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(54) Title: CATALYST COMPOSITION COMPRISING FLUORIDED SUPPORT AND PROCESSES FOR USE THEREOF

Figure 1a. GPC-3D Characterization of PE produced with supported catalyst a-1.

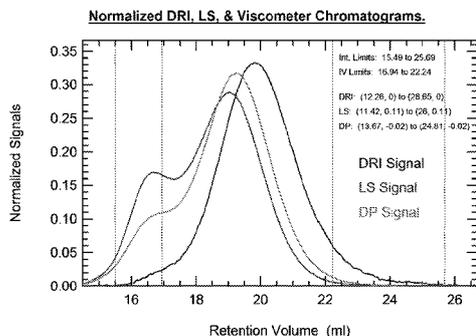
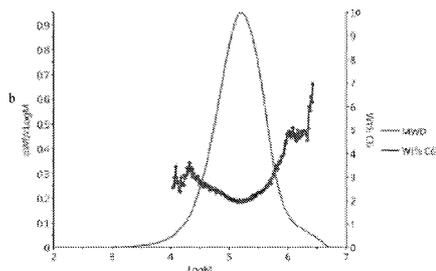


Figure 1b. GPC-IR Characterization of PE produced with supported catalyst a-1



(57) Abstract: This invention relates to a catalyst system comprising fluorided silica, alkylalumoxane activator and at least two metallocene catalyst compounds, where the first metallocene is a bridged monocyclopentadienyl group 4 transition metal compound and the second metallocene is a biscyclopentadienyl group 4 transition metal compound, where the fluorided support has not been calcined at a temperature of 400°C or more, and is preferably produced using a west mixing method, such as an aqueous method.

WO 2016/171807 A1

Catalyst Composition Comprising Fluorided Support and Processes for Use Thereof**CROSS-REFERENCE TO RELATED APPLICATIONS**

[0001] This application claims the benefit of Provisional Application No. 62/149799, filed April 20, 2015 and EP Application No. 15172225.3, filed June 15, 2015, the disclosures of which are hereby incorporated by reference in their entireties.

FIELD OF THE INVENTION

[0002] This invention relates to novel catalyst compositions comprising a monocyclopentadienyl transition metal compound, a biscyclopentadienyl transition metal compound, a fluorided support, and an optional activator and uses thereof.

BACKGROUND OF THE INVENTION

[0003] Olefin polymerization catalysts are of great use in industry. Hence, there is interest in finding new catalyst systems that increase the commercial usefulness of the catalyst and allow the production of polymers having improved properties. Catalysts for olefin polymerization are often based on cyclopentadienyl transition metal compounds as catalyst precursors, which are activated either with an alumoxane or with an activator containing a non-coordinating anion.

[0004] A typical metallocene catalyst system includes a metallocene catalyst, a support, and an activator. Supported catalyst systems are used in many polymerization processes, often in slurry or gas phase polymerization processes. For example, US 6,846,770 and US 6,664,348 disclose catalyst compositions containing at least one metallocene, and least one activator and a support that has been fluorided using a fluoride containing compound. *See also*, WO 05/075525; US 2002/007023; WO 2003/025027; US 2005/0288461; and US 2014/0031504.

[0005] Metallocenes are often combined with other catalysts, or even other metallocenes, to attempt to modify polymer properties. *See, for example*, US 8,088,867. Likewise, US 5,516,848 discloses the use of two different cyclopentadienyl based transition metal compounds activated with alumoxane or non-coordinating anions. In particular, the examples disclose, among other things, catalyst compounds in combination, such as $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-c-Ci}_2\text{H}_{23})\text{TiCl}_2$ and $\text{rac-Me}_2\text{Si}(\text{H}_4\text{Ind})\text{ZrCl}_2$, or $\text{Me}_2\text{Si}(\text{Me}_4\text{C}_5)(\text{N-c-Ci}_2\text{H}_{23})\text{TiCl}_2$ and $\text{Me}_2\text{Si}(\text{Ind})_2\text{HfMe}_2$, (Ind=indenyl) activated with activators such as methylalumoxane or N,N-dimethyl anilinium tetrakis(pentafluorophenyl)borate to produce polypropylenes having bimodal molecular weight distributions (Mw/Mn), varying amounts of isotacticity (from 12 to 52 weight % isotactic PP in the product in Ex 2, 3 and 4), and

having weight average molecular weights over 100,000, and some even as high as 1,200,000 for use as thermoplastics. *See also*, US 4,701,432; US 5,077,255; US 7,141,632; US 6,207,606; US 8,598,061; Hong et al. in *Immobilized Me₂Si(C₃Me)₄(N-t-Bu)TiCl₂/(nBuCp)₂ZrCh Hybrid Metallocene Catalyst System for the Production of Poly(ethylene-co-hexene) with Pseudo-bimodal Molecular Weight and Inverse Comonomer Distribution*, (Polymer Engineering and Science-2007, DOI 10.1002/pen, pages 131-139, published online in Wiley InterScience (www.interscience.wiley.com) 2007 Society of Plastics Engineers); US 2012/0130032; US 7,192,902; US 8,110,518; US 7,355,058; US 5,382,630; US 5,382,631; US 8,575,284, US 6,069,213; Kim, J. D. *et al*, J. Polym. Sci. Part A: Polym Chem, 38, 1427 (2000); Iedema, P.D. *et al*, Ind. Eng. Chem. Res., 43, 36 (2004); US 6,656,866; US 8,815,357; US 2004/259722; US 2014/0031504; US 5,135,526; US 7,385,015; WO 2007/080365; WO 2012/006272; WO 2014/0242314; WO 00/12565; WO 02/060957; WO 2004/046214; WO 2009/146167; and EP 2 374 822 A.

[0006] There is still a need in the art for new and improved catalyst systems for the polymerization of olefins, in order to achieve increased activity or specific polymer properties, such as high melting point, high molecular weights, to increase conversion or comonomer incorporation, or to alter comonomer distribution without deteriorating the resulting polymer's properties. It is therefore also an object of the present invention to provide novel supported catalysts systems and processes for the polymerization of olefins using such catalyst systems.

SUMMARY OF THE INVENTION

[0007] This invention relates to a catalyst system comprising fluorided silica, alkylaluminum activator and at least two metallocene catalyst compounds, where the first metallocene is a bridged monocyclopentadienyl group 4 transition metal compound and the second metallocene is a biscyclopentadienyl group 4 transition metal compound, where the fluorided support has not been calcined at a temperature of 400°C or more.

[0008] This invention also relates to a process to produce ethylene polymer comprising: i) contacting, in the gas phase or slurry phase, ethylene and C₃ to C₂₀ comonomer with a catalyst system comprising a fluorided support, an alkyl aluminum activator, and at least two metallocene catalyst compounds, where the first metallocene is a bridged monocyclopentadienyl group 4 transition metal compound and the second metallocene is a biscyclopentadienyl group 4 transition metal compound, where the fluorided support has not been calcined at a temperature of 400°C or more, and ii) obtaining a polymer comprising at

least 50 mol% ethylene.

[0009] This invention also relates to a catalyst system comprising a fluorided support, an alkylaluminum activator, and at least two metallocene catalyst compounds, where the metallocenes are represented by the formula:



5 wherein each Cp is, independently, a cyclopentadienyl group (such as cyclopentadiene, indene or fluorene) which may be substituted or unsubstituted, M is a group 4 transition metal, for example, titanium, zirconium, hafnium, G is a heteroatom group represented by the formula JR^*_z where J is N, P, O or S, and R^* is a C_1 to C_{20} hydrocarbyl group and z is 1 or 2,
 10 T is a bridging group, and y is 0 or 1, X is a leaving group (such as a halide, a hydride, an alkyl group, an alkenyl group or an arylalkyl group), and $m=1$ or 2, $n=0, 1, 2$ or 3, $q=0, 1, 2$ or 3, and the sum of $m+n+q$ is equal to the oxidation state of the transition metal; wherein $m = 1, n = 1$ and $y = 1$ in the first metallocene catalyst compound; and $n = 0$ and $m = 2$ in the second metallocene catalyst compound, provided that when $y = 1$ in the second metallocene
 15 compound, then at least one Cp is preferably not an indene group.

