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CATALYST COMPOSITION COMPRISING SHUTTLING AGENT FOR ETHYLENE COPOLYMER FORMATION

Cross Reference Statement

5 This application claims the benefit of U.S. Provisional Application No. 60/553,906, filed March 17, 2004. For purposes of United States patent practice, the contents of this provisional application are herein incorporated by reference.

Background of the Invention

10 The present invention relates to compositions for polymerizing ethylene, 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 methods of using these polymers in applications requiring unique combinations of physical properties. In still another aspect, the invention relates to the articles prepared from these polymers.

15 The inventive polymers comprise two or more differing regions or segments (blocks) causing the polymer to possess unique physical properties. These multi-block copolymers and polymeric 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.

20 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.

 It has long been known that polymers containing a block-type structure often have superior properties compared to random copolymers and blends. For example, triblock copolymers of styrene and butadiene (SBS) and hydrogenated versions of the same (SEBS) have an excellent

25 combination of heat resistance and elasticity. Other block copolymers are also known in the art. Generally, block copolymers known as thermoplastic elastomers (TPE) have desirable properties due to the presence of "soft" or elastomeric block segments connecting "hard" either crystallizable or glassy blocks in the same polymer. At temperatures up to the melt temperature or glass transition temperature of the hard segments, the polymers demonstrate elastomeric character. At higher

30 temperatures, the polymers become flowable, exhibiting thermoplastic behavior. Known methods of preparing block copolymers include anionic polymerization and controlled free radical polymerization. Unfortunately, these methods of preparing block copolymers require sequential monomer addition and batch processing and the types of monomers that can be usefully employed in such methods are relatively limited. For example, in the anionic polymerization of styrene and



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butadiene to form a SBS type block copolymer, each polymer chain requires a stoichiometric amount of initiator and the resulting polymers have extremely narrow molecular weight distribution, Mw/Mn, preferably from 1.0 to 1.3. Additionally, anionic and free-radical processes are relatively slow, resulting in poor process economics.

5 It would be desirable to produce block copolymers catalytically, that is, in a process wherein more than one polymer molecule is produced for each catalyst or initiator molecule. In addition, it would be highly desirable to produce multi-block copolymers having both highly crystalline and amorphous blocks or segments, from a single monomer, ethylene, which is generally unsuited for use in anionic or free-radical polymerizations. Finally, it would be highly desirable to
10 be able to use a continuous process for production of the present multi-block copolymers.

Previous researchers have stated that certain homogeneous coordination polymerization catalysts can be used to prepare polymers having a substantially "block-like" structure by suppressing chain-transfer during the polymerization, for example, by conducting the polymerization process in the absence of a chain transfer agent and at a sufficiently low temperature
15 such that chain transfer by β -hydride elimination or other chain transfer processes is essentially eliminated. Under such conditions, the sequential addition of different monomers was said to result in formation of polymers having sequences or segments of different monomer content. Several examples of such catalyst compositions and processes are reviewed by Coates, Hustad, and Reinartz in Angew. Chem., Int. Ed., 41, 2236-2257 (2002) as well as US-A-2003/0114623.

20 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
25 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.

30 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 from propylene.

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
5 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
10 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 $\text{Zn}(\text{i-Pr})_2$. 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
15 distribution. However, after analysis of time-dependent product distribution, the authors concluded this reaction was, “not a simple catalyzed chain growth reaction.” The reference fails to disclose the use of two or more catalysts in combination with a chain shuttling agent to make multi-block copolymers. Similar processes employing single catalysts have been described in USP’s 5,210,338, 5,276,220, and 6,444,867.

Earlier workers have claimed to have formed block copolymers using a single Ziegler-Natta
20 type catalyst in multiple reactors arranged in series, see for example USP’s 3,970,719 and 4,039,632. Additional Ziegler-Natta based processes and polymers are disclosed in USP’s 4,971,936; 5,089,573; 5,118,767; 5,118,768; 5,134,209; 5,229,477; 5,270,276; 5,270,410; 5,294,581; 5,543,458; 5,550,194; and 5,693,713, as well as in EP-A-470,171 and EP-A-500,530.

It is known that random defects occur in polymers prepared from single monomers using,
25 for example, Ni and Pd –diimine catalysts. The catalyst engages in “chain walking” during polymerization forming branched chains, highly branched (hyper-branched), or even dendrimeric branched chains in the resulting polymer. Examples of this type of polymerization are found in Chem. Rev., 100, 1169-1203 (2000), Macromolecular Chemistry and Physics, 205, 897-906, (2004),
30 and elsewhere. It is also known that long chain branched polymer units may be prepared from ethylene using certain homogeneous polymerization catalysts such as 1-, and 2- *t*-butyldimethylsiloxy substituted bis(indenyl)zirconium complexes with methylalumoxane cocatalyst. Examples of this type of polymerization are found in J. Mol. Catal. A: Chemical, 102

59-65 (1995); Macromolecules, 21, 617-622 (1988); J. Mol. Catal. A: Chemical, 185, 57-64 (2002), and J. Am. Chem. Soc., 117, 6414-6415 (1995).

Despite the advances by the foregoing researchers, there remains a need in the art for a polymerization process that is capable of preparing block like copolymers, especially multi-block copolymers, and most especially linear multi-block copolymers, in high yield and selectivity from a single monomer, ethylene, by the use of a shuttling agent. In addition it would be desirable to provide such an improved process that is capable of preparing multi-block copolymers, especially linear multi-block copolymers, having a relatively narrow molecular weight distribution. It would further be desirable to provide an improved process for preparing copolymers having more than two segments or blocks. Furthermore, it would be desirable to provide a process for identifying combinations of catalysts and chain shuttling agents capable of making such multi-block copolymers. Even further, it would be desirable to provide a process for independent control of the order of the various polymer blocks, especially a process for preparing olefin block copolymers containing terminal blocks having high crystallinity and/or functionality from a single olefin reagent. Finally, it would be desirable to provide an improved process for preparing any of the foregoing desirable polymer products in a continuous process, without required sequential addition of two or more monomers. Highly desirably, such process allows for independent control of the quantity and/or identity of the shuttling agent(s) and/or catalysts used.

Summary of the Invention

According to the present invention there are now provided a composition for use in the polymerization of ethylene to form a segmented copolymer (multi-block copolymer), said copolymer containing therein two or more, preferably three or more segments or blocks differing in one or more chemical or physical properties as further disclosed here in, the composition comprising the admixture or reaction product resulting from combining:

- (A) a first olefin polymerization catalyst,
- (B) a second olefin polymerization catalyst capable of preparing polymers differing in chemical or physical properties from the polymer prepared by catalyst (A) under equivalent polymerization conditions,
- at least one of catalyst (A) or catalyst (B) being capable of forming a branched polymer by means of chain walking or reincorporation of in situ formed olefinic polymer chains, and
- (C) a chain shuttling agent.

Preferably the admixture or reaction product results from combining:

(A) a first olefin polymerization catalyst capable of forming a highly crystalline ethylene homopolymers by ethylene polymerization;

(B) a second olefin polymerization catalyst capable of forming a branched polymer upon polymerization by means of chain walking or reincorporation of in situ formed olefinic polymer chains, and

(C) a chain shuttling agent.

In another embodiment of the invention, there is provided a method for selecting an admixture of catalysts (A) and (B) and chain shuttling agent (C) capable of producing multi-block copolymers according to the invention.

In a further embodiment of the present invention there is provided a process for preparing a segmented copolymer, said process comprising contacting ethylene under addition polymerization conditions with a composition comprising:

the admixture or reaction product resulting from combining:

(A) a first olefin polymerization catalyst,

(B) a second olefin polymerization catalyst capable of preparing polymers differing in chemical or physical properties from the polymer prepared by catalyst (A) under equivalent polymerization conditions,

at least one of catalyst (A) or catalyst (B) being capable of forming a branched polymer by means of chain walking or reincorporation of in situ formed olefinic polymer chains, and

(C) a chain shuttling agent.

Preferably, the foregoing process takes the form of a continuous solution process for forming block copolymers, especially multi-block copolymers, preferably linear multi-block copolymers, using multiple catalysts that are incapable of interconversion. That is the catalysts are chemically distinct. Under continuous solution polymerization conditions, the process is ideally suited for polymerization of ethylene at high monomer conversions. Under these polymerization conditions, shuttling from the chain shuttling agent to the catalyst becomes advantaged compared to chain growth, and multi-block copolymers, especially linear multi-block copolymers according to the invention are formed in high efficiency.

In another embodiment of the invention there is provided a high molecular weight, segmented copolymer (multi-block copolymer) prepared from ethylene, containing therein two or more, preferably three or more segments differing in density or other chemical or physical property. Highly preferably the copolymer possesses a molecular weight distribution, M_w/M_n , of less than 3.0, preferably less than 2.8.

In yet another embodiment of the invention, there are provided functionalized derivatives of the foregoing segmented or multi-block copolymers.

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 and a copolymerizable comonomer, and (2) a high molecular weight, multi-block copolymer according to the present invention or prepared according to the process of the present invention. In a desirable embodiment component (1) is a matrix polymer comprising high density polyethylene or isotactic polypropylene and component (2) is an elastomeric multi-block copolymer. In a preferred embodiment, component (2) comprises occlusions of the matrix polymer formed during compounding of components (1) and (2).

Brief Description of the Drawings

Figure 1 is a schematic representation of the process of polymer chain shuttling involving two catalyst sites.

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 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 component, step or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any 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 conventional homopolymers, that is, homogeneous polymers prepared from a single monomer, and copolymers (interchangeably referred to herein as
5 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 C₃₋₈ α-olefins in which ethylene comprises at least 50 mole percent. The term "crystalline" if employed, refers to a polymer that possesses a first order
10 transition or crystalline melting point (T_m) 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 "multi-block copolymer" or "segmented copolymer" refers to a polymer comprising two or more chemically distinct regions or segments (referred to as "blocks") preferably
15 joined in a linear manner, that is, a polymer comprising chemically differentiated units which are joined end-to-end with respect to polymerized ethylenic functionality, rather than in pendent or grafted fashion. In a preferred embodiment, the blocks differ in the density, the amount of crystallinity, the crystallite size attributable to a polymer of such composition, the amount of chain branching, the homogeneity, or any other chemical or physical property attributable to an olefin
20 polymer. Compared to block copolymers of the prior art, including copolymers produced by sequential monomer addition, fluxional catalysts, or anionic polymerization techniques, certain of the polymers of the invention are characterized by unique distributions of both polymer polydispersity (PDI or Mw/Mn), block length distribution, and/or block number distribution, due, in a preferred embodiment, to the effect of the shuttling agent(s) in combination with multiple
25 catalysts. More specifically, the polymers desirably possess PDI from 1.7 to 2.9, preferably from 1.8 to 2.5.

Because the respective distinguishable segments or blocks are joined into single polymer chains, the polymer cannot be completely fractionated using standard selective extraction techniques. For example, polymers containing regions that are relatively crystalline (high density
30 segments) and regions that are relatively amorphous (lower density segments) cannot be selectively extracted or fractionated using differing solvents. In a preferred embodiment the quantity of extractable polymer using either a dialkyl ether- or an alkane- solvent is less than 10 percent, more preferably less than 5 percent and most preferably less than 2 percent of the total polymer weight.

In addition, the multi-block copolymers of the invention desirably possess a PDI fitting a Schutz-Flory distribution rather than a Poisson distribution. The use of the present polymerization process results in a product having both a polydisperse block distribution as well as a polydisperse distribution of block sizes. This ultimately results in the formation of polymer products having improved and distinguishable physical properties. The theoretical benefits of a polydisperse block distribution have been previously modeled and discussed in Potemkin, Physical Review E (1998) 57(6), p. 6902-6912, and Dobrynin, J. Chem. Phys. (1997) 107(21), p 9234-9238.

In a further embodiment, the polymers of the invention, especially those made in a continuous, solution polymerization reactor, possess a most probable distribution of block lengths. Most preferred polymers according to the invention are multi-block copolymers containing 4 or more blocks or segments including terminal blocks.

The following mathematical treatment of the resulting polymers is based on theoretically derived parameters that are believed to apply to the present invented polymers and demonstrate that, especially in a steady-state, continuous, well-mixed reactor, the block lengths of the resulting polymer prepared using 2 or more catalysts will each conform to a most probable distribution, derived in the following manner, wherein p_i is the probability of propagation with respect to block sequences from catalyst i . The theoretical treatment is based on standard assumptions and methods known in the art and used in predicting the effects of polymerization kinetics on molecular architecture, including the use of mass action reaction rate expressions that are not affected by chain or block lengths. Such methods have been previously disclosed in W. H. Ray, J. Macromol. Sci., Rev. Macromol. Chem., C8, 1 (1972) and A. E. Hamielec and J. F. MacGregor, "Polymer Reaction Engineering", K.H. Reichert and W. Geisler, Eds., Hanser, Munich, 1983. In addition it is assumed that adjacent sequences formed by the same catalyst form a single block. For catalyst i , the fraction of sequences of length n is given by $X_i[n]$, where n is an integer from 1 to infinity representing the number of monomer units in the block.

$$X_i[n] = (1-p_i) p_i^{(n-1)} \quad \text{most probable distribution of block lengths}$$

$$N_i = \frac{1}{1-p_i} \quad \text{number average block length}$$

Each catalyst has a probability of propagation (p_i) and forms a polymer segment having a unique average block length and distribution. In a most preferred embodiment, the probability of propagation is defined as:

$$p_i = \frac{R_p[i]}{R_p[i] + R_t[i] + R_s[i] + [C_i]} \quad \text{for each catalyst } i = \{1, 2, \dots\}, \text{ where,}$$

$$R_p[i] = \text{Rate of monomer consumption by catalyst } i, (\text{moles/L}),$$

Rt[i] = Total rate of chain transfer and termination for catalyst i, (moles/L),

Rs[i] = Rate of chain shuttling with dormant polymer to other catalysts, (moles/L), and

[C_i] = Concentration of catalyst i (moles/L).

Dormant polymer chains refers to polymer chains that are attached to a CSA.

5 The overall monomer consumption or polymer propagation rate, Rp[i], is defined using an apparent rate constant, $\overline{k_{pi}}$, multiplied by a total monomer concentration, [M], as follows:

$$Rp[i] = \theta \overline{k_{pi}} [M][C_i]$$

The total chain transfer rate is given below including values for chain transfer to hydrogen (H₂), beta hydride elimination, and chain transfer to chain shuttling agent (CSA). The reactor
10 residence time is given by θ and each subscripted k value is a rate constant.

$$Rt[i] = \theta k_{H_2i}[H_2][C_i] + \theta k_{\beta i}[C_i] + \theta k_{ai}[CSA][C_i]$$

For a dual catalyst system, the rate of chain shuttling of polymer between catalysts 1 and 2 is given as follows:

$$Rs[1] = Rs[2] = \theta k_{a1}[CSA] \theta k_{a2}[C_1][C_2].$$

15 If more than 2 catalysts are employed then added terms and complexity in the theoretical relation for Rs[i] result, but the ultimate conclusion that the resulting block length distributions are most probable is unaffected.

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
20 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,
25 B, S, Si, Sb, Al, Sn, As, Se and Ge. The term "amorphous" refers to a polymer lacking a crystalline melting point as determined by differential scanning calorimetry (DSC) or equivalent technique.

The term, "hydrocarbyl" refers to univalent substituents containing only hydrogen and carbon atoms, including branched or unbranched, saturated or unsaturated, cyclic, polycyclic or
30 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 a single or multiple covalent bond or a coordinating or other donative bond. Thus, an alkyl group substituted with a heterocycloalkyl-, aryl- substituted heterocycloalkyl-, heteroaryl-, alkyl- 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 cyanomethyl-, benzoylmethyl-, (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. Examples of aromatic ring(s) 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, "branching index", refers to the percent branched polymer containing segments in a polymer prepared under representative ethylene polymerization conditions by the catalyst under consideration in the absence of other polymerization catalysts, ideally under steady-state, continuous solution polymerization conditions in a hydrocarbon diluent at 100 °C, 4.5 MPa reactor pressure, and greater than 92 percent, preferably greater than 95 percent ethylene conversion. The selection of metal complexes or catalyst compositions having the greatest difference in branching indices results in multi-block copolymers having the largest difference in block or segment properties, such as density.

The branching index for polymers formed from catalysts capable of chain walking may be determined directly, for example by the use of NMR spectroscopic techniques, since linear, high

density polyethylene is normally produced by catalysts that are incapable of chain walking polymerization.

Monomers

5 The present invention results by polymerization of a single monomer, ethylene, as previously explained. In addition, it is understood by the skilled artisan that one or more addition polymerizable comonomers may be present during the present polymerization without departing from the scope of the present invention, so long as the objects stated herein are attained. Preferably, however, the present invention takes place in the substantial absence of any comonomer, and most
10 preferably the only olefin monomer employed in the process is ethylene.

Chain shuttling agents

 The term, "shuttling agent" refers to a compound or mixture of compounds employed in the composition of the present invention that is capable of causing polymeryl exchange between at least
15 two active catalyst sites of the catalysts included in the composition under the conditions of the polymerization. That is, transfer of a polymer fragment occurs both to and from one or more of the active catalyst sites. 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. Preferably, the shuttling agent has an activity ratio R_{A-B}/R_{B-A} of from 0.01 and
20 100, more preferably from 0.1 to 10, most preferably from 0.5 to 2.0, and most highly preferably from 0.8 to 1.2, wherein R_{A-B} is the rate of polymeryl transfer from catalyst A active site to catalyst B active site via the shuttling agent, and R_{B-A} is the rate of reverse polymeryl transfer, i.e., the rate of exchange starting from the catalyst B active site to catalyst A active site via the shuttling agent. Desirably, the intermediate formed between the shuttling agent and the polymeryl chain is
25 sufficiently stable that chain termination is relatively rare. Desirably, less than 90 percent, preferably less than 75 percent, more preferably less than 50 percent and most desirably less than 10 percent of shuttle-polymeryl products are terminated prior to attaining 3 distinguishable polymer segments or blocks. Ideally, the rate of chain shuttling (defined by the time required to transfer a polymer chain from a catalyst site to the chain shuttling agent and then back to a catalyst site) is
30 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. This permits polymer block formation on the same time scale as polymer propagation.

 By selecting different combinations of catalysts having differing branching indices as well as differing reactivities, and by pairing various shuttling agents or mixtures of agents with these

catalyst combinations, polymer products having segments of different densities or branching indices, different block lengths, and different numbers of such segments or blocks in each copolymer can be prepared. For example, if the activity of the shuttling agent is low relative to the catalyst polymer chain propagation rate of one or more of the catalysts, longer block length multi-block copolymers and polymer blends may be obtained. Contrariwise, if shuttling is very fast relative to polymer chain propagation, a copolymer having a more random chain structure and shorter block lengths is obtained. An extremely fast shuttling agent may produce a multi-block copolymer having substantially random copolymer properties. By proper selection of both catalyst mixture and shuttling agent, relatively pure block copolymers, copolymers containing relatively large polymer segments or blocks, and/or blends of the foregoing with various ethylene polymers can be obtained.

A suitable composition comprising Catalyst A, Catalyst B, and a chain shuttling agent can be selected for this invention by the following multi-step procedure specially adapted for block differentiation based on branching index:

I. Ethylene is polymerized using a mixture comprising a potential catalyst and a potential chain shuttling agent. This polymerization test is desirably performed using a batch or semi-batch reactor (that is, without resupply of catalyst or shuttling agent), preferably with relatively constant ethylene concentration, operating under solution polymerization conditions, typically using a molar ratio of catalyst to chain shuttling agent from 1:5 to 1:500. After forming a suitable quantity of polymer, the reaction is terminated by addition of a catalyst poison and the polymer's properties (branching index, Mw, Mn, and Mw/Mn or PDI) measured.

II. The foregoing polymerization and polymer testing are repeated for several different reaction times, providing a series of polymers having a range of yields and PDI values.

III. Catalyst/ shuttling agent pairs demonstrating significant polymer transfer both to and from the shuttling agent are characterized by a polymer series wherein the minimum PDI is less than 2.0, more preferably less than 1.5, and most preferably less than 1.3. Furthermore, if chain shuttling is occurring, the Mn of the polymer will increase, preferably nearly linearly, as conversion is increased. Most preferred catalyst/ shuttling agent pairs are those giving polymer Mn as a function of conversion (or polymer yield) fitting a line with a statistical precision (R^2) of greater than 0.95, preferably greater than 0.99.

Steps I-III are then carried out for one or more additional pairings of potential catalysts and/or putative shuttling agents.

A suitable composition comprising Catalyst A, Catalyst B, and one or more chain shuttling agents according to the invention is then selected such that the two catalysts each undergo chain

shuttling with one or more of the chain shuttling agents, and one of the catalysts (designated as catalyst (B)), forms polymer having a higher branching index compared to Catalyst A under the reaction conditions chosen. Most preferably, at least one of the chain shuttling agents undergoes polymer transfer in both the forward and reverse directions (as identified in the foregoing test) with both Catalyst A and Catalyst B. In addition, it is preferable that the chain shuttling agent does not reduce the catalyst activity (measured in weight of polymer produced per weight of catalyst per unit time) of either catalyst (compared to activity in the absence of a shuttling agent) by more than 60 percent, more preferably such catalyst activity is not reduced by more than 20 percent. Highly desirably, catalyst activity of at least one of the catalysts is actually increased in the presence of the chain shuttling agent.

Alternatively, it is also possible to detect desirable catalyst/shuttling agent pairs by performing a series of ethylene polymerizations under standard batch reaction conditions and measuring the resulting number average molecular weights, PDI, branching index, and polymer yield or production rate. Suitable shuttling agents are characterized by lowering of the resultant M_n without significant broadening of PDI or loss of activity (reduction in yield or rate).

The foregoing tests are readily adapted to rapid throughput screening techniques using automated reactors and analytic probes and to formation of polymer blocks having different distinguishing properties. For example, a number of potential shuttling agent candidates can be pre-identified or synthesized *in situ* by combination of various organometal compounds with various proton sources and the compound or reaction product added to a polymerization reaction employing an olefin polymerization catalyst composition. Several polymerizations are conducted at varying molar ratios of shuttling agent to catalyst. As a minimum requirement, suitable shuttling agents are those that produce a minimum PDI of less than 2.0 in variable yield experiments as described above, while not significantly adversely affecting catalyst activity, and preferably improving catalyst activity, as above described.

Regardless of the method for identifying, *a priori*, a shuttling agent, the term is meant to refer to a compound that is capable of preparing the presently identified multi-block copolymers or usefully employed under the polymerization conditions herein disclosed. Highly desirably, multi-block copolymers having an average number of blocks or segments per average chain (as defined as the average number of blocks of different composition divided by the M_n of the polymer) greater than 3.0 more preferably greater than 3.5, even more preferably greater than 4.0, and less than 25, preferably less than 15, more preferably less than 10.0, most preferably less than 8.0 are formed according to the invention.

Suitable shuttling agents for use herein include Group 1, 2, 12 or 13 metal compounds or complexes 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-butyl)dimethylsiloxide, 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).

It will be appreciated by the skilled artisan that a suitable shuttling agent for one catalyst or catalyst combination may not necessarily be as good or even satisfactory for use with a different catalyst or catalyst combination. Some potential shuttling agents may adversely affect the performance of one or more catalysts and may be undesirable for use for that reason as well. Accordingly, the activity of the chain shuttling agent desirably is balanced with the catalytic activity of the catalysts to achieve the desired polymer properties. In some embodiments of the invention, best results may be obtained by use of shuttling agents having a chain shuttling activity (as measured by a rate of chain transfer) that is less than the maximum possible rate.

Generally however, preferred shuttling agents possess the highest 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. In addition, such shuttling agents result in production of the shortest possible polymer block lengths. 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.

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 3-10 or the Lanthanide series of the Periodic Table of the Elements. It is preferred that any catalyst employed herein, not significantly detrimentally affect the performance of the other catalyst under the conditions of the present polymerization. Desirably, no catalyst is reduced in activity by greater than 25 percent, more preferably greater than 10 percent under the conditions of the present polymerization.

Metal complexes for use herein as Catalyst A include complexes of transition 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 4-8, 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
5 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;

10 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.

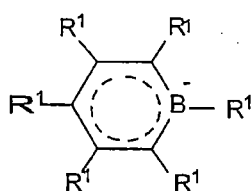
Suitable metal complexes include those containing from 1 to 3 π -bonded anionic or neutral
15 ligand groups, which may be cyclic or non-cyclic delocalized π -bonded anionic ligand groups. Exemplary of such π -bonded groups are conjugated or nonconjugated, cyclic or non-cyclic diene and dienyl groups, 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.

20 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
25 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,
30 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-butyl dimethylsilyl, 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 alkyleneithio groups bonded to the transition metal or Lanthanide metal, and bonded to the hydrocarbyl group, π -bonded group, or hydrocarbyl- substituted heteroatom.

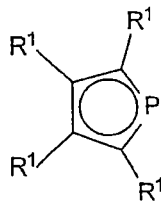
Examples of suitable anionic, delocalized π -bonded groups include cyclopentadienyl, indenyl, fluorenyl, tetrahydroindenyl, tetrahydrofluorenyl, octahydrofluorenyl, pentadienyl, cyclohexadienyl, dihydroanthracenyl, hexahydroanthracenyl, decahydroanthracenyl groups, phosphole, and boratabenzyl groups, 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(*D*))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 germynyl, 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 R¹ is as previously defined.

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

5 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;

10 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;

15 k is an integer from 0 to 3;

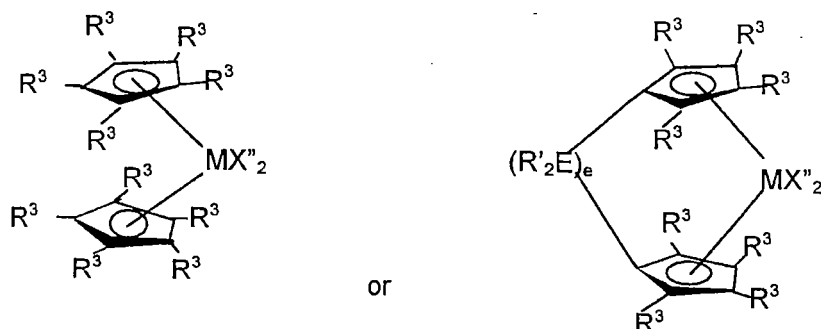
x is an integer from 1 to 4;

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
20 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,
25 phenyl, methoxy, ethoxy or phenoxy.

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



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-tetramethyl)-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 C₁₋₂₀ hydrocarbyl groups.

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

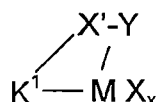
- 5 bis(cyclopentadienyl)zirconiumdimethyl,
bis(cyclopentadienyl)zirconium dibenzyl,
bis(cyclopentadienyl)zirconium methyl benzyl,
bis(cyclopentadienyl)zirconium methyl phenyl,
bis(cyclopentadienyl)zirconiumdiphenyl,
- 10 bis(cyclopentadienyl)titanium-allyl,
bis(cyclopentadienyl)zirconiummethoxymethoxide,
bis(cyclopentadienyl)zirconiummethylchloride,
bis(pentamethylcyclopentadienyl)zirconiumdimethyl,
bis(pentamethylcyclopentadienyl)titaniumdimethyl,
- 15 bis(indenyl)zirconiumdimethyl,
indenylfluorenyl zirconiumdimethyl,
bis(indenyl)zirconiummethyl(2-(dimethylamino)benzyl),
bis(indenyl)zirconiummethyltrimethylsilyl,
bis(tetrahydroindenyl)zirconiummethyltrimethylsilyl,
- 20 bis(pentamethylcyclopentadienyl)zirconiummethylbenzyl,
bis(pentamethylcyclopentadienyl)zirconiumdibenzyl,
bis(pentamethylcyclopentadienyl)zirconiummethoxymethoxide,
bis(pentamethylcyclopentadienyl)zirconiummethylchloride,
bis(methylethylcyclopentadienyl)zirconiumdimethyl,
- 25 bis(butylcyclopentadienyl)zirconiumdibenzyl,
bis(t-butylcyclopentadienyl)zirconiumdimethyl,
bis(ethyltetramethylcyclopentadienyl)zirconiumdimethyl,
bis(methylpropylcyclopentadienyl)zirconiumdibenzyl,
bis(trimethylsilylcyclopentadienyl)zirconiumdibenzyl,
- 30 dimethylsilylbis(cyclopentadienyl)zirconiumdichloride,
dimethylsilylbis(cyclopentadienyl)zirconiumdimethyl,
dimethylsilylbis(tetramethylcyclopentadienyl)titanium (III) allyl
dimethylsilylbis(t-butylcyclopentadienyl)zirconiumdichloride,
dimethylsilylbis(n-butylcyclopentadienyl)zirconiumdichloride,

- (dimethylsilylbis(tetramethylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,
 (dimethylsilylbis(n-butylcyclopentadienyl)titanium(III) 2-(dimethylamino)benzyl,
 dimethylsilylbis(indenyl)zirconiumdichloride,
 dimethylsilylbis(indenyl)zirconiumdimethyl,
 5 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(4,5,6,7-tetrahydroinden-1-yl)zirconiumdichloride,
 10 dimethylsilylbis(4,5,6,7-tetrahydroinden-1-yl)zirconiumdimethyl,
 dimethylsilylbis(tetrahydroindenyl)zirconium(II) 1,4-diphenyl-1,3-butadiene,
 dimethylsilylbis(tetramethylcyclopentadienyl)zirconium dimethyl
 dimethylsilylbis(fluorenyl)zirconiumdimethyl,
 dimethylsilylbis(tetrahydrofluorenyl)zirconium bis(trimethylsilyl),
 15 ethylenebis(indenyl)zirconiumdichloride,
 ethylenebis(indenyl)zirconiumdimethyl,
 ethylenebis(4,5,6,7-tetrahydroindenyl)zirconiumdichloride,
 ethylenebis(4,5,6,7-tetrahydroindenyl)zirconiumdimethyl,
 (isopropylidene)(cyclopentadienyl)(fluorenyl)zirconiumdibenzyl, and
 20 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.

- 25 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.

- 30 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,
 5 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
 10 derivative thereof;

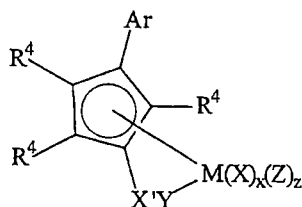
x is 1 or 2;

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,
 15 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,

20 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-
 25 substituted hydrocarbyl, hydrocarbyloxy- substituted hydrocarbyl, trihydrocarbyl silyl- 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 R⁴ groups may be joined together forming a polycyclic fused ring group;

M is titanium;

X' is SiR⁶₂, CR⁶₂, SiR⁶₂SiR⁶₂, CR⁶₂CR⁶₂, CR⁶=CR⁶, CR⁶₂SiR⁶₂, BR⁶, BR⁶L, or GeR⁶₂;

5 Y is -O-, -S-, -NR⁵-, -PR⁵-, -NR⁵₂, or -PR⁵₂;

R⁵, independently each occurrence, is hydrocarbyl, trihydrocarbylsilyl, or trihydrocarbylsilylhydrocarbyl, said R⁵ having up to 20 atoms other than hydrogen, and optionally two R⁵ groups or R⁵ together with Y or Z form a ring system;

10 R⁶, independently each occurrence, is hydrogen, or a member selected from hydrocarbyl, hydrocarbyloxy, silyl, halogenated alkyl, halogenated aryl, -NR⁵₂, and combinations thereof, said R⁶ having up to 20 non-hydrogen atoms, and optionally, two R⁶ groups or R⁶ together with Z forms a ring system;

Z is a neutral diene or a monodentate or polydentate Lewis base optionally bonded to R⁵, R⁶, or X;

15 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.

20 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,

25 (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;

30 (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,

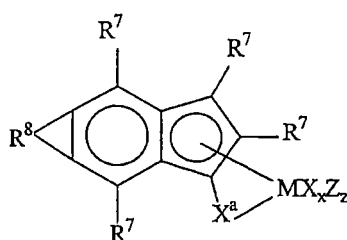
(3-(1-methylpyrrol-3-yl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium (II) 1,4-diphenyl-1,3-butadiene;

(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
 5 dichloride,
 (3-(3-N,N-dimethylamino)phenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium
 dimethyl,
 (3-(3-N,N-dimethylamino)phenyl)cyclopentadien-1-yl)dimethyl(t-butylamido)silanetitanium
 (II) 1,4-diphenyl-1,3-butadiene;
 10 (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;
 15 (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
 20 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;
 25 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
 30 (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,
 5 (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-
 10 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;
 15 (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 as catalyst (A) herein are
 20 polycyclic complexes corresponding to the formula:



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

R⁷ independently each occurrence is hydride, hydrocarbyl, silyl, germyl, halide,
 hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbyl)amino,
 25 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;

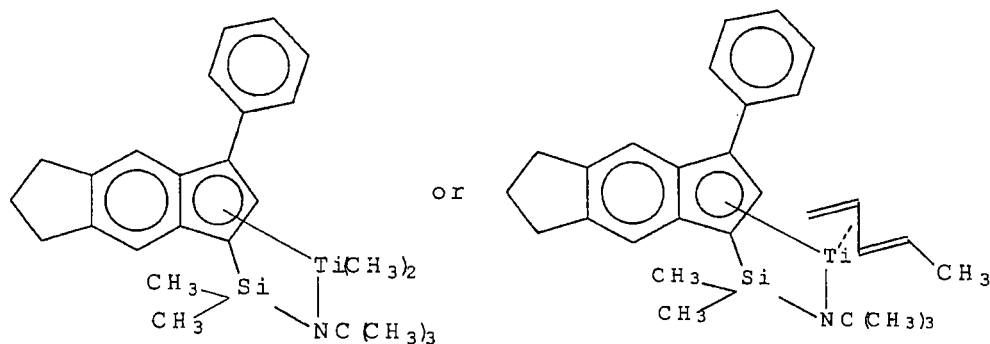
X is a monovalent anionic ligand group having up to 60 atoms exclusive of the class of ligands that are cyclic, delocalized, π -bound ligand groups and optionally two X groups together form a divalent ligand group;

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

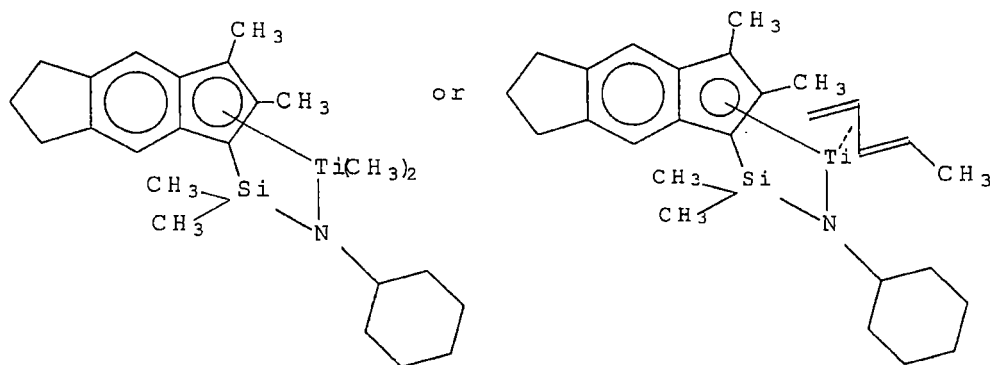
x is 0, 1 or 2; and

z is zero or 1.

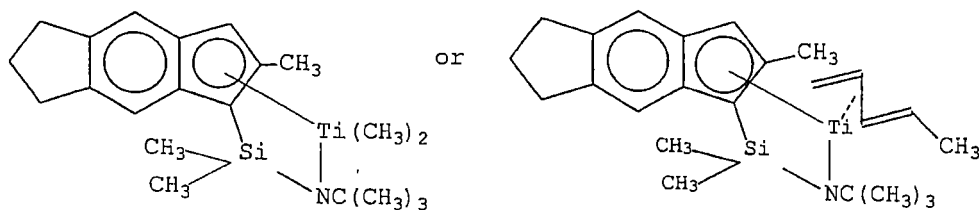
Preferred examples of such complexes are 3-phenyl-substituted s-indecenyl complexes corresponding to the formula:



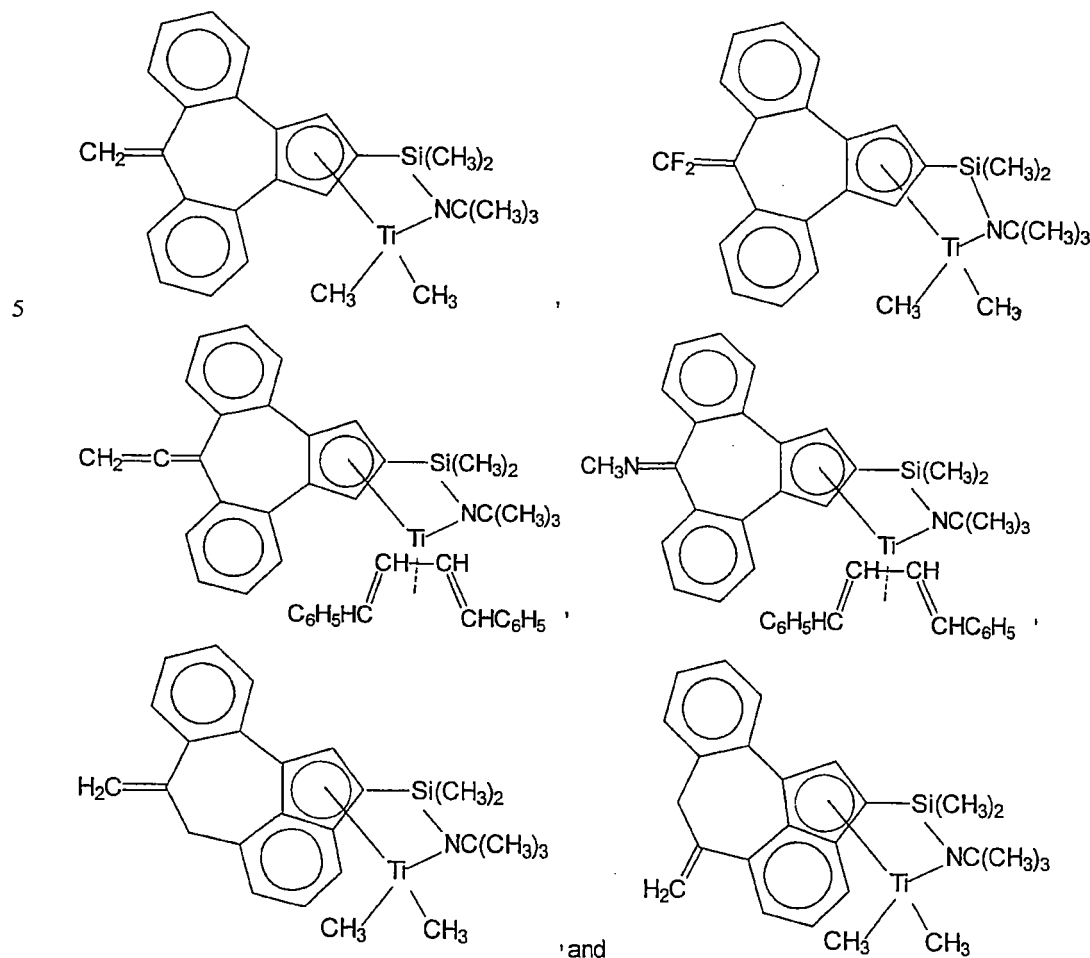
2,3-dimethyl-substituted s-indecenyl complexes corresponding to the formulas:



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



Additional examples of metal complexes that are usefully employed as catalyst (A) according to the present invention include those of the formula:



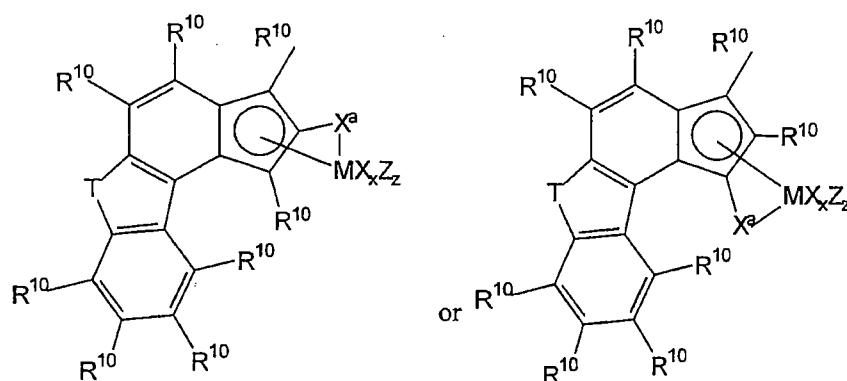
Specific metal complexes include:

- (8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilylanamide
titanium (II) 1,4-diphenyl-1,3-butadiene,
(8-methylene-1,8-dihydrodibenzo[*e,h*]azulen-1-yl)-N-(1,1-dimethylethyl)dimethylsilylanamide
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,
- 5 (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,
- 10 (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,
- 15 (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,
- 20 (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,
- 25 (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,
- 30 (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 -NR⁹- or -O-;

R⁹ is hydrocarbyl, silyl, germyl, dihydrocarbylboryl, or halo-hydrocarbyl or up to 10 atoms not counting hydrogen;

R¹⁰ 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 R¹⁰ group having up to 40 atoms not counting hydrogen atoms, and optionally two or more of the foregoing adjacent R¹⁰ groups may together form a divalent derivative thereby forming a saturated or unsaturated fused ring;

X^a 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(CH₃), X is halo or hydrocarbyl, x is 2, X' is dimethylsilane, z is 0, and R¹⁰ 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 R¹⁰ 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),
- 5 (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,
- 10 (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,
- 15 (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),
- 20 (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,
- 25 (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,
- 30 (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:

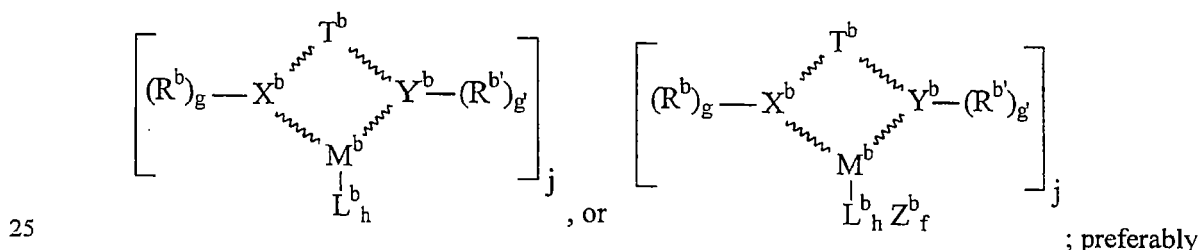
(tert-butylamido)(1,1-dimethyl-2,3,4,9,10- η -1,4,5,6,7,8-hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,
 (tert-butylamido)(1,1,2,3-tetramethyl-2,3,4,9,10- η -1,4,5,6,7,8-hexahydronaphthalenyl)dimethylsilanetitaniumdimethyl,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl) dimethylsilanetitanium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

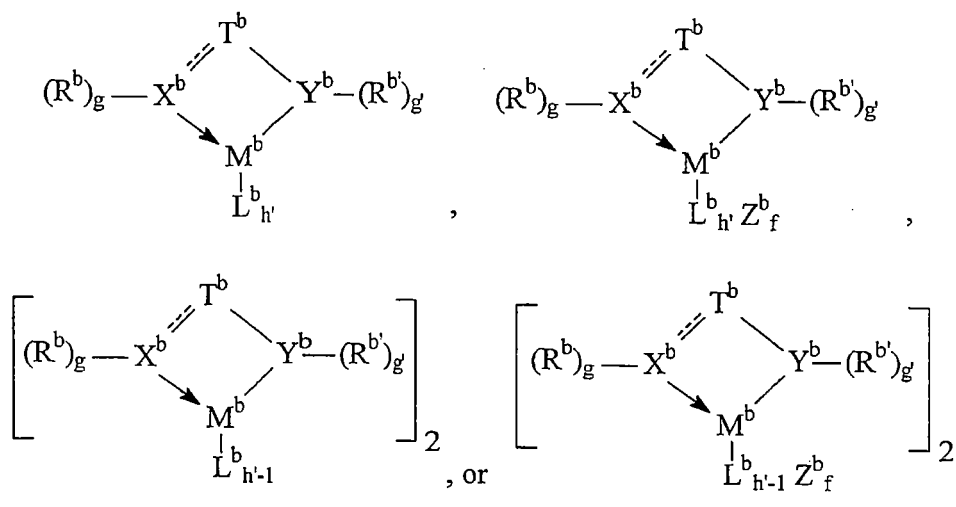
- 1,3-pentadiene,
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 1,4-diphenyl-1,3-butadiene,
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,
 5 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 2,3-dimethyl-1,3-butadiene,
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) isoprene,
 (tert-butylamido)(2-methylindenyl)dimethylsilanetitanium (IV) 1,3-butadiene,
 (tert-butylamido)(2,3-dimethylindenyl)dimethylsilanetitanium (IV)
 10 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
 15 (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,
 20 (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,
 25 (tert-butylamido)(2-methyl-4-phenylindenyl)dimethylsilanetitanium (II) 2,4-hexadiene,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (IV)
 1,3-butadiene,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (IV)
 2,3-dimethyl-1,3-butadiene,
 30 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (IV)
 isoprene,
 (tert-butylamido)(tetramethyl- η^5 -cyclopentadienyl)dimethylsilanetitanium (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,
 5 (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
 10 (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)
 15 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:
 20 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 as catalyst (A) are complexes of polyvalent Lewis bases, such as compounds corresponding to the formula:





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,

- 5 R^b and $\text{R}^{b'}$ 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 $\text{R}^{b'}$ 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 R^b and $\text{R}^{b'}$ 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;

- 15 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 $h \times j$ 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, aryloxy carbonyl, di(hydrocarbyl)amine, tri(hydrocarbyl)silyl, and nitrile groups. Preferred Z^b groups include triphenylphosphine, tetrahydrofuran, pyridine, and 1,4-diphenylbutadiene;

5 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;

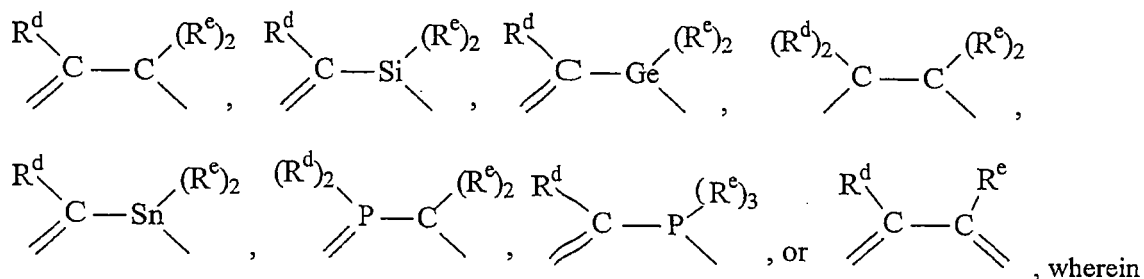
h is an integer from 1 to 6, preferably from 1 to 4, more preferably from 1 to 3;

10 ~~~~~ indicates any form of electronic interaction, 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.

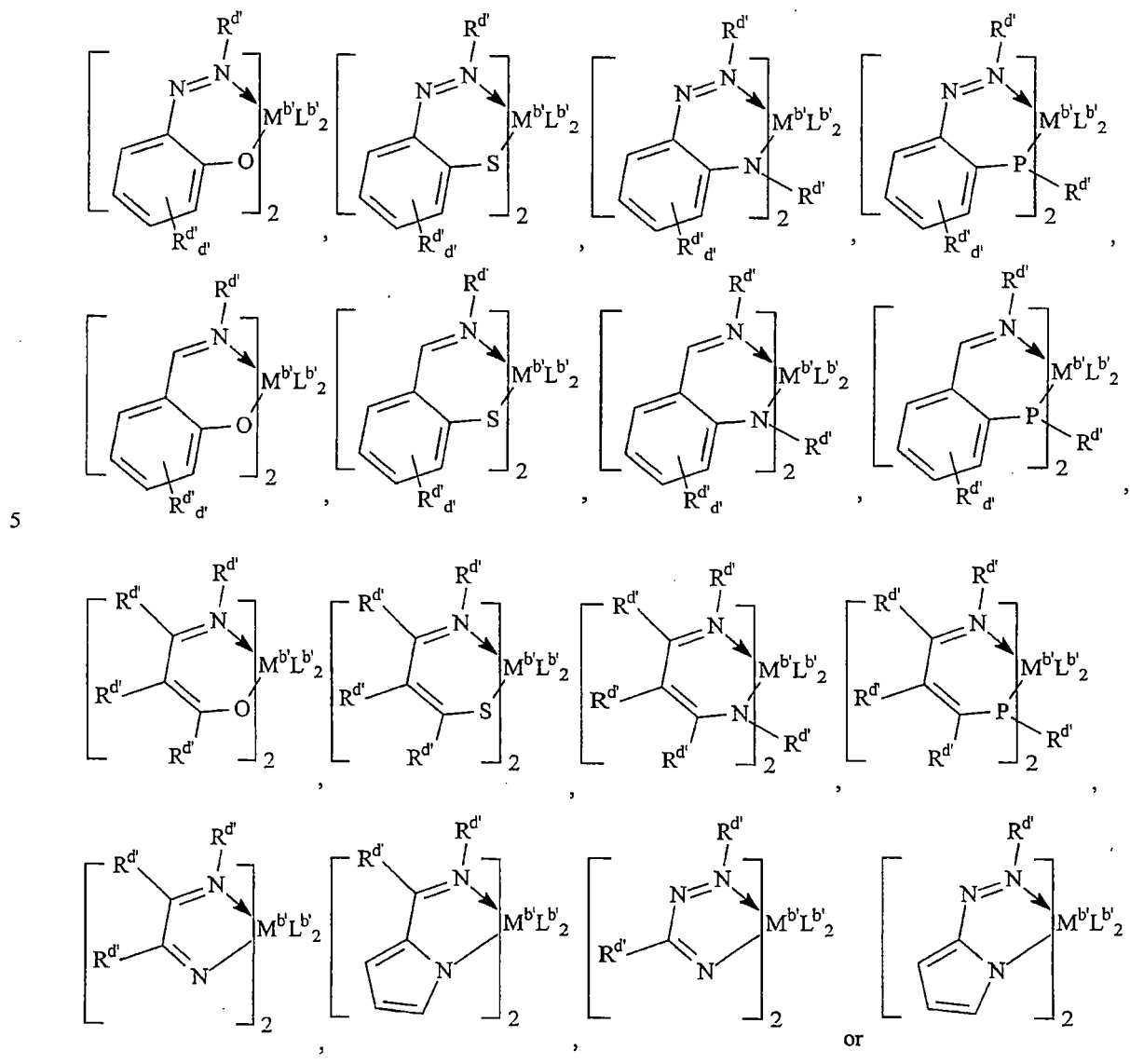
25 Examples of preferred T^b groups are structures corresponding to the following formulas:



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

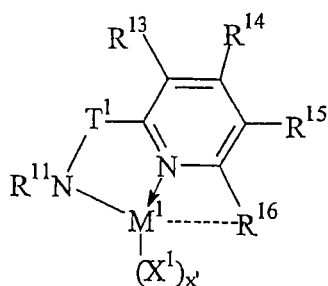
or R^e groups, or mixtures of R_d and R_e groups may together form a polyvalent derivative of a hydrocarbyl group, such as, 1,4-butylene, 1,5-pentylene, or a multicyclic, fused ring, polyvalent hydrocarbyl- or heterohydrocarbyl- group, such as naphthalene-1,8-diyl.

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 C₁₋₅₀ 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;

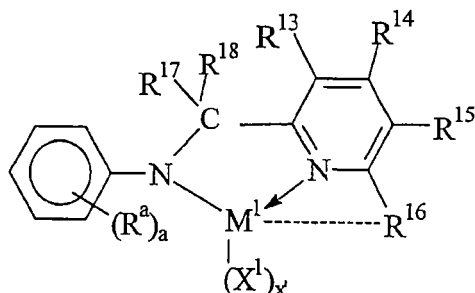


, wherein

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

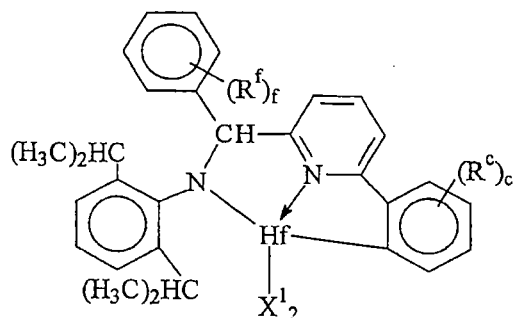
- M^1 , X^1 , and x' are as previously defined,

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 as catalyst (A) correspond to the formula:

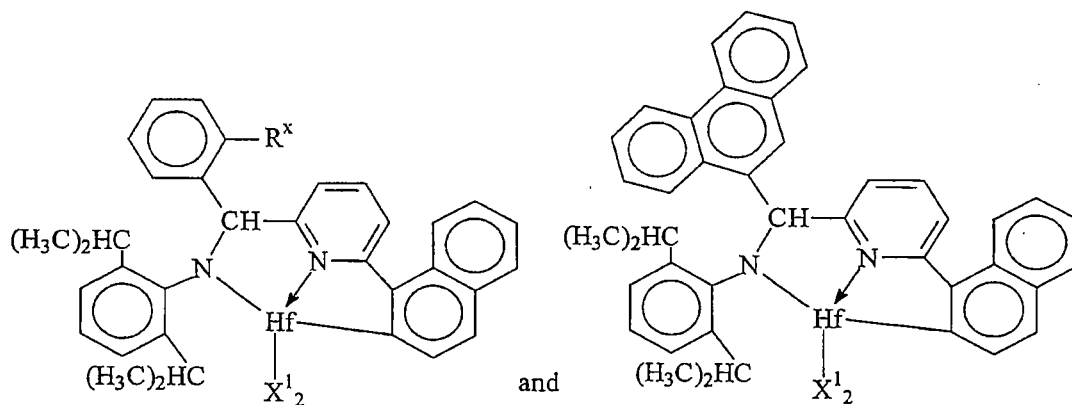


wherein X^1 each occurrence is halide, N,N-dimethylamido, or C_{1-4} alkyl, and preferably each occurrence X^1 is methyl;

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 as catalyst (A) 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 as catalyst (A) 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;

5 [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;

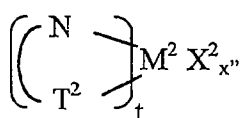
10 [N-(2,6-di(1-methylethyl)phenyl)amido](phenanthren-5-yl)(α-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl;

[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.

15 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
20 electron pair of the nitrogen atom.

Group 4-10 derivatives corresponding to the formula:



wherein

25 M² 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;

T² is a nitrogen, oxygen or phosphorus containing group;

X² is halo, hydrocarbyl, or hydrocarbyloxy;

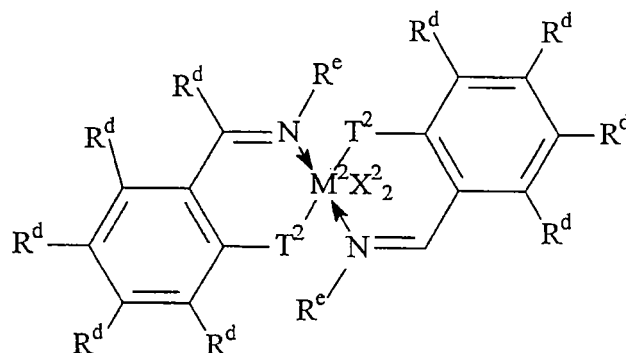
t is one or two;

x'' is a number selected to provide charge balance;

30 and T² 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.

Examples of the foregoing metal complexes include aromatic diimine or aromatic dioximine complexes of Group 4 metals, especially zirconium, corresponding to the formula:



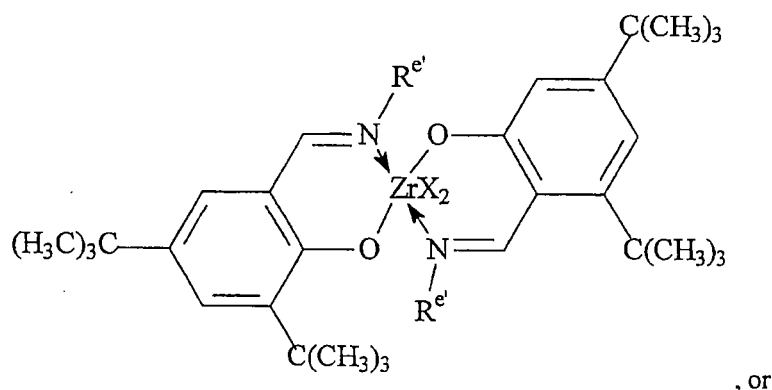
wherein;

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

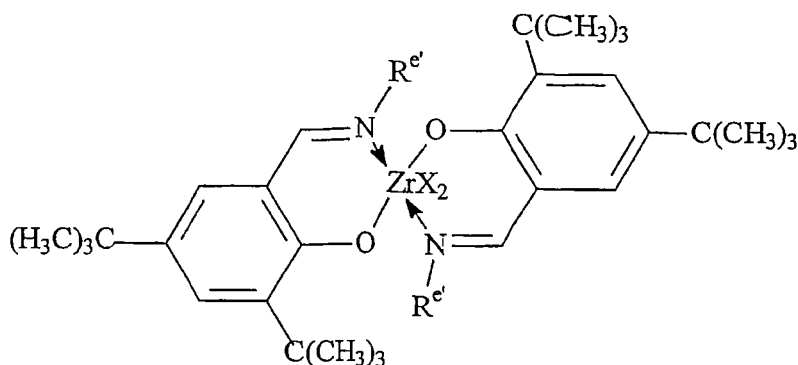
R^d independently each occurrence is hydrogen, halogen, or R^e ; and

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 dioximine complexes of zirconium, corresponding to the formula:



, or



wherein;

X^2 is as previously defined, preferably C_{1-10} hydrocarbonyl, 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 disclosed in EP-A-890581. These complexes correspond to the formula:

$[(R^f)_3-P=N]_f M(K^2)(R^f)_{3-f}$, wherein:

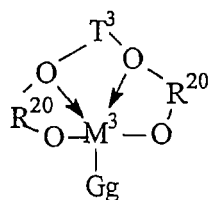
R^f is a monovalent ligand or two R^f groups together are a divalent ligand, preferably R^f is hydrogen or C_{1-4} alkyl;

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.

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



, where:

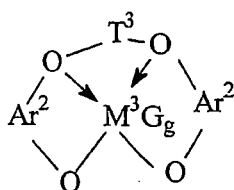
R^{20} is an aromatic or inertly substituted aromatic group containing from 5 to 20 atoms not counting hydrogen, or a polyvalent derivative thereof;

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:

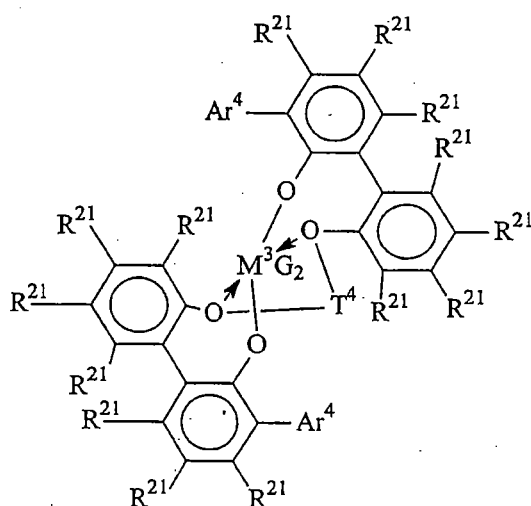
T^3 is a divalent bridging group of from 2 to 20 atoms not counting hydrogen, preferably a substituted or unsubstituted, C_{3-6} alkylene group; and

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 G 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;

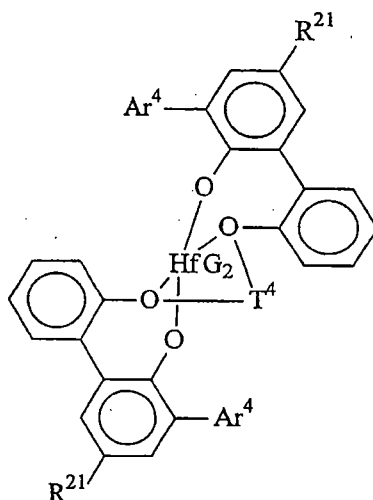
Ar^4 is C_{6-20} aryl or inertly substituted derivatives thereof, especially 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl, and

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:



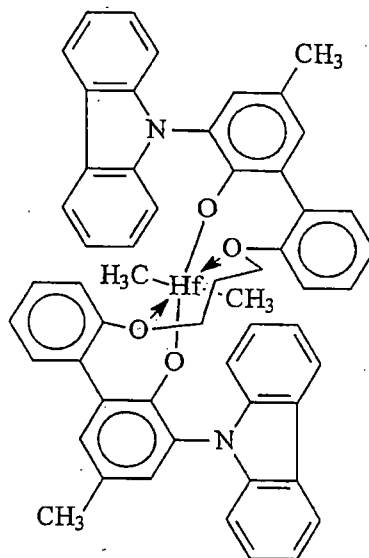
wherein Ar^4 is 3,5-di(isopropyl)phenyl, 3,5-di(isobutyl)phenyl, dibenzo-1H-pyrrole-1-yl, or anthracen-5-yl,

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.

Additional metal complexes are those of the foregoing formula:



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.

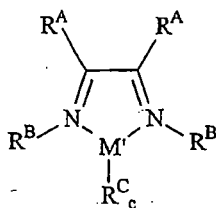
Suitable metal compounds for use as catalyst (B) include the foregoing metal compounds mentioned with respect to catalyst (A) as well as other metal compounds, with the proviso, that they result in formation of at least some hyperbranch- or long chain branch- formation.

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 olefin terminated polymer may be reincorporated into a growing polymer chain, provided that vinyl terminated polymer chains are present, normally as a result of β -hydride elimination, resulting in the formation of long chain branches, that is, branches of a carbon length greater than result from the monomer itself. Long chain branching of olefin polymers is further described in USP's 5,272,236, 5,278,272, and 5,665,800.

Alternatively, and more preferably, branching, including hyper-branching, is induced in a particular segment of the present multi-block copolymers by the use of specific catalysts known to result in "chain-walking" in the resulting polymer. Preferred catalysts are those based on the higher transition metal complexes, especially nickel and palladium diimines.

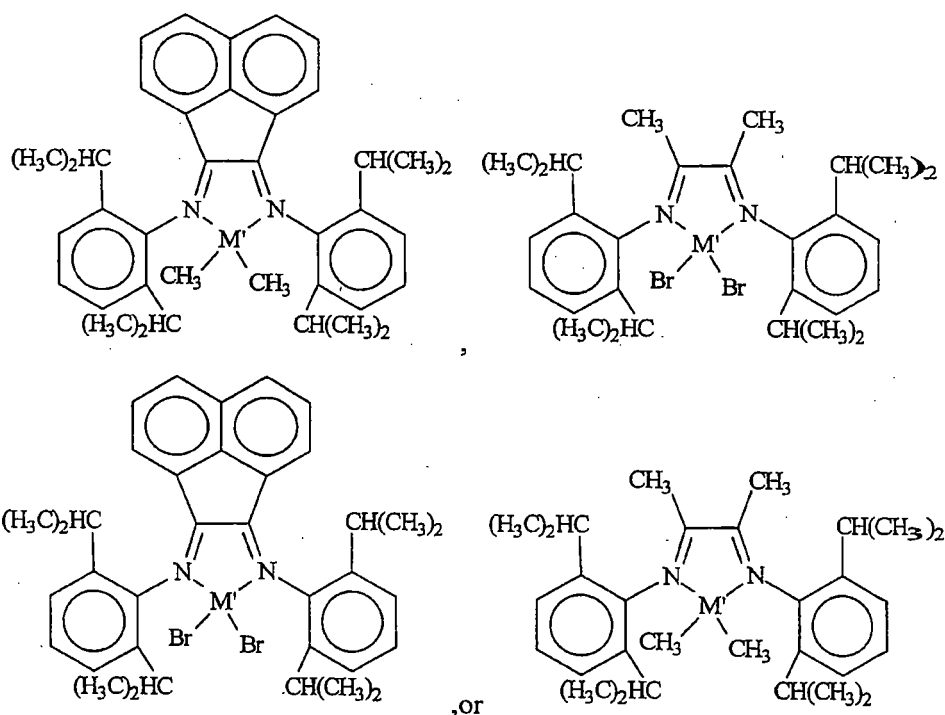
5 In one embodiment of the invention, the presence of such branching (long chain branching, 1,3-addition, or hyper-branching) in the polymers of the invention can be confined to only the blocks or segments resulting from activity of catalyst B. Accordingly, in one embodiment of the invention a multi-block copolymer containing blocks or segments differing in the presence of such branching in combination with other segments or blocks substantially lacking such branching
10 (especially high density or highly crystalline polymer blocks), can be produced from a single monomer containing reaction mixture, that is, without the addition of a deliberately added comonomer. Highly preferably, in a specific embodiment of the invention, a multi-block copolymer comprising alternating unbranched, ethylene homopolymer segments and branched polyethylene segments, especially ethylene/propylene copolymer segments, may be prepared from an initial
15 reaction mixture consisting essentially of ethylene as the addition polymerizable monomer. The presence of such branching in the multi-block copolymers of the invention can be detected by certain physical properties of the resulting copolymers, such as reduced surface imperfections during melt extrusion (reduced melt fracture), reduced melting point, T_g, for the amorphous segments compared to a non-branched polymer segment, and/or the presence of 1,3-addition
20 sequences or hyper-branching as detected by NMR techniques. The quantity of the foregoing types of branching present in the polymers of the invention (as a portion of the blocks or segments containing the same), is normally in the range from 0.01 to 10 branches per 1,000 carbons.

In addition to the previously identified metal complexes for use as catalyst (A), the following metal compounds or inertly coordinated derivatives thereof are especially suited for use
25 as catalyst (B): racemic ethylene bisindenyl complexes of Group 4 metals, especially Zr, and inertly substituted derivatives thereof, such as 1-, or 2- t-butyl dimethylsiloxy- substituted ethylene bis(indenyl) zirconium complexes, as disclosed in Macromolecules 33, 9200-9204 (2000), ethylenebis(4,5,6,7-tetrahydro-1-indenyl) zirconium- complexes, racemic ethylene bis(indenyl)zirconium complexes, and metal complexes of the formula:



where M' is a metal of Groups 4-13, preferably Groups 8-10, most preferably Ni or Pd;
 R^A , R^B and R^C are univalent or neutral substituents, which also may be joined together to
form one or more divalent substituents, and
c is a number chosen to balance the charge of the metal complex.

5 Preferred examples of the foregoing metal complexes for use as catalysts (B) are
compounds corresponding to the formula:



wherein M' is Pd or Ni.

Cocatalysts

Each of the metal complex catalysts (A) and (B) (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. In
15 a preferred embodiment, the shuttling agent is employed both for purposes of chain shuttling and as
the cocatalyst component of the catalyst composition.

The metal complexes desirably are rendered catalytically active by combination with a
cation forming cocatalyst, such as those previously known in the art for use with Group 4 metal
olefin polymerization complexes. Suitable cation forming cocatalysts for use herein include neutral
20 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.

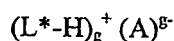
Combinations of neutral Lewis acids, especially the combination of a trialkyl aluminum compound having from 1 to 4 carbons in each alkyl group and a halogenated tri(hydrocarbyl)boron compound having from 1 to 20 carbons in each hydrocarbyl group, especially tris(pentafluorophenyl)borane, further combinations 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
5 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:



10 wherein:

L^* is a neutral Lewis base;

$(L^*-H)^+$ 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.

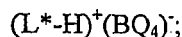
15 More preferably A^{g-} corresponds to the formula: $[M'Q_4]^-$;

wherein:

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

Q independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxy, halosubstituted-hydrocarbyl, halosubstituted hydrocarbyloxy, and
20 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 hydrocarbyloxy 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
25 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:



wherein:

L^* is as previously defined;

30 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 C₁₂₋₄₀ 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
5 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,
10 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,
15 N,N-dimethylanilinium tetrakis(4-(t-butyl)dimethylsilyl)-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,
20 dimethyloctadecylammonium tetrakis(pentafluorophenyl) borate,
methyldioctadecylammonium tetrakis(pentafluorophenyl) borate,
dialkyl ammonium salts such as:

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

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

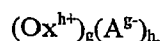
diphenyloxonium tetrakis(pentafluorophenyl) borate,
di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and
di(octadecyl)oxonium tetrakis(pentafluorophenyl) borate;

di-substituted sulfonium salts such as:

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

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



10 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
15 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:

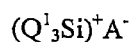


wherein:

$[C]^+$ 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 triphenylmethyl.

25 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:



wherein:

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

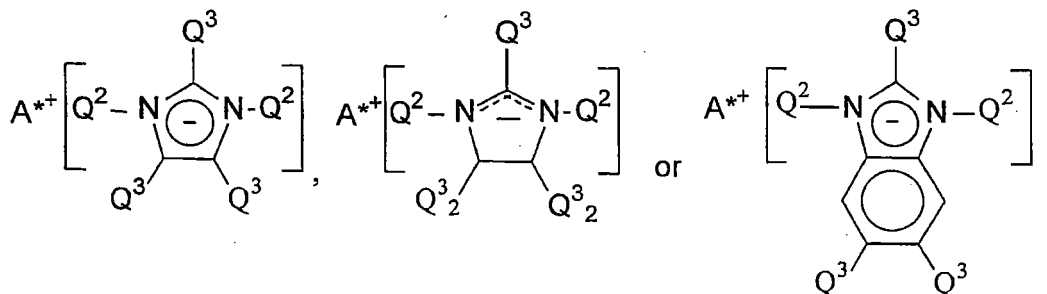
30 Preferred silylium salt activating cocatalysts are trimethylsilylium
tetrakis(pentafluorophenyl)borate, triethylsilylium tetrakis(pentafluorophenyl)borate and ether
substituted adducts thereof. Silylium salts have been previously generically disclosed in J. Chem
Soc. Chem. Comm., 1993, 383-384, as 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,
 5 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,
 10 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,
 15 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,
 20 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.

25 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
 30 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.

The process of the invention employing catalyst A, catalyst B, one or more cocatalysts, and chain shuttling agent C may be further elucidated by reference to Figure 1, where there are illustrated activated catalyst site A, 10, which under polymerization conditions forms a polymer chain, 13, attached to the active catalyst site, 12. Similarly, active catalyst site B, 20, produces a differentiated polymer chain, 23, attached to the active catalyst site, 22. A chain shuttling agent C1, attached to a polymer chain produced by active catalyst B, 14, exchanges its polymer chain, 23, for the polymer chain, 13, attached to catalyst site A. Additional chain growth under polymerization conditions causes formation of a multi-block copolymer, 18, attached to active catalyst site A. Similarly, chain shuttling agent C2, attached to a polymer chain produced by active catalyst site A, 24, exchanges its polymer chain, 13, for the polymer chain, 23, attached to catalyst site B. Additional chain growth under polymerization conditions causes formation of a multi-block copolymer, 28, attached to active catalyst site B. The growing multi-block copolymers are repeatedly exchanged between active catalyst A and active catalyst B by means of shuttling agent C resulting in formation of a block or segment of differing properties whenever exchange to the opposite active catalyst site occurs. The growing polymer chains may be recovered while attached to a chain shuttling agent and functionalized if desired. Alternatively, the resulting polymer may be recovered by scission from the active catalyst site or the shuttling agent, through use of a proton source or other killing agent.

It is believed (without wishing to be bound by such belief), that the composition of the respective segments or blocks, and especially of the end segments of the polymer chains, may be influenced through selection of process conditions or other process variables. In the polymers of the invention, the nature of the end segments is determined by the relative rates of chain transfer or termination for the respective catalysts as well as by the relative rates of chain shuttling. Possible chain termination mechanisms include, but are not limited to, β -hydrogen elimination, β -hydrogen transfer to monomer, β -methyl elimination, and chain transfer to hydrogen or other chain-

terminating reagent such as an organosilane or chain functionalizing agent. Accordingly, when a low concentration of chain shuttling agent is used, the majority of polymer chain ends will be generated in the polymerization reactor by one of the foregoing chain termination mechanisms and the relative rates of chain termination for catalyst (A) and (B) will determine the predominant chain terminating moiety. That is, the catalyst having the fastest rate of chain termination will produce relatively more chain end segments in the finished polymer.

In contrast, when a high concentration of chain shuttling agent is employed, the majority of the polymer chains within the reactor and upon exiting the polymerization zone are attached or bound to the chain shuttling agent. Under these reaction conditions, the relative rates of chain transfer of the polymerization catalysts and the relative rate of chain shuttling of the two catalysts primarily determines the identity of the chain terminating moiety. If catalyst (A) has a faster chain transfer and/or chain shuttling rate than catalyst (B), then the majority of the chain end segments will be those produced by catalyst (A).

At intermediate concentrations of chain shuttling agent, all three of the aforementioned factors are instrumental in determining the identity of the final polymer block. The foregoing methodology may be expanded to the analysis of multi-block polymers having more than two block types and for controlling the average block lengths and block sequences for these polymers. For example, using a mixture of catalysts 1, 2, and 3 with a chain shuttling agent, for which each catalyst type makes a different type of polymer block, produces a linear block copolymer with three different block types. Furthermore, if the ratio of the shuttling rate to the propagation rate for the three catalysts follows the order $1 > 2 > 3$, then the average block length for the three block types will follow the order $3 > 2 > 1$, and there will be fewer instances of 2-type blocks adjacent to 3-type blocks than 1-type blocks adjacent to 2-type blocks.

It follows that a method exists for controlling the block length distribution of the various block types. For example, by selecting catalysts 1, 2, and 3 (wherein 2 and 3 produce substantially the same polymer block type), and a chain shuttling agent, and the shuttling rate follows the order $1 > 2 > 3$, the resulting polymer will have a bimodal distribution of block lengths made from the 2 and 3 catalysts.

During the polymerization, the reaction mixture comprising the monomer to be polymerized is contacted with the activated catalyst composition according to any suitable polymerization conditions. The process is 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 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. The skilled artisan will appreciate that the ratio of chain shuttling agent to one or more catalysts and or monomers in the process of the present invention may be varied in order to produce polymers differing in one or more chemical or physical properties.

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, shuttling agent(s), monomers, and optionally solvent, adjuvants, scavengers, and polymerization aids are continuously supplied to the reaction zone 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.

The catalyst compositions can be advantageously employed in a high pressure, solution, slurry, or gas phase polymerization process. 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 where either the metal complex or the cocatalyst is only poorly soluble is disclosed in US-A-5,783,512. A solution process to prepare the novel polymers of the present invention, especially a continuous solution process is preferably carried out at a temperature between 80°C and 250°C, more preferably between 100°C and 210°C, and most preferably between 110°C and 210°C. 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
5 polymerization are from 30°C, preferably from 60°C up to 115°C, preferably up to 100°C. 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 employing two or more active polymerization
10 catalyst species, allows the use of elevated reactor temperatures which results in the economical production of multi-block or segmented copolymers in high yields and efficiencies. Both homogeneous and plug-flow type reaction conditions may be employed. The latter conditions are preferred where tapering of the block composition is desired.

Both catalyst compositions (A) and (B) may be prepared as a homogeneous composition by
15 addition of the requisite metal 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 the shuttling agent may be combined with the catalyst composition either prior to, simultaneously with, or after combination with the monomers to be polymerized and any additional reaction diluent.

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

Without limiting in any way the scope of the invention, one means for carrying out such a
25 polymerization process is as follows. In a stirred-tank reactor, the monomers to be polymerized are introduced continuously together with any solvent or diluent. The reactor contains a liquid phase composed substantially of monomers together with any solvent or diluent and dissolved polymer. Preferred solvents include C₄₋₁₀ 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.

30 Catalysts (A) and (B) along with cocatalyst and chain shuttling agent are continuously or intermittently introduced in the reactor liquid phase or any recycled portion thereof. The reactor temperature and pressure may be controlled by adjusting the solvent/monomer ratio, the catalyst addition rate, as well as by cooling or heating coils, jackets or both. The polymerization rate is controlled by the rate of catalyst addition. The ethylene content of the polymer product is

determined by the ratio of ethylene to comonomer 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 chain transfer agent, as is well known in the art. Upon exiting the reactor, the effluent is contacted with a catalyst kill agent such as water, steam or an alcohol. The polymer solution is optionally heated, and the polymer product is recovered by flashing off gaseous monomers as well as residual solvent 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 continuous loop reactor with or without a monomer, catalyst or shuttling agent gradient established between differing regions thereof, optionally accompanied by separated addition of catalysts and/or chain transfer agent, and operating under adiabatic or non-adiabatic solution polymerization conditions or combinations of the foregoing reactor conditions. Examples of suitable loop reactors and a variety of suitable operating conditions for use therewith are found in USP's 5,977,251, 6,319,989 and 6,683,149.

Although not as desired, 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 an 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.

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 according to the invention. 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.

Examples of 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 multi-block copolymers 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, for example, the reaction product of a metallated polymer with an oxygen source and then with water to form a hydroxyl terminated polymer. In another embodiment, sufficient air or other quench agent is added to cleave some or all of the shuttling agent-polymer bonds thereby converting

at least a portion of the polymer to a hydroxyl terminated polymer. Additional examples include olefin terminated polymers formed by β -hydride elimination and ethylenic unsaturation in the resulting polymer.

In one embodiment of the invention the multi-block copolymer may be functionalized by maleation (reaction with maleic anhydride or its equivalent), metallation (such as with an alkyl lithium reagent, optionally in the presence of a Lewis base, especially an amine, such as tetramethylethylenediamine). Techniques for functionalization of polymers are well known, and disclosed for example in USP 5,543,458, and elsewhere.

Because a substantial fraction of the polymeric product exiting the reactor is terminated with the chain 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-, ketone-, ester-, nitrile-, 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 polymers, including multi-block copolymers, are readily prepared. Highly desirably, the polymers are interpolymers comprising in polymerized form ethylene, having blocks of segments characterized by the presence of hyper-branching and other segments of highly crystalline polyethylene.

The multi-block copolymers of the invention are believed to be characterized by the presence of differentiated blocks within the polymer chains, having both crystalline and amorphous nature. The presence of such differentiated blocks in the interpolymers of the invention can be identified by unique TREF elution curves as well as ATREFF or other standard analytical techniques.

In the various embodiments of the invention, unless indicated otherwise, the inventive polymers preferably possess a heat of fusion of 130 J/g or less, an ethylene content (that is $-\text{CH}_2-\text{CH}_2$ polymer segments) of at least 50 weight percent, preferably at least 90 percent, a glass transition temperature, T_g , of less than -25°C , more preferably less than -30°C , and/or one and only one T_m .

Additionally, 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 10000 g/mole to 500,000 g/mole, and especially from 10,000 g/mole to 300,000 g/mole. The density of the invented polymers can be from 0.80 to 0.99 g/cm³ and preferably for ethylene containing polymers from 0.85 g/cm³ to 0.97 g/cm³.

Moreover, the present polymers may be prepared using techniques to influence the degree or level of blockiness. That is the amount of branching and length of each polymer block or segment can be altered by controlling the ratio and type of catalysts and shuttling agent as well as the temperature of the polymerization, and other polymerization variables. A surprising benefit of this phenomenon is the discovery that as the degree of blockiness is increased, the optical properties, tear strength, and high temperature recovery properties of the resulting polymer are improved. In particular, haze decreases while clarity, tear strength, and high temperature recovery properties increase as the average number of blocks in the polymer increases. By selecting shuttling agents and catalyst combinations having the desired chain transferring ability (high rates of shuttling with low levels of chain termination) other forms of polymer termination are effectively suppressed. Accordingly, little if any β -hydride elimination is observed in the polymerization according to the invention, and the resulting crystalline blocks are highly, or substantially completely, linear, possessing little or no long chain branching.

Another surprising benefit of the invention is that polymers wherein chain ends are highly crystalline can be selectively prepared. In certain applications, reducing the relative quantity of polymer that terminates with an amorphous block reduces the intermolecular dilutive effect on crystalline regions. This result can be obtained by choosing chain shuttling agents and catalysts having an appropriate response to hydrogen or other chain terminating agents. Specifically, if the catalyst which produces highly crystalline polymer is more susceptible to chain termination (such as by use of hydrogen) than the catalyst responsible for producing the less crystalline polymer segment (such as through chain walking or long chain branched polymer formation), then the highly crystalline polymer segments will preferentially populate the terminal portions of the polymer. Not only are the resulting terminated groups crystalline, but upon termination, the highly crystalline polymer forming catalyst site is once again available for reinitiation of polymer formation. The initially formed polymer is therefore another highly crystalline polymer segment. Accordingly, both ends of the resulting multi-block copolymer are preferentially highly crystalline.

Additional components of the present formulations usefully employed according to the present invention include various other ingredients in amounts that do not detract from the properties of the resultant composition. These ingredients include, but are not limited to, activators

such as calcium or magnesium oxide; fatty acids such as stearic acid and salts thereof; fillers and reinforcers such as calcium or magnesium carbonate, silica, and aluminum silicates; plasticizers such as dialkyl esters of dicarboxylic acids; antidegradants; softeners; waxes; and pigments.

5 Applications and End Uses

 The polymers of the invention can be useful 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
10 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, additives, reinforcing agents, ignition resistant additives, antioxidants, stabilizers, colorants, extenders, crosslinkers, blowing agents, and plasticizers. Of particular utility are multi-component fibers such as core/sheath fibers, having an outer surface layer, comprising at least in
15 part, one or more polymers of the invention.

 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
20 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, calendered 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
25 injection molding, blow molding process, or rotomolding processes. Compositions comprising the polymers of the present invention 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
30 or formulations comprising the same. Frothed foams comprising the invented polymers can also be formed, as disclosed in PCT application No. 2004/027593, filed August 25, 2004. 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.

Additives and adjuvants may be included in any formulation comprising the present polymers. Suitable additives include fillers, such as organic or inorganic particles, including clays, talc, carbon black, titanium dioxide, zeolites, powdered metals, organic or inorganic fibers, including carbon fibers, silicon nitride fibers, steel wire or mesh, and nylon or polyester cording, nano-sized particles, clays, and so forth; tackifiers, oil extenders, including paraffinic or naphthenic oils; and other natural and synthetic polymers, including other polymers according to the invention.

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 polymers.

Suitable end uses for the foregoing products include elastic films and fibers; soft touch goods, such as tooth brush handles and appliance handles; gaskets and profiles; adhesives (including hot melt adhesives and pressure sensitive adhesives); footwear (including shoe soles and shoe liners); auto interior parts and profiles; foam goods (both open and closed cell); impact modifiers for other thermoplastic polymers such as high density polyethylene, isotactic polypropylene, or other olefin polymers; coated fabrics; hoses; tubing; weather stripping; cap liners; flooring; and viscosity index modifiers, also known as pour point modifiers, for lubricants.

In a highly desired embodiment of the invention thermoplastic compositions comprising a thermoplastic matrix polymer, especially isotactic polypropylene, and an elastomeric multi-block copolymer of ethylene and a copolymerizable comonomer according to the invention, are uniquely capable of forming core-shell type particles having hard crystalline or semi-crystalline blocks in the form of a core surrounded by soft or elastomeric blocks forming a "shell" around the occluded

domains of hard polymer. These particles are formed and dispersed within the matrix polymer by the forces incurred during melt compounding or blending. This highly desirable morphology is believed to result due to the unique physical properties of the multi-block copolymers which enable compatible polymer regions such as the matrix and higher comonomer content elastomeric regions of the multi-block copolymer to self-assemble in the melt due to thermodynamic forces. Shearing forces during compounding are believed to produce separated regions of matrix polymer encircled by elastomer. Upon solidifying, these regions become occluded elastomer particles encased in the polymer matrix.

Particularly desirable blends are thermoplastic polyolefin blends (TPO), thermoplastic elastomer blends (TPE), thermoplastic vulcanisites (TPV) and styrenic polymer blends. TPE and TPV blends may be prepared by combining the invented multi-block polymers, including functionalized or unsaturated derivatives thereof with an optional rubber, including conventional block copolymers, especially an SBS block copolymer, and optionally a crosslinking or vulcanizing agent. TPO blends are generally prepared by blending the invented multi-block copolymers with a polyolefin, and optionally a crosslinking or vulcanizing agent. The foregoing blends may be used in forming a molded object, and optionally crosslinking the resulting molded article. A similar procedure using different components has been previously disclosed in USP 6,797,779.

Suitable conventional block copolymers for this application desirably possess a Mooney viscosity (ML 1+4 @ 100°C.) in the range from 10 to 135, more preferably from 25 to 100, and most preferably from 30 to 80. Suitable polyolefins especially include linear or low density polyethylene, polypropylene (including atactic, isotactic, syndiotactic and impact modified versions thereof) and poly(4-methyl-1-pentene). Suitable styrenic polymers include polystyrene, rubber modified polystyrene (HIPS), styrene/acrylonitrile copolymers (SAN), rubber modified SAN (ABS or AES) and styrene maleic anhydride copolymers.

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 multiblock copolymers, this temperature may be above 130° C., most generally above 145° C., and most preferably 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, calenders, and the like. 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. Typically, a TPE or TPV composition will have a higher loading of cross-linkable polymer (typically the conventional block

copolymer containing unsaturation) compared to TPO compositions. Generally, for TPE and TPV compositions, the weight ratio of block copolymer to multi-block copolymer may be from about 90:10 to 10:90, more preferably from 80:20 to 20:80, and most preferably from 75:25 to 25:75. For TPO applications, the weight ratio of multi-block copolymer to polyolefin may be from about 49:51 to about 5:95, more preferably from 35:65 to about 10:90. For modified styrenic polymer applications, the weight ratio of multi-block copolymer to polyolefin may also be from about 49:51 to about 5:95, more preferably from 35:65 to about 10:90. The ratios may be changed by changing the viscosity ratios of the various components. There is considerable literature illustrating techniques for changing the phase continuity by changing the viscosity ratios of the constituents of a blend and a person skilled in this art may consult if necessary.

The blend compositions may contain processing oils, plasticizers, and processing aids. Rubber processing oils have a certain ASTM designations and paraffinic, naphthenic 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 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.

It is known that non-hydrogenated rubbers such as those comprising polymerized forms of butadiene or isoprene, including block copolymers (here-in-after diene rubbers), have lower resistance to UV, ozone, and oxidation, compared to mostly or highly saturated rubbers. In applications such as tires made from compositions containing higher concentrations of diene based rubbers, it is known to incorporate carbon black to improve rubber stability, along with anti-ozone additives and anti-oxidants. Multi-block copolymers according to the present invention possessing extremely low levels of unsaturation, find particular application as a protective surface layer (coated, coextruded or laminated) or weather resistant film adhered to articles formed from conventional diene elastomer modified polymeric compositions.

For conventional TPO, TPV, and TPE applications, carbon black is the additive of choice for UV absorption and stabilizing properties. Representative examples of carbon blacks include ASTM N110, N121, N220, N231, N234, N242, N293, N299, S315, N326, N330, M332, N339, N343, N347, N351, N358, N375, N539, N550, N582, N630, N642, N650, N683, N754, N762, N765, N774, N787, N907, N908, N990 and N991. These carbon blacks have iodine absorptions ranging from 9 to 145 g/kg and average pore volumes ranging from 1.0 to 150 cm³/100 g. Generally,

smaller particle sized carbon blacks are employed, to the extent cost considerations permit. For many such applications the present multi-block copolymers and blends thereof require little or no carbon black, thereby allowing considerable design freedom to include alternative pigments or no pigments at all. Multi-hued tires or tires matching the color of the vehicle are one possibility.

5 Compositions, including thermoplastic blends according to the invention may also contain anti-ozonants or anti-oxidants that are known to a rubber chemist 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
10 di(dimethylbenzyl) phenol, p-phenylenediamines, butylated reaction products of p-cresol and dicyclopentadiene (DCPD), polyphenolic antioxidants, 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
15 antioxidant, Wingstay™ K antioxidant, Wingstay™ 29 antioxidant, Wingstay™ SN-1 antioxidant, and Irganox™ antioxidants. In some applications, the anti-oxidants and anti-ozonants 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™
20 144, 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
25 anti-oxidants, anti-ozonants, carbon black, UV absorbers, and/or light stabilizers to form a masterbatch, and subsequently to form polymer blends there from.

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,
30 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 about 0.5 to about 4, preferably about 0.8 to about 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 about 0.05 to about 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, dithiocarbamate 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 Elastomer", Vol. 74, No 3, July-August 2001.

When the multi-block copolymer containing composition is at least partially crosslinked, the degree of crosslinking may be measured by dissolving the composition in a solvent for specified duration, and calculating the percent gel or unextractable component. 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 multi-block copolymers of the invention as well as blends thereof possess improved processability compared to prior art compositions, due, it is believed, to lower melt viscosity. Thus, the composition or blend demonstrates an improved surface appearance, especially when formed into a molded or extruded article. At the same time, the present compositions and blends thereof uniquely possess improved melt strength properties, thereby allowing the present multi-block copolymers and blends thereof, especially TPO blends, to be usefully employed in foam and thermoforming applications where melt strength is currently inadequate.

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, 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, wollastonite, graphite, zeolites, and ceramics, such as silicon carbide, silicon nitride or titanias. Silane based or other coupling agents may also be employed for better filler bonding.

5 The thermoplastic 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.

10 Testing Methods

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

Standard CRYSTAF Method

15 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.

20 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
25 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. To calculate the CRYSTAF curve, the preferred processing parameters are with a temperature limit of 70°C and with smoothing parameters above the temperature limit of 0.1, and below the temperature limit of 0.3.

30 **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 about 175°C and then air-cooled to room temperature (25°C). 3-10 mg Of material is then cut into a 6 mm diameter

disk, accurately weighed, placed in a light aluminum pan (ca 50 mg), and 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.

10 Abrasion Resistance

Abrasion resistance is measured on compression molded plaques according to ISO 4649. The average value of 3 measurements is reported. Plaques for the test are 6.4 mm thick and 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 minutes, followed by 1.3 MPa for 3 minutes, and then 2.6 MPa for 3 minutes. Next the plaques are cooled in the press with running cold water at 1.3 MPa for 1 minute and removed for testing.

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)): $M_{\text{polyethylene}} = 0.431(M_{\text{polystyrene}})$.

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

5 **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

Samples for density measurement are prepared according to ASTM D 1928. Measurements are made within one hour of sample pressing using ASTM D792, Method B.

15 **Flexural/Secant Modulus/ Storage Modulus**

Samples are compression molded using ASTM D 1928. Flexural and 2 percent secant moduli are measured according to ASTM D-790. Storage modulus is measured according to ASTM D 5026-01 or equivalent technique.

Optical properties

20 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.

25 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.

30 **Mechanical Properties - Tensile, Hysteresis, and Tear**

Stress-strain behavior in uniaxial tension is measured using ASTM D 1708 microtensile specimens. Samples are stretched with an Instron at 500 % 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 using ASTM D 1708 microtensile specimens 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:

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

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:

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

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 (Penetration Temperature) 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 Strength

Pellets (150 g) are loaded into a 2" (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 Index

Melt index, or I_2 , is measured in accordance with ASTM D 1238, Condition 190°C/2.16 kg. Melt index, or I_{10} is also measured in accordance with ASTM D 1238, Condition 190°C/10 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.

Polymer Fractionation by TREF

Large-scale TREF fractionation is carried by dissolving 15-20 g of polymer in 2 liters of 1,2,4-trichlorobenzene (TCB) by stirring for 4 hours at 160°C. The polymer solution is forced by 15 psig (100 kPa) nitrogen onto a 3 inch by 4 foot (7.6 cm x 12 cm) steel column packed with a 60:40 (v:v) mix of 30-40 mesh (600-425 μ m) spherical, technical quality glass beads (available from Potters Industries, HC 30 Box 20, Brownwood, TX, 76801) and stainless steel, 0.028" (0.7mm) diameter cut wire shot (available from Pellets, Inc. 63 Industrial Drive, North Tonawanda, NY, 14120). The column is immersed in a thermally controlled oil jacket, set initially to 160 °C. The column is first cooled ballistically to 125 °C, then slow cooled to 20 °C at 0.04 °C per minute and held for one hour. Fresh TCB is introduced at about 65 ml/min while the temperature is increased at 0.167 °C per minute.

Approximately 2000 ml portions of eluant from the preparative TREF column are collected in a 16 station, heated fraction collector. The polymer is concentrated in each fraction using a rotary evaporator until about 50 to 100 ml of the polymer solution remains. The concentrated solutions are allowed to stand overnight before adding excess methanol, filtering, and rinsing (approx. 300-500 ml of methanol including the final rinse). The filtration step is performed on a 3 position vacuum assisted filtering station using 5.0 μ m polytetrafluoroethylene coated filter paper (available from Osmonics Inc., Cat# Z50WP04750). The filtrated fractions are dried overnight in a vacuum oven at 60 °C and weighed on an analytical balance before further testing.

¹³C NMR Analysis

The samples are prepared by adding approximately 3g of a 50/50 mixture of tetrachloroethane-d₂/orthodichlorobenzene to 0.4 g sample in a 10 mm NMR tube. The samples are dissolved and homogenized by heating the tube and its contents to 150°C. The data is collected using a JEOL Eclipse™ 400MHz spectrometer or a Varian Unity Plus™ 400MHz spectrometer, corresponding to a ¹³C resonance frequency of 100.5 MHz. The data is acquired using 4000 transients per data file with a 6 second pulse repetition delay. To achieve minimum signal-to-noise for quantitative analysis, multiple data files are added together. The spectral width is 25,000 Hz with a minimum file size of 32K data points. The samples are analyzed at 130 °C in a 10 mm broadband probe. The comonomer incorporation is determined using Randall's triad method (Randall, J.C.; JMS-Rev. Macromol. Chem. Phys., C29, 201-317 (1989).

Atomic Force Microscopy (AFM)

Sections are collected from the sample material using a Leica UCT™ microtome with a FC cryo-chamber operated at -80 °C. A diamond knife is used to section all sample material to a thickness of 120 nm. Sections are placed on freshly cleaved mica surfaces, and mounted on
5 standard AFM specimen metal support disks with a double carbon tape. The sections are examined with a DI NanoScope IV™ Multi-Mode AFM, in tapping mode with phase detection. Nano-sensor tips are used in all experiments.

Specific Embodiments

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

1. A composition comprising the admixture or reaction product resulting from combining:
 (A) a first olefin polymerization catalyst,
 (B) a second olefin polymerization catalyst capable of preparing polymers differing in
15 chemical or physical properties from the polymer prepared by catalyst (A) under equivalent polymerization conditions,
 at least one of catalyst (A) or catalyst (B) being capable of forming a branched polymer by means of chain walking or reincorporation of in situ formed olefinic polymer chains, and
 (C) a chain shuttling agent.
- 20 2. A composition comprising the admixture or reaction product resulting from combining:
 (A) a first olefin polymerization catalyst capable of forming a highly crystalline ethylene homopolymers by ethylene polymerization;
 (B) a second olefin polymerization catalyst capable of forming a branched polymer upon
polymerization by means of chain walking or reincorporation of in situ formed olefinic polymer
25 chains, and
 (C) a chain shuttling agent.
3. A process for preparing a high molecular weight, multi-block copolymer comprising contacting ethylene under addition polymerization conditions with a composition comprising:
the admixture or reaction product resulting from combining:
30 (A) a first olefin polymerization catalyst,
 (B) a second olefin polymerization catalyst capable of preparing polymers differing in chemical or physical properties from the polymer prepared by catalyst (A) under equivalent polymerization conditions,

at least one of catalyst (A) or catalyst (B) being capable of forming a branched polymer by means of chain walking or reincorporation of in situ formed olefinic polymer chains, and

(C) a chain shuttling agent.

4. A process for preparing a high molecular weight, multi-block copolymer comprising
5 contacting ethylene under addition polymerization conditions with a composition comprising:
the admixture or reaction product resulting from combining:

(A) a first olefin polymerization catalyst capable of forming a highly crystalline ethylene homopolymer by ethylene polymerization;

- (B) a second olefin polymerization catalyst capable of forming a branched polymer upon
10 polymerization by means of chain walking or reincorporation of in situ formed olefinic polymer chains, and

(C) a chain shuttling agent.

5. A multi-block copolymer formed from a reaction mixture consisting essentially of
ethylene as the addition polymerizable monomer, said copolymer containing therein two or more,
15 preferably three or more segments or blocks differing in branching index, said copolymer
possessing a molecular weight distribution, M_w/M_n , of less than 3.0, more preferably less than 2.8.

6. A multi-block copolymer formed from a reaction mixture consisting essentially of
ethylene as the addition polymerizable monomer, said copolymer containing therein two or more,
preferably three or more segments or blocks differing in branching index.

- 20 7. A multi-block copolymer according to embodiment 6 possessing a molecular weight
distribution, M_w/M_n , of less than 3.0, more preferably less than 2.8.

8. A functionalized derivative of the multi-block copolymer of any one of embodiments 5-
7.

9. A crosslinked derivative of a polymer according to any one of embodiments 5-7.

- 25 10. A crosslinked derivative of a polymer according to embodiment 8.

11. A polymer according to any one of embodiments 5-7, or preparable by the method of
embodiment 3 or 4, or a composition comprising the same in the form of a film, at least one layer of
a multilayer film, at least one layer of a laminated article, a foamed article, a fiber, a nonwoven
fabric, an injection molded article, a blow molded article, a roto-molded article, or an adhesive.

- 30 12. A polymer according to embodiment 8 or a composition comprising the same in the
form of a film, at least one layer of a multilayer film, at least one layer of a laminated article, a
foamed article, a fiber, a nonwoven fabric, an injection molded article, a blow molded article, a
roto-molded article, or an adhesive.

13. A polymer according to embodiment 9 or a composition comprising the same in the form of a film, at least one layer of a multilayer film, at least one layer of a laminated article, a foamed article, a fiber, a nonwoven fabric, an injection molded article, a blow molded article, a roto-molded article, or an adhesive.

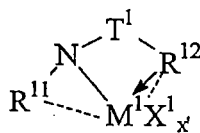
14. A polymer according to embodiment 10 or a composition comprising the same in the form of a film, at least one layer of a multilayer film, at least one layer of a laminated article, a foamed article, a fiber, a nonwoven fabric, an injection molded article, a blow molded article, a roto-molded article, or an adhesive.

15. A composition according to embodiment 1 or 2 wherein the shuttling agent is a trihydrocarbyl aluminum- or dihydrocarbyl zinc- compound containing from 1 to 12 carbons in each hydrocarbyl group.

16. A composition according to embodiment 15 wherein the shuttling agent is triethylaluminum or diethylzinc.

17. A composition according to embodiment 1 or 2 wherein catalyst (A) comprises a complex comprising a transition metal selected from Groups 4-8 of the Periodic Table of the Elements and one or more delocalized, π -bonded ligands or polyvalent Lewis base ligands.

18. A composition according to embodiment 17 wherein catalyst (A) corresponds 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;

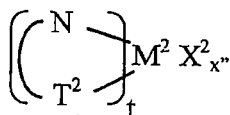
M^1 is a Group 4 metal, preferably hafnium;

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.

19. A composition according to embodiment 18 wherein catalyst (B) corresponds 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.

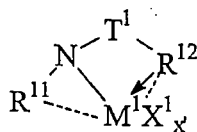
20. A process according to embodiment 3 or 4 which is a continuous process.

21. A process according to embodiment 20 which is a solution process.

22. A process according to embodiment 21 wherein ethylene conversion in the reactor is at least 92 percent.

22. A process according to embodiment 22 wherein the ethylene conversion in the reactor is at least 95 percent.

23. A process according to embodiment 20 wherein catalyst (A) corresponds to the formula:



wherein:

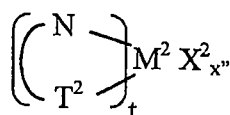
R^{11} is selected from alkyl, cycloalkyl, heteroalkyl, cycloheteroalkyl, aryl, and inertly substituted derivatives thereof containing from 1 to 30 atoms not counting hydrogen or a divalent derivative thereof;

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^1 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
 5 lines and arrows respectively.

24. A process according to embodiment 23 wherein catalyst (B) corresponds 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.

25. A process according to embodiment 3 or 4 in which the ratio of chain shuttling agent to one or more catalysts and or monomers is varied in order to produce polymers differing in one or more chemical or physical properties.

26. A polymer mixture comprising: (1) an organic or inorganic polymer, preferably a homopolymer of ethylene or propylene and/or a copolymer of ethylene and a copolymerizable comonomer, and (2) a polymer according to any one of embodiments 5-7, or preparable by the method of embodiment 3 or 4.

27. A polymer mixture according to embodiment 26 wherein component (1) is an organic thermoplastic polymer.

28. A polymer mixture according to embodiment 27 wherein component (1) is an ethylene or propylene homopolymers or a copolymer of ethylene and a C_{3-8} α -olefin.

29. A polymer mixture according to embodiment 27 wherein component (2) is an elastomeric ethylene polymer.

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

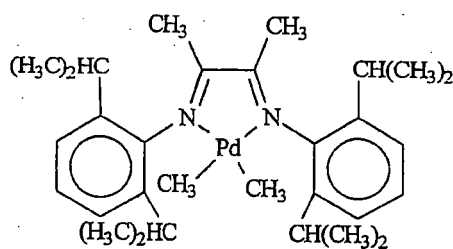
Examples

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 C₆₋₉ 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 bis(indenyl)zirconium dimethyl.

Catalyst (B1) is:



prepared according to the teachings of Macromolecular Chemistry and Physics, (2004), 205, 897-906.

Cocatalyst 1 A mixture of methyldi(C₁₄₋₁₈ 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(C₆F₅)₄], substantially as disclosed in USP 5,919,9883, Ex. 2.

Shuttling Agents The shuttling agents employed are diethylzinc (DEZ) and, trioctylaluminum (TOA)

25 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. Polymerizations are conducted at 120°C using 1.2 equivalents of cocatalyst 1 based on total catalyst used. The 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 μ L. Each cell is temperature and pressure controlled with stirring provided by individual stirring paddles. The monomer gas and quench gas 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, cocatalyst, shuttling agent, and catalyst. After quenching with CO, 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.

Example 1

A 6-mL reaction vessel containing a glass vial insert is charged with mixed alkanes (3.295 mL), and then pressurized to 200 psi (1.4 MPa) with ethylene. Cocatalyst 1 (1.23 mM in toluene, 0.205 mL, 2.52 μ mol) and DEZ (2.5 mM in toluene, 0.200 mL, 0.5 μ mol) are sequentially added via syringe. A mixture of catalyst A1 (1.0 mM in toluene, 0.10 mL, 100 nmol) and B1 (10 mM in toluene, 0.20 mL, 2.0 μ mol) is added via syringe. After 1200 seconds, the reaction is quenched by addition of CO. The glass insert is removed and volatile components removed under vacuum. GPC analysis shows PDI < 2.0.

Example 2

A 6-mL reaction vessel containing a glass vial insert is charged with mixed alkanes (3.296 mL), and then pressurized to 200 psi (1.4 MPa) with ethylene. Cocatalyst 1 (1.23 mM in toluene, 0.205 mL, 2.52 μ mol) and TOA (2.5 mM in toluene, 0.200 mL, 0.5 μ mol) are sequentially added via syringe. A mixture of catalyst A1 (1.0 mM in toluene, 0.10 mL, 100 nmol) and B1 (10 mM in toluene, 0.20 mL, 2.0 μ mol) is added via syringe. After 1200 seconds, the reaction is quenched by addition of CO. The glass insert is removed and volatile components removed under vacuum. GPC analysis shows PDI < 2.0.

Comparative A

A 6-mL reaction vessel containing a glass vial insert is charged with mixed alkanes (3.292 mL), and then pressurized to 200 psi (1.4 MPa) with ethylene. Cocatalyst 1 (1.23 mM in toluene, 0.205 mL, 2.52 mmol) and MMAO (50 mM in toluene, 0.210 mL, 10.5 mmol) are sequentially

added via syringe. A mixture of catalysts A1 (1.0 mM in toluene, 0.10 mL, 100 nmol) and B1 (10 mM in toluene, 0.20 mL, 2.0 mmol) is added via syringe. After 1200 seconds, the reaction is quenched by addition of CO. The glass insert is removed and volatile components removed under vacuum. GPC analysis shows PDI > 2.0.

Examples 1-2 demonstrate the synthesis of linear block copolymers by the present invention as evidenced by the formation of a very narrow MWD, essentially monomodal copolymer when DEZ or TOA is present and a bimodal, broad molecular weight distribution product (a mixture of linear and branched polyethylene polymers) in the absence of a chain shuttling agent (comparative A). Due to the fact that Catalyst (A1) produces polymer chains with different branching characteristics than Catalyst (B1), the different blocks or segments of the resulting multi-block copolymers are distinguishable based on branching frequency.

Continuous Solution Polymerization

Continuous solution polymerizations are carried out in a computer controlled autoclave reactor equipped with an internal stirrer. Purified mixed alkanes solvent (Isopar™ E available from ExxonMobil, Inc.), ethylene, and hydrogen (where used) are supplied to a 3.8 L reactor equipped with a jacket for temperature control and an internal thermocouple. The solvent feed to the reactor is measured by a mass-flow controller. A variable speed diaphragm pump controls the solvent flow rate and pressure to the reactor. At the discharge of the pump, a side stream is taken to provide flush flows for the catalyst and cocatalyst 1 injection lines and the reactor agitator. These flows are measured by Micro-Motion mass flow meters and controlled by control valves or by the manual adjustment of needle valves. The remaining solvent is combined with ethylene and hydrogen (where used) and fed to the reactor. A mass flow controller is used to deliver hydrogen to the reactor as needed. The temperature of the solvent/monomer solution is controlled by use of a heat exchanger before entering the reactor. Temperature of the reactor is maintained at the desired temperature, typically between 70 – 170 °C. This stream enters the bottom of the reactor. The catalyst component solutions are metered using pumps and mass flow meters and are combined with the catalyst flush solvent and introduced into the bottom of the reactor. The reactor is run liquid-full at 500 psig (3.45 MPa) with vigorous stirring. Product is removed through exit lines at the top of the reactor. All exit lines from the reactor are steam traced and insulated. Polymerization is stopped by the addition of a small amount of water into the exit line along with any stabilizers or other additives and passing the mixture through a static mixer. The product stream is then heated

by passing through a heat exchanger before devolatilization. The polymer product is recovered by extrusion using a devolatilizing extruder and water cooled pelletizer.

5 The reactor temperature and monomer concentration are used to control the composition or density of the polymer segment or block produced by each catalyst, enabling production of polymer segments or blocks from the two catalysts that are distinguishable based on branching or density. Suitable blocks comprising linear polyethylene and branched polyethylene can be produced by achieving the correct ethylene concentration, catalyst ratios, and amount of chain shuttling agent (DEZ) added. Monomer conversion is regulated at the desired level by adjusting the feeds of the catalysts. The overall composition of the polymer, meaning the amount of linear and branched
10 polyethylene, is controlled by modifying either the catalyst feed ratio or the reactor temperature or monomer concentration. Hydrogen and/or DEZ is used to control molecular weight of the polymer. When hydrogen alone is used for control of molecular weight, the product can display bimodal molecular weight and composition distributions. This copolymer blend can be separated by techniques commonly used by those skilled in the art. Conversely, when DEZ is used for molecular
15 weight control, the copolymer displays narrow molecular weight and composition distributions consistent with a multi-block polymer.

The inventive polymer samples from the above continuous solution polymerization procedure can display several enhanced characteristics relative to comparative examples or linear or branched ethylene polymers. For example, high temperature resistance properties, as evidenced by
20 TMA temperature testing, pellet blocking strength, high temperature recovery, high temperature compression set and storage modulus ratio, $G'(25^{\circ}\text{C})/G'(100^{\circ}\text{C})$, can all be achieved. At a given composition, the inventive copolymers can also display a high melting temperature, T_m , and a low glass transition temperature, T_g , with $T_m \geq 135^{\circ}\text{C}$, and $T_g \leq -40^{\circ}\text{C}$.

CLAIMS:

1. A composition comprising the admixture or reaction product resulting from combining:
 - (A) a first olefin polymerization catalyst,
 - (B) a second olefin polymerization catalyst capable of preparing polymers differing in
5 chemical or physical properties from the polymer prepared by catalyst (A) under equivalent polymerization conditions,
at least one of catalyst (A) or catalyst (B) being capable of forming a branched polymer by means of chain walking or reincorporation of in situ formed olefinic polymer chains, and
(C) a chain shuttling agent.
- 10 2. A composition comprising the admixture or reaction product resulting from combining:
 - (A) a first olefin polymerization catalyst capable of forming a highly crystalline ethylene homopolymers by ethylene polymerization;
 - (B) a second olefin polymerization catalyst capable of forming a branched polymer upon
polymerization by means of chain walking or reincorporation of in situ formed olefinic polymer
15 chains, and
(C) a chain shuttling agent.
- 20 3. A process for preparing a high molecular weight, multi-block copolymer comprising contacting ethylene under addition polymerization conditions with a composition comprising:
the admixture or reaction product resulting from combining:
 - (A) a first olefin polymerization catalyst,
 - (B) a second olefin polymerization catalyst capable of preparing polymers differing in
chemical or physical properties from the polymer prepared by catalyst (A) under equivalent
polymerization conditions,
at least one of catalyst (A) or catalyst (B) being capable of forming a branched polymer by
25 means of chain walking or reincorporation of in situ formed olefinic polymer chains, and
(C) a chain shuttling agent.
- 30 4. A process for preparing a high molecular weight, multi-block copolymer comprising contacting ethylene under addition polymerization conditions with a composition comprising:
the admixture or reaction product resulting from combining:
 - (A) a first olefin polymerization catalyst capable of forming a highly crystalline ethylene
homopolymer by ethylene polymerization;
 - (B) a second olefin polymerization catalyst capable of forming a branched polymer upon
polymerization by means of chain walking or reincorporation of in situ formed olefinic polymer
chains, and
35 (C) a chain shuttling agent.

5. A multi-block copolymer formed from a reaction mixture consisting essentially of ethylene as the addition polymerizable monomer, said copolymer containing therein two or more segments or blocks differing in branching index, said copolymer possessing a molecular weight distribution, M_w/M_n , of less than 3.0.

5 6. A multi-block copolymer formed from a reaction mixture consisting essentially of ethylene as the addition polymerizable monomer, said copolymer containing therein two or more segments or blocks differing in branching index.

7. A multi-block copolymer according to claim 6 possessing a molecular weight distribution, M_w/M_n , of less than 3.0.

10 8. A functionalized derivative of the multi-block copolymer of any one of claims 5-7.

9. A crosslinked derivative of a polymer according to any one of claims 5-7.

10. A crosslinked derivative of a polymer according to claim 8.

11. A polymer according to any one of claims 5-7, or preparable by the method of claim 3 or 4, or a composition comprising the same in the form of a film, at least one layer of a multilayer film, at least one layer of a laminated article, a foamed article, a fiber, a nonwoven fabric, an injection molded article, a blow molded article, a roto-molded article, or an adhesive.

12. A polymer according to claim 8 or a composition comprising the same in the form of a film, at least one layer of a multilayer film, at least one layer of a laminated article, a foamed article, a fiber, a nonwoven fabric, an injection molded article, a blow molded article, a roto-molded article, or an adhesive.

13. A polymer according to claim 9 or a composition comprising the same in the form of a film, at least one layer of a multilayer film, at least one layer of a laminated article, a foamed article, a fiber, a nonwoven fabric, an injection molded article, a blow molded article, a roto-molded article, or an adhesive.

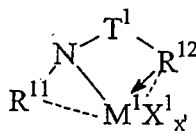
14. A polymer according to claim 10 or a composition comprising the same in the form of a film, at least one layer of a multilayer film, at least one layer of a laminated article, a foamed article, a fiber, a nonwoven fabric, an injection molded article, a blow molded article, a roto-molded article, or an adhesive.

15. A composition according to claim 1 or 2 wherein the shuttling agent is a trihydrocarbyl aluminum- or dihydrocarbyl zinc- compound containing from 1 to 12 carbons in each hydrocarbyl group.

16. A composition according to claim 15 wherein the shuttling agent is triethylaluminum or diethylzinc.

17. A composition according to claim 1 or 2 wherein catalyst (A) comprises a complex comprising a transition metal selected from Groups 4-8 of the Periodic Table of the Elements and one or more delocalized, π -bonded ligands or polyvalent Lewis base ligands.

18. A composition according to claim 17 wherein catalyst (A) corresponds 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; and

R^{12} is a C_{5-20} heteroaryl group containing Lewis base functionality;

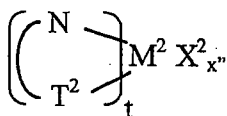
M^1 is a Group 4 metal;

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.

19. A composition according to claim 18 wherein catalyst (B) corresponds 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.

20. A process according to claim 3 or 4 which is a continuous process.

21. A process according to claim 20 which is a solution process.

22. A process according to claim 21 wherein ethylene conversion in the reactor is at least 92 percent.

22. A process according to claim 22 wherein the ethylene conversion in the reactor is at least 95 percent.

23. A process according to claim 20 wherein catalyst (A) corresponds to the formula:



wherein:

- 5 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; 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;

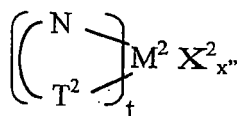
- 10 M^1 is a Group 4 metal;

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.

- 15 24. A process according to claim 23 wherein catalyst (B) corresponds 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;

- 20 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.

- 25 25. A process according to claim 3 or 4 in which the ratio of chain shuttling agent to one or more catalysts and or monomers is varied in order to produce polymers differing in one or more chemical or physical properties.

26. A polymer mixture comprising: (1) an organic or inorganic polymer, and (2) a polymer according to any one of claims 5-7, or preparable by the method of claim 3 or 4.

- 30 27. A polymer mixture according to claim 26 wherein component (1) is an organic thermoplastic polymer.

28. A polymer mixture according to claim 27 wherein component (1) is an ethylene or propylene homopolymers or a copolymer of ethylene and a C₃₋₈ α -olefin.

29. A polymer mixture according to claim 27 wherein component (2) is an elastomeric ethylene polymer.