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(54) POLYMERIZATION CATALYST SYSTEMS COMPRISING SUBSTITUTED HAFNOCENES

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See application file for complete search history.

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(57) ABSTRACT

The present invention relates to a process for the polymerization of monomers utilizing a bulky ligand hafnium transition metal metallocene-type catalyst compound, to the catalyst compound itself and to the catalyst compound in combination with an activator. The hafnocene comprises at least one cyclopentadienyl ligand including at least one linear or isoalkyl substituent of at least 3 carbon atoms.

23 Claims, No Drawings

POLYMERIZATION CATALYST SYSTEMS COMPRISING SUBSTITUTED HAFNOCENES

Matter enclosed in heavy brackets [ ] appears in the original patent but forms no part of this reissue specification; matter printed in italics indicates the additions made by reissue.

FIELD OF THE INVENTION

This invention relates to catalysts, catalyst systems and their use in olefin polymerization. The invention more particularly relates to substituted hafnium metallocene-type catalyst compounds, catalyst systems thereof and their use in a polymerizing process.

BACKGROUND OF THE INVENTION

The use of bulky ligand transition metal catalyst compounds in polymerization processes to produce a diverse array of new polymers for use in a wide variety of applications and products is well known in the art. Typical bulky ligand transition metal compounds, known as metallocene-type compounds, are generally described as containing one or more ligands capable of η-5 bonding to the transition metal atom, usually, cyclopentadienyl derived ligands or moieties, in combination with a transition metal selected from Group 4, 5 or 6 or from the lanthanide and actinide series of the Periodic Table of Elements. Predomiantly in the literature the transition metal is from Group 4, particularly either titanium, zirconium or hafnium, and the cyclopentadienyl derived ligand or moiety is substituted with various radicals, typically alkyl radicals, or two or more cyclopentadienyl ligands are joined by a structural bridge, usually an organic or inorganic group, typically, a carbon or silicon atom containing group.

Other forms of these metallocene-type catalyst compounds contain a cyclopentadienyl derived ligand or moiety and a heteroatom containing group bonded to a transition metal, typically titanium, where the cyclopentadienyl ligand or moiety and the heteroatom containing group are joined by a structural bridge, usually a silicon atom containing group. These and other metallocene-type catalyst compounds in combination with an activator form metallocene-type catalyst systems capable of polymeriig various olefin(s), alone or in combination with other olefin(s). Exemplary of the development of these and other metallocene-type catalyst compounds and catalyst systems are described in U.S. Pat. Nos. 5,017,714, 5,055,438, 5,096,867, 5,198,401, 5,229,478, 5,264,405, 5,278,119, 5,324,800, 5,384,299, 5,408,017, 5,491,207 and 5,621,126 all of which are herein fully incorporated by reference.

It is well known in the art, although not fully understood, that where the transition metal of these metallocene-type catalyst compounds is hafnium, often referred to as a "hafnocene", hafnocene catalyst systems generally, among other characteristics, perform relatively poorly in comparison to their titanium, especially their zirconium equivalents, often referred to as "zirconocenes". Although hafnocenes will typically polymerize polymers having higher molecular weights than their zirconocene equivalents under similar polymerization conditions, their overall poor activity make them inferior polymerization catalysts. For example, European patent EP 0 284 707 B1 granted Aug. 30, 1995, which is fully incorporated herein by reference, describes a process for polymerizing olefins using a catalyst system, in liquid form containing a chiral, sterorigid bridged hafnium metallocene catalyst compound and an aluminum compound.

Thus, it would be highly advantageous to have a hafnium metallocene-type catalyst system capable of polymerizing olefin(s) with improved catalyst performance.

SUMMARY OF THE INVENTION

This invention relates to a substituted bulky ligand hafnium transition metal metallocene-type catalyst compound and a catalyst system thereof. The invention also relates to a polymerization process for polymerizing one or more olefin(s) utilizing the substituted bulky ligand hafnium transition metal metallocene-type catalyst compound.

In one embodiment, the invention provides for a catalyst system of a bulky ligand hafnium metallocene-type compound where at least one bulky ligand is substituted with a substituent having at least 3 or more non-hydrogen atoms, and an activator. Preferably, the bulky ligand is substituted with a substituent having at least 3 or more carbon atoms or silicon atoms or combinations thereof. In a preferred embodiment, the invention provides for an activated catalyst system of a bully ligand hafnium metallocenetype catalyst complex where the bulky ligand is capable of η-5 bonding to the hafnium transition metal and is substituted with an alkyl substituent having 3 or more carbon atoms, preferably where the alkyl substituent has 3 to 5 carbon atoms, more preferably the alkyl substituent is a linear alky. In one preferred embodiment, the alkyl substituent is at least one n-butyl group, most preferably at least one n-propyl group, substituted to at least one of the bulky ligands.

In yet another embodiment, the invention is directed to a process for polymerizing, preferably in a continuous process, one or more monomer(s) in the presence of the catalyst system or activated catalyst complex described above.

In one preferred embodiment, the above process of the invention is a continuous slurry or gas phase polymerization process.

In another embodiment, the invention is directed to a polymer product produced using the hafnocene catalyst systems or complexes described above, wherein the polymer product contains less than 2 ppm hafnium, preferably less than 1 ppm hafnium.

DETAILED DESCRIPTION OF THE INVENTION

Introduction

The invention is directed toward a hafnium transition metal metallocene-type catalyst system for polymerizing one or more olefin(s). It has been surprisingly discovered that by properly substituting the cyclopentadienyl derived ligand or moiety of a hafiocene results in an improved catalyst system. Unexpectedly where the substituent on the bulky ligand or moiety is a substituent having 3 or more non-hydrogen atoms, preferably 3 or more carbon atoms, preferably an alkyl substituent, for example n-propyl or n-butyl, the catalyst activity of the hafnocene metallocene-type catalyst system is substantially improved. Along with a sufficiently commercially acceptable activity, the hafnocene catalyst systems of the invention produces polymers having higher molecular weights in comparison to its zirconocene equivalents at the same or similar polymerization conditions. It was surprising that the substituted hafnocene of the invention will tend to produce lower density polymer products than its zirconocene equivalent at substantially the same molecular weight.

Catalyst Components and Catalyst Systems

Preferred metallocene catalysts of the invention, for example, are typically those bulky ligand transition metal complexes described by formula (I):

$$\{[(L^{p})_{m}M(A^{q})_{n}]^{+k}\}_{h}[B'^{-j}]_{i}$$

where L is a substituted bulky ligand bonded to M, p is the anionic charge of L and m is the number of L ligands and m is 1, 2 or 3; at least one L is substituted with at least one substituent having 3 or more non-hydrogen atoms, preferably having 3 or more carbon atoms or silicon atoms or combination thereof; A is a ligand bonded to M and capable of inserting an olefin between the M—A bond, q is the anionic charge of A and n is the number of A ligands and n is 1, 2, 3 or 4, M is the transition metal hafnium (Hf), and $(p\times m)+(q\times n)+k$ corresponds to the formal oxidation state of the metal center, where k is the charge on the cation and k is 1, 2, 3 or 4, and B' is a chemically stable, non-nucleophillic anionic complex, preferably having a molecular diameter of 4 Å or greater and j is the anionic charge on B', h is the number of cations of charge k, and i the number of anions of charge j such that $h\times k=j\times i$.

Any two L and/or A ligands may be bridged to each other and/or unbridged. The catalyst compound may be fit-sandwich compounds having two or more ligands L, which include cyclopentadienyl derived ligands or substituted cyclopentadienyl derived ligands, or half-sandwich compounds having one ligand L, which is a cyclopentadienyl derived ligand or heteroatom substituted cyclopentadienyl derived ligand or hydrocarbyl substituted cyclopentadienyl derived ligand or moiety such as an indenyl ligand, a benzindenyl ligand or a fluorenyl ligand and the like including hydrogenated versions thereof or any other ligand capable of η-5 bonding to the transition metal atom. One or more of these bulky ligands is π-bonded to the transition metal atom. At least one L is substituted with at least one substituent having 3 or more non-hydrogen atoms, preferably having 3 or more carbon atoms or 3 or more non-hydrogen atoms of which at least one is a silicon atom, in addition, L can be substituted with a combination of additional substituents, which can be the same or different. Non-limiting examples of non-hydrogen atoms include silicon, germanium, tin, oxygen, nitrogen or carbon and combinations thereof. Non-limiting examples of additional substituents include hydrogen or a linear, branched or cyclic alkyl, alkenyl or aryl radical or combination thereof having from 1 to 30 carbon atoms. The at least one substituent or the additional substituents can also be substituted with hydrogen or a linear, branched or cyclic alkyl, alkenyl or aryl radical having from 1 to 30 carbon atoms or non-hydrogen atoms. L may also be other types of bulky ligands including but not limited to bulky amides, phosphides, alkoxides, aryloxides, imides, carbolides, borollides, porphyrins, phthalocyanines, corrins and other polyazomacrocycles. Other ligands may be bonded to the hafnium transition metal, such as a leaving group, such as but not limited to weak bases such amines, phosphines, ether and the like. In addition to the transition metal, these ligands may be optionally bonded to A or L. Non-limiting examples of catalyst components and catalyst systems are discussed in for example, U.S. Pat. Nos. 4,530,914, 4,871,705, 4,937,299, 5,124,418, 5,017,714, 5,120,867, 5,210,352, 5,278,264, 5,278,119, 5,304,614, 5,324,800, 5,347,025, 5,350,723, 5,391,790, 5,391,789, 5,399,636, 5,539,124, 5,455,366, 5,534,473, 5,684,098 and 5,693,730 all of which are herein fully incorporated by reference. Also, the disclosures of European publications EP-A-0 591 756, EP-A-0 520 732, EP-A-0 420 436, EP-B1 0 485 822, EP-B1 0 485 823 and EP-A2-0 743 324 and PCT publications WO 91/04257, WO 92/00333, WO 93/08221, WO 93/08199, WO 94/01471, WO 96/20233, WO 97/15582 and WO 97/19959 are all herein fully incorporated by reference.

In one embodiment, the activated catalyst of the invention is formed from a hafnocene catalyst compound represented by the general formula (II):

$$(L^p)_mM(A^q)_n(E^r)_o$$

where L is a bulky ligand substituted with at least one substituent having 3 or more non-hydrogen atoms, preferably 3 or more carbon atoms, preferably an alkyl substituent having 3 or more carbon atoms, even more preferably a linear allyl substituent having 3 or more carbon atoms, M is Hf, A, and p, m, q and n are as defined above and E is an anionic leaving group such as but not limited to hydrocarbyl, hydride, halide or combination thereof or any other anionic ligands; r is the anionic charge of E and o is the number of E ligands and o is 1, 2, 3 or 4 such that $(p\times m)+(q\times n)+(r\times o)$ is equal to the formal oxidation state of the metal center; and an alnum alkyl, alumoxane, modified alumoxane or any other oxy-containing organometallic compound or non-coordinating ionic activators, or a combination thereof.

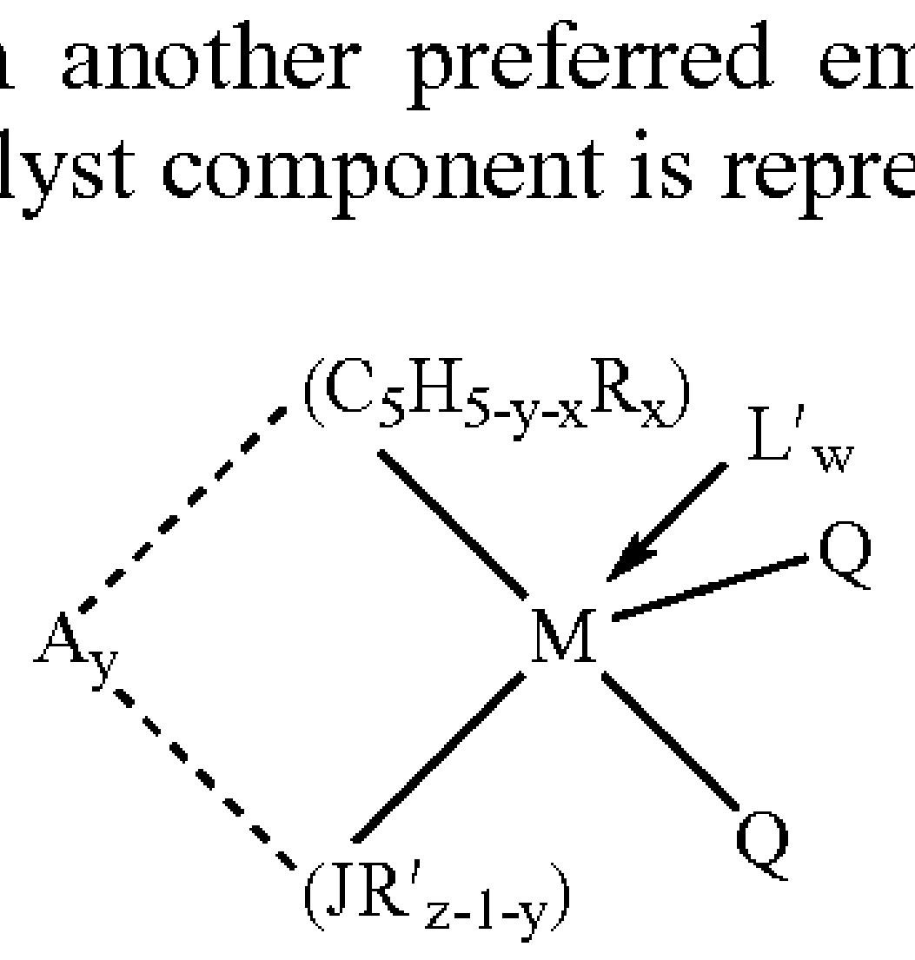
In one embodiment of the invention the substituted hafnocene catalyst compound of the invention includes monocyclopentadienyl heteroatom containing hafnium transition metal metallocene-type compounds. This metallocene-type compound is activated by either an alumoxane, modified alumoxane, a non-coordinating ionic activator, a Lewis acid or a combination thereof to form an active polymerization catalyst system. These types of catalyst systems are described in, for example, PCT publication WO 92/00333, WO 94/07928, WO 91/04257, WO 94/03506, WO 96/00244 and WO 97/15602 and U.S. Pat. Nos. 5,057,475, 5,096,867, 5,055,438, 5,198,401, 5,227,440 and 5,264,405 and European publication EP-A-0 420 436, all of which are herein fully incorporated by reference. Additionally it is within the scope of this invention that the metallocene catalysts and catalyst systems may be those described in U.S. Pat. Nos. 5,064,802, 5,145,819, 5,149,819, 5,243,001, 5,239,022, 5,276,208, 5,296,434, 5,321,106, 5,329,031, 5,304,614 and 5,677,401, and PCT publications WO 93/08221, WO 93/08199 and WO 95/07140 and European publications EP-A-0 578 838 and EP-A-0 638 595 all of which are herein fully incorporated by reference.

In another embodiment, the catalyst component is represented by the formula (III):

$$(C_5H_{5-d-f}R''_d)_eR'''_fMQ_{g-e}$$

wherein M is a Hf transition metal, $(C_5H_{5-d-f}R''_d)$ is an unsubstituted or substituted cyclopentadienyl ligand bonded to M, wherein at least one $(C_5H_{5-d-f}R''_d)$ has at least one R" that is an alkyl substituent having 3 or more carbon atoms, each additional R", which can be the same or different is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R"' is one or more or a combination of carbon, germanium, silicon, phosphorous or nitrogen atoms containing radical bridging two $(C_5H_{5-d-f}R''_d)$ rings, or bridging one $(C_5H_{5-d-f}R''_d)$ ring to M; each Q which can be the same or different is a hydride, substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides or any other univalent anionic ligand or combination thereof, also, two Q's together form an allylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand, where g is an integer corresponding to the formal oxidation state of M, d is 0, 1, 2, 3, 4 or 5, f is 0or 1 and e is 1,2 or 3.

In another preferred embodiment of this invention the catalyst component is represented by the formula (IV):



wherein M is Hf; $(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring which is substituted with from at least one to 5 substituent groups R, "x" is 1, 2, 3, 4 or 5 denoting the degree of substitution, and at least one R is a non-hydrogen atom, preferably R is at least 3 carbon atoms or silicon atoms or a combination thereof more preferably R is an alkyl having 3 or more carbon atoms, for example n-propyl or n-butyl, and each additional substituent group R is, independently, a radical selected from a group consisting of C_1–C_{20} hydrocarbyl radicals, substituted C_1–C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, C_1–C_{20} hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group 14 of the Periodic Table of Elements, and halogen radicals or $(C_5H_{5-y-x}R_x)$ is a cyclopentadienyl ring in which two adjacent R-groups are joined forming C_4–C_{20} ring to give a saturated or unsaturated polycyclic cyclopentadienyl ligand such as indenyl, tetrahydroindenyl, fluorenyl or octahydrofluorenyl;

- (JR'_{z-1-y}) is a heteroatom ligand in which J is an element with a coordination number of three from Group 15 or an element with a coordination number of two from Group 16 of the Periodic Table of Elements, preferably nitrogen, phosphorus, oxygen or sulfur with nitrogen being preferred, and each R' is, independently a radical selected from a group consisting of C_1–C_{20} hydrocarbyl radicals wherein one or more hydrogen atoms is replaced by a halogen atom, y is 0 or 1, and "z" is the coordination number of the element J;
- each Q is, independently any univalent anionic ligand such as halogen, hydride, or substituted or unsubstituted C_1–C_{30} hydrocarbyl, alkoxide, aryloxide, amide or phosphide, provided that two Q may be an alkylidene, a cyclometallated hydrocarbyl or any other divalent anionic chelating ligand;
- A is a covalent bridging groups containing a Group 15 or 14 element such as, but not limited to, a dialkyl, alkylaryl or diaryl silicon or germanium radical, alkyl or aryl phosphine or amine radical, or a hydrocarbyl radical such as methylene, ethylene and the like;
- L' is a Lewis base such as diethylether, tetraethylammonium chloride, tetrahydrofran, dimethylaniline, aniline, trimethylphosphine, n-butylamine, and the like; and w is a number from 0 to 3. Additionally, L' may be bonded to any of R, R' or Q.

In one embodiment of the bulky ligand hafnium transition metal metallocene-type catalyst compounds described above, at least one bulky ligand is substituted with a substituent having 3 or more carbon atoms, preferably 3 to 20 carbon atoms, more preferably 3 to 10 and most preferably 3 to 5 carbon atoms. In another preferred embodiment, the hafnium transition metal metallocene-type catalyst system has two bulky ligands that are each substituted with a linear or branched, preferably linear, alkyl having 3 or more carbon atoms, preferably 3 to 10 carbon atoms, most preferably 3 to 5 carbon atoms, where at least one bulky ligand is a cyclopentadienyl derived ligand, preferably a cyclopentadienyl ring. In a preferred embodiment the bulky ligands of the hafnium transition metal metallocene are both cyclopentadienyl rings at least one of which is substituted with one or more branched or linear alkyls having 3 or more carbon atoms, preferably both cyclopentadienyl rings are substituted with at least one n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, or combination thereof In a more preferred embodiment the hafnium transition metal metallocene-type catalyst compound has two bulky ligands that are each substituted with n-propyl, n-butyl or n-pentyl or combination thereof in the same or different positions, preferably in the same position on the bulky ligands.

In another preferred embodiment, the hafnium transition metal metallocene-type catalyst system has two bulky ligands that are each substituted with a linear or branched, preferably linear, silyl having 3 or more non-hydrogen atoms, preferably 3 to 10 non-hydrogen atoms, most preferably 3 to 5 non-hydrogen atoms, where at least one bulky ligand is a cyclopentadienyl derived ligand, preferably a cyclopentadienyl ring. In a preferred embodiment the bulky ligands of the hafnium transition metal metallocene are both cyclopentadienyl rings at least one of which is substituted with one or more branched or linear silylalkyls having 3 or more non-hydrogen atoms. In one embodiment, the substituent has at least 3 or more non-hydrogen atoms of which at least one is a silicon atom, for example trimethyl silyl alkyl, tributyl silyl alkyl or tripropyl silyl alkyl or even cyclopropyl silyl. Other non-hydrogen substituent atoms include oxygen and/or nitrogen.

It is contemplated that the substituted bulky ligands of the hafnium transition metal metallocene-type catalyst compound of the invention are asymmetrically substituted in terms of additional substituents or types of substituents, and/or unbalanced in terms of the number of additional substituents on the bulky ligands.

Non-limiting examples of hafnocenes of the invention include bis(n-propyl cyclopentadienyl) hafnium dichloride, dimethyl or dihydride, bis(n-butyl cyclopentadienyl) hafnium dichloride or dimethyl, bis(n-pentyl cyclopentadienyl) hafnium dichloride or dimethyl, (n-propyl cyclopentadienyl)(n-butyl cyclopentadienyl) hafnium dichloride or dimethyl, bis[(2-trimethylsilyl-ethyl) cyclopentadienyl] hafnium dichloride or dimethyl, bis (trimethylsilyl cyclopentadienyl) hafnium dichloride or dimethyl or dihydride, bis(2-n-propyl indenyl) hafnium dichloride or dimethyl, bis(2-n-butyl indenyl) hafnium dichloride or dimethyl, dimethylsilyl bis(n-propyl cyclopentadienyl) hafnium dichloride or dimethyl, dimethylsilyl bis(n-butyl cyclopentadienyl) hafnium dichloride or dimethyl, bis(9-n-propyl fluorenyl) hafnium dichloride or dimethyl bis(9-n-butyl fluorenyl) hafnium dichloride or dimethyl, (9-n propyl fluorenyl)(2-n-propyl indenyl) hafnium dichloride or dimethyl, bis(1,2-n-propyl, methyl cyclopentadienyl) hafnium dichloride or dimethyl (n-propyl cyclopentadienyl) (1,3-n-propyl, n-butyl cyclopentadienyl) hafnium dichloride or dimethyl and the like.

In one preferred embodiment the hafnocenes of the invention are unbridged mono- and bis- hafnocenes where a structural bridge is not required for stereorigidity. It is also contemplated that in one embodiment, the hafnocenes of the invention include their structural or optical isomers and mixtures thereof.

For the purposes of this patent specification and appended claims, the term "activator" is defined to be any compound or component which can activate a bulky ligand transition metal metallocenetype catalyst compound as described above, for example, a Lewis acid or a non-coordinating ionic activator or ionizing activator or any other compound that can convert a neutral metallocene catalyst component to a metallocene cation. It is within the scope of this invention to use alumoxane or modified alumoxane as an activator, and/or to also use ionizing activators, neutral or ionic, such as tri (n-butyl) ammonium tetrakis(pentafluorophenyl) boron or a trisperfluorophenyl boron metalloid precursor which ionizes the neutral metallocene compound.

There are a variety of methods for preparing alumoxane and modified alumoxanes, non-limiting examples of which are described in U.S. Pat. Nos. 4,665,208, 4,952,540, 5,091,352, 5,206,199, 5,204,419, 4,874,734, 4,924,018, 4,908,463, 4,968,827, 5,308,815, 5,329,032, 5,248,801, 5,235,081, 5,157,137, 5,103,031, 5,391,793, 5,391,529, 5,693,838 and European publications EP-A-0 561 476, EP-B1-0 279 586 and EP-A-0 594-218, and PCT publication WO 94/10180, all of which are herein fully incorporated by reference.

Ionizing compounds may contain an active proton, or some other cation associated with but not coordinated or only loosely coordinated to the remaining ion of the ionizing compound. Such compounds and the like are described in European publications EP-A-0 570 982, EP-A-0 520 732, EP-A-0 495 375, EP-A-0 426 637, EP-A-500 944, EP-A-0 277 003 and EP-A-0 277 004, and U.S. Pat. Nos. 5,153,157, 5,198,401, 5,066,741, 5,206,197, 5,241,025, 5,387,568, 5,384,299 and 5,502,124 and U.S. patent application Ser. No. 08/285,380, filed Aug. 3, 1994, now abandoned all, of which are herein fully incorporated by reference. Combinations of activators are also contemplated by the invention, for example, alumoxanes and ionizing activators in combinations, see for example, PCT publications WO 94/07928 and WO 95/14044 and U.S. Pat. Nos. 5,153,157 and 5,453,410 all of which are herein fully incorporated by reference.

In an embodiment of the invention two or more bulky ligand hafnium transition metal metallocene-type catalyst compounds as described above can be combined to form a catalyst system useful in the invention. For example, those mixed catalysts described in U.S. Pat. Nos. 5,281,679, 5,359,015 and 5,470,811, all of which are herein fully incorporated herein reference. In another embodiment of the catalyst system of the invention combinations of one or more of catalyst components of the formulas (III) and/or (IV) are contemplated.

In one embodiment, metallocene catalyst components can be combined to form the blend compositions as described in PCT publication WO 90/03414 published Apr. 5, 1990, herein fully incorporated by reference. In yet another embodiment of the invention mixed metallocenes as described in U.S. Pat. Nos. 4,937,299 and 4,935,474, both are herein fully incorporated herein by reference, can be used to produce polymers having a broad molecular weight distribution and/or a multimodal molecular weight distribution.

In another embodiment of the invention at least one metallocene catalyst of the invention can be combined with a non-metallocene or traditional Ziegler-Natta catalyst or catalyst system, or chromium based catalysts or catalyst systems, non-limiting examples are described in U.S. Pat. Nos. 4,159,965, 4,325,837, 4,701,432, 5,124,418, 5,077,255, 5,183,867, 5,391,660, 5,395,810 and 5,691,264, all of which are herein fully incorporated by reference.

It is within the scope of this invention that Ni^{2+} and Pd^{2+} complexes described in the articles Johnson, et al., "New Pd(II)- and Ni(II)- Based Catalysts for Polymerization of Ethylene and a-Olefins", J. Am. Chem. Soc. 1995, 117, 6414–6415 and Johnson, et al., "Copolymerization of Ethylene and Propylene with Functionalaled Vinyl Monomers by Palladium(II) Catalysts", J. Am. Chem. Soc., 1996, 118, 267–268, and WO 96/23010 published Aug. 1, 1996 which are all herein fully incorporated by reference, can be used as catalysts in combination with the hafnocenes of the invention. These complexes can be either dialkyl ether adducts, or alkylated reaction products of the described dihalide complexes that can be activated to a cationic state by the activators of this invention. It is also within the scope of the process of this invention that the above described complexes can be combined with one or more of the catalyst compounds represented by formula (III) and (IV), with one or more activators, and with one or more of the support materials using one of the support methods that are described below.

For purposes of this patent specification the terms "carrier" or "support" are interchangeable and can be any support material, preferably a porous support material, for example, talc, inorganic oxides, inorganic chlorides, and magnesium chloride, and resinous support materials such as polystyrene or polystyrene divinyl benzene polyolefins or polymeric compounds or any other organic or inorganic support material and the like, or mixtures thereof.

The preferred support materials are inorganic oxide materials, which include those of Groups 2, 3, 4, 5, 13 or 14 metal oxides. In a preferred embodiment, the catalyst support materials include silica, alumina, silica-alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina and magnesia, titania, zirconia, and the like.

It is preferred that the carrier of the catalyst of this invention has a surface area in the range of from about 10 to about 700 m^2/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 10 to about 500 μm. More preferably, the surface area is in the range of from about 50 to about 500 m^2/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 20 to about 200 μm. Most preferably the surface area range is from about 100 to about 400 m^2/g, pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about 20 to about 100 μm. The average pore size of the carrier of the invention typically has pore size in the range of from 10 to 1000 Å, preferably 50 to about 500 Å, and most preferably 75 to about 350 Å.

The catalyst system of the invention can be made and used in a variety of different ways as described below. In one embodiment the catalyst is unsupported, preferably in liquid form such as described in U.S. Pat. Nos. 5,317,036 and 5,693,727 and European publication EP-A-0 593 083, all of which are herein incorporated by reference. In the preferred embodiment, the catalyst system of the invention is supported. Examples of supporting the catalyst system used in the invention are described in U.S. Pat. Nos. 4,701,432, 4,808,561, 4,912,075, 4,925,821, 4,937,217, 5,008,228, 5,238,892, 5,240,894, 5,332,706, 5,346,925, 5,422,325, 5,466,649, 5,466,766, 5,468,702, 5,529,965, 5,554,704, 5,629,253, 5,639,835, 5,625,015, 5,643,847 and 5,665,665 and U.S. application Ser. Nos. 271,598 filed Jul. 7, 1994, now U.S. Pat. No. 5,468,702, and 788,736 filed Jan. 23, 1997, now U.S. Pat. No. 6,090,740, and PCT publications WO 95/32995, WO 95/14044, WO 96/06187 and WO 97/02297 all of which are herein fully incorporated by reference.

In another embodiment, the catalyst system of the invention contains a polymer bound ligand as described in U.S. Pat. No. 5,473,202 which is herein fully incorporated by reference. In one embodiment the catalyst system of the invention is spray dried as described in U.S. Pat. No. 5,648,310 which is fully incorporated herein by reference. In an embodiment the support of the invention is functionalized as described in European publication EP-A-0 802 203 or at least one substituent or leaving group is selected as described in U.S. Pat. No. 5,688,880, both of which are herein fully incorporated by reference.

In one embodiment of the process of the invention, olefin(s), preferably C_2 to C_{20} olefin(s) or alpha-olefin(s), preferably ethylene or propylene or combinations thereof are prepolymerized in the presence of the catalyst or catalyst system of the invention prior to the main polymerization. The prepolymerization can be carried out batchwise or continuously in gas, solution or slurry phase including at elevated pressures. The prepolymerization can take place with any alpha-olefin monomer or combination and/or in the presence of any molecular weight controlling agent such as hydrogen. For details on prepolymerization see U.S. Pat. Nos. 4,923,833, 4,921,825 and 5,283,278 and European publication EP-B-0279 863 all of which are herein fully incorporated by reference.

In another embodiment of the invention, the supported catalyst system of the invention includes an antistatic agent or surface modifier, for example, those described in U.S. Pat. No. 5,283,278 and PCT publication WO 96/11960 which are herein fully incorporated by reference. Non-limiting examples of antistatic agents and surface modifiers include alcohol, thiol, silanol, diol, ester, ketone, aldehyde, acid, amnine, and ether compounds. Tertiary amines, ethoxylated amines, and polyether compounds are preferred. The antistatic agent can be added at any stage in the formation of the supported catalyst system of the invention, however, it is preferred that it is added after the supported catalyst system of the invention is formed, in either a slurry or dried state.

A preferred method for producing the catalyst of the invention is described below and an be found in U.S. application Ser. Nos. 265,533, filed Jun. 24, 1994, now abandoned and 265,532, filed Jun. 24, 1994, now abandoned and PCT publications WO 96/00245 and WO 96/00243 both published Jan. 4, 1996, all of which are herein fully incorporated by reference. In a preferred embodiment, the metallocene-type catalyst component is slurried in a liquid to form a metallocene solution and a separate solution is formed containing an activator and a liquid. The liquid can be any compatible solvent or other liquid capable of forming a solution or the like with at least one metallocene catalyst component and/or at least one activator. In the preferred embodiment the liquid is a cyclic aliphatic or aromatic hydrocarbon, most preferably toluene. The metallocene and activator solutions are mixed together and added to a porous support or the porous support is added to the solutions such that the total volume of the metallocene solution and the activator solution or the metallocene and activator solution is less than four times the pore volume of the porous support, more preferably less than three times, even more preferably less than two times; preferred ranges being from 1.1 times to 3.5 times range and most preferably in the 1.2 to 3 times range.

Procedures for measuring the total pore volume of a porous support are well known in the art. Details of one of these procedures is discussed in Volume 1, Experimental Methods in Catalytic Research (Academic Press, 1968) (specifically see pages 67–96). This preferred procedure involves the use of a classical BET apparatus for nitrogen absorption. Another method well know in the art is described in Innes, Total Porosity and Particle Density of Fluid Catalysts By Liquid Titration, Vol. 28, No. 3, Analytical Chemistry 332–334 (March, 1956).

The mole ratio of the metal of the activator component to the transition metal of the metallocene component is in the range of ratios between 0.3:1 to 1000:1, preferably 20:1 to 800:1, and most preferably 50:1 to 500:1. Where the activator is an aluminum-free ionizing activator such as those based on the anion tetrakis(pentafluorophenyl)boron, the mole ratio of the metal of the activator component to the transition metal component is preferably in the range of ratios between 0.3:1 to 3:1.

In another embodiment the catalyst loading in millimoles (mmoles) of metallocene to weight of support catalyst in grams (g) is in the range of from about 0.001 to about 2.0 mmoles of metallocene per g of support material, preferably from about 0.005 to about 1.0, more preferably from about 0.005 to 0.5 and most preferably from about 0.01 to 0.05.

In one embodiment, the catalyst of the invention has a catalyst productivity of greater than 1000 grams of polymer per gram of the metallocene catalyst, preferably greater than 1400 grams of polymer per gram of metallocene catalyst, more preferably greater than 1800 grams of polymer per gram of metallocene catalyst, even more preferably greater than 2000 grams of polymer per gram of metallocene catalyst, and most preferably greater than 2500 grams of polymer per gram of metallocene catalyst.

Polymerization Process of the Invention

The substituted bulky ligand hafnium transition metal metallocene-type catalyst compounds and catalyst systems of this invention are suited for the polymerization of monomers, and optionally one or more comonomers, in any polymerization process, solution phase, gas phase or slurry phase, most preferably a gas or slurry phase process is used.

In an embodiment, this invention is directed toward the solution, slurry or gas phase polymerization or copolymerization reactions involving the polymerization of one or more of the monomers having from 2 to 30 carbon atoms, preferably 2–12 carbon atoms, and more preferably 2 to 8 carbon atoms. The invention is particularly well suited to the copolymerization reactions involving the polymerization of one or more of the monomers, for example alpha-olefin monomers of ethylene, propylene, butene-1, pentene-1, 4-methyl-pentene-1, hexene-1, octene-1, decene-1, and cyclic olefins such as cyclopentene, and styrene or a combination thereof. Other monomers can include polar vinyl monomers, diolefins such as dienes, polyenes, norbornene, norbarnadiene, acetylene and aldehyde monomers. Preferably a copolymer of ethylene or propylene is produced. Preferably the comonomer is an alpha-olefin having from 3 to 15 carbon atoms, preferably 4 to 12 carbon atoms and most preferably 4 to 8 carbon atoms. In another embodiment ethylene or propylene is polymerized with at least two different comonomers to form a terpolymer and the like, the preferred comonomers are a combination of alpha-olefin monomers having 3 to 10 carbon atoms, more preferably 4 to 8 carbon atoms.

In another embodiment ethylene or propylene is polymerized with at least two different comonomers to form a terpolymer and the like, the preferred comonomers are a combination of alpha-olefin monomers having 3 to 10 carbon atoms, more preferably 3 to 8 carbon atoms, optionally with at least one diene monomer. The preferred terpolymers include the combinations such as ethylene/butene-1/hexene-1, ethylene/propylene/butene-1, propylene/ethylene/butene-1, propylene/ethylene/hexene-1, ethylene/propylene/norbornadiene and the like.

In the most preferred embodiment the process of the invention relates to the polymerization of ethylene and at least one comonomer having from 4 to 8 carbon atoms. Particularly, the comonomers are butene-1, 4-methylpentene-1, hexene-1 and octene-1, the most preferred being hexene-1.

Typically in a gas phase polymerization process a continuous cycle is employed where in one part of the cycle of a reactor, a cycling gas stream, otherwise known as a recycle stream or fluidizing medium, is heated in the reactor by the heat of polymerization. This heat is removed in another part of the cycle by a cooling system external to the reactor. (See for example U.S. Pat. Nos. 4,543,399, 4,588,790, 5,028,670, 5,317,036, 5,352,749, 5,405,922, 5,436,304, 5,453,471, 5,462,999, 5,616,661 and 5,668,228 all of which are fully incorporated herein by reference.)

Generally, in a gas fluidized bed process for producing polymers, a gaseous stream containing one or more monomers is continuously cycled through a fluidized bed in the presence of a catalyst under reactive conditions. The gaseous stream is withdrawn from the fluidized bed and recycled back into the reactor. Simultaneously, polymer product is withdrawn from the reactor and fresh monomer is added to replace the polymerized monomer. The reactor pressure may vary from about 100 psig (680 kPag) to about 500 psig (3448 kPag), preferably in the range of from about 200 psig (1379 kPag) to about 400 psig (2759 kPag), more preferably in the range of from about 250 psig (1724 kPag) to about 350 psig (2414 kPag). The reactor temperature may vary between about 60° C. and about 120° C., preferably about 60° C. to about 115° C., and more preferably in the range of from about 70° C. to 110° C., and most preferably in the range of from about 70° C. to 95° C. The settled bulk density for the polymers produced by the process of invention are in the range of from about 10 to 35 lb/ft^3 (160 to 561 kg/m^3), preferably from about 12 to 35 lb/ft^3 (193 to 561 kg/m^3), more preferably from about 14 to 32 lb/ft^3 (224 to 513 kg/m^3), and most preferably from about 15 to 30 lb/ft^3 (240 to 481 kg/m^3).

Other gas phase processes contemplated by the process of the invention include those described in U.S. Pat. Nos. 5,627,242, 5,665,818 and 5,677,375, and European publications EP-A-0 794 200, EP-A-0 802 202 and EP-B-634 421 all of which are herein fully incorporated by reference.

A preferred process of the invention is where the process, preferably a slurry or gas phase process, most preferably a gas phase process, is operated in the absence of or essentially free of any scavengers, such as triethylaluminum, trimethylaluminun trisobutylaluminum and tri-n-hexylaluminum and diethyl aluminum chloride and the like. This preferred process is described in PCT publication WO 96/08520, which is herein fully incorporated by reference.

A slurry polymerization process generally uses pressures in the range of about 1 to about 50 atmospheres and even greater and temperatures in the range of 0° C. to about 200° C. In a slimy polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization medium to which ethylene and comonomers and often hydrogen along with catalyst are added. The liquid employed in the polymerization medium can be alkane or cycloalkane, or an aromatic hydrocarbon such as toluene, ethylbenzene or xylene. The medium employed should be liquid under the conditions of polymerization and relatively inert. Preferably, hexane or isobutane medium is employed.

In one embodiment a preferred polymerization technique of the invention is referred to as a particle form, or slurry process where the temperature is kept below the temperature at which the polymer goes into solution. Such technique is well known in the art, see for instance U.S. Pat. No. 3,248,179 which is fully incorporated herein by reference. The preferred temperature in the particle form process is within the range of about 185° F. (85° C.)to about 230° F. (110° C.). Two preferred polymerization methods for the slurry process are those employing a loop reactor and those utilizing a plurality of stirred reactors in series, parallel, or combinations thereof. Non-limiting examples of slurry processes include continuous loop or stirred tank processes. Also, other examples of slurry processes are described in U.S. Pat. No. 4,613,484, which is herein fully incorporated by reference.

It is also contemplated in an embodiment of the invention, that the process is a multistage polymerization process where one reactor is operating in slurry phase that feeds into a reactor operating in a gas phase as described in U.S. Pat. No. 5,684,097, which is fuilly incorporated herein by reference.

In one embodiment the reactor utilized in the present invention is capable of producing greater than 500 lbs/hr (227 Kg/hr) to about 200,000 lbs/hr (90,900 Kg/hr)or higher of polymer, preferably greater than 1000 lbs/hr (455 Kg/hr), more preferably greater than 10,000 lbs/hr (4540 Kg/hr), even more preferably greater than 25,000 lbs/hr (11,300 Kg/hr), still more preferably greater than 35,000 lbs/hr (15, 900 Kg/hr), still even more preferably greater than 50,000 lbs/hr (22,700 Kg/hr) and most preferably greater than 65,000 lbs/hr (29,000 Kg/hr) to greater than 100,000 lbs/hr (45,500 Kg/hr).

The productivity of the catalyst or catalyst system is influenced by the main monomer partial pressure. The preferred mole percent of the main monomer, ethylene or propylene, preferably ethylene is from about 25 to 90 mole percent and the monomer partial pressure is in the range of from about 75 psia (517 kPa) to about 300 psia (2069 kPa), which are typical conditions in a gas phase polymerization process.

In another embodiment of the invention where the hafnocene of the invention is in particular an unbridged metallocene-type catalyst, the process of the invention is capable of producing a polymer product having a melt index of less than 0.1 dg/min without the addition of hydrogen to the process.

Polymer Product of the Invention

The polymers produced by this invention can be used in a wide variety of products and end-use applications. The polymers typically have a density in the range of from 0.86g/cc to 0.97 g/cc, preferably in the range of from 0.88 g/cc to 0.965 g/cc, more preferably in the range of from 0.900 g/cc to 0.96 g/cc, even more preferably in the range of from 0.905 g/cc to 0.95 g/cc, yet even more preferably in the range from 0.910 g/cc to 0.940 g/cc, and most preferably greater than 0.910 g/cc, preferably greater than 0.915 g/cc. The polymers of the invention typically have a narrow molecular weight distribution, a weight average molecular weight to number average molecular weight (M_w/M_n) of greater than 1.5 to about 4, particularly greater than 2 to about 3, more preferably greater than about 2.2 to less than 3. Also, the polymers of the invention typically have a narrow composition distribution. In another embodiment, the polymers produced by the process of the invention, particularly in a slurry and gas phase process, contain less than 2 ppm hafnium, preferably less than 1.5 ppm hafnium, more preferably less than 1 ppm hafnium. In an embodiment, the polymer of the invention contains in the range of from about 0.01 ppm to about 2 ppm hafnium, preferably in the range of from about 0.01 ppm to about 1.5 ppm hafnium, more preferably in the range of from about 0.01 ppm to 1 or less ppm hafnium.

Polymers produced by the process of the invention are usefiil in such forming operations as film, sheet, and fiber extrusion and co-extrusion as well as blow molding, injection molding and rotary molding. Films include blown or cast films formed by coextrusion or by lamination useful as shrink film, cling film, stretch film, sealing films, oriented films, snack packaging, heavy duty bags, grocery sacks, baked and frozen food packaging, medical packaging, industrial liners, membranes, etc. in food-contact and non-food contact applications. Fibers include melt spinning, solution spinning and melt blown fiber operations for use in woven or non-woven form to make filters, diaper fabrics, medical garments, geotextiles, etc. Extruded articles include medical tubing, wire and cable coatings, geomembranes, and pond liers. Molded articles include single and multi-layered constructions in the form of bottles, tanks, large hollow articles, rigid food containers and toys, etc.

EXAMPLES

In order to provide a better understanding of the present invention including representative advantages thereof, the following examples are offered.

The properties of the polymer were determined by the following test methods:

Density is measured in accordance with ASTM-D-1238.

MWD, or polydispersity, is a well-known characteristic of polymers. MWD is generally descried as the ratio of the weight average molecular weight (Mw) to the number average molecular weight (Mn). The ratio of Mw/Mn can be measured by gel permeation chromatography techniques, or indirectly, by measuring the ratio of I_{21} to I_2 (melt index) as described in ASTM D-1238-F and a ASTM D-1238-E respectively.

In all the Examples below the methylalumoxane (MAO) is a 30 weight percent MAO solution in toluene available from Albemarle Corporation, Baton Rouge, La., the Davision 948 silica is available from W. R. Grace, Davison Chemical Division, Baltimore, Md. and the N,N-bis(2-hydroxylethyl) octadecylamine is available as Kemamine AS-990 from ICI Specialties, Wilmington, Del. The metallocene components of the examples were prepared in accordance with procedures well known in the art.

Example 1

Preparation of Catalyst

A solution of methylalumoxane and metallocene was formed by adding 11 cm^3 of 30 wt-% MAO solution in toluene onto 0.202 g of bis (n-propylcyclopentadienyl) hafnium dichloride in a vial. 40 cm^3 of fresh toluene was added, and the mixture stirred for 1 hour at 25° C. This pre-mixed solution of the MAO and the metallocene was then added onto 10 g of Davison 948 silica dried to 600° C. The resulting slurry was stirred for 1.5 hours at 25° C. The final catalyst was then dried to free-flowing powder under vacuum at 65° C.

Polymerization

A sample of the dry catalyst formed in the above Example 1 was then used in a polymerization process of ethylenell-butene in a 2-liter semi-batch gas-phase reactor at 85° C. The pressure in the reactor, about 155 psig (1069 kPag), was held constant by continuously feeding 5 mol-% 1-butene in ethylene to compensate for any pressure changes due to polymerization. After 1 h (hour), the polymer formed was separated from the seed bed material and analyzed for the molecular properties shown in Table 1 below as Run 1 and 2.

Example 2

Preparation of Catalyst

A solution of methylalumoxane and metallocene was formed by adding 66.5 cm^3 of 30 wt-% MAO solution in toluene onto 1.21 g of bis (n-propylcyclopentadienyl) hafnium dichloride in a vial. 50 cm^3 of fresh toluene was added, and the mixture stirred for 1.5 hours at 25° C. This pre-mixed solution of the MAO and the metalocene was then added onto 60 g of Davison 948 silica dried to 600° C. The resulting slurry was stirred for 1.5 hours at 25° C. Then a solution of 0.41 g of N,N-bis(2-hydroxylethyl) octadecylamnine in 50 cm^3 toluene was added, and stirring continued for another 30 minutes. The final catalyst was then dried to free-flowing powder under vacuum at 65° C.

Polymerization

A sample of the dry catalyst formed in Example 2 was then used in a polymerization process of ethylene/1-butene in a 2-liter semi-batch gas-phase reactor at 85° C. The pressure in the reactor, about 158 psig (1089 kPag), was held constant by continuously feeding 5 mol-% 1-butene in ethylene to compensate for any pressure change due to polymerization. After 1 h, the polymer formed was separated from the seed bed material and analyzed for the molecular properties shown as Run 3 in Table 1 below.

Example 3

Preparation of Catalyst

a) Methylalumoxane (1155 cm^3 of 30 wt-% solution in toluene) was charged into a 2-gallon reaction vessel. 1970 cm^3 of fresh toluene was added. Then a solution of 20.2 g of bis(n-propylcyclopentadienyl) hafnium dichloride in 355 cm^3 toluene was added. The temperature was maintained at 27° C. and the mixture stirred for 1.5 hour.

b) 1000 g of a Davison 948 silica dehydrated at 600° C. was charged into a 2-gallon reaction vessel at 27° C. The solution of methylalumoxane and metallocene from above was added onto the silica in two equal portions. Then an additional 250 cm^3 toluene was added to the slurry. After 1 hour, a solution of 6.7 g of N,N-bis(2-hydroxylethyl) octadecylamine in 70 cm^3 toluene was added and stirring continued for another 20 minutes. The final catalyst was then dried to free-flowing powder at 68° C. under vacuum.

Polymerization

Samples of the dry catalyst formed in Example 3 each were then used in a polymerization process of ethylene/1-butene in a 2-liter semi-batch gas-phase reactor at 85° C. The pressure in the reactor, about 158 psig (1089 kPag), was held constant by continuously feeding 5 mol-% 1-butene in ethylene to compensate for any pressure change due to polymerization. After 1 h, the polymer formed was separated from the seed bed material and ayzed for the molecular properties shown as Runs 4–6 in Table 1 below.

Example 4

Preparation of Catalyst

A solution of methylalumoxane and metallocene was formed by adding 27.8 cm^3 of 30 wt-% MAO solution in toluene onto 0.536 g of bis (n-butylcyclopentadienyl) hafnium dichloride in a vial. 60 cm^3 of fresh toluene was added, and the mixture stirred for 1.5 hours at 25° C. This pre-mixed solution of the MAO and the metallocene was then added onto 25 g of Davison 948 silica dried to 600° C. The resulting slurry was stirred for 1.5 hours at 25° C. Then a solution of 0.166 g of N,N-bis(2-hydroxylethyl) octadecylamine in 40 cm^3 toluene was added, and stirring continued for another 30 minutes. The final catalyst was then dried to free-flowing powder under vacuum at 65° C.

Polymerization

Samples of the dry catalyst formed in Example 4 then were each used in a polymerization process of ethylene/1-butene in a 2-liter semi-batch gas-phase reactor at 85° C. The pressure in the reactor, about 155 psig (1069 kPag), was held constant by continuously feeding 5 mol-% 1-butene in ethylene to compensate for any pressure change due to polymerization. After 1 h, the polymer formed was separated from the seed bed material and analyzed for the molecular properties shown as Runs 7–9 in Table 1 below.

Comparative Example 5

Preparation of Catalyst

A solution of methylalumoxane and metallocene was formed by adding 27.7 cm^3 of 30 wt-% MAO solution in toluene onto 0.413 g of bis (cyclopentadienyl) hafnium dichloride in a vial. 50 cm^3 of fresh toluene was added, and the mixture stirred for 1.5 hours at 25° C. This pre-mixed solution of the MAO and the metalocene was then added onto 25 g of Davison 948 silica dried to 600° C. The resulting shiny was stirred for 1.5 hours at 25° C. Then a solution of 0.166 g of N,N-bis(2-hydroxylethyl) octadecylamine in 40 cm^3 toluene was added, and stirring continued for another 30 minutes. The final catalyst was then dried to free-flowing powder under vacuum at 65° C.

Polymerization

Samples of the dry catalyst formed in Comparative Example 5 were then each used in a polymerization process of ethylene/1-butene in a 2-liter semi-batch gas-phase reactor at 85° C. The pressure in the reactor, about 158 psig (1089 kPag), was held constant by continuously feeding 5 mol-% 1-butene in ethylene to compensate for any pressure change due to polymerization. After 1 h, the polymer formed was separated from the seed bed material and analyzed for the molecular properties shown as Runs C1 and C2 in Table 1 below.

Comparative Example 6

Preparation of Catalyst

A solution of methylalumoxane and metallocene was formed by adding 27.8 cm^3 of 30 wt-% MAO solution in toluene onto 0.444 g of bis (methylcyclopentadienyl) hafnium dichloride in a vial. 60 cm^3 of fresh toluene was added, and the mixture stirred for 1.5 hours at 25° C. This pre-mixed solution of the MAO and the metallocene was then added onto 25 g of Davison 948 silica dried to 600° C. The resulting slurry was stirred for 1.5 hours at 25° C. Then a solution of 0.169 g of N,N-bis(2-hydroxylethyl) octadecylamine in 50 cm^3 toluene was added, and stirring continued for another 30 minutes. The final catalyst was then dried to freeflowing powder under vacuum at 65° C.

Polymerization

A sample of the dry catalyst formed in Comparative Example 6 was then used in a polymerization process of ethylene/1-butene in a 2-liter semi-batch gas-phase reactor at 85° C. The pressure in the reactor, about 154 psig (1062 kPag), was held constant by continuously feeding 5 mol-% 1-butene in ethylene to compensate for pressure changes due to polymerization. After 1 h, the polymer formed was separated from the seed bed material and analyzed for the molecular properties shown as Run C3 in Table 1 below.

Comparative Example 7

Preparation of Catalyst

A solution of methylalumoxane and metallocene was formed by adding 27.8 cm^3 of 30 wt-% MAO solution in toluene onto 0.475 g of bis (ethylcyclopentadienyl) hafnium dichloride in a vial. 60 cm^3 of fresh toluene was added, and the mixture stirred for 1.5 hours at 25° C. This pre-mixed solution of the MAO and the metallocene was then added onto 25 g of Davison 948 silica dried to 600° C. The resulting slurry was stirred for 1.5 hours at 25° C. Then a solution of 0.167 g of N,N-bis(2-hydroxylethyl octadecylamine in 50 cm^3 toluene was added, and stirring continued for another 30 minutes. The final catalyst was then dried to free-flowing powder under vacuum at 65° C.

Polymerization

A sample of the dry catalyst formed above in Comparative Example 7 was then used in a polymerization process of ethylene/1-butene in a 2-liter semi-batch gas-phase reactor at 85° C. The pressure in the reactor, about 160 psig (1103 kPag), was held constant by continuously feeding 5 mol-% 1-butene in ethylene to compensate for any pressure change due to polymerization. After 1 h, the polymer formed was separated from the seed bed material and analyzed for the molecular properties shown as Run C4 in Table 1 below.

Comparative Example 8

Preparation of Catalyst

A solution of methylalumoxane and metallocene was formed by adding 28 cm^3 of 30 wt-% MAO solution in toluene onto 0.585 g of Me_2Si (Indenyl)$_2$ hafnium dichloride in a vial. 60 cm^3 of fresh toluene was added, and the mixture stirred for 1.5 hours at 25° C. This pre-mixed solution of the MAO and the metallocene was then added onto 25 g of Davison 948 silica dried to 600° C. The resulting slurry was stirred for 1.5 hours at 25° C. Then a solution of 0.167 g of N,N-bis(2-hydroxylethyl) octadecylamine in 40 cm^3 toluene was added, and stirring continued for another 30 nmnutes. The final catalyst was then dried to free-flowing powder under vacuum at 65° C.

Polymerization

Samples of the dry catalyst formed above in Comparative Example 8 were then each used in a polymerization process of ethylene/1-butene in a 2-liter semibatch gas-phase reactor at 85° C. The pressure in the reactor, about 158 psig (1089 kPag), was held constant by continuously feeding 5 mol-% 1-butene in ethylene to compensate for any pressure change due to polymerization. After 1 h, the polymer formed was separated from the seedbed material and analyzed for the molecular properties shown as Runs C5–C7 in Table 1 below.

While the present invention has been described and illustrated by reference to particular embodiments, those of ordinary skill in the art will appreciate that the invention lends itself to variations not necessarily illustrated herein. It is contemplated that the catalyst system of this invention can be used in combination with other catalyst systems comprising more than one catalyst system of the invention. For this reason, then, reference should be made solely to the appended claims for purposes of determining the true scope of the present invention.

TABLE 1

Run #	Catalyst (mg)	Polymer Yield (g)	Activity[1]	Density (g/cc)	I_2 (dg/min)	I_{21} (dg/min)	Mw	MWD
				$(nPrCp)_2HfCl_2$				
1	100	211	2126	0.9061	0.096	2.26	278942	2.88
2	50	117	2363	0.9025	0.089	2.5	275100	2.61
3	50	136	2674	NM	NM	1.83	NM	NM
4	50	159	3159	0.9064	NM	1.76	283282	2.82
5	50	117	2325	0.9091	NM	1.77	272925	2.80
6	50	117	2356	0.9081	NM	2.0	316801	2.88
				$(nBuCp)_2HfCl_2$				
7	150	271	1821	0.9057	NM	1.2	322890	2.46
8	150	225	1479	0.9056	NM	0.83	NM	NM
9	100	195	1935	0.9070	NM	1.51	NM	NM
				$(Cp)_2HfCl_2$				
C1	300	12	40	0.9310	NM	0.42	361692	3.98
C2	500	18	36	0.9273	NM	0.67	NM	NM
				$(MeCp)_2HfCl_2$				
C3	150	17	112	0.9234	NM	0.68	291412	3.24
				$(EtCp)_2HfCl_2$				
C4	150	16	107	0.9275	NM	0.36	375772	3.20
				$Me_2Si(Ind)_2HfCl_2$				
C5	150	7	48	0.9365	NM	1.74	232475	3.44
C6	150	6	37	0.9265	NM	1.21	263758	4.16
C7	500	25	49	0.9239	NM	1.73	239161	3.40

Note
[1] Catalyst activity expressed as $g_{PE}/(gcAT \cdot h \cdot 150\ psi)$
NM - - Not Measured; "Ind" is indenyl

We claim:

1. A *gas-phase* process for polymerizing olefin(s), excluding cyclic olefin(s), in the presence of a catalyst system comprising a hafnium metallocene catalyst compound **[**having at least one cyclopentadienyl or cyclopentadienyl derived ligand substituted with at least one linear or iso alkyl group having from 3 to 10 carbon atoms, and an activator**]** *represented by the formula:*

$$(C_5H_{5-d-f}R''_d)_eR'''_fHfQ_{4-e}$$

wherein $(C_5H_{5-d-f}R''_d)$ *is a substituted cyclopentadienyl ligand bonded to Hf, wherein at least one* $(C_5H_{5-d-f}R''_d)$ *is substituted with at least one R", wherein said R" is selected from one or more of n-propyl, or n-pentyl, each additional R", which can be the same or different is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R''' is one or more or a combination of the group consisting of carbon, germanium, silicon, phosphorous and nitrogen atoms containing radical bridging two* $(C_5H_{5-d-f}R''_d)$ *rings, or bridging one* $(C_5H_{5-d-f}R''_d)$ *ring to Hf; each Q which can be the same or different is selected from the group consisting of a hydride, substituted and unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides and combination thereof; two Q's together form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand; d is 1, 2, 3, or 4, f is 0 or 1, and e is 1, 2 or 3, said catalyst system further comprising an activator and a support, wherein the activator and the hafnium metallocene catalyst compound are premixed in a solvent, and then combined with the support and then dried, to produce a free-flowing powder, and wherein the catalyst has a catalyst productivity of greater than 1000 (g polymer)/(g catalyst*h*150 psi) at 85° C.*

2. The process in accordance with claim **1** **[**where the linear or iso alkyl group has 3 to 5 carbon atoms**]** *wherein said hafnium metallocene catalyst compound is one of:*

bis (n-propyl cyclopentadienyl) hafnium dichloride, dimethyl, or dihydride; bis (n-pentyl cyclopentadienyl) hafnium dichloride, or dimethyl; (n-propyl cyclopentadienyl)(n-butyl cyclopentadienyl) hafnium dimethyl or dichloride; bis (2-n-propyl indenyl) hafnium dichloride or dimethyl; bis (1,2-n-propyl, methyl cyclopentadienyl) hafnium dichloride or dimethyl; (n-propyl cyclopentadienyl) (1,3-n-propyl, n-butyl cyclopentadienyl) hafnium dimethyl or dichloride.

[3. The process in accordance with claim **1** wherein the ligand is one or more cyclopentadienyl ligands, wherein one of the cyclopentadienyl ligands is substituted with at least one linear or iso alkyl having 3 or 4 carbon atoms.**]**

[4. The process in accordance with claim **1** wherein the ligands are two cyclopentadienyl rings each substituted with at least one linear or iso alkyl group having 3 to 10 carbon atoms.**]**

[5. The process in accordance with claim **2** wherein the linear or iso alkyl group is selected from one or more of the group consisting of n-propyl, isopropyl, n-butyl, isobutyl and n-pentyl.**]**

6. The process in accordance with claim **1** wherein the olefin(s) are alpha-olefins having from 2 to 12 carbon atoms.

7. The process in accordance with claim **1** wherein the olefin(s) are ethylene in combination with one or more other alpha-olefin(s) having from 3 to 10 carbon atoms.

[8. The process in accordance with claim **1** wherein the process is a gas phase process.**]**

[**9**. The process in accordance with claim **1** wherein the catalyst system further comprises a support.]

10. The process in accordance with claim **1** wherein the hafnium metallocene catalyst compound is bis(n-propylcyclopentadienyl) hafnium dichloride.

11. A continuous gas phase process for polymerizing olefin(s), excluding cyclic olefin(s), in a fluidized bed gas phase reactor in the presence of a catalyst system to produce a polymer product, the catalyst system comprising an activator and a hafnium metallocene catalyst compound [having at least one cyclopentadienyl or cyclopentadienyl derived ligand substituted with at least one linear or iso alkyl group having from 3 to 10 carbon atoms,] *represented by the formula:*

$$(C_5H_{5-d-f}R''_d)_eR'''_fHfQ_{4-e}$$

wherein $(C_5H_{5-d-f}R''_d)$ *is a substituted cyclopentadienyl ligand bonded to Hf, wherein at least one* $(C_5H_{5-d-f}R''_d)$ *is substituted with at least one R", wherein said R" is selected from one or more of n-propyl, or n-pentyl, each additional R", which can be the same or different is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R''' is one or more or a combination of the group consisting of carbon, germanium, silicon, phosphorous and nitrogen atoms containing radical bridging two* $(C_5H_{5-d-f}R''_d)$ *rings, or bridging one* $(C_5H_{5-d-f}R''_d)$ *ring to Hf; each Q which can be the same or different is selected from the group consisting of a hydride, substituted and unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides and combination thereof; two Q's together form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand; d is 1, 2, 3, or 4, f is 0 or 1, and e is 1, 2 or 3, said catalyst system further comprising a support, wherein the activator and the hafnium metallocene catalyst compound are premixed in a solvent, and then combined with the support and then dried, to produce a free-flowing powder, and wherein the catalyst has a catalyst productivity of greater than 1000 (g polymer)/(g catalyst*h*150 psi) at 85° C.,* and the polymer product comprising less than 2 ppm hafnium.

12. The process of claim **11** wherein the polymer product comprises less than 1 ppm hafnium.

13. The process in accordance with claim **11** wherein [the catalyst system is supported] *said hafnium metallocene catalyst compound is one of:*

bis (n-propyl cyclopentadienyl) hafnium dichloride, dimethyl, or dihydride; bis (n-pentyl cyclopentadienyl) hafnium dichloride, or dimethyl; (n-propyl cyclopentadienyl)(n-butyl cyclopentadienyl) hafnium dimethyl or dichloride; bis (2-n-propyl indenyl) hafnium dichloride or dimethyl; bis (1,2-n-propyl, methyl cyclopentadienyl) hafnium dichloride or dimethyl; (n-propyl cyclopentadienyl) (1,3-n-propyl, n-butyl cyclopentadienyl) hafnium dimethyl or dichloride.

14. The process in accordance with claim **11** wherein the polymer product has a density greater than 0.915 g/cc.

15. The process in accordance with claim **11** wherein the olefin(s) are ethylene and at least one alpha-olefin(s) having 3 to 8 carbon atoms.

16. The process in accordance in accordance with claim **11** wherein the catalyst system is represented by the formula:

$$(C_5H_{5-d-f}R''_d)_eR'''_fHfQ_{g-e}$$

wherein $(C_5H_{5-d-f}R''_d)$ is an unsubstituted or substituted cyclopentadienyl ligand bonded to Hf, wherein at least one $(C_5H_{5-d-f}R''_d)$ is substituted with at least one R" which is an alkyl group selected from the group consisting of n-propyl, isopropyl, isobutyl and n-pentyl, each additional R", which can be the same or different, is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof, or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R''' is one or more or a combination of the group consisting of carbon, germanium, silicon, phosphorous and nitrogen atoms containing radical bridging two $(C_5H_{5-d-f}R''_d)$ rings, or bridging one $(C_5H_{5-d-f}R''_d)$ ring to Hf; each Q which can be the same or different is selected from the group consisting of a hydride, substituted and unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides and combination thereof; two Q's together form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand; where g is an integer corresponding to the formal oxidation state of Hf, d is 0, 1, 2, 3, 4, or 5, f is 0 or 1 and e is 1, 2, or 3, [and] the polymer product has a melt index less than 0.1 dg/min without the addition of hydrogen to the process *and wherein the hafnium metallocene catalyst compound is bis(n-propyl-cyclopentadienyl) hafnium dichloride and said activator is alumoxane.*

17. A continuous slurry phase process for polymerizing olefin(s), excluding cyclic olefin(s), in the presence of a catalyst system to produce a polymer product in a liquid polymerization medium, the catalyst system comprising an activator, *a support* and a hafnium metallocene catalyst compound [having at least one cyclopentadienyl or cyclopentadienyl derived ligand substituted with at least one linear or iso alkyl group having from 3 to 10 carbon atoms] *represented by the formula:*

$$(C_5H_{5-d-f}R''_d)_eR'''_fHfQ_{4-e}$$

wherein $(C_5H_{5-d-f}R''_d)$ *is a substituted cyclopentadienyl ligand bonded to Hf, wherein at least one* $(C_5H_{5-d-f}R''_d)$ *is substituted with at least one R", wherein said R" is selected from one or more of n-propyl, or n-pentyl, each additional R", which can be the same or different is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R''' is one or more or a combination of the group consisting of carbon, germanium, silicon, phosphorous and nitrogen atoms containing radical bridging two* $(C_5H_{5-d-f}R''_d)$ *rings, or bridging one* $(C_5H_{5-d-f}R''_d)$ *ring to Hf; each Q which can be the same or different is selected from the group consisting of a hydride, substituted and unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides and combination thereof; two Q's together form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand; d is 1, 2, 3, or 4, f is 0 or 1, and e is 1, 2 or 3, wherein the activator and the hafnium metallocene cata-*

*lyst compound are premixed in a solvent, and then combined with the support and then dried, to produce a free-flowing powder, and wherein the catalyst has a catalyst productivity of greater than 1000 (g polymer)/(g catalyst*h*150 psi) at 85° C.,* and the polymer product comprising less than 2 ppm hafnium.

18. The process in accordance with claim **17** wherein the polymer product comprises less than 1 ppm hafnium *and wherein said hafnium metallocene catalyst compound is one of:*

- *bis (n-propyl cyclopentadienyl) hafnium dichloride, dimethyl, or dihydride; bis (n-pentyl cyclopentadienyl) hafnium dichloride, or dimethyl; (n-propyl cyclopentadienyl)(n-butyl cyclopentadienyl) hafnium dimethyl or dichloride; bis (2-n-propyl indenyl) hafnium dichloride or dimethyl; bis (1,2-n-propyl, methyl cyclopentadienyl) hafnium dichloride or dimethyl; (n-propyl cyclopentadienyl) (1,3-n-propyl, n-butyl cyclopentadienyl) hafnium dimethyl or dichloride.*

19. The process in accordance with claim **[17]** *18* wherein the density is greater than 0.900 g/cc.

20. The process in accordance with claim **[17]** *19* wherein the olefins are ethylene and at least one alpha-olefin(s) having 3 to 8 carbon atoms.

21. The process in accordance with claim **17** wherein the **[**catalyst system is represented by the formula:

$$(C_5H_{5-d-f}R''_d)_eR'''_fHfQ_{g-e}$$

wherein $(C_5H_{5-d-f}R''_d)$ is an unsubstituted or substituted cyclopentadienyl ligand bonded to Hf, wherein at least one $(C_5H_{5-d-f}R''_d)$ is substituted with at least one R" which is a linear or iso alkyl group having from 3 to 10 carbon atoms, each additional R", which can be the same or different is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R''' is one or more or a combination of the group consisting of carbon, germanium, silicon, phosphorous and nitrogen atoms containing radical bridging two $(C_5H_{5-d-f}R''_d)$ rings, or bridging one $(C_5H_{5-d-f}R''_d)$ ring to Hf; each Q which can be the same or different is selected from the group consisting of hydride, substituted and unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides and combinations thereof; two Q's together form an alkylidene ligand or a cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand; where g is an integer corresponding to the formal oxidation state of Hf, d is 0, 1, 2, 3, 4 or 5, f is 0 or 1 and e is 1, 2 or 3, and the**]** polymer product has a melt index less than 0.1 dg/min (ASTM D-1238-F or ASTM D-1238-E) without the addition of hydrogen to the process, *wherein the hafnium metallocene catalyst compound is bis(n-propyl-cyclopentadienyl) hafnium dichloride and wherein said activator is alumoxane.*

[22. The process in accordance with claim **3** wherein the linear or iso alkyl group has 3 carbon atoms.**]**

23. A *continuous* process for polymerizing olefin(s), excluding cyclic olefin(s), in the presence of a catalyst system comprising a hafnium transition metal **[**metalloccne**]** *metallocene* catalyst **[**having at least one cyclopentadienyl ring substituted with at least one alkyl group selected from group consisting of n-propyl, isopropyl, isobutyl and n-pentyl, and an activator**]** *represented by the formula:*

$$(C_5H_{5-d-f}R''_d)_eR'''_fHfQ_{g-e}$$

*wherein $(C_5H_{5-d-f}R''_d)$ is a substituted cyclopentadienyl ligand bonded to Hf, wherein at least one $(C_5H_{5-d-f}R''_d)$ is substituted with at least one R", wherein said R" is selected from one or more of n-propyl, or n-pentyl, each additional R", which can be the same or different is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R''' is one or more or a combination of the group consisting of carbon, germanium, silicon, phosphorous and nitrogen atoms containing radical bridging two $(C_5H_{5-d-f}R''_d)$ rings, or bridging one $(C_5H_{5-d-f}R''_d)$ ring to Hf; each Q which can be the same or different is selected from the group consisting of a hydride, substituted and unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides and combination thereof; two Q's together form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand; d is 1, 2, 3, or 4, f is 0 or 1, and e is 1, 2 or 3, a support and an activator, wherein the activator and the hafnium metallocene catalyst compound are premixed in a solvent, and then combined with the support and then dried, to produce a free-flowing powder, and wherein the catalyst has a catalyst productivity of greater than 1000 (g polymer)/(g catalyst*h*150 psi) at 85° C.*

24. A continuous gas phase process for polymerizing olefins, excluding cyclic olefin, in a fluidized bed gas phase reactor in the presence of a catalyst system to produce a polymer product, the catalyst system comprising an activator, *a support* and a **[**bulky ligand**]** hafnium transition metal metallocene catalyst represented by the formula:

$$(C_5H_{5-d-f}R''_d)_eR'''_fHfQ_{g-e}$$

wherein $(C_5H_{5-d-f}R''_d)$ is an unsubstituted or substituted cyclopentadienyl ligand bonded to Hf, wherein at least one $(C_5H_{5-d-f}R''_d)$ is substituted with at least one R" which is an alkyl group selected from the group consisting of n-propyl, **[**isopropyl, isobutyl**]** and n-pentyl, each additional R", which can be the same or different, is hydrogen or a substituted or unsubstituted hydrocarbyl having from 1 to 30 carbon atoms or combinations thereof, or two or more carbon atoms are joined together to form a part of a substituted or unsubstituted ring or ring system having 4 to 30 carbon atoms, R''' is one or more or a combination of the group consisting of carbon, germanium, silicon, phosphorous and nitrogen atoms containing radical bridging two $(C_5H_{5-d-f}R''_d)$ rings, or bridging one $(C_5H_{5-d-f}R''_d)$ ring to Hf; each Q which can be the same or different is selected from the group consisting of hydride, substituted and unsubstituted hydrocarbyl having from 1 to 30 carbon atoms, halogen, alkoxides, aryloxides, amides, phosphides and combinations thereof; two Q's together form an alkylidene ligand or cyclometallated hydrocarbyl ligand or other divalent anionic chelating ligand; where g is an integer corresponding to the formal oxidation state of Hf, d is 0, 1, 2, 3, 4 or 5, f is 0 or 1 and e is 1, 2 or 3, *wherein the activator and the hafnium metallocene catalyst compound are premixed in a solvent, and then combined with the support and then dried, to produce a free-flowing powder, and wherein the catalyst has a catalyst productivity of greater than 1000 (g polymer)/(g catalyst*h*150 psi) at 85° C.,* and the polymer product has a melt index less than 10 dg/min (ASTM D-1238-F or ASTM D-1238-E) without the addition of hydrogen to the process.

[25. The process in accordance with claim **1** wherein the hafnium metallocene catalyst compound is a bis-cyclopentadienyl hafnium metallocene compound.**]**

26. The process in accordance with claim **1** wherein the activator is alumoxane.

27. The process in accordance with claim **[4** where in the linear or iso alkyl group has from 3 to 5 carbon atoms**]** *24, wherein the hafnium metallocene catalyst compound is bis (n-propyl-cyclopentadienyl) hafnium dichloride and said activator is alumoxane*.

[28. The process in accordance with claim **1** wherein the linear or iso alkyl group has 3 carbon atoms.**]**

*29. A continuous gas-phase process for polymerizing olefins, excluding cyclic olefin(s), comprising: combining a) one or more of ethylene, propylene, butene-1, pentene-1, 4-methyl-1-pentene, hexene-1 and octene-1 b) a catalyst comprising a bis n-propyl cyclopentadienyl hafnium dichloride, an activator selected from the group consisting of alumoxane, methyl alumoxane, modified alumoxane, and ionizing activators, and a support, wherein the activator and the catalyst are premixed in a solvent, and then combined with the support and then dried, to produce a free-flowing powder, and wherein the catalyst has a catalyst productivity of greater than 1000 (g polymer)/(g catalyst*h*150 psi) at 85° C.*

*30. A continuous gas-phase process for polymerizing olefins, excluding cyclic olefin(s), comprising: combining a) one or more of ethylene, propylene, butene-1, pentene-1, 4-methyl-1-pentene, hexene-1 and octene-1 b) a catalyst consisting essentially of a bis n-propyl cyclopentadienyl hafnium dichloride, an activator selected from the group consisting of alumoxane, methyl alumoxane, modified alumoxane, and ionizing activators, and a support, wherein the activator and catalyst are premixed in a solvent, and then combined with the support and then dried, to produce a free-flowing powder, and wherein the catalyst has a catalyst productivity of greater than 1000 (g polymer)/(g catalyst*h*150 psi) at 85° C.*

*31. A continuous gas-phase process for polymerizing olefins, excluding cyclic olefin(s), comprising: combining a) one or more of ethylene, propylene, butene-1, pentene-1, 4-methyl-1-pentene, hexene-1 and octene-1 b) a catalyst consisting of a bis n-propyl cyclopentadienyl hafnium dichloride, an activator selected from the group consisting of alumoxane, methyl alumoxane, modified alumoxane, and ionizing activators, and a support, wherein the activator and the catalyst are premixed in a solvent, and then combined with the support and then dried, to produce a free-flowing powder, and wherein the catalyst has a catalyst productivity of greater than 1000 (g polymer)/(g catalyst*h*150 psi) at 85° C.*

* * * * *