BRIEF DESCRIPTION OF THE FIGURES

[0010] Figure 1a is the GPC-3D graph for PE produced with supported catalyst **a-1**.
 Figure 1b is the GPC-IR graph for PE produced with supported catalyst **a-1**.
 Figure 2a is the GPC-3D graph for PE produced with supported catalyst **b-1**.
 20 Figure 2b is the GPC-IR graph for PE produced with supported catalyst **b-1**.
 Figure 3a is the GPC-3D graph for PE produced with supported catalyst **c-1**.
 Figure 3b is the GPC-IR graph for PE produced with supported catalyst **c-1**.
 Figure 4 is the GPC-3D graph for PE produced with supported catalyst **d-1**.
 Figure 5a is the GPC-3D graph for PE produced with supported catalyst **e-1**.
 25 Figure 5b is the GPC-4D graph for PE produced with supported catalyst **e-1**.
 Figure 5c is the TREF of PE produced from supported catalyst **e-1**.
 Figure 6a is the GPC-4D of PE produced with supported catalyst **f-1**.
 Figure 6b is the TREF of PE produced with supported catalyst **f-1**.
 Figure 6c is the CFC graph for PE produced with supported catalyst **f-1**.
 30 Figure 7 is the TREF of PE produced with supported catalyst **g-2**.
 Figure 8a is the TREF of PE produced with supported catalyst **h-1**.
 Figure 8b is the CFC of PE produced with supported catalyst **h-1**.

Figure 9 is a proton NMR trace for four supports, from top to bottom: 1) reaction mixture of $(\text{NH}_4)_2\text{SiF}_6$ and MAO solution; 2) reaction mixture of silica-1 and MAO solution; 3) reaction mixture of silica-2 and MAO solution.

DETAILED DESCRIPTION

5 [0011] For the purposes of this invention and the claims thereto, the new numbering scheme for the Periodic Table Groups is used as described in **CHEMICAL AND ENGINEERING NEWS**, 63(5), pg. 27 (1985), e.g., a "Group 4 metal" is an element from Group 4 of the Periodic Table, e.g., Hf, Ti, or Zr.

[0012] An "olefin," alternatively referred to as "alkene," is a linear, branched, or cyclic
10 compound of carbon and hydrogen having at least one double bond. For purposes of this specification and the claims appended thereto, when a polymer or copolymer is referred to as comprising an olefin, the olefin present in such polymer or copolymer is the polymerized form of the olefin. For example, when a copolymer is said to have an "ethylene" content of 35 wt% to 55 wt%, it is understood that the mer unit in the copolymer is derived from
15 ethylene in the polymerization reaction and said derived units are present at 35 wt% to 55 wt%, based upon the weight of the copolymer. A "polymer" has two or more of the same or different mer units. A "homopolymer" is a polymer having mer units that are the same. A "copolymer" is a polymer having two or more mer units that are different from each other. A "terpolymer" is a polymer having three mer units that are different from each other.
20 "Different" as used to refer to mer units indicates that the mer units differ from each other by at least one atom or are different isomerically. Accordingly, the definition of copolymer, as used herein, includes terpolymers and the like. An "ethylene polymer" or "ethylene copolymer" is a polymer or copolymer comprising at least 50 mole% ethylene derived units, a "propylene polymer" or "propylene copolymer" is a polymer or copolymer comprising at
25 least 50 mole% propylene derived units, and so on.

[0013] For the purposes of this invention, ethylene shall be considered an a-olefin.

[0014] For purposes of this invention and claims thereto, the term "substituted" means
30 that a hydrogen group has been replaced with a heteroatom, or a heteroatom containing group. For example, a "substituted hydrocarbyl" is a radical made of carbon and hydrogen where at least one hydrogen is replaced by a heteroatom or heteroatom containing group.

[0015] As used herein, Mn is number average molecular weight, Mw is weight average molecular weight, and Mz is z average molecular weight, wt% is weight percent, and mol% is mole percent. Molecular weight distribution (MWD), also referred to as polydispersity, is

defined to be Mw divided by Mn. Unless otherwise noted, all molecular weight units (e.g., Mw, Mn, Mz) are g/mol. The following abbreviations may be used herein: Me is methyl, Et is ethyl, Pr is propyl, cPr is cyclopropyl, nPr is n-propyl, iPr is isopropyl, Bu is butyl, nBu is normal butyl, iBu is isobutyl, sBu is sec-butyl, tBu is tert-butyl, Oct is octyl, Ph is phenyl, Bn is benzyl, Cp is cyclopentadienyl, Cp* is pentamethyl cyclopentadienyl, Ind is indenyl, Flu is fluorenyl, and MAO is methylalumoxane.

[0016] For purposes of this invention and the claims thereto, a "catalyst system" is the combination of at least two catalyst compounds, at least one activator, an optional co-activator, and fluorided support material. For the purposes of this invention and the claims thereto, when catalyst systems are described as comprising neutral stable forms of the components, it is well understood by one of ordinary skill in the art, that the ionic form of the component is the form that reacts with the monomers to produce polymers.

[0017] In the description herein, the metallocene catalyst may be described as a catalyst precursor, a pre-catalyst compound, metallocene catalyst compound or a transition metal compound, and these terms are used interchangeably.

[0018] A metallocene catalyst is defined as an organometallic transition metal compound with at least one π -bound cyclopentadienyl moiety (or substituted cyclopentadienyl moiety) and more frequently two π -bound cyclopentadienyl moieties or substituted cyclopentadienyl moieties bound to a transition metal.

[0019] For purposes of this invention and claims thereto in relation to metallocene catalyst compounds, the term "substituted" means that a hydrogen group has been replaced with a hydrocarbyl group, a heteroatom, or a heteroatom containing group. For example, methyl cyclopentadiene (Cp) is a Cp group substituted with a methyl group.

[0020] For purposes of this invention and claims thereto, "alkoxides" include those where the alkyl group is a C₁ to C₁₀ hydrocarbyl. The alkyl group may be straight chain, branched, or cyclic. The alkyl group may be saturated or unsaturated. In some embodiments, the alkyl group may comprise at least one aromatic group.

[0021] This invention relates to a catalyst system comprising a fluorided support, an alkylalumoxane activator, and at least two metallocene catalyst compounds, where the first metallocene is a bridged monocyclopentadienyl group 4 transition metal compound and the second metallocene is a biscyclopentadienyl group 4 transition metal compound, preferably the metallocenes are represented by the formula:



wherein Cp is a cyclopentadienyl group (such as cyclopentadiene, indene or fluorene) which may be substituted or unsubstituted, M is a group 4 transition metal, for example, titanium, zirconium, hafnium, G is a heteroatom group represented by the formula JR^*_z where J is N, P, O or S, and R^* is a C_1 to C_{20} hydrocarbyl group and z is 1 or 2, T is a bridging group, and
5 y is 0 or 1, X is a leaving group (such as a halide, a hydride, an alkyl group, an alkenyl group or an arylalkyl group), and $m=1$ or 2, $n=0, 1, 2$ or 3, $q=0, 1, 2$ or 3, and the sum of $m+n+q$ is equal to the oxidation state of the transition metal (preferably 2, 3, 4, 5 or 6, preferably 4); wherein $m = 1, n = 1$ and $y = 1$ in the first metallocene catalyst compound and $n = 0$ and $m = 2$ in the second metallocene catalyst compound, provided that when $y = 1$ in the second
10 metallocene compound, then at least one Cp is preferably not an indene group.

[0022] Generally, two or more different catalyst compounds are present in the catalyst system used herein. When two transition metal compound based catalysts are used as a mixed catalyst system, the two transition metal compounds are preferably chosen such that the two are compatible. A simple screening method such as by 1H or ^{13}C NMR, known to
15 those of ordinary skill in the art, can be used to determine which transition metal compounds are compatible. It is preferable to use the same activator for the transition metal compounds, however, two different activators, such as a non-coordinating anion activator and an alumoxane can be used in combination. If one or more transition metal compounds contain an X_1 or X_2 ligand which is not a hydride, hydrocarbyl, or substituted hydrocarbyl, then the
20 alumoxane may be contacted with the transition metal compounds prior to addition of the non-coordinating anion activator.

[0023] The two transition metal compounds (pre-catalysts) may be used in any ratio. Preferred molar ratios of (A) monocyclopentadienyl transition metal compound to (B) biscyclopentadienyl transition metal compound fall within the range of (A:B) 1:1000 to
25 1000:1, alternatively 1:100 to 500:1, alternatively 1:10 to 200:1, alternatively 1:1 to 100:1, and alternatively 1:1 to 75:1, and alternatively 5:1 to 50:1. The particular ratio chosen will depend on the exact pre-catalysts chosen, the method of activation, and the end product desired. In a particular embodiment, when using the two pre-catalysts, where both are activated with the same activator, useful mole percents, based upon the molecular weight of
30 the pre-catalysts, are 10 to 99.9% A to 0.1 to 90%B, alternatively 25 to 99% A to 0.5 to 50% B, alternatively 50 to 99% A to 1 to 25% B, and alternatively 75 to 99% A to 1 to 10% B.

[0024] The combined catalyst compounds are present on the support at 1 to 100 $\mu\text{mol/g}$ supported catalyst, preferably 20-60 $\mu\text{mol/g}$ supported catalyst.

[0025] This invention also relates to metallocene catalyst compositions comprising the reaction product of at least four components: (1) one or more bridged metallocenes having one cyclopentadienyl group; (2) one or more metallocenes having two or three cyclopentadienyl groups; (3) one or more alkylaluminum activators; and (4) one or more fluorided support compositions, where the fluorided support composition has not been calcined at 400°C or more, preferably the fluorided support composition has been calcined at a temperature of 100°C to 395°C, alternately 125°C to 350°C, alternately 150°C to 300°C).

[0026] Typically, the fluorided supports described herein are prepared by combining an aqueous solution of fluorinating agent (such as SiF₄ or (NH₄)₂SiF₆) with a slurry of support (such as a toluene slurry of silica), then drying until it is free flowing, and optionally, calcining (typically at temperatures over 100°C for at least 1 hour). The supports are then combined with activator(s) and catalyst compounds (separately or together).

Fluorided Supports

[0027] As used herein, the phrases "fluorided support" and "fluorided support composition" mean a support, desirably particulate and porous, which has been treated with at least one inorganic fluorine containing compound. For example, the fluorided support composition can be a silicon dioxide support wherein a portion of the silica hydroxyl groups has been replaced with fluorine or fluorine containing compounds. Likewise, the term "support composition" means a support, desirably particulate and porous, which has been treated with at least one fluorine containing compound. Suitable fluorine containing compounds include, but are not limited to, inorganic fluorine containing compounds and/or organic fluorine containing compounds.

[0028] Supports suitable for use in this invention are generally porous materials and can include organic materials, inorganic materials and inorganic oxides. Desirably, supports suitable for use in this invention include talc, clay, silica, alumina, magnesia, zirconia, iron oxides, boria, calcium oxide, zinc oxide, barium oxide, thoria, aluminum phosphate gel, polyvinylchloride and substituted polystyrene and mixtures thereof. Other useful support materials include zeolites, clays, organoclays, or any other organic or inorganic support material and the like, or mixtures thereof.

[0029] Preferably, the support material is an inorganic oxide in a finely divided form. Suitable inorganic oxide materials for use in the catalyst systems described herein include Groups 2, 4, 13, and 14 metal oxides, such as silica, alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, or

alumina are magnesia, titania, zirconia, and the like. Other suitable support materials, however, can be employed, for example, finely divided functionalized polyolefins, such as finely divided polyethylene. Particularly useful supports include magnesia, titania, zirconia, montmorillonite, phyllosilicate, zeolites, talc, clays, and the like. Also, combinations of these support materials may be used, for example, silica-chromium, silica-alumina, silica-titania, and the like. Preferred support materials include Al_2O_3 , ZrO_2 , SiO_2 , and combinations thereof, more preferably SiO_2 , Al_2O_3 , or $\text{SiO}_2/\text{Al}_2\text{O}_3$. In a preferred embodiment, of the invention, the support is silica.

[0030] It is preferred that the support material, preferably an inorganic oxide, preferably silica, has a surface area in the range of from about 10 to about 800 m^2/g (alternately 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 5 to about 500 μm . More preferably, the surface area of the support material is in the range of from about 50 to about 500 m^2/g , pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 10 to about 200 μm . Most preferably, the surface area of the support material is in the range 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 5 to about 100 μm . The average pore size of the support material useful in the invention is in the range of from 10 to 1000 \AA , preferably 50 to about 500 \AA , and most preferably 75 to about 350 \AA . In some embodiments, the support material is a high surface area, amorphous silica (surface area=300 m^2/gm ; pore volume of 1.65 cm^3/gm). Useful silicas are marketed under the trade names of DAVISON™ 952, DAVISON™ 948 or DAVISON™ 955 by the Davison Chemical Division of W.R. Grace and Company. Total surface area, also referred to as "surface area" and total pore volume, also referred to as "pore volume", and average pore diameter are measured by the Brunauer-Emmett-Teller (BET) method using adsorption-desorption of nitrogen (temperature of liquid nitrogen, 77 K) with a Micromeritics Tristar II 3020 instrument after degassing of the powders for 4 hrs. at 350°C. More information regarding the method can be found, for example, in *"Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density"*, S. Lowell et al, Springer, 2004. Average particle size, also referred to as "particle size," or "particle diameter" is determined using a Mastersizer™ 3000 (range of 1 to 3500 μm) available from Malvern Instruments, Ltd. Worcestershire, England.

[0031] In a particularly useful embodiment, the support is silica, is desirably porous, and has a surface area in the range of from about 10 to about 800 m^2/g , a total pore volume in the

range of from about 0.1 to about 4.0 cc/g and an average particle diameter in the range of from about 10 to about 500 μm . More desirably, the surface area is in the range of from about 50 to about 500 m^2/g , the pore volume is in the range of from about 0.5 to about 3.5 cc/g and the average particle diameter is in the range of from about 15 to about 150 μm .
5 Most desirably the surface area is in the range of from about 100 to about 400 m^2/g , the pore volume is in the range of from about 0.8 to about 3.0 cc/g and the average particle diameter is in the range of from about 20 to about 100 μm . The average pore diameter of typical porous silicon dioxide support materials is in the range of from about 10 to about 1000 \AA . Desirably, the support material has an average pore diameter of from about 50 to about 500 \AA , and most
10 desirably from about 75 to about 350 \AA .

[0032] The fluorine compounds suitable for providing fluorine for the support may be organic or inorganic fluorine compounds and are desirably inorganic fluorine containing compounds. Such inorganic fluorine containing compounds may be any compound containing a fluorine atom as long as it does not contain a carbon atom. Particularly
15 desirable are inorganic fluorine-containing compounds selected from the group consisting of NH_4BF_4 , $(\text{NH}_4)_2\text{SiF}_6$, NH_4PF_6 , NH_4F , $(\text{NH}_4)_2\text{TaF}_7$, NH_4NbF_4 , $(\text{NH}_4)_2\text{GeF}_6$, $(\text{NH}_4)_2\text{SmF}_6$, $(\text{NH}_4)_2\text{TiF}_6$, $(\text{NH}_4)_2\text{ZrF}_6$, MoF_6 , ReF_6 , GaF_3 , S_2Cl_2 , F_2 , SiF_4 , SF_6 , ClF_3 , ClF_5 , BrF_5 , IF_7 , NF_3 , HF , BF_3 , NHF_2 and NH_4HF_2 . Of these, ammonium hexafluorosilicate and ammonium tetrafluoroborate are useful. Combinations of these compounds may also be used.

[0033] Ammonium hexafluorosilicate and ammonium tetrafluoroborate fluorine compounds are typically solid particulates as are the silicon dioxide supports. A useful method of treating the support with the fluorine compound is to dry mix the two components by simply blending at a concentration of from 0.01 to 10.0 millimole F/g of support, desirably in the range of from 0.05 to 6.0 millimole F/g of support, and most desirably in the
25 range of from 0.1 to 3.0 millimole F/g of support. The fluorine compound can be dry mixed with the support either before or after charging to a vessel for dehydration or calcining the support. Accordingly, the fluorine concentration present on the support is preferably in the range of from 0.1 to 25 wt%, alternately 0.19 to 19 wt%, alternately from 0.6 to 3.5 wt %, based upon the weight of the support.

[0034] Another method of treating the support with the fluorine compound is to dissolve the fluorine compound in a solvent, such as water, and then contact the support (dry or combined with water or hydrocarbon solvent) with the fluorine compound containing

solution. When water is used and silica is the support, it is desirable to use a quantity of water which is less than the total pore volume of the support.

[0035] A disadvantage of typical dry mix methods is that the density difference between fluorinating agent (such as ammonium hexafluorosilicate - density about 2.1 g/cm³) and silica
5 (e.g., such as Davison™ 948 - density about 0.7 g/cm³) makes it difficult to evenly/homogeneously distribute the fluorinating agent in the silica support. The density difference has also led to settling of ammonium hexafluorosilicate in fluorided silica derived from dry mix method. Over a period of two weeks, a vertical gradient of ammonium hexafluorosilicate concentrations in fluorided silica (made via dry mix method) stored in a
10 bottle was observed. Such settling can lead to operational problems on a commercial scale.

[0036] To overcome these problems, an alternative method (wet-mixing) has been developed. The aqueous (wet-mixing) method employs a minimal amount of a polar solvent (e.g., water, or methanol, ethanol, isopropanol, any solvent capable of dissolving the fluoride compound (such as ammonium hexafluorosilicate) to dissolve the fluorinating agent (e.g.,
15 ammonium hexafluorosilicate). The fluoride compound solution (such as an ammonium hexafluorosilicate solution) is then added to a slurry of silica in a non-polar solvent (e.g., toluene, or benzene, chloroform, etc.), followed by vigorous stirring of the resulting mixture. The polar/hydrophilic nature of the fluoride compound (such as ammonium hexafluorosilicate) leads to its absorption onto the hydrophilic silica surface. When the non-
20 polar solvent is removed (by filtration), silica with an even distribution of fluorinating agent (such as ammonium hexafluorosilicate) is obtained, and ready for subsequent drying and calcination steps.

[0037] The fluorided support material is then typically slurried in a non-polar solvent and the resulting slurry is contacted with a solution of a metallocene compounds and activator. In
25 some embodiments, the slurry of the fluorided support material is first contacted with the activator for a period of time in the range of from about 0.5 hours to about 24 hours, from about 1 hour to about 16 hours, or from about 2 hours to about 8 hours. The solution of the metallocene compound is then contacted with the isolated fluorided support/activator. In some embodiments, the supported catalyst system is generated in situ. In alternate
30 embodiment, the slurry of the fluorided support material is first contacted with the catalyst compound for a period of time in the range of from about 0.5 hours to about 24 hours, from about 1 hour (or 2 hours) to about 16 hours, or from about 2 hours (or 4 hours) to about 8

hours. The slurry of the supported metallocene compound is then contacted with the activator solution.

[0038] The mixture of the metallocenes, activator and fluorided support may be heated to about 0°C to about 70°C, preferably to about 23°C to about 60°C, preferably at room temperature. Contact times typically range from about 0.5 hours to about 24 hours, from about 2 hours to about 16 hours, or from about 4 hours to about 8 hours.

[0039] In a preferred embodiment of the invention, the fluorided support material in slurried in a non-polar solvent and the resulting slurry is contacted with a solution of methylalumoxane (typically 30 wt% MAO in toluene). The fluorided support/MAO mixture is then heated to elevated temperature (30°C to 120°C, preferably 80 to 100°C) with vigorous stirring for a period of time (0.1 to 24 hours, preferably 1 to 3 hours). The support/activator is isolated by filtration, rinsed with non-polar solvent (e.g., toluene, pentane, hexane, etc.), and dried. The isolated support/activator is then slurried in a non-polar solvent (e.g., toluene), and a solution of metallocene compound/compounds is then contacted with the support/activator slurry. Vigorous stirring may then be applied.

[0040] In a preferred embodiment of the invention, the fluorided support material is slowly added in solid form to a solution of MAO in non-polar solvent (e.g., toluene) (typically at room temperature) with vigorous stirring. This addition sequence, namely slow and portion-wise addition of fluorided silica to MAO solution, is referred to as "reversed addition". After the addition of fluorided silica is completed, the fluorided support/MAO mixture is then heated to elevated temperature (30°C to 120°C, preferably 80 to 100°C) with vigorous stirring for a period of time (0.1 to 24 hours, preferably 1 to 3 hours). The support/activator is isolated by filtration, rinsed with non-polar solvent (e.g., toluene, pentane, hexane, etc.), and dried. The isolated support/activator is then slurried in a non-polar solvent (e.g., toluene), and a solution of metallocene compound/compounds is then contacted with the support/activator slurry. Vigorous stirring may be applied.

[0041] Under otherwise identical conditions, the "reversed addition" method for immobilizing MAO on fluorided silica surface offers higher polymerization activity for a wide variety of catalysts, compared to the "traditional addition" method where MAO solution is added to a slurry of fluorided silica in non-polar solvent.

[0042] Suitable non-polar solvents are materials in which all of the reactants used herein, i.e., the activator, and the metallocene compound, are at least partially soluble and which are liquid at reaction temperatures. Preferred non-polar solvents are alkanes, such as isopentane,

hexane, n-heptane, octane, nonane, and decane, although a variety of other materials including cycloalkanes, such as cyclohexane, aromatics, such as benzene, toluene, and ethylbenzene, may also be employed.

[0043] In a preferred embodiment of the invention, the fluorided supports described
5 herein are prepared by combining an aqueous solution of fluorinating agent (such as $(\text{NH}_4)_2\text{SiF}_6$) with a slurry of support (such as a toluene slurry of silica), drying until free flowing, optionally, calcining (typically at temperatures from 100°C to 400°C for at least 1 hour), then combining with activators and catalyst compounds (the activators and catalyst compounds may be added to the support separately or together).

10 [0044] In another embodiment of the invention, the water to solvent ratio (by weight) is between 1:10 to 1:1000, preferably between 1:20 to 1:50.

[0045] In another embodiment of the invention, the fluorided silica support can immobilize greater than 5.0 mmol "Al" per gram silica, and preferably greater than 6.0 mmol "Al" per gram silica. The amount of "Al" (from alkylaluminum, such as MAO) that can be
15 immobilized on 1 gram of fluorided silica is determined by an aluminum titration experiment. The titration is done at 100°C at ambient pressure allowing the aluminum (15 mmol Al) and the 1 gram of fluorided silica to react for 3 hours. Thereafter, the silica is washed with toluene (10ml, 3 times) and then washed with pentane (10 ml, 3 times). The solid is then
20 collected and dried in vacuo for 8 hours until solvent is removed. Then the sample is weighed and the difference in weight is divided by the Mw of the aluminum compound (Mw as reported in the **CHEMICAL AND ENGINEERING NEWS**, 63(5), pg. 27 (1985)). Methyl aluminum is defined to be Me-Al-O. The "Al" uptake for silica-1 in the examples below was about 5.5 mmol Al/gram, whereas the "Al" uptake for silica-2 was about 6.8 mmol/gram. Higher Al uptake (or loading) is often desirable as it is thought to offer higher polymerization
25 activity, provided the silica and the catalyst precursor stay unchanged. In a useful embodiment of the invention, the catalyst system comprising the fluorided silica support immobilizes greater than 5.0 mmol "Al" per gram of silica, and preferably greater than 6.0 mmol "Al" per gram of silica.

[0046] Alternately, the fluorided silica support preferably contains less than 0.05
30 mmol/gram fluorinating agent (such as $(\text{NH}_4)_2\text{SiF}_6$), preferably less than 0.02 mmol/gram fluorinating agent, as measured by ^1H NMR.

[0047] Alternately, the surface area of the fluorided silica support is greater than 200 m^2/g , preferably greater than 250 m^2/g , as determined by BET. Alternatively, the surface

area of combined fluorided silica support and activator (such as MAO) is greater than 250 m^2/g , preferably greater than 350 m^2/g , as determined by BET.

[0048] In embodiments where SiF_4 and/or $(NH_4)_2SiF_6$ is/are the fluoriding agent, immediately after combination of the alkylaluminum with the fluorided support the combination preferably contains less than 0.04 mmoles per gram of silica (preferably less than 0.02 mmoles, preferably less than 0.01 mmoles) of tetraalkylsilane per gram of support as determined by 1H NMR (where the alkyl is derived from the alkylaluminum).

[0049] In useful embodiments, the ratio of mmol of fluorine per gram of silica in the fluorided support is between 0.1 and 1.5, preferably between 0.2 and 1.2, preferably between 0.4 and 1.0.

[0050] For fluorided silica prepared using $(NH_4)_2SiF_6$, the amount of residual $(NH_4)_2SiF_6$ in the silica should be equal or less than 0.04 mmol $(NH_4)_2SiF_6/g$ silica, preferably equal or less than 0.02 mmol $(NH_4)_2SiF_6/g$ silica, more preferably equal or less than 0.01 mmol $(NH_4)_2SiF_6/g$ silica.

15 Catalyst Compounds

[0051] Useful catalysts include compounds represented by the formula: $T_yCp_mMG_nX_q$ wherein Cp is a cyclopentadienyl group (such as cyclopentadiene, indene or fluorene) which may be substituted or unsubstituted, M is a Group 4 transition metal, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, G is a heteroatom group represented by the formula JR^*_z where J is a group 15 or 16 element, preferably N, P, O or S, and R^* is a C_1 to C_{20} hydrocarbyl group and z is 1 or 2, T is a bridging group, and y is 0 or 1, each X is, independently, a leaving group, or two X are joined and bound to the metal atom to form a metallocycle ring, or two X are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand; and $m=1$ or 2, $n=0, 1, 2$ or 3, $q=0, 1, 2$ or 3, and the sum of $m+n+q$ is equal to the oxidation state of the transition metal (preferably 2, 3, 4, 5, or 6, preferably 4 or 5, preferably 4). In the present invention at least two metallocenes are present on the support where in the first metallocene m is 1, n is 1, and y is 1 and in the second metallocene n is 0 and m is 2, provided that when y = 1 in the second metallocene compound, then at least one Cp is preferably not an indene group.

[0052] In a preferred embodiment of the invention, M is a Group 4 transition metal (preferably Hf, Ti and/or Zr) and the two catalyst compounds may have the same or different M. In an embodiment when M is Ti, then m is 1. In another embodiment when M is Zr, then m is 2 or 3. In an embodiment when M is Ti, then m is 1 and when M is Zr, then m is 2. In a

useful embodiment, in the first metallocene M is Ti and in the second metallocene M is Hf or Zr.

[0053] Typically, each G is, independently, a heteroatom group represented by the formula JR^*_z where J is a group 15 or 16 element, preferably N, P, O or S (preferably N or O, preferably N), and R^* is a C_1 to C_{20} hydrocarbyl group. Typically, a linear branched or cyclic hydrocarbyl group having from one to twenty carbon atoms (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, or an isomer thereof, including t-butyl, cyclododecyl, cyclooctyl and the like) and z is 1 or 2.

[0054] In an embodiment, when m is one, n is preferably 1 and G is a heteroatom group represented by the formula JR^*_z where J is a group 15 or 16 element, preferably N, P, O or S (preferably N or O, preferably N), and R^* is a linear branched or cyclic hydrocarbyl group having from one to twenty carbon atoms (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl or an isomer thereof, including t-butyl, cyclododecyl, cyclooctyl and the like) and z is 1 or 2, preferably JR^*_z is cyclododecyl amido, t-butyl amido, and or 1-adamantyl amido.

[0055] In an embodiment, when m is 2 or 3, n is 0.

[0056] In an embodiment each X may be, independently, a halide, a hydride, an alkyl group, an alkenyl group or an arylalkyl group.

[0057] Alternately, each X is, independently, selected from the group consisting of hydrocarbyl radicals having from 1 to 20 carbon atoms, aryls, hydrides, amides, alkoxides, sulfides, phosphides, halides, dienes, amines, phosphines, ethers, and a combination thereof, (two X's may form a part of a fused ring or a ring system), preferably each X is independently selected from halides, aryls and C_1 to C_5 alkyl groups, preferably each X is a phenyl, methyl, ethyl, propyl, butyl, pentyl, or chloro group.

[0058] Typically, each Cp group is, independently, a substituted or unsubstituted cyclopentadiene, a substituted or unsubstituted indene, or a substituted or unsubstituted fluorene.

[0059] Independently, each Cp group may be substituted with a combination of substituent groups R. Non-limiting examples of substituent groups R include one or more from the group selected from hydrogen, or linear, branched alkyl radicals, or alkenyl radicals, alkynyl radicals, cycloalkyl radicals or aryl radicals, acyl radicals, alkoxy radicals, aryloxy radicals, alkylthio radicals, dialkylamino radicals, alkoxycarbonyl radicals, aryloxycarbonyl radicals, carbamoyl radicals, alkyl- or dialkyl- carbamoyl radicals, acyloxy radicals,

acylamino radicals, aroylamino radicals, straight, branched or cyclic, alkylene radicals, or combination thereof. In a preferred embodiment, substituent groups R have up to 50 non-hydrogen atoms, preferably from 1 to 30 carbon, that can also be substituted with halogens or heteroatoms or the like. Non-limiting examples of alkyl substituents R include methyl, ethyl, 5 propyl, butyl, pentyl, hexyl, cyclopentyl, cyclohexyl, benzyl or phenyl groups and the like, including all their isomers, for example, tertiary butyl, isopropyl and the like. Other hydrocarbyl radicals include fluoromethyl, fluoroethyl, difluoroethyl, iodopropyl, bromohexyl chlorobenzyl and hydrocarbyl substituted organometalloid radicals including trimethylsilyl, trimethylgermyl, methyldiethylsilyl and the like; and halocarbyl-substituted 10 organometalloid radicals including tris(trifluoromethyl)-silyl, methylbis(difluoromethyl)silyl, bromomethyldimethylgermyl and the like; and disubstituted boron radicals including dimethylboron for example; and disubstituted pnictogen radicals including dimethylamine, dimethylphosphine, diphenylamine, methylphenylphosphine, chalcogen radicals including methoxy, ethoxy, propoxy, phenoxy, methylsulfide and ethylsulfide. Non-hydrogen 15 substituents R include the atoms carbon, silicon, boron, aluminum, nitrogen, phosphorus, oxygen, tin, sulfur, germanium and the like, including olefins such as, but not limited to, olefinically unsaturated substituents including vinyl-terminated ligands, for example but-3-enyl, prop-2-enyl, hex-5-enyl and the like. Also, at least two R groups, preferably two adjacent R groups, may be joined to form a ring structure having from 3 to 30 atoms selected 20 from carbon, nitrogen, oxygen, phosphorus, silicon, germanium, aluminum, boron or a combination thereof.

[0060] In an embodiment of the Cp group, the substituent(s) R are, independently, hydrocarbyl groups, heteroatoms, or heteroatom containing groups, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl or an isomer 25 thereof, N, O, S, P, or a C₁ to C₂₀ hydrocarbyl substituted with an N, O, S and or P heteroatom or heteroatom containing group (typically having up to 12 atoms, including the N, O, S and P heteroatoms).

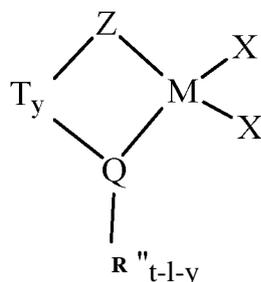
[0061] Non-limiting examples of Cp groups include cyclopentadienyl ligands, cyclopentaphenanthrenyl ligands, indenyl ligands, benzindenyl ligands, fluorenyl ligands, 30 octahydrofluorenyl ligands, cyclooctatetraenyl ligands, cyclopentacyclododecene ligands, azenyl ligands, azulene ligands, pentalene ligands, phosphoyl ligands, phosphinimine ligands (WO 99/40125), pyrrolyl ligands, pyrazolyl ligands, carbazolyl ligands, borabenzene ligands and the like, including hydrogenated versions thereof, for example tetrahydroindenyl ligands.

In another embodiment, each Cp may, independently comprise one or more heteroatoms, for example, nitrogen, silicon, boron, germanium, sulfur and phosphorus, in combination with carbon atoms to form an open, acyclic, or preferably a fused, ring or ring system, for example, a heterocyclopentadienyl ancillary ligand. Other Cp ligands include but are not limited to porphyrins, phthalocyanines, corrins and other polyazamacrocycles.

[0062] Preferably, T is present and is a bridging group containing at least one Group 13, 14, 15, or 16 element, in particular boron or a Group 14, 15 or 16 element. Examples of suitable bridging groups include $P(=S)R'$, $P(=Se)R'$, $P(=O)R'$, R'_2C , R'_2Si , R'_2Ge , $R'_2CCR'_2$, $R'_2CCR'_2CR'_2$, $R'_2CCR'_2CR'_2CR'_2$, $R'C=CR'$, $R'C=CR'CR'_2$, $R'_2CCR'=CR'CR'_2$, $R'C=CR'CR'=CR'$, $R'C=CR'CR'_2CR'_2$, $R'_2CSiR'_2$, $R'_2SiSiR'_2$, $R'_2SiOSiR'_2$, $R'_2CSiR'_2CR'_2$, $R'_2SiCR'_2SiR'_2$, $R'C=CR'SiR'_2$, $R'_2CGeR'_2$, $R'_2GeGeR'_2$, $R'_2CGeR'_2CR'_2$, $R'_2GeCR'_2GeR'_2$, $R'_2SiGeR'_2$, $R'C=CR'GeR'_2$, $R'B$, R'_2C-BR' , $R'_2C-BR'-CR'_2$, $R'_2C-O-CR'_2$, $R'_2CR'_2C-O-CR'_2$, $R'_2C-O-CR'_2CR'_2$, $R'_2C-O-CR'_2=CR'$, $R'_2C-S-CR'_2$, $R'_2CR'_2C-S-CR'_2$, $R'_2C-S-CR'_2CR'_2$, $R'_2C-S-CR'_2=CR'$, $R'_2C-Se-CR'_2$, $R'_2CR'_2C-Se-CR'_2$, $R'_2C-Se-CR'_2CR'_2$, $R'_2C-Se-CR'_2=CR'$, $R'_2C-N=CR'$, $R'_2C-NR'-CR'_2$, $R'_2C-NR'-CR'_2CR'_2$, $R'_2C-NR'-CR'_2=CR'$, $R'_2CR'_2C-NR'-CR'_2$, $R'_2C-P=CR'$, $R'_2C-PR'-CR'_2$, O, S, Se, Te, NR', PR', AsR', SbR', O-O, S-S, R'N-NR', R'P-PR', O-S, O-NR', O-PR', S-NR', S-PR', and R'N-PR' where R' is hydrogen or a C₁-C₂₀ containing hydrocarbyl, substituted hydrocarbyl, halocarbyl, substituted halocarbyl, silylcarbyl or germylcarbyl substituent and optionally two or more adjacent R' may join to form a substituted or unsubstituted, saturated, partially unsaturated or aromatic, cyclic or polycyclic substituent. Preferred examples for the bridging group T include CH₂, CH₂CH₂, SiMe₂, SiPh₂, SiMePh, Si(CH₂)₃, Si(CH₂)₄, O, S, NPh, PPh, NMe, PMe, NEt, NPr, NBu, PEt, PPr, Me₂SiOSiMe₂, and PBu.

[0063] In a preferred embodiment of the invention in any embodiment of any formula described herein, T is represented by the formula R^a_2J or $(R^a_2J)_2$, where J is C, Si, or Ge, and each R^a is, independently, hydrogen, halogen, C₁ to C₂₀ hydrocarbyl (such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, or dodecyl) or a C₁ to C₂₀ substituted hydrocarbyl, and two R^a can form a cyclic structure including aromatic, partially saturated, or saturated cyclic or fused ring system. Preferably, T is a bridging group comprising carbon or silica, such as dialkylsilyl, preferably T is selected from CH₂, CH₂CH₂, C(CH₃)₂, SiMe₂, SiPh₂, SiMePh, silylcyclobutyl (Si(CH₂)₃), (Ph)₂C, (p-Et)₃SiPh)₂C, Me₂SiOSiMe₂, and cyclopentasilylene (Si(CH₂)₄).

[0064] Useful bridged metallocene compounds having one cyclopentadienyl ring include those represented by the formula:



wherein

5 M is the same as M described above, preferably M is titanium, zirconium or hafnium, preferably titanium;

Z is a substituted or unsubstituted Cp group (useful Z groups are represented by the formula: $(C_5H_{4-d}S^*_d)$, where d is 1, 2, 3 or 4, S* is hydrocarbyl groups, heteroatoms, or heteroatom containing groups, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, 10 decyl, undecyl, dodecyl or an isomer thereof, N, O, S, P, or a C₁ to C₂₀ hydrocarbyl substituted with an N, O, S and or P heteroatom or heteroatom containing group (typically having up to 12 atoms, including the N, O, S and P heteroatoms) and two S* may form a cyclic or multicyclic group, preferably Z is tetramethylcyclopentadienyl;

T is a bridging group as described above that is bonded to Z and Q, y is one;

15 Q is a heteroatom with a coordination number of three from Group 15 or with a coordination number of two from Group 16 of the Periodic Table of Elements, such as N, O, S or P and preferably Q is nitrogen;

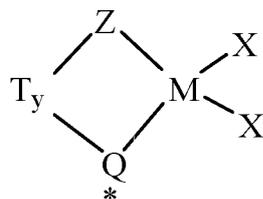
R'' is selected from a C₃-C₁₀₀ substituted or unsubstituted monocyclic or polycyclic ring structure substituent that is partially unsaturated, unsaturated or aromatic; or a C₂-C₁₀₀ 20 substituted or unsubstituted, unsaturated or partially unsaturated, linear or branched alicyclic hydrocarbyl substituent; or a C₁-C₁₀₀ substituted or unsubstituted saturated hydrocarbyl radical (preferably R'' is selected from methyl, ethyl, all propyl isomers, all butyl isomers, phenyl, benzyl, phenethyl, 1-adamantyl, cyclododecyl, cyclohexyl and norbornyl);

t is the coordination number of the heteroatom Q where "t-l-y" indicates the number of R'' 25 substituents bonded to Q; and

each X is, independently, a univalent anionic ligand, or two X are joined and bound to the metal atom to form a metallocycle ring, or two X are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand.

[0065] Useful metallocenes having two or three cyclopentadienyl rings are represented

by the formula:



wherein

M is the same as M described above, preferably M is titanium, zirconium or hafnium, Zr or Hf;

Z and Q* are, independently, a substituted or unsubstituted Cp group (useful Z and Q* groups are represented by the formula: $(C_5H_{4-d}S^*_d)$, where d is 1, 2, 3 or 4, S* is hydrocarbyl groups, heteroatoms, or heteroatom containing groups, such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl or an isomer thereof, N, O, S, P, or a Ci to C₂₀ hydrocarbyl substituted with an N, O, S and or P heteroatom or heteroatom containing group (typically having up to 12 atoms, including the N, O, S and P heteroatoms) and two S* may form a cyclic or multicyclic group;

T is a bridging group as described above that is bonded to Z and Q*, y is zero or one; and each X is, independently, a univalent anionic ligand, or two X are joined and bound to the metal atom to form a metallocycle ring, or two X are joined to form a chelating ligand, a diene ligand, or an alkylidene ligand provided that when y is one then at least one of Z and Q* is preferably not an indene group, alternately both of Z and Q* are not indene. In an alternate embodiment, when y is one, Z and Q* are not 2, 4 substituted indene, preferably are not 2-methyl, 4-phenyl indene.

[0066] Particularly useful combinations of catalysts include:

$SiMe_2(Me_4Cp)(cCi2N)TiMe_2$ and $bis(1-Bu,3-Me-Cp) ZrCl_2$;

$SiMe_2(Me_4Cp)(cCi2N)TiMe_2$ and $(SiMe_2) bis(indenyl)ZrCl_2$;

$SiMe_2(Me_4Cp)(cCi2N)TiMe_2$ and $(SiMe_2)_2O bis(indenyl)ZrCl_2$;

$SiMe_2(Me_4Cp)(cCi2N)TiMe_2$ and $(SiMe_2)_2O bis(indenyl)ZrMe_2$;

$SiMe_2(Me_4Cp)(cCi2N)TiMe_2$ and $SiMe_2(3-neopentylCp)((Me_4Cp)HfCl_2$;

$SiMe_2(Me_4Cp)(cCi2N)TiMe_2$ and $SiMe_2(3-neopentylcyclopentadienyl)(Me_4Cp)HfMe_2$;

$SiMe_2(Me_4Cp)(1-adamantylamido)TiMe_2$ and $bis(1-Bu,3-MeCp)ZrCl_2$; and

$SiMe_2(Me_4Cp)(1-t-butylamido)TiMe_2$ and $bis(1-Bu,3-MeCp)ZrCl_2$.

[0067] In a useful embodiment a third catalyst is present, such as $(Me_2Si)_2O(Ind)_2ZrCl_2$,

2,6-Bis[1-(2-chloro-4,6-dimethylphenylimino)ethyl]pyridine iron(II) dichloride, typically the

third catalyst is a different metallocene.

[0068] For purposes of this invention one metallocene catalyst compound is considered different from another if they differ by at least one atom. For example "bisindenyl zirconium dichloride" is different from (indenyl)(2-methylindenyl) zirconium dichloride" which is
5 different from "(indenyl)(2-methylindenyl) hafnium dichloride." Catalyst compounds that differ only by isomer are considered the same for purposes of this invention, e.g., *rac*-dimethylsilylbis(2-methyl 4-phenyl)hafnium dimethyl is considered to be the same as *meso*-dimethylsilylbis(2-methyl 4-phenyl)hafnium dimethyl.

[0069] Synthesis of monocyclopentadienyl complexes is known in the art, and for
10 example, has been disclosed in WO93/19103, US5096867 and US 5264405.

[0070] Synthesis of bis cyclopentadienyl complexes is known in the art, and for example, has been disclosed in US 4,530,914; US 4,542,199; US 4,769,910; US 4,808,561; US 4,871,705; US 4,933,403; US 4,937,299; US 5,017,714; US 5,026,798; US 5,057,475; US 5,120,867; US 5,278,119; US 5,304,614; US 5,324,800; US 5,350,723; US 5,391,790; and
15 US 7,141,632, each fully incorporated herein by reference.

Activators

[0071] The terms "cocatalyst" and "activator" are used herein interchangeably and are defined to be any compound which can activate any one of the catalyst compounds described above by converting the neutral catalyst compound to a catalytically active catalyst
20 compound cation. Non-limiting activators, for example, include alumoxanes, aluminum alkyls, ionizing activators, which may be neutral or ionic, and conventional-type cocatalysts. Preferred activators typically include alumoxane compounds, modified alumoxane compounds, used alone or in combination with ionizing anion precursor compounds that abstract a reactive, σ -bound, metal ligand making the metal complex cationic and providing a
25 charge-balancing noncoordinating or weakly coordinating anion.

Alumoxane Activators

[0072] Alumoxane activators are utilized as activators in the catalyst systems described herein. Alumoxanes are generally oligomeric compounds containing $-A^R-O-$ sub-units, where R^1 is an alkyl group. Examples of alumoxanes include methylalumoxane (MAO),
30 modified methylalumoxane (MMAO), ethylalumoxane and isobutylalumoxane. Alkylalumoxanes and modified alkylalumoxanes are suitable as catalyst activators, particularly when the abstractable ligand is an alkyl, halide, alkoxide or amide. Mixtures of different alumoxanes and modified alumoxanes may also be used. It may be preferable to use

a visually clear methylalumoxane. A cloudy or gelled alumoxane can be filtered to produce a clear solution or clear alumoxane can be decanted from the cloudy solution. A useful alumoxane is a modified methyl alumoxane (MMAO) cocatalyst type 3A (commercially available from Akzo Chemicals, Inc. under the trade name Modified Methylalumoxane type
5 3A, covered under patent number U.S. Patent No. 5,041,584).

Non Coordinating Anion Activators

[0073] In alternate embodiments, the alkylalumoxanes can be used in combination with non-coordinating anion activators. The term "non-coordinating anion" (NCA) means an anion which either does not coordinate to a cation or which is only weakly coordinated to a
10 cation thereby remaining sufficiently labile to be displaced by a neutral Lewis base. "Compatible" non-coordinating anions are those which are not degraded to neutrality when the initially formed complex decomposes. Further, the anion will not transfer an anionic substituent or fragment to the cation so as to cause it to form a neutral transition metal compound and a neutral by-product from the anion. Non-coordinating anions useful in
15 accordance with this invention are those that are compatible, stabilize the transition metal cation in the sense of balancing its ionic charge at +1, and yet retain sufficient lability to permit displacement during polymerization.

[0074] The terms "cocatalyst" and "activator" are used herein interchangeably and are defined to be any compound which can activate any one of the catalyst compounds described
20 above by converting the neutral catalyst compound to a catalytically active catalyst compound cation.

Optional Scavengers or Co-Activators

[0075] In addition to the activator compounds, scavengers, chain transfer agents or co-activators may be used. Aluminum alkyl or organoaluminum compounds which may be
25 utilized as scavengers or co-activators include, for example, trimethylaluminum, triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, and diethyl zinc.

Preparation of the Supported Catalyst

[0076] In an embodiment, this invention describes the preparation of fluorided supports
30 (such as silica) through the addition of a solution of polar solvent (such as water) and fluorine compound (such as $(\text{NH}_4)_2\text{SiF}_6$) to a slurry of support (such as a toluene slurry of silica). This preparation method contributes to an even distribution of the fluoride compound (such as $(\text{NH}_4)_2\text{SiF}_6$) onto the support surface (such as the silica surface), in contrast to a less

homogeneous distribution observed when the solid salt is combined with the solid silica as described in US 2002/0123582 A1. Metallocenes supported on the fluorided support from this preparation exhibit comparable or higher activity compared to supported metallocenes on fluorided supports made through solid/solid mixing.

5 [0077] In an embodiment, a solution of polar solvent (such as water) and fluorinating agent (such as $(\text{NH}_4)_2\text{SiF}_6$) is added to a slurry of support (such as a toluene slurry of silica). Vigorous stirring of the mixture allows the dissolved fluorine compound (preferably in water) to be evenly absorbed onto the hydrophilic support surface. After filtration, the wet support is allowed to air dry until it is free flowing, and then may be calcined (typically at
10 temperatures over 100°C for at least 1 hour).

Polymerization Processes

[0078] In embodiments herein, the invention relates to polymerization processes where monomer (such as ethylene), and optionally comonomer (such as hexene), are contacted with a catalyst system comprising the result of the combination of an activator, a fluorided
15 support, and at least two metallocene compounds, as described above. The catalyst compounds, support and activator may be combined in any order, and are combined typically prior to contacting with the monomer.

[0079] Monomers useful herein include substituted or unsubstituted C2 to C40 alpha olefins, preferably C2 to C20 alpha olefins, preferably C2 to C12 alpha olefins, preferably
20 ethylene, propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene and isomers thereof. In a preferred embodiment of the invention, the monomers comprises ethylene and optional comonomers comprising one or more C3 to C40 olefins, preferably C4 to C20 olefins, or preferably C₆ to C12 olefins. The C3 to C40 olefin monomers may be linear, branched, or cyclic. The C3 to C40 cyclic olefins may be strained
25 or unstrained, monocyclic or polycyclic, and may optionally include heteroatoms and/or one or more functional groups.

[0080] Polymerization processes of this invention can be carried out in any manner known in the art. Any suspension, homogeneous, bulk, solution, slurry, or gas phase polymerization process known in the art can be used. Such processes can be run in a batch,
30 semi-batch, or continuous mode. Gas phase polymerization processes and slurry processes are preferred. (A homogeneous polymerization process is defined to be a process where at least 90 wt% of the product is soluble in the reaction media.) A bulk homogeneous process is particularly preferred. (A bulk process is defined to be a process where monomer

concentration in all feeds to the reactor is 70 volume % or more.) Alternately, no solvent or diluent is present or added in the reaction medium, (except for the small amounts used as the carrier for the catalyst system or other additives, or amounts typically found with the monomer; e.g., propane in propylene). In another embodiment, the process is a slurry
5 process. As used herein the term "slurry polymerization process" means a polymerization process where a supported catalyst is employed and monomers are polymerized on the supported catalyst particles. At least 95 wt% of polymer products derived from the supported catalyst are in granular form as solid particles (not dissolved in the diluent).

Gas phase polymerization

10 [0081] Generally, in a fluidized gas bed process used 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
15 monomer. (See for example U.S. Patents 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.)

Slurry phase polymerization

[0082] A slurry polymerization process generally operates between 1 to about 50
20 atmosphere pressure range (15 psi to 735 psi, 103 kPa to 5068 kPa) or even greater and temperatures in the range of 0°C to about 120°C. In a slurry polymerization, a suspension of solid, particulate polymer is formed in a liquid polymerization diluent medium to which monomer and comonomers, along with catalysts, are added. The suspension including diluent is intermittently or continuously removed from the reactor where the volatile
25 components are separated from the polymer and recycled, optionally after a distillation, to the reactor. The liquid diluent employed in the polymerization medium is typically an alkane having from 3 to 7 carbon atoms, preferably a branched alkane. The medium employed should be liquid under the conditions of polymerization and relatively inert. When a propane medium is used, the process must be operated above the reaction diluent critical temperature
30 and pressure. Preferably, a hexane or an isobutane medium is employed.

Polyolefin Products

[0083] This invention also relates to compositions of matter produced by the methods described herein.

[0084] In a preferred embodiment, the process described herein produces ethylene homopolymers or ethylene copolymers, such as ethylene-alphaolefin (preferably C₃ to C₂₀) copolymers (such as ethylene-butene copolymers, ethylene-hexene and / or ethylene-octene copolymers) having: a Mw/Mn of greater than 1 to 4 (preferably greater than 1 to 3).

5 [0085] Likewise, the process of this invention produces ethylene copolymers. In a preferred embodiment, the copolymers produced herein have from 0 to 25 mole% (alternately from 0.5 to 20 mole%, alternately from 1 to 15 mole%, preferably from 3 to 10 mole%) of one or more C₃ to C₂₀ olefin comonomer (preferably C₃ to C₁₂ alpha-olefin, preferably propylene, butene, hexene, octene, decene, dodecene, preferably propylene, butene, hexene,
10 octene).

[0086] In a preferred embodiment, the monomer is ethylene and the comonomer is hexene, preferably from 1 to 15 mole% hexene, alternately 1 to 10 mole%.

[0087] Typically, the polymers produced herein have an Mw of 5,000 to 1,000,000 g/mol (preferably 25,000 to 750,000 g/mol, preferably 50,000 to 500,000 g/mol), and/or an Mw/Mn
15 of greater than 1 to 40 (alternately 1.2 to 20, alternately 1.3 to 10, alternately 1.4 to 5, 1.5 to 4, alternately 1.5 to 3).

[0088] In a preferred embodiment, the polymer produced herein has a unimodal or multimodal molecular weight distribution as determined by Gel Permeation Chromatography (GPC). By "unimodal" is meant that the GPC trace has one peak or inflection point. By
20 "multimodal" is meant that the GPC trace has at least two peaks or inflection points. An inflection point is that point where the second derivative of the curve changes in sign (e.g., from negative to positive or vice versus).

[0089] Unless otherwise indicated Mw, Mn, MWD are determined by GPC as described the Experimental section below.

25 [0090] In a preferred embodiment, the polymer produced herein has a composition distribution breadth index (CDBI) of 50% or more, preferably 60% or more, preferably 70 % or more. CDBI is a measure of the composition distribution of monomer within the polymer chains and is measured by the procedure described in PCT publication WO 93/03093, published February 18, 1993, specifically columns 7 and 8 as well as in Wild et al, J. Poly.
30 Sci., Poly. Phys. Ed., Vol. 20, p. 441 (1982) and US 5,008,204, including that fractions having a weight average molecular weight (Mw) below 15,000 are ignored when determining CDBI.

[0091] In another embodiment, the polymer produced herein has two peaks in the TREF

measurement (see below). Two peaks in the TREF measurement as used in this specification and the appended claims means the presence of two distinct normalized ELS (evaporation mass light scattering) response peaks in a graph of normalized ELS response (vertical or y axis) versus elution temperature (horizontal or x axis with temperature increasing from left to right) using the TREF method below. A "peak" in this context means where the general slope of the graph changes from positive to negative with increasing temperature. Between the two peaks is a local minimum in which the general slope of the graph changes from negative to positive with increasing temperature. "General trend" of the graph is intended to exclude the multiple local minimums and maximums that can occur in intervals of 2°C. or less. Preferably, the two distinct peaks are at least 3°C. apart, more preferably at least 4°C. apart, even more preferably at least 5°C. apart. Additionally, both of the distinct peaks occur at a temperature on the graph above 20°C. and below 120°C. where the elution temperature is run to 0°C. or lower. This limitation avoids confusion with the apparent peak on the graph at low temperature caused by material that remains soluble at the lowest elution temperature.

Two peaks on such a graph indicates a bi-modal composition distribution (CD). Bimodal CD may also be determined by other methods known to those skilled in the art. One such alternate method for TREF measurement then can be used if the above method does not show two peaks is disclosed in B. Monrabal, "Crystallization Analysis Fractionation: A New Technique for the Analysis of Branching Distribution in Polyolefins," *Journal of Applied Polymer Science*, Vol. 52, 491-499 (1994).

TREF Method

[0092] Temperature Rising Elution Fractionation (TREF) analysis is done using a CRYSTAF-TREF 200+ instrument from Polymer Char, S.A., Valencia, Spain. The principles of TREF analysis and a general description of the particular apparatus to be used are given in the article Monrabal, B.; del Hierro, P. *Anal. Bioanal. Chem.* **2011**, *399*, 1557. Fig. 3 of the article is an appropriate schematic of the particular apparatus used; however, the connections to the 6-port valve shown in Fig. 3 differ from the apparatus to be used in that the tubing connected to the 11-o'clock port is connected to the 9-o'clock port and the tubing connected to the 9-o'clock port is connected to the 11-o'clock port. Pertinent details of the analysis method and features of the apparatus to be used are as follows.

[0093] 1,2-Dichlorobenzene (ODCB) solvent stabilized with approximately 380 ppm of 2,6-bis(1,1-dimethylethyl)-4-methylphenol (butylated hydroxytoluene) is used for preparing the sample solution and for elution. The sample to be analyzed (approximately 25 mg but as

low as approximately 10 mg) is dissolved in ODCB (25 ml metered at ambient temperature) by stirring at 150°C for 60 min. A small volume (0.5 ml) of the solution is introduced into a column (15-cm long by 3/8" o.d.) packed with an inert support (of stainless steel balls) at 150°C, and the column temperature is stabilized at 140°C for 45 min. The sample volume is then allowed to crystallize in the column by reducing the temperature to 30°C at a cooling rate of 1°C/min. The column is kept at 30°C for 15 min before injecting the ODCB flow (1 ml/min) into the column for 10 min to elute and measure the polymer that did not crystallize (soluble fraction). The infrared detector used (Polymer Char IR4) generates an absorbance signal that is proportional to the concentration of polymer in the eluting flow. A complete TREF curve is then generated by increasing the temperature of the column from 30 to 140°C at a rate of 2°C/min while maintaining the ODCB flow at 1 ml/min to elute and measure the dissolving polymer.

Films

[0094] Specifically, any of the foregoing polymers, such as the foregoing ethylene copolymers or blends thereof, may be used in a variety of end-use applications. Such applications include, for example, mono- or multi-layer blown, extruded, and/or shrink films. These films may be formed by any number of well-known extrusion or coextrusion techniques, such as a blown bubble film processing technique, wherein the composition can be extruded in a molten state through an annular die and then expanded to form a uni-axial or biaxial orientation melt prior to being cooled to form a tubular, blown film, which can then be axially slit and unfolded to form a flat film. Films may be subsequently unoriented, uniaxially oriented, or biaxially oriented to the same or different extents.

Experimental

[0095] Room temperature is 23°C unless otherwise noted.

[0096] MAO is methyl alumoxane (30 wt% in toluene) obtained from Albemarle.

Gel Permeation Chromatography with Three Detectors (GPC-3D)

[0097] M_w , M_n and M_w/M_n are determined by using a High Temperature Gel Permeation Chromatography (Agilent PL-220), equipped with three in-line detectors, a differential refractive index detector (DRI), a light scattering (LS) detector, and a viscometer. Experimental details, including detector calibration, are described in: T. Sun, P. Brant, R. R. Chance, and W. W. Graessley, *Macromolecules*, Volume 34, Number 19, pp. 6812-6820, (2001) and references therein. Three Agilent PLgel 10 μ m Mixed-B LS columns are used. The nominal flow rate is 0.5 mL/min, and the nominal injection volume is 300 μ L. The

various transfer lines, columns, viscometer and differential refractometer (the DRI detector) are contained in an oven maintained at 145°C. Solvent for the experiment is prepared by dissolving 6 grams of butylated hydroxy toluene as an antioxidant in 4 liters of Aldrich reagent grade 1,2,4-trichlorobenzene (TCB). The TCB mixture is then filtered through a 0.1
 5 μm Teflon filter. The TCB is then degassed with an online degasser before entering the GPC-3D. Polymer solutions are prepared by placing dry polymer in a glass container, adding the desired amount of TCB, then heating the mixture at 160°C with continuous shaking for about 2 hours. All quantities are measured gravimetrically. The TCB densities used to express the polymer concentration in mass/volume units are 1.463 g/ml at room temperature
 10 and 1.284 g/ml at 145°C. The injection concentration is from 0.5 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples. Prior to running each sample the DRI detector and the viscometer are purged. Flow rate in the apparatus is then increased to 0.5 ml/minute, and the DRI is allowed to stabilize for 8 hours before injecting the first sample. The LS laser is turned on at least 1 to 1.5 hours before running the samples.
 15 The concentration, c , at each point in the chromatogram is calculated from the baseline-subtracted DRI signal, $\frac{3}{4} \text{RI}$, using the following equation:

$$c = K_{DRI} I_{DRI} / (dn/dc)$$

where K_{DRI} is a constant determined by calibrating the DRI, and (dn/dc) is the refractive index increment for the system. The refractive index, $n = 1.500$ for TCB at 145°C and $\lambda =$
 20 690 nm. Units on parameters throughout this description of the GPC-3D method are such that concentration is expressed in g/cm^3 , molecular weight is expressed in g/mole , and intrinsic viscosity is expressed in dL/g