wherein;

M^2, X^2 and T^2 are as previously defined;

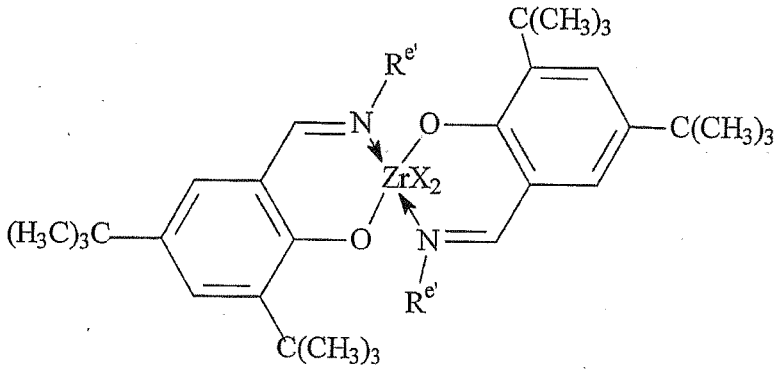
R^d independently each occurrence is hydrogen, halogen, or R^e; and

R^e independently each occurrence is C_{1-20} hydrocarbyl or a heteroatom-, especially a F, N, S or P- substituted derivative thereof, more preferably C_{1-10} hydrocarbyl or a F or N substituted derivative thereof, most preferably alkyl, dialkylaminoalkyl, pyrrolyl, piperidenyl, perfluorophenyl, cycloalkyl, (poly)alkylaryl, or aralkyl.

Most preferred examples of the foregoing metal complexes are aromatic dioxyimine complexes of zirconium, corresponding to the formula:



, or



wherein;

X^2 is as previously defined, preferably C_{1-10} hydrocarbyl, most preferably methyl or benzyl; and

$R^{e'}$ is methyl, isopropyl, t-butyl, cyclopentyl, cyclohexyl, 2-methylcyclohexyl, 2,4-dimethylcyclohexyl, 2-pyrrolyl, N-methyl-2-pyrrolyl, 2-piperidenyl, N-methyl-2-piperidenyl, benzyl, o-tolyl, 2,6-dimethylphenyl, perfluorophenyl, 2,6-di(isopropyl)phenyl, or 2,4,6-trimethylphenyl.

The foregoing complexes also include certain phosphinimine complexes are disclosed in EP-A-890581. These complexes correspond to the formula: $[(R^f)_3\text{-}P{=}N]_fM(K^2)(R^f)_{3-f}$, wherein:

R^f is a monovalent ligand or two R^f groups together are a divalent ligand, preferably R^f is hydrogen or C_{1-4} alkyl;

M is a Group 4 metal,

K^2 is a group containing delocalized π-electrons through which K^2 is bound to M, said K^2 group containing up to 50 atoms not counting hydrogen atoms, and

f is 1 or 2.

Catalysts having high comonomer incorporation properties are also known to reincorporate *in situ* prepared long chain olefins resulting incidentally during the polymerization through β-hydride elimination and chain termination of growing polymer, or other process. The concentration of such long chain olefins is particularly enhanced by use of continuous solution polymerization conditions at high conversions, especially ethylene conversions of 95 percent or greater, more preferably at ethylene conversions of 97 percent or greater. Under such conditions a small but detectable quantity of vinyl group terminated polymer may be reincorporated into a growing polymer chain, resulting in the formation of long chain branches, that is, branches of a carbon length greater than would result from other deliberately added comonomer. Moreover, such chains reflect the presence of other comonomers present in the reaction mixture. That is, the chains may include short chain or long chain branching as well, depending on the comonomer composition of the reaction mixture. However, the presence of an MSA or CSA during polymerization can seriously limit the incidence of long chain branching since the vast majority of the polymer chains become attached to an MSA or CSA species and are prevented from undergoing β-hydride elimination.

Cocatalysts

Each of the metal complexes (also interchangeably referred to herein as procatalysts) may be activated to form the active catalyst composition by combination with a cocatalyst, preferably a cation forming cocatalyst, a strong Lewis acid, or a combination thereof.

Suitable cation forming cocatalysts include those previously known in the art for use with Group 4 metal olefin polymerization complexes. Examples include neutral Lewis acids, such as C_{1-30} hydrocarbyl substituted Group 13 compounds, especially tri(hydrocarbyl)aluminum- or tri(hydrocarbyl)boron compounds and halogenated (including perhalogenated) derivatives thereof, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, more especially perfluorinated tri(aryl)boron compounds, and most especially tris(pentafluoro-phenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially the use of ammonium-, phosphonium-, oxonium-, carbonium-, silylium- or sulfonium- salts of compatible, noncoordinating anions, or ferrocenium-, lead- or silver salts of compatible, noncoordinating anions; and combinations of the foregoing cation forming cocatalysts and techniques. The foregoing activating cocatalysts and activating techniques have been previously taught with respect to different metal complexes for olefin polymerizations in the following references: EP-A-277,003, US-A-5,153,157, US-A-5,064,802, US-A-5,321,106, US-A-5,721,185, US-A-5,350,723, US-A-5,425,872, US-A-5,625,087, US-A-5,883,204, US-A-5,919,983, US-A-5,783,512, WO 99/15534, and WO99/42467.

Combinations of neutral Lewis acids, especially the combination of a trialkyl aluminum compound having from 1 to 4 carbons in each alkyl group and a halogenated tri(hydrocarbyl)boron compound having from 1 to 20 carbons in each hydrocarbyl group, especially tris(pentafluorophenyl)borane, further combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane may be used as activating cocatalysts. Preferred molar ratios of metal complex:tris(pentafluorophenyl-borane:alumoxane are from 1:1:1 to 1:5:20, more preferably from 1:1:1.5 to 1:5:10.

Suitable ion forming compounds useful as cocatalysts in one embodiment of the present invention comprise a cation which is a Bronsted acid capable of donating a proton, and a compatible, noncoordinating anion, A^-. As used herein, the term "noncoordinating" means an anion or substance which either does not coordinate to the Group 4 metal containing precursor complex and the catalytic derivative derived there from, or which is only weakly coordinated to such complexes thereby remaining sufficiently labile to be displaced by a neutral Lewis base. A noncoordinating anion specifically refers to an anion which when functioning as a charge balancing anion in a cationic metal complex does not transfer an anionic substituent or fragment thereof to said cation thereby forming neutral complexes. "Compatible anions" are anions which are not degraded to neutrality when the initially formed complex decomposes and are noninterfering with desired subsequent polymerization or other uses of the complex.

Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is capable of balancing the charge of the active catalyst species (the metal cation) which may be formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum, gold and platinum. Suitable metalloids include, but are not limited to, boron, phosphorus, and silicon. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

Preferably such cocatalysts may be represented by the following general formula:

$$(L^*\text{-}H)_g^+ (A)^{g-}$$

wherein:

L* is a neutral Lewis base;

$(L^*\text{-}H)^+$ is a conjugate Bronsted acid of L*;

A^{g-} is a noncoordinating, compatible anion having a charge of g-, and

g is an integer from 1 to 3.

More preferably A^{g-} corresponds to the formula: $[MiQ_4]^-$;

wherein:

Mi is boron or aluminum in the +3 formal oxidation state; and

Q independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxide, halosubstituted-hydrocarbyl, halosubstituted hydrocarbyloxy, and halo- substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl- perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with the proviso that in not more than one occurrence is Q halide. Examples of suitable hydrocarbyloxide Q groups are disclosed in US-A-5,296,433.

In a more preferred embodiment, d is one, that is, the counter ion has a single negative charge and is A^-. Activating cocatalysts comprising boron which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:

$$(L^*\text{-}H)^+(BQ_4)^-;$$

wherein:

L* is as previously defined;

B is boron in a formal oxidation state of 3; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

Preferred Lewis base salts are ammonium salts, more preferably trialkylammonium salts containing one or more C_{12-40} alkyl groups. Most preferably, Q is each occurrence a fluorinated aryl group, especially, a pentafluorophenyl group.

Illustrative, but not limiting, examples of boron compounds which may be used as an activating cocatalyst in the preparation of the improved catalysts of this invention are tri-substituted ammonium salts such as:

trimethylammonium tetrakis(pentafluorophenyl) borate,
triethylammonium tetrakis(pentafluorophenyl) borate,
tripropylammonium tetrakis(pentafluorophenyl) borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate,
N,N-dimethylanilinium benzyltris(pentafluorophenyl) borate,

N,N-dimethylanilinium tetrakis(4-(t-butyldimethylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,
N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl) borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl) borate,
dimethyloctadecylammonium tetrakis(pentafluorophenyl) borate,
methyldioctadecylammonium tetrakis(pentafluorophenyl) borate,
dialkyl ammonium salts such as:

di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate,
methyloctadecylammonium tetrakis(pentafluorophenyl) borate,
methyloctadodecylammonium tetrakis(pentafluorophenyl) borate, and
dioctadecylammonium tetrakis(pentafluorophenyl) borate;
tri-substituted phosphonium salts such as:

triphenylphosphonium tetrakis(pentafluorophenyl) borate,
methyldioctadecylphosphonium tetrakis(pentafluorophenyl) borate, and
tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate;
di-substituted oxonium salts such as:

diphenyloxonium tetrakis(pentafluorophenyl) borate,
di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and
di(octadecyl)oxonium tetrakis(pentafluorophenyl) borate;
di-substituted sulfonium salts such as:

di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and
methylcotadecylsulfonium tetrakis(pentafluorophenyl) borate.

Preferred $(L^*\text{-}H)^+$ cations are methyldioctadecylammonium cations, dimethyloctadecylammonium cations, and ammonium cations derived from mixtures of trialkyl amines containing one or 2 $C_{14\text{-}18}$ alkyl groups.

Another suitable ion forming, activating cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula:

$$(Ox^{h+})_g(A^{g-})_h,$$

wherein:

Ox^{h+} is a cationic oxidizing agent having a charge of h+;

h is an integer from 1 to 3; and

A^{g-} and g are as previously defined.

Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^+, or Pb^{+2}. Preferred embodiments of A^{g-} are those anions previously defined with

respect to the Bronsted acid containing activating cocatalysts, especially tetrakis(pentafluorophenyl)borate.

Another suitable ion forming, activating cocatalyst comprises a compound which is a salt of a carbenium ion and a noncoordinating, compatible anion represented by the formula:

$$[C]^+ A^-$$

wherein:

$[C]^+$ is a C_{1-20} carbenium ion; and

A^- is a noncoordinating, compatible anion having a charge of -1. A preferred carbenium ion is the trityl cation, that is triphenylmethylium.

A further suitable ion forming, activating cocatalyst comprises a compound which is a salt of a silylium ion and a noncoordinating, compatible anion represented by the formula:

$$(Q^1{}_3Si)^+A^-$$

wherein:

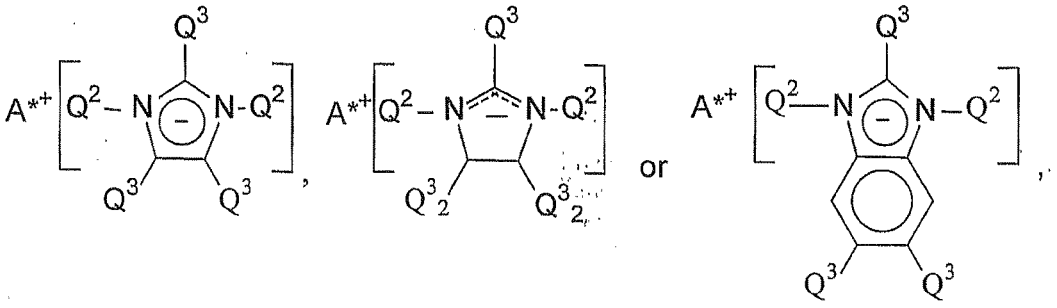
Q^1 is C_{1-10} hydrocarbyl, and A^- is as previously defined.

Preferred silylium salt activating cocatalysts are trimethylsilylium tetrakispentafluorophenylborate, triethylsilylium tetrakispentafluorophenylborate and ether substituted adducts thereof. Silylium salts have been previously generically disclosed in J. Chem Soc. Chem. Comm., 1993, 383-384, as well as Lambert, J. B., et al., Organometallics, 1994, 13, 2430-2443. The use of the above silylium salts as activating cocatalysts for addition polymerization catalysts is disclosed in US-A-5,625,087.

Certain complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are also effective catalyst activators and may be used according to the present invention. Such cocatalysts are disclosed in US-A-5,296,433.

Suitable activating cocatalysts for use herein also include polymeric or oligomeric alumoxanes, especially methylalumoxane (MAO), triisobutyl aluminum modified methylalumoxane (MMAO), or isobutylalumoxane; Lewis acid modified alumoxanes, especially perhalogenated tri(hydrocarbyl)aluminum- or perhalogenated tri(hydrocarbyl)boron modified alumoxanes, having from 1 to 10 carbons in each hydrocarbyl or halogenated hydrocarbyl group, and most especially tris(pentafluorophenyl)borane modified alumoxanes. Such cocatalysts are previously disclosed in US Patents 6,214,760, 6,160,146, 6,140,521, and 6,696,379.

A class of cocatalysts comprising non-coordinating anions generically referred to as expanded anions, further disclosed in US Patent 6,395,671, may be suitably employed to activate the metal complexes of the present invention for olefin polymerization. Generally, these cocatalysts (illustrated by those having imidazolide, substituted imidazolide, imidazolinide, substituted imidazolinide, benzimidazolide, or substituted benzimidazolide anions) may be depicted as follows:



wherein:

A^{*+} is a cation, especially a proton containing cation, and preferably is a trihydrocarbyl ammonium cation containing one or two C_{10-40} alkyl groups, especially a methyldi (C_{14-20} alkyl)ammonium cation,

Q^3, independently each occurrence, is hydrogen or a halo, hydrocarbyl, halocarbyl, halohydrocarbyl, silylhydrocarbyl, or silyl, (including mono-, di- and tri(hydrocarbyl)silyl) group of up to 30 atoms not counting hydrogen, preferably C_{1-20} alkyl, and

Q^2 is tris(pentafluorophenyl)borane or tris(pentafluorophenyl)alumane).

Examples of these catalyst activators include trihydrocarbylammonium- salts, especially, methyldi(C_{14-20} alkyl)ammonium- salts of:

bis(tris(pentafluorophenyl)borane)imidazolide,
bis(tris(pentafluorophenyl)borane)-2-undecylimidazolide,
bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolide,
bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolide,
bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolide,
bis(tris(pentafluorophenyl)borane)imidazolinide,
bis(tris(pentafluorophenyl)borane)-2-undecylimidazolinide,
bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolinide,
bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolinide,
bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolinide,
bis(tris(pentafluorophenyl)borane)-5,6-dimethylbenzimidazolide,
bis(tris(pentafluorophenyl)borane)-5,6-bis(undecyl)benzimidazolide,

bis(tris(pentafluorophenyl)alumane)imidazolide,
bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolide,
bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolide,
bis(tris(pentafluorophenyl)alumane)imidazolinide,

bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolinide,
bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolinide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolinide,
bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolinide,
bis(tris(pentafluorophenyl)alumane)-5,6-dimethylbenzimidazolide, and
bis(tris(pentafluorophenyl)alumane)-5,6-bis(undecyl)benzimidazolide.

Other activators include those described in PCT publication WO 98/07515 such as tris (2, 2', 2"-nonafluorobiphenyl)fluoroaluminate. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, EP-A-0 573120, PCT publications WO 94/07928 and WO 95/14044 and US Patents 5,153,157 and 5,453,410. WO 98/09996 describes activating catalyst compounds with perchlorates, periodates and iodates, including their hydrates. WO 99/18135 describes the use of organoboroaluminum activators. WO 03/10171 discloses catalyst activators that are adducts of Bronsted acids with Lewis acids. Other activators or methods for activating a catalyst compound are described in for example, US Patents 5,849,852, 5,859, 653, 5,869,723, EP-A-615981, and PCT publication WO 98/32775. All of the foregoing catalyst activators as well as any other know activator for transition metal complex catalysts may be employed alone or in combination according to the present invention, however, for best results alumoxane containing cocatalysts are avoided.

The molar ratio of catalyst/cocatalyst employed preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:1000 to 1:1. Alumoxane, when used by itself as an activating cocatalyst, is employed in large quantity, generally at least 100 times the quantity of metal complex on a molar basis. Tris(pentafluorophenyl)borane, where used as an activating cocatalyst is employed in a molar ratio to the metal complex of from 0.5:1 to 10:1, more preferably from 1:1 to 6:1 most preferably from 1:1 to 5:1. The remaining activating cocatalysts are generally employed in approximately equimolar quantity with the metal complex.

During the polymerization, the reaction mixture is contacted with the activated catalyst composition according to any suitable polymerization conditions. The process is desirably characterized by use of elevated temperatures and pressures. Hydrogen may be employed as a chain transfer agent for molecular weight control according to known techniques, if desired. As in other similar polymerizations, it is highly desirable that the monomers and solvents employed be of sufficiently high purity that catalyst deactivation or premature chain termination does not occur. Any suitable technique for monomer purification such as devolatilization at reduced pressure, contacting with molecular sieves or high surface area alumina, or a combination of the foregoing processes may be employed.

Supports may be employed in the present invention, especially in slurry or gas-phase polymerizations. Suitable supports include solid, particulated, high surface area, metal oxides, metalloid oxides, or mixtures thereof (interchangeably referred to herein as an inorganic oxide). Examples include: talc, silica, alumina, magnesia, titania, zirconia, Sn_2O_3, aluminosilicates, borosilicates, clays, and mixtures thereof. Suitable supports preferably have a surface area as determined by nitrogen porosimetry using the B.E.T. method from 10 to 1000 m^2/g, and preferably from 100 to 600 m^2/g. The average particle size typically is from 0.1 to 500 μm, preferably from 1 to 200 μm, more preferably 10 to 100 μm.

In one embodiment of the invention the present catalyst composition and optional support may be spray dried or otherwise recovered in solid, particulated form to provide a composition that is readily transported and handled. Suitable methods for spray drying a liquid containing slurry are well known in the art and usefully employed herein. Preferred techniques for spray drying catalyst compositions for use herein are described in US-A's-5,648,310 and 5,672,669.

The polymerization is desirably carried out as a continuous polymerization, preferably a continuous, solution polymerization, in which catalyst components, monomers, and optionally solvent, adjuvants, scavengers, and polymerization aids are continuously supplied to one or more reactors or zones and polymer product continuously removed there from. Within the scope of the terms "continuous" and "continuously" as used in this context are those processes in which there are intermittent additions of reactants and removal of products at small regular or irregular intervals, so that, over time, the overall process is substantially continuous. While the multi-centered shuttling agent and the chain shuttling agent(s) (if used) may be added at any point during the polymerization including in the first reactor or zone, at the exit or slightly before the exit of the first reactor, between the first reactor or zone and any subsequent reactor or zone, or even solely to the second reactor or zone, if present, both are preferably added at the initial stages of the polymerization. If there exists any difference in monomers, temperatures, pressures or other polymerization condition within a reactor or between two or more reactors or zones connected in series, polymer segments of differing composition such as comonomer content, crystallinity, density, tacticity, regio-regularity, or other chemical or physical difference, within the same molecule are formed in the polymers of the invention. In such event, the size of each segment or block is determined by the polymer reaction conditions, and preferably is a most probable distribution of polymer sizes.

If multiple reactors are employed, each can be independently operated under high pressure, solution, slurry, or gas phase polymerization conditions. In a multiple zone polymerization, all zones operate under the same type of polymerization, such as solution, slurry, or gas phase, but, optionally, at different process conditions. For a solution polymerization process, it is desirable to

employ homogeneous dispersions of the catalyst components in a liquid diluent in which the polymer is soluble under the polymerization conditions employed. One such process utilizing an extremely fine silica or similar dispersing agent to produce such a homogeneous catalyst dispersion wherein normally either the metal complex or the cocatalyst is only poorly soluble is disclosed in US-A-5,783,512. A high pressure process is usually carried out at temperatures from 100°C to 400°C and at pressures above 500 bar (50 MPa). A slurry process typically uses an inert hydrocarbon diluent and temperatures of from 0°C up to a temperature just below the temperature at which the resulting polymer becomes substantially soluble in the inert polymerization medium. Preferred temperatures in a slurry polymerization are from 30°C, preferably from 60°C up to 115°C, preferably up to 100°C, depending on the polymer being prepared. Pressures typically range from atmospheric (100 kPa) to 500 psi (3.4 MPa).

In all of the foregoing processes, continuous or substantially continuous polymerization conditions are preferably employed. The use of such polymerization conditions, especially continuous, solution polymerization processes, allows the use of elevated reactor temperatures which results in the economical production of the present block copolymers in high yields and efficiencies.

The catalyst may be prepared as a homogeneous composition by addition of the requisite metal complex or multiple complexes to a solvent in which the polymerization will be conducted or in a diluent compatible with the ultimate reaction mixture. The desired cocatalyst or activator and, optionally, a shuttling agent may be combined with the catalyst composition either prior to, simultaneously with, or after combination of the catalyst with the monomers to be polymerized and any additional reaction diluent. Desirably, the MSA is added at the same time.

At all times, the individual ingredients as well as any active catalyst composition must be protected from oxygen, moisture and other catalyst poisons. Therefore, the catalyst components, multi-centered shuttling agent and activated catalysts must be prepared and stored in an oxygen and moisture free atmosphere, preferably under a dry, inert gas such as nitrogen.

Without limiting in any way the scope of the invention, one means for carrying out such a polymerization process is as follows. In one or more well stirred tank or loop reactors operating under solution polymerization conditions, the monomers to be polymerized are introduced continuously together with any solvent or diluent at one part of the reactor. The reactor contains a relatively homogeneous liquid phase composed substantially of monomers together with any solvent or diluent and dissolved polymer. Preferred solvents include C_{4-10} hydrocarbons or mixtures thereof, especially alkanes such as hexane or mixtures of alkanes, as well as one or more of the monomers employed in the polymerization. Examples of suitable loop reactors and a variety of

suitable operating conditions for use therewith, including the use of multiple loop reactors, operating in series, are found in USP's 5,977,251, 6,319,989 and 6,683,149.

Catalyst along with cocatalyst and multi-centered shuttling agent are continuously or intermittently introduced in the reactor liquid phase or any recycled portion thereof at a minimum of one location. The reactor temperature and pressure may be controlled by adjusting the solvent/monomer ratio, the catalyst addition rate, as well as by use of cooling or heating coils, jackets or both. The polymerization rate is controlled by the rate of catalyst addition. The content of a given monomer in the polymer product is influenced by the ratio of monomers in the reactor, which is controlled by manipulating the respective feed rates of these components to the reactor. The polymer product molecular weight is controlled, optionally, by controlling other polymerization variables such as the temperature, monomer concentration, or by the previously mentioned multi-centered shuttling agent, or a chain terminating agent such as hydrogen, as is well known in the art.

In one embodiment of the invention, a second reactor is connected to the discharge of the reactor, optionally by means of a conduit or other transfer means, such that the reaction mixture prepared in the first reactor is discharged to the second reactor without substantially termination of polymer growth. Between the first and second reactors, a differential in at least one process condition may be established. Preferably for use in formation of a copolymer of two or more monomers, the difference is the presence or absence of one or more comonomers or a difference in comonomer concentration. Additional reactors, each arranged in a manner similar to the second reactor in the series may be provided as well. Further polymerization is ended by contacting the reactor effluent with a catalyst kill agent such as water, steam or an alcohol or with a coupling agent if a coupled reaction product is desired.

The resulting polymer product is recovered by flashing off volatile components of the reaction mixture such as residual monomer(s) or diluent at reduced pressure, and, if necessary, conducting further devolatilization in equipment such as a devolatilizing extruder. In a continuous process the mean residence time of the catalyst and polymer in the reactor generally is from 5 minutes to 8 hours, and preferably from 10 minutes to 6 hours.

Alternatively, the foregoing polymerization may be carried out in a plug flow reactor optionally with a monomer, catalyst, multi-centered shuttling agent, temperature or other gradient established between differing zones or regions thereof, further optionally accompanied by separate addition of catalysts and/or chain shuttling agent, and operating under adiabatic or non-adiabatic polymerization conditions.

The catalyst composition may also be prepared and employed as a heterogeneous catalyst by adsorbing the requisite components on an inert inorganic or organic particulated solid, as previously disclosed. In a preferred embodiment, a heterogeneous catalyst is prepared by co-

precipitating the metal complex and the reaction product of an inert inorganic compound and an active hydrogen containing activator, especially the reaction product of a tri (C_{1-4} alkyl) aluminum compound and an ammonium salt of a hydroxyaryltris(pentafluorophenyl)borate, such as an ammonium salt of (4-hydroxy-3,5-ditertiarybutylphenyl)tris(pentafluorophenyl)borate. When prepared in heterogeneous or supported form, the catalyst composition may be employed in a slurry or a gas phase polymerization. As a practical limitation, slurry polymerization takes place in liquid diluents in which the polymer product is substantially insoluble. Preferably, the diluent for slurry polymerization is one or more hydrocarbons with less than 5 carbon atoms. If desired, saturated hydrocarbons such as ethane, propane or butane may be used in whole or part as the diluent. As with a solution polymerization, the α-olefin comonomer or a mixture of different α-olefin monomers may be used in whole or part as the diluent. Most preferably at least a major part of the diluent comprises the α-olefin monomer or monomers to be polymerized.

Preferably for use in gas phase polymerization processes, the support material and resulting catalyst has a median particle diameter from 20 to 200 μm, more preferably from 30 μm to 150 μm, and most preferably from 50 μm to 100 μm. Preferably for use in slurry polymerization processes, the support has a median particle diameter from 1 μm to 200 μm, more preferably from 5 μm to 100 μm, and most preferably from 10 μm to 80 μm.

Suitable gas phase polymerization process for use herein are substantially similar to known processes used commercially on a large scale for the manufacture of polypropylene, ethylene/ α-olefin copolymers, and other olefin polymers. The gas phase process employed can be, for example, of the type which employs a mechanically stirred bed or a gas fluidized bed as the polymerization reaction zone. Preferred is the process wherein the polymerization reaction is carried out in a vertical cylindrical polymerization reactor containing a fluidized bed of polymer particles supported or suspended above a perforated plate or fluidization grid, by a flow of fluidization gas.

The gas employed to fluidize the bed comprises the monomer or monomers to be polymerized, and also serves as a heat exchange medium to remove the heat of reaction from the bed. The hot gases emerge from the top of the reactor, normally via a tranquilization zone, also known as a velocity reduction zone, having a wider diameter than the fluidized bed and wherein fine particles entrained in the gas stream have an opportunity to gravitate back into the bed. It can also be advantageous to use a cyclone to remove ultra-fine particles from the hot gas stream. The gas is then normally recycled to the bed by means of a blower or compressor and one or more heat exchangers to strip the gas of the heat of polymerization.

A preferred method of cooling of the bed, in addition to the cooling provided by the cooled recycle gas, is to feed a volatile liquid to the bed to provide an evaporative cooling effect, often

referred to as operation in the condensing mode. The volatile liquid employed in this case can be, for example, a volatile inert liquid, for example, a saturated hydrocarbon having 3 to 8, preferably 4 to 6, carbon atoms. In the case that the monomer or comonomer itself is a volatile liquid, or can be condensed to provide such a liquid, this can suitably be fed to the bed to provide an evaporative cooling effect. The volatile liquid evaporates in the hot fluidized bed to form gas which mixes with the fluidizing gas. If the volatile liquid is a monomer or comonomer, it will undergo some polymerization in the bed. The evaporated liquid then emerges from the reactor as part of the hot recycle gas, and enters the compression/heat exchange part of the recycle loop. The recycle gas is cooled in the heat exchanger and, if the temperature to which the gas is cooled is below the dew point, liquid will precipitate from the gas. This liquid is desirably recycled continuously to the fluidized bed. It is possible to recycle the precipitated liquid to the bed as liquid droplets carried in the recycle gas stream. This type of process is described, for example in EP-89691; U.S. 4,543,399; WO-94/25495 and U.S. 5,352,749. A particularly preferred method of recycling the liquid to the bed is to separate the liquid from the recycle gas stream and to reinject this liquid directly into the bed, preferably using a method which generates fine droplets of the liquid within the bed. This type of process is described in WO-94/28032.

The polymerization reaction occurring in the gas fluidized bed is catalyzed by the continuous or semi-continuous addition of catalyst composition as previously disclosed. The catalyst composition may be subjected to a prepolymerization step, for example, by polymerizing a small quantity of olefin monomer in a liquid inert diluent, to provide a catalyst composite comprising supported catalyst particles embedded in olefin polymer particles as well.

The polymer is produced directly in the fluidized bed by polymerization of the monomer or mixture of monomers on the fluidized particles of catalyst composition, supported catalyst composition or prepolymerized catalyst composition within the bed. Start-up of the polymerization reaction is achieved using a bed of preformed polymer particles, which are preferably similar to the desired polymer, and conditioning the bed by drying with inert gas or nitrogen prior to introducing the catalyst composition, the monomers and any other gases which it is desired to have in the recycle gas stream, such as a diluent gas, hydrogen chain transfer agent, or an inert condensable gas when operating in gas phase condensing mode. The produced polymer is discharged continuously or semi-continuously from the fluidized bed as desired.

The gas phase processes most suitable for the practice of this invention are continuous processes which provide for the continuous supply of reactants to the reaction zone of the reactor and the removal of products from the reaction zone of the reactor, thereby providing a steady-state environment on the macro scale in the reaction zone of the reactor. Products are readily recovered by exposure to reduced pressure and optionally elevated temperatures (devolatilization) according

to known techniques. Typically, the fluidized bed of the gas phase process is operated at temperatures greater than 50°C, preferably from 60°C to 110°C, more preferably from 70°C to 110°C.

Suitable gas phase processes which are adaptable for use in the process of this invention are disclosed in US Patents: 4,588,790; 4,543,399; 5,352,749; 5,436,304; 5,405,922; 5,462,999; 5,461,123; 5,453,471; 5,032,562; 5,028,670; 5,473,028; 5,106,804; 5,556,238; 5,541,270; 5,608,019; and 5,616,661.

As previously mentioned, functionalized derivatives of polymers are also included within the present invention. Examples include metallated polymers wherein the metal is the remnant of the catalyst or chain shuttling agent employed, as well as further derivatives thereof. Because a substantial fraction of the polymeric product exiting the reactor is terminated with the multi-centered shuttling agent, further functionalization is relatively easy. The metallated polymer species can be utilized in well known chemical reactions such as those suitable for other alkyl-aluminum, alkyl-gallium, alkyl-zinc, or alkyl-Group 1 compounds to form amine-, hydroxy-, epoxy-, silane, vinylic, and other functionalized terminated polymer products. Examples of suitable reaction techniques that are adaptable for use here in are described in Negishi, "Organometallics in Organic Synthesis", Vol. 1 and 2, (1980), and other standard texts in organometallic and organic synthesis.

Polymer Products

Utilizing the present process, novel polymer compositions, including pseudo-block copolymers of one or more olefin monomers having the present bimodal molecular weight distribution, are readily prepared. Preferred polymers comprise in polymerized form at least one monomer selected from the group consisting of ethylene, propylene and 4-methyl-1-pentene. Highly desirably, the polymers are interpolymers comprising in polymerized form ethylene, propylene or 4-methyl-1-pentene and at least one different C_{2-20} α-olefin comonomer, and optionally one or more additional copolymerizable comonomers. Suitable comonomers are selected from diolefins, cyclic olefins, and cyclic diolefins, halogenated vinyl compounds, and vinylidene aromatic compounds. Preferred polymers are interpolymers of ethylene with 1-butene, 1-hexene or 1-octene. Desirably, the polymer compositions of the invention have an ethylene content from 1 to 99 percent, a diene content from 0 to 10 percent, and a styrene and/or C_{3-8} α-olefin content from 99 to 1 percent, based on the total weight of the polymer. Further preferably, the polymers of the invention have a weight average molecular weight (Mw) from 10,000 to 2,500,000.

The polymers of the invention can have a melt index, I_2, from 0.01 to 2000 g/10 minutes, preferably from 0.01 to 1000 g/10 minutes, more preferably from 0.01 to 500 g/10 minutes, and

especially from 0.01 to 100 g/10 minutes. Desirably, the invented polymers can have molecular weights, M_w, from 1,000 g/mole to 5,000,000 g/mole, preferably from 1000 g/mole to 1,000,000, more preferably from 1000 g/mole to 500,000 g/mole, and especially from 1,000 g/mole to 300,000 g/mole. The density of the invented polymers can be from 0.80 to 0.99 g/cm^3 and preferably, for ethylene containing polymers, from 0.85 g/cm^3 to 0.97 g/cm^3.

The polymers of the invention may be differentiated from conventional, random copolymers, physical blends of polymers, and block copolymers prepared via sequential monomer addition, fluxional catalysts, or by anionic or cationic living polymerization techniques, due to the previously mentioned unique molecular weight distribution. If present, the separate regions or blocks within each polymer are relatively uniform, depending on the uniformity of reactor conditions, and chemically distinct from each other. That is, the comonomer distribution, tacticity, or other property of segments within the polymer are relatively uniform within the same block or segment. However, the average block length is not a narrow distribution, but desirably is a most probable distribution. Such polymer products having two or more blocks or segments and a broader size distribution than a conventional block copolymer prepared by anionic techniques, are referred to herein as pseudo-block copolymers. The polymers have properties approximating in many respects, those of pure block copolymers, and in some aspects exceeding the properties of pure block copolymers.

Various additives may be usefully incorporated into the present compositions in amounts that do not detract from the properties of the resultant composition. These additives include reinforcing agents, fillers including conductive and non-conductive materials, ignition resistant additives, antioxidants, heat and light stabilizers, colorants, extenders, crosslinkers, blowing agents, plasticizers, flame retardants, anti-drip agents, lubricants, slip additives, anti-blocking aids, antidegradants, softeners, waxes, and pigments.

Applications and End Uses

The polymer composition of the invention can be employed in a variety of conventional thermoplastic fabrication processes to produce useful articles, including objects comprising at least one film layer, such as a monolayer film, or at least one layer in a multilayer film, prepared by cast, blown, calendered, or extrusion coating processes; molded articles, such as blow molded, injection molded, or rotomolded articles; extrusions; fibers; and woven or non-woven fabrics. Thermoplastic compositions comprising the present polymers, include blends with other natural or synthetic polymers and additives, including the previously mentioned reinforcing agents, fillers, ignition resistant additives, antioxidants, heat and light stabilizers, colorants, extenders, crosslinkers,

blowing agents, plasticizers, flame retardants, anti-drip agents, lubricants, slip additives, anti-blocking aids, antidegradants, softeners, waxes, and pigments.

Fibers that may be prepared from the present polymers or blends include staple fibers, tow, multicomponent, sheath/core, twisted, and monofilament. Suitable fiber forming processes include spinbonded, melt blown techniques, as disclosed in USP's 4,430,563, 4, 663,220, 4,668,566, and 4,322,027, gel spun fibers as disclosed in USP 4,413,110, woven and nonwoven fabrics, as disclosed in USP 3,485,706, or structures made from such fibers, including blends with other fibers, such as polyester, nylon or cotton, thermoformed articles, extruded shapes, including profile extrusions and co-extrusions, calendared articles, and drawn, twisted, or crimped yarns or fibers. The new polymers described herein are also useful for wire and cable coating operations, as well as in sheet extrusion for vacuum forming operations, and forming molded articles, including the use of injection molding, blow molding process, or rotomolding processes. Compositions comprising the olefin polymers can also be formed into fabricated articles such as those previously mentioned using conventional polyolefin processing techniques which are well known to those skilled in the art of polyolefin processing.

Dispersions (both aqueous and non-aqueous) can also be formed using the present polymers or formulations comprising the same. Frothed foams comprising the invented polymers can also be formed, using for example the process disclosed in WO04/021622. The polymers may also be crosslinked by any known means, such as the use of peroxide, electron beam, silane, azide, or other cross-linking technique. The polymers can also be chemically modified, such as by grafting (for example by use of maleic anhydride (MAH), silanes, or other grafting agent), halogenation, amination, sulfonation, or other chemical modification.

Suitable polymers for blending with the polymers of the invention include thermoplastic and non-thermoplastic polymers including natural and synthetic polymers. Exemplary polymers for blending include polypropylene, (both impact modifying polypropylene, isotactic polypropylene, atactic polypropylene, and random ethylene/propylene copolymers), various types of polyethylene, including high pressure, free-radical LDPE, Ziegler Natta LLDPE, metallocene PE, including multiple reactor PE ("in reactor" blends of Ziegler-Natta PE and metallocene PE, such as products disclosed in USP's 6,545,088, 6,538,070, 6,566,446, 5,844,045, 5,869,575, and 6,448,341, ethylene-vinyl acetate (EVA), ethylene/ vinyl alcohol copolymers, polystyrene, impact modified polystyrene, ABS, styrene/butadiene block copolymers and hydrogenated derivatives thereof (SBS and SEBS), and thermoplastic polyurethanes. Homogeneous polymers such as olefin plastomers and elastomers, ethylene and propylene-based copolymers (for example polymers available under the trade designation VERSIFY™ available from The Dow Chemical Company and VISTAMAXX™

available from ExxonMobil can also be useful as components in blends comprising the present polymer composition.

The blends may be prepared by mixing or kneading the respective components at a temperature around or above the melt point temperature of one or both of the components. For most of the present compositions, this temperature may be above 130° C., 145° C., or even above 150° C. Typical polymer mixing or kneading equipment that is capable of reaching the desired temperatures and melt plastifying the mixture may be employed. These include mills, kneaders, extruders (both single screw and twin-screw), Banbury mixers, and calenders. The sequence of mixing and method may depend on the final composition. A combination of Banbury batch mixers and continuous mixers may also be employed, such as a Banbury mixer followed by a mill mixer followed by an extruder.

The blend compositions may contain processing oils, plasticizers, and processing aids. Rubber processing oils have a certain ASTM designations and paraffinic, napthenic or aromatic process oils are all suitable for use. Generally from 0 to 150 parts, more preferably 0 to 100 parts, and most preferably from 0 to 50 parts of oil per 100 parts of total polymer composition are employed. Higher amounts of oil may tend to improve the processing of the resulting product at the expense of some physical properties. Additional processing aids include conventional waxes, fatty acid salts, such as calcium stearate or zinc stearate, (poly)alcohols including glycols, (poly)alcohol ethers, including glycol ethers, (poly)esters, including (poly)glycol esters, and metal salt-, especially Group 1 or 2 metal or zinc-, salt derivatives thereof.

Compositions according to the invention may also contain anti-ozonants and anti-oxidants that are known to a person of ordinary skill. The anti-ozonants may be physical protectants such as waxy materials that come to the surface and protect the part from oxygen or ozone or they may be chemical protectors that react with oxygen or ozone. Suitable chemical protectors include styrenated phenols, butylated octylated phenol, butylated di(dimethylbenzyl) phenol, p-phenylenediamines, butylated reaction products of p-cresol and dicyclopentadiene (DCPD), polyphenolic anitioxidants, hydroquinone derivatives, quinoline, diphenylene antioxidants, thioester antioxidants, and blends thereof. Some representative trade names of such products are Wingstay™ S antioxidant, Polystay™ 100 antioxidant, Polystay™ 100 AZ antioxidant, Polystay™ 200 antioxidant, Wingstay™ L antioxidant, Wingstay™ LHLS antioxidant, Wingstay™ K antioxidant, Wingstay™ 29 antioxidant, Wingstay™ SN-1 antioxidant, and Irganox™ antioxidants. In some applications, the antioxidants and antiozonants used will preferably be non-staining and non-migratory.

For providing additional stability against UV radiation, hindered amine light stabilizers (HALS) and UV absorbers may be also used. Suitable examples include Tinuvin™ 123, Tinuvin™

144, Tinuvin™ 622, Tinuvin™ 765, Tinuvin™ 770, and Tinuvin™ 780, available from Ciba Specialty Chemicals, and Chemisorb™ T944, available from Cytex Plastics, Houston, TX, USA. A Lewis acid may be additionally included with a HALS compound in order to achieve superior surface quality, as disclosed in USP 6,051,681.

For some compositions, additional mixing process may be employed to pre-disperse the anti-oxidants, anti-ozonants, pigment, UV absorbers, and/or light stabilizers to form a masterbatch, and subsequently to form polymer blends therefrom.

Certain compositions according to the invention, especially those containing the remnant of a conjugated diene comonomer, may be subsequently crosslinked to form cured compositions. Suitable crosslinking agents (also referred to as curing or vulcanizing agents) for use herein include sulfur based, peroxide based, or phenolic based compounds. Examples of the foregoing materials are found in the art, including in USP's: 3,758,643, 3,806,558, 5,051,478, 4,104,210, 4,130,535, 4,202,801, 4,271,049, 4,340,684, 4,250,273, 4,927,882, 4,311,628 and 5,248,729.

When sulfur based curing agents are employed, accelerators and cure activators may be used as well. Accelerators are used to control the time and/or temperature required for dynamic vulcanization and to improve the properties of the resulting cross-linked article. In one embodiment, a single accelerator or primary accelerator is used. The primary accelerator(s) may be used in total amounts ranging from 0.5 to 4, preferably 0.8 to 1.5, phr, based on total composition weight. In another embodiment, combinations of a primary and a secondary accelerator might be used with the secondary accelerator being used in smaller amounts, such as from 0.05 to 3 phr, in order to activate and to improve the properties of the cured article. Combinations of accelerators generally produce articles having properties that are somewhat better than those produced by use of a single accelerator. In addition, delayed action accelerators may be used which are not affected by normal processing temperatures yet produce a satisfactory cure at ordinary vulcanization temperatures. Vulcanization retarders might also be used. Suitable types of accelerators that may be used in the present invention are amines, disulfides, guanidines, thioureas, thiazoles, thiurams, sulfenamides, dithiocarbamates and xanthates. Preferably, the primary accelerator is a sulfenamide. If a second accelerator is used, the secondary accelerator is preferably a guanidine, dithiocarbarnate or thiuram compound. Certain processing aids and cure activators such as stearic acid and ZnO may also be used. When peroxide based curing agents are used, co-activators or coagents may be used in combination therewith. Suitable coagents include trimethylolpropane triacrylate (TMPTA), trimethylolpropane trimethacrylate (TMPTMA), triallyl cyanurate (TAC), triallyl isocyanurate (TAIC), among others. Use of peroxide crosslinkers and optional coagents used for partial or complete dynamic vulcanization are known in the art and disclosed for example in the publication, "Peroxide Vulcanization of Elastomers", Vol. 74, No 3, July-August 2001.

The degree of crosslinking in a cured composition according to the invention may be measured by dissolving the composition in a solvent for a specified duration, and calculating the percent gel or unextractable rubber. The percent gel normally increases with increasing crosslinking levels. For cured articles according to the invention, the percent gel content is desirably in the range from 5 to 100 percent.

The present compositions and blends thereof uniquely possess improved melt strength properties due to the presence of the high molecular weight component and unique molecular weight distribution, thereby allowing the present compositions and blends thereof to be usefully employed in foam and in thermoforming applications where high melt strength is desired.

Thermoplastic compositions according to the invention may also contain organic or inorganic fillers or other additives such as starch, talc, calcium carbonate, glass fibers, polymeric fibers (including nylon, rayon, cotton, polyester, and polyaramide), metal fibers, wire, mesh, flakes or particles, expandable layered silicates, phosphates or carbonates, such as clays, mica, silica, alumina, aluminosilicates or aluminophosphates, carbon whiskers, carbon fibers, nanoparticles including nanotubes and nonofibers, wollastonite, graphite, zeolites, and ceramics, such as silicon carbide, silicon nitride or titanias. Silane based oils or other coupling agents may also be employed for better filler bonding. Additional suitable additives include tackifiers; oils, including paraffinic or napthelenic oils; and other natural and synthetic polymers, including other polymers according to the invention.

The polymer compositions of this invention, including the foregoing blends, may be processed by conventional molding techniques such as injection molding, extrusion molding, thermoforming, slush molding, over molding, insert molding, blow molding, and other techniques. Films, including multi-layer films, may be produced by cast or tentering processes, including blown film processes.

Testing Methods

In the foregoing characterizing disclosure and the examples that follow, the following analytical techniques may be employed:

Molecular Weight Determination

Molecular weights are determined by optical analysis techniques including deconvoluted gel permeation chromatography coupled with a low angle laser light scattering detector (GPC-LALLS) as described by Rudin, A., "Modern Methods of Polymer Characterization", John Wiley & Sons, New York (1991) pp. 103-112.

Standard CRYSTAF Method

Branching distributions are determined by crystallization analysis fractionation (CRYSTAF) using a CRYSTAF 200 unit commercially available from PolymerChar, Valencia, Spain. The samples are dissolved in 1,2,4 trichlorobenzene at 160 °C (0.66 mg/mL) for 1 hr and stabilized at 95°C for 45 minutes. The sampling temperatures range from 95 to 30 °C at a cooling rate of 0.2 °C/min. An infrared detector is used to measure the polymer solution concentrations. The cumulative soluble concentration is measured as the polymer crystallizes while the temperature is decreased. The analytical derivative of the cumulative profile reflects the short chain branching distribution of the polymer.

The CRYSTAF peak temperature and area are identified by the peak analysis module included in the CRYSTAF Software (Version 2001.b, PolymerChar, Valencia, Spain). The CRYSTAF peak finding routine identifies a peak temperature as a maximum in the dW/dT and the area between the largest positive inflections on either side of the identified peak in the derivative curve.

DSC Standard Method

Differential Scanning Calorimetry results are determined using a TAI model Q1000 DSC equipped with an RCS cooling accessory and an autosampler. A nitrogen purge gas flow of 50 ml/min is used. The sample is pressed into a thin film and melted in the press at 175°C and then air-cooled to room temperature (25 °C). About 10 mg of material in the form of a 5-6 mm diameter disk is accurately weighed and placed in an aluminum foil pan (ca 50 mg) which is then crimped shut. The thermal behavior of the sample is investigated with the following temperature profile. The sample is rapidly heated to 180°C and held isothermal for 3 minutes in order to remove any previous thermal history. The sample is then cooled to -40°C at 10°C/min cooling rate and held at -40°C for 3 minutes. The sample is then heated to 150 °C at 10°C/min. heating rate. The cooling and second heating curves are recorded.

The DSC melting peak is measured as the maximum in heat flow rate (W/g) with respect to the linear baseline drawn between -30 °C and end of melting. The heat of fusion is measured as the area under the melting curve between -30 °C and the end of melting using a linear baseline.

Abrasion Resistance

Abrasion resistance is measured on compression molded plaques according to ISO 4649. The average value of 3 measurements is reported. Plaques of 6.4 mm thick are compression molded using a hot press (Carver Model #4095-4PR1001R). The pellets are placed between polytetrafluoroethylene sheets, heated at 190 °C at 55 psi (380 kPa) for 3 min, followed by 1.3 MPa for 3 min, and then 2.6 MPa for 3 min. Next the film is cooled in the press with running cold water at 1.3 MPa for 1 min.

GPC Method

The gel permeation chromatographic system consists of either a Polymer Laboratories Model PL-210 or a Polymer Laboratories Model PL-220 instrument. The column and carousel compartments are operated at 140 °C. Three Polymer Laboratories 10-micron Mixed-B columns are used. The solvent is 1,2,4 trichlorobenzene. The samples are prepared at a concentration of 0.1 grams of polymer in 50 milliliters of solvent containing 200 ppm of butylated hydroxytoluene (BHT). Samples are prepared by agitating lightly for 2 hours at 160°C. The injection volume used is 100 microliters and the flow rate is 1.0 ml/minute.

Calibration of the GPC column set is performed with 21 narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 to 8,400,000, arranged in 6 "cocktail" mixtures with at least a decade of separation between individual molecular weights. The standards are purchased from Polymer Laboratories (Shropshire, UK). The polystyrene standards are prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000 and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards are dissolved at 80 °C with gentle agitation for 30 minutes. The narrow standards mixtures are run first and in order of decreasing highest molecular weight component to minimize degradation. The polystyrene standard peak molecular weights are converted to polyethylene molecular weights using the following equation (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)): $M_{polyethylene} = 0.431(M_{polystyrene})$.

Polyetheylene equivalent molecular weight calculations are performed using Viscotek TriSEC software Version 3.0.

Compression Set

Compression set is measured according to ASTM D 395. The sample is prepared by stacking 25.4 mm diameter round discs of 3.2 mm, 2.0 mm, and 0.25 mm thickness until a total thickness of 12.7 mm is reached. The discs are cut from 12.7 cm x 12.7 cm compression molded plaques molded with a hot press under the following conditions: zero pressure for 3 min at 190°C, followed by 86 MPa for 2 min at 190°C, followed by cooling inside the press with cold running water at 86 MPa.

Density

Density measurement are conducted according to ASTM D 1928. Measurements are made within one hour of sample pressing using ASTM D792, Method B.

Flexural/Secant Modulus

Samples are compression molded using ASTM D 1928. Flexural and 2 percent secant moduli are measured according to ASTM D-790.

Optical properties, tensile, hysteresis, and tear

Films of 0.4 mm thickness are compression molded using a hot press (Carver Model #4095-4PR1001R). The pellets are placed between polytetrafluoroethylene sheets, heated at 190 °C at 55 psi (380 kPa) for 3 min, followed by 1.3 MPa for 3 min, and then 2.6 MPa for 3 min. The film is then cooled in the press with running cold water at 1.3 MPa for 1 min. The compression molded films are used for optical measurements, tensile behavior, recovery, and stress relaxation.

Clarity is measured using BYK Gardner Haze-gard as specified in ASTM D 1746.

45° gloss is measured using BYK Gardner Glossmeter Microgloss 45° as specified in ASTM D-2457

Internal haze is measured using BYK Gardner Haze-gard based on ASTM D 1003 Procedure A. Mineral oil is applied to the film surface to remove surface scratches.

Stress-strain behavior in uniaxial tension is measured using ASTM D 1708 microtensile specimens. Samples are stretched with an Instron at 500 percent (%) min^{-1} at 21°C. Tensile strength and elongation at break are reported from an average of 5 specimens.

100% and 300% Hysteresis is determined from cyclic loading to 100% and 300% strains according to ASTM D 1708 with an Instron™ instrument. The sample is loaded and unloaded at 267 % min^{-1} for 3 cycles at 21°C. Cyclic experiments at 300% and 80°C are conducted using an environmental chamber. In the 80 °C experiment, the sample is allowed to equilibrate for 45 minutes at the test temperature before testing. In the 21 °C, 300% strain cyclic experiment, the retractive stress at 150% strain from the first unloading cycle is recorded. Percent recovery for all experiments are calculated from the first unloading cycle using the strain at which the load returned to the base line. The percent recovery is defined as:

$$\%\,\mathrm{Recovery} = \frac{\varepsilon_f - \varepsilon_s}{\varepsilon_f} \times 100$$

where ε_f is the strain taken for cyclic loading and ε_s is the strain where the load returns to the baseline during the 1st unloading cycle.

Stress relaxation is measured at 50 percent strain and 37 °C for 12 hours using an Instron™ instrument equipped with an environmental chamber. The gauge geometry was 76 mm x 25 mm x 0.4 mm. After equilibrating at 37°C for 45 min in the environmental chamber, the sample was stretched to 50% strain at 333% min^{-1}. Stress was recorded as a function of time for 12 hours. The percent stress relaxation after 12 hours was calculated using the formula:

$$\%\ Stress\ Relaxation = \frac{L_0 - L_{12}}{L_0} \times 100$$

where L_0 is the load at 50% strain at 0 time and L_{12} is the load at 50 percent strain after 12 hours.

Tensile notched tear experiments are carried out on samples having a density of 0.88 g/cc or less using an Instron™ instrument. The geometry consists of a gauge section of 76 mm x 13 mm x 0.4 mm with a 2 mm notch cut into the sample at half the specimen length. The sample is stretched at 508 mm min^{-1} at 21 °C until it breaks. The tear energy is calculated as the area under the stress-elongation curve up to strain at maximum load. An average of at least 3 specimens are reported.

TMA

Thermal Mechanical Analysis is conducted on 30mm diameter x 3.3 mm thick, compression molded discs, formed at 180°C and 10 MPa molding pressure for 5 minutes and then air quenched. The instrument used is a TMA 7, brand available from Perkin-Elmer. In the test, a probe with 1.5 mm radius tip (P/N N519-0416) is applied to the surface of the sample disc with 1N force. The temperature is raised at 5°C/min from 25°C. The probe penetration distance is measured as a function of temperature. The experiment ends when the probe has penetrated 1 mm into the sample.

DMA

Dynamic Mechanical Analysis (DMA) is measured on compression molded disks formed in a hot press at 180°C at 10 MPa pressure for 5 minutes and then water cooled in the press at 90°C / min. Testing is conducted using an ARES controlled strain rheometer (TA instruments) equipped with dual cantilever fixtures for torsion testing.

A 1.5mm plaque is pressed and cut in a bar of dimensions 32x12mm. The sample is clamped at both ends between fixtures separated by 10mm (grip separation ΔL) and subjected to successive temperature steps from -100°C to 200°C (5°C per step). At each temperature the torsion modulus G' is measured at an angular frequency of 10 rad/s, the strain amplitude being maintained between 0.1 percent and 4 percent to ensure that the torque is sufficient and that the measurement remains in the linear regime.

An initial static force of 10 g is maintained (auto-tension mode) to prevent slack in the sample when thermal expansion occurs. As a consequence, the grip separation ΔL increases with the temperature, particularly above the melting or softening point of the polymer sample. The test stops at the maximum temperature or when the gap between the fixtures reaches 65 mm.

Pellet Blocking Behavior

Pellets (150 g) are loaded into a 2 inch (5 cm) diameter hollow cylinder that is made of two halves held together by a hose clamp. A 2.75 lb (1.25 kg) load is applied to the pellets in the cylinder at 45 °C for 3 days. After 3 days, the pellets loosely consolidate into a cylindrical shaped plug. The plug is removed from the form and the pellet blocking force measured by loading the cylinder of blocked pellets in compression using an Instron™ instrument to measure the compressive force needed to break the cylinder into pellets.

Melt Properties

Melt Flow Rate (MFR) and Melt index, or I_2, are measured in accordance with ASTM D1238, Condition 190°C/2.16 kg.

ATREF

Analytical temperature rising elution fractionation (ATREF) analysis is conducted according to the method described in USP 4,798,081. The composition to be analyzed is dissolved in trichlorobenzene and allowed to crystallize in a column containing an inert support (stainless steel shot) by slowly reducing the temperature to 20 °C at a cooling rate of 0.1 °C/min. The column is equipped with an infrared detector. An ATREF chromatogram curve is then generated by eluting the crystallized polymer sample from the column by slowly increasing the temperature of the eluting solvent (trichlorobenzene) from 20 to 120 °C at a rate of 1.5 °C/min.

Specific Embodiments

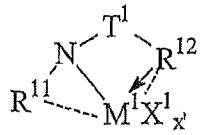
The following specific embodiments of the invention and combinations thereof are especially desirable and hereby delineated in order to provide detailed disclosure for the appended claims.

1. A process for the polymerization of one or more addition polymerizable monomers to form a polymer composition, said process comprising contacting an addition polymerizable monomer or mixture of monomers in a reactor or reactor zone with a composition comprising at least one polymerization catalyst and a cocatalyst under polymerization conditions, terminating the polymerization, and recovering the terminated polymer, characterized in that at least a portion of said polymerization is conducted in the presence of a multi-centered shuttling agent, thereby causing the composition to have a broadened molecular weight distribution.

2. An olefin polymer composition, especially such a copolymer comprising in polymerized form ethylene and a copolymerizable comonomer, propylene and at least one copolymerizable comonomer having from 4 to 20 carbons, or 4-methyl-1-pentene and at least one different copolymerizable comonomer having from 4 to 20 carbons, said polymer composition having a bimodal molecular weight distribution with the mean molecular weight of the higher molecular weight component exceeding the mean molecular weight of the lower molecular weight component by approximately an integer multiple.

3. A polymer mixture comprising: (1) an organic or inorganic polymer, preferably a homopolymer of ethylene, a copolymer of ethylene and a copolymerizable comonomer, or a homopolymer of propylene; and (2) a polymer composition according to the present invention or prepared according to the process of the present invention.

4. A process according to embodiment 1 wherein the catalyst comprises a metal complex corresponding to the formula:



wherein:

R^{11} is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen or a divalent derivative thereof;

T^1 is a divalent bridging group of from 1 to 41 atoms other than hydrogen, preferably 1 to 20 atoms other than hydrogen, and most preferably a mono- or di- C_{1-20} hydrocarbyl substituted methylene or silane group; and

R^{12} is a C_{5-20} heteroaryl group containing Lewis base functionality, especially a pyridin-2-yl- or substituted pyridin-2-yl group or a divalent derivative thereof;

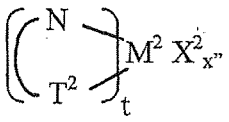
M^1 is a Group 4 metal, preferably hafnium;

X^1 is an anionic, neutral or dianionic ligand group;

x' is a number from 0 to 5 indicating the number of such X^1 groups; and

bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively, or

a metal complex corresponding to the formula:



wherein

M^2 is a metal of Groups 4-10 of the Periodic Table of the elements;

T^2 is a nitrogen, oxygen or phosphorus containing group;

X^2 is halo, hydrocarbyl, or hydrocarbyloxy;

t is one or two;

x" is a number selected to provide charge balance;

and T^2 and N are linked by a bridging ligand.

5. A process according to any one of embodiments 1 or 4, characterized by producing a polymer composition according to embodiment 2 or by producing a polymer mixture according to embodiment 3.

6. A process for preparing an α,ω-difunctionalized polymer comprising:

a) contacting an addition polymerizable monomer or mixture of monomers in a reactor or reactor zone with a composition comprising at least one polymerization catalyst and a cocatalyst under polymerization conditions in the presence of a di-centered shuttling agent capable of transferring metal center containing moieties to both termini of the growing polymer chain,

b) recovering a polymer terminally substituted at both termini with a metal center containing moiety; and

c) exchanging the terminal metal center moieties for the desired functionality.

7. The process of embodiment 6 wherein the monomer or monomer mixture comprises one or more C_{2-20} α-olefins.

8. The process of embodiment 6 wherein ethylene is homopolymerized to prepare a polymer having a Mw from 500 to 10,000.

9. The process of any one of embodiments 6-8 wherein the exchange is an oxidation or displacement reaction and the resulting product is the corresponding dihydroxyl- or divinyl-functionalized polymer.

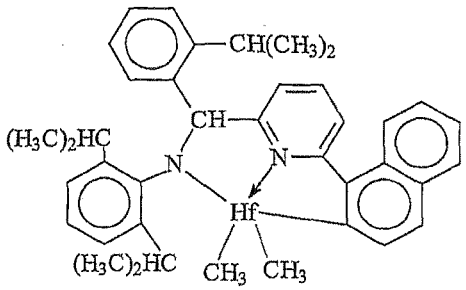
The skilled artisan will appreciate that the invention disclosed herein may be practiced in the absence of any component which has not been specifically disclosed.

Examples

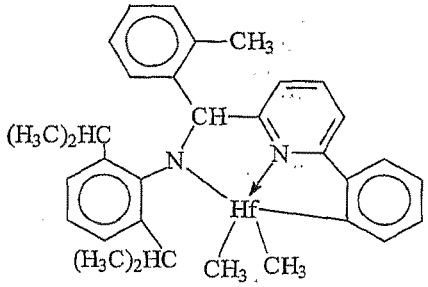
The following examples are provided as further illustration of the invention and are not to be construed as limiting. The term "overnight", if used, refers to a time of approximately 16-18 hours, the term "room temperature", refers to a temperature of 20-25 °C, and the term "mixed alkanes" refers to a commercially obtained mixture of C_{6-9} aliphatic hydrocarbons available under the trade designation Isopar E®, from Exxon Mobil Chemicals Inc. In the event the name of a compound herein does not conform to the structural representation thereof, the structural representation shall control. The synthesis of all metal complexes and the preparation of all screening experiments were carried out in a dry nitrogen atmosphere using dry box techniques. All solvents used were HPLC grade and were dried before their use.

MMAO refers to modified methylalumoxane, a triisobutylaluminum modified methylalumoxane available commercially from Akzo-Noble Corporation.

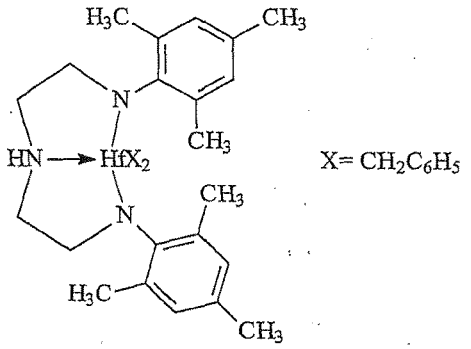
Catalyst (A1) is [N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl, prepared according to the teachings of WO 03/40195, 2003US0204017, USSN 10/429,024, filed May 2, 2003, and WO 04/24740.



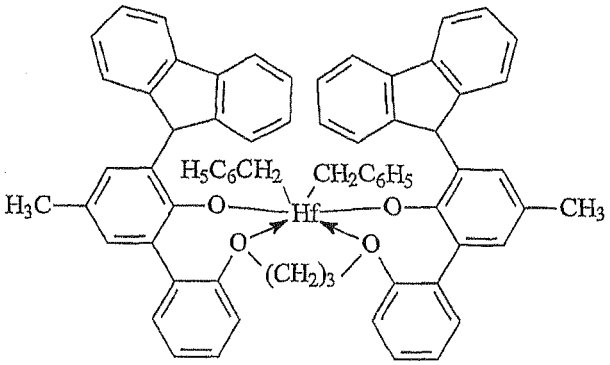
Catalyst (A2) is [N-(2,6-di(1-methylethyl)phenyl)amido)(2-methylphenyl)(1,2-phenylene-(6-pyridin-2-diyl)methane)]hafnium dimethyl, prepared according to the teachings of WO 03/40195, 2003US0204017, USSN 10/429,024, filed May 2, 2003, and WO 04/24740.



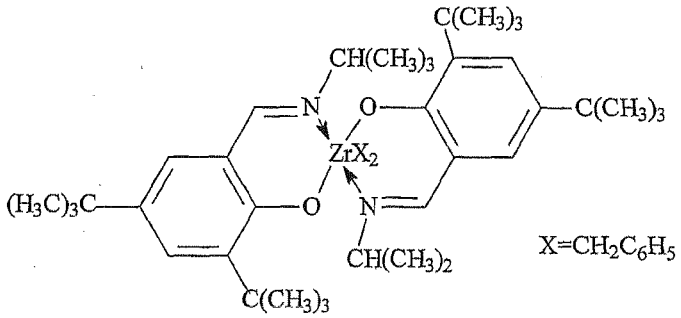
Catalyst (A3) is bis[N,N'''-(2,4,6-tri(methylphenyl)amido)ethylenediamine]hafnium dibenzyl.



Catalyst (A4) is bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxymethyl)cyclohexane-1,2-diyl zirconium (IV) dibenzyl, prepared substantially according to the teachings of US-A-2004/0010103.



Catalyst (A5) is (bis-(1-methylethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)immino)zirconium dibenzyl.



The preparation of catalyst (A5) is conducted as follows.

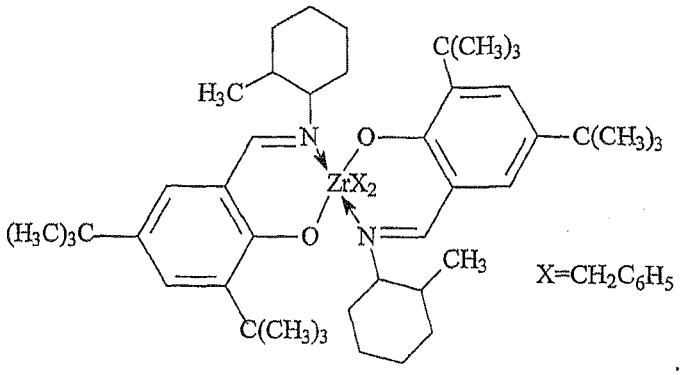
a) Preparation of (1-methylethyl)(2-hydroxy-3,5-di(t-butyl)phenyl)imine

3,5-Di-t-butylsalicylaldehyde (3.00 g) is added to 10 mL of isopropylamine. The solution rapidly turns bright yellow. After stirring at ambient temperature for 3 hours, volatiles are removed under vacuum to yield a bright yellow, crystalline solid (97 percent yield).

b) Preparation of (bis-(1-methylethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)immino) zirconium dibenzyl

A solution of (1-methylethyl)(2-hydroxy-3,5-di(t-butyl)phenyl)imine (605 mg, 2.2 mmol) in 5 mL toluene is slowly added to a solution of $Zr(CH_2Ph)_4$ (500 mg, 1.1 mmol) in 50 mL toluene. The resulting dark yellow solution is stirred for 30 min. Solvent is removed under reduced pressure to yield the desired product as a reddish-brown solid.

Catalyst (A6) is bis-(1-(2-methylcyclohexyl)ethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)immino) zirconium dibenzyl



The preparation of catalyst (A6) is conducted as follows.

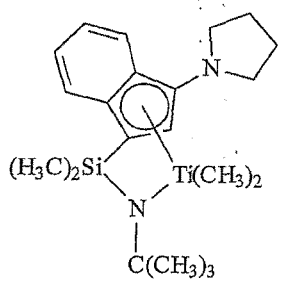
a) Preparation of (1-(2-methylcyclohexyl)ethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)imine

2-Methylcyclohexylamine (8.44 mL, 64.0 mmol) is dissolved in methanol (90 mL), and di-t-butylsalicaldehyde (10.00 g, 42.67 mmol) is added. The reaction mixture is stirred for three hours and then cooled to -25 °C for 12 hrs. The resulting yellow solid precipitate is collected by filtration and washed with cold methanol (2 x 15 mL), and then dried under reduced pressure. The yield is 11.17 g of a yellow solid. ^{1}H NMR is consistent with the desired product as a mixture of isomers.

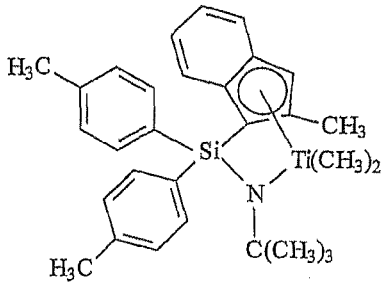
b) Preparation of bis-(1-(2-methylcyclohexyl)ethyl)(2-oxoyl-3,5-di(t-butyl)phenyl) immino)zirconium dibenzyl

A solution of (1-(2-methylcyclohexyl)ethyl)(2-oxoyl-3,5-di(t-butyl)phenyl)imine (7.63 g, 23.2 mmol) in 200 mL toluene is slowly added to a solution of $Zr(CH_2Ph)_4$ (5.28 g, 11.6 mmol) in 600 mL toluene. The resulting dark yellow solution is stirred for 1 hour at 25 °C. The solution is diluted further with 680 mL toluene to give a solution having a concentration of 0.00783 M.

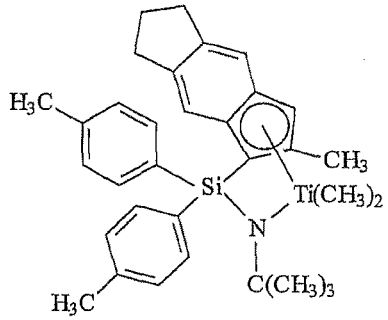
Catalyst (A7) is (t-butylamido)dimethyl(3-N-pyrrolyl-1,2,3,3a,7a-η-inden-1-yl)silanetitanium dimethyl prepared substantially according to the techniques of USP 6,268,444:



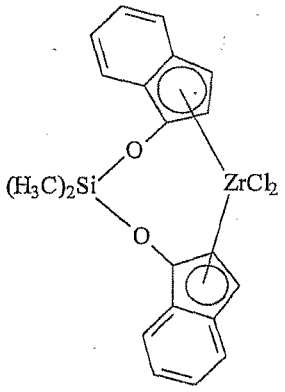
Catalyst (A8) is (t-butylamido)di(4-methylphenyl)(2-methyl-1,2,3,3a,7a-η-inden-1-yl)silanetitanium dimethyl prepared substantially according to the teachings of US-A-2003/004286:



Catalyst (A9) is (t-butylamido)di(4-methylphenyl)(2-methyl-1,2,3,3a,8a-η-s-indacen-1-yl)silanetitanium dimethyl prepared substantially according to the teachings of US-A-2003/004286:



Catalyst (A10) is bis(dimethyldisiloxane)(indene-1-yl)zirconium dichloride available from Sigma-Aldrich:



Cocatalyst 1 A mixture of methyldi(C_{14-18} alkyl)ammonium salts of tetrakis(pentafluorophenyl)borate (here-in-after armeenium borate), prepared by reaction of a long chain trialkylamine (Armeen™ M2HT, available from Akzo-Nobel, Inc.), HCl and $Li[B(C_6F_5)_4]$, substantially as disclosed in USP 5,919,9883, Ex. 2.

Cocatalyst 2 Mixed C_{14-18} alkyldimethylammonium salt of bis(tris(pentafluorophenyl)-alumane)-2-undecylimidazolide, prepared according to USP 6,395,671, Ex. 16.

Multi-centered Shuttling Agents The multi-centered shuttling agents employed include (1,2-ethylene) di(zinc chloride) (MSA1), (1,2-ethylene)di(zinc bromide) (MSA2), (1,2-ethylene)-di(ethylzinc) (MSA3), (1,2-ethylene)bis((trimethyl)silylzinc) (MSA4), (1,4-butylene)di(zinc-

chloride) (MSA5), (1,4-butylene)di(zincbromide) (MSA6), (1,4-butylene)di(ethylzinc) (MSA7), (1,4-butylene)bis((trimethyl)silylzinc) (MSA8), bis(1,2-ethylenedizinc) (MSA9), bis(1,3-propylenedizinc) (MSA10), bis(1,4-butylenedizinc) (SA11), methyltri(1,2-ethylenezincchloride) (SA12) and (1,2-ethylene)bis(diethylaluminum) (SA13).

General High Throughput Parallel Polymerization Conditions

Polymerizations are conducted using a high throughput, parallel polymerization reactor (PPR) available from Symyx technologies, Inc. and operated substantially according to USP's 6,248,540, 6,030,917, 6,362,309, 6,306,658, and 6,316,663. Ethylene copolymerizations are conducted at 130 °C and 80 psi (550 kPa) with ethylene on demand using 1.2 equivalents of cocatalyst 2 based on total catalyst used. A series of polymerizations are conducted in a parallel pressure reactor (PPR) comprised of 48 individual reactor cells in a 6 x 8 array that are fitted with a pre-weighed glass tube. The working volume in each reactor cell is 6000 μL. Each cell is temperature and pressure controlled with stirring provided by individual stirring paddles. The monomer gas and quench gas (air) are plumbed directly into the PPR unit and controlled by automatic valves. Liquid reagents are robotically added to each reactor cell by syringes and the reservoir solvent is mixed alkanes. The order of addition is mixed alkanes solvent (4 ml), ethylene, 1-octene comonomer (143 mg), 0.419 μmol cocatalyst, multi-centered shuttling agent in the indicated amounts, and finally, 0.3495 μmol catalyst A3. After quenching, the reactors are cooled and the glass tubes are unloaded. The tubes are transferred to a centrifuge/vacuum drying unit, and dried for 12 hours at 60 °C. The tubes containing dried polymer are weighed and the difference between this weight and the tare weight gives the net yield of polymer. The resulting polymer compositions are measured for molecular weight (Mw and Mn) using GPC-LALLS. Polydispersity Index (PDI=Mw/Mn) is calculated for each polymer. The presence of a broader polydispersity (Mw/Mn) and distinct bimodal distribution indicates an effective multi-centered shuttling agent according to the invention.

CLAIMS:

1. A process for the polymerization of one or more addition polymerizable monomers to form a polymer composition, said process comprising:

contacting an addition polymerizable monomer or mixture of monomers in a reactor or reactor zone with a composition comprising at least one polymerization catalyst and a cocatalyst under polymerization conditions and in the presence of a multi-centered shuttling agent comprising at least a first chain shuttling moiety and a second chain shuttling moiety and having the following formula:

$(M')_mA$

wherein

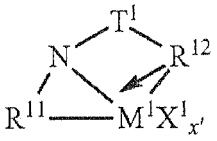
M' is a chain shuttling moiety,

A is a linking group, the linking group being an organic group, and

m is an integer from 2 to 6; and

forming a polymer composition comprising a first polymer free of the second chain shuttling moiety and a second polymer comprising the second chain shuttling moiety.

2. The process according to claim 1 wherein the catalyst comprises a metal complex corresponding to the formula:



wherein:

R^{11} is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen or a divalent derivative thereof;

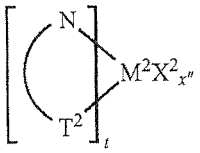
T^1 is a divalent bridging group of from 1 to 41 atoms other than hydrogen, preferably 1 to 20 atoms other than hydrogen, and most preferably a mono- or di-C_{1-20} hydrocarbyl substituted methylene or silane group; and

R^{12} is a C_{5-20} heteroaryl group containing Lewis base functionality, especially a pyridin-2-yl- or substituted pyridin-2-yl group or a divalent derivative thereof;

M^1 is a Group 4 metal, preferably hafnium;

X^1 is an anionic, neutral or dianionic ligand group;

x' is a number from 0 to 5 indicating the number of such X^1 groups; and bonds, optional bonds and electron donative interactions are represented by lines, dotted lines and arrows respectively, or a metal complex corresponding to the formula:



wherein

M^2 is a metal of Groups 4-10 of the Periodic Table of the elements;

T^2 is a nitrogen, oxygen or phosphorus containing group;

X^2 is halo, hydrocarbyl, or hydrocarbyloxy;

t is one or two;

x" is a number selected to provide charge balance; and

T^2 and N are linked by a bridging ligand.

3. The process of claim 1 comprising forming a substantially homogeneously polymer composition having a bimodal molecular weight distribution.

4. The process of claim 1 comprising forming a second polymer with a molecular weight at least about two times the molecular weight of the first polymer.

5. The process of claim 1 comprising dividing the multi-centered chain shuttling agent into the first chain shuttling moiety and the second chain shuttling moiety.

6. The process of claim 5 comprising regenerating, after the attaching, a multi-centered chain shuttling agent comprising a polymer segment attached thereto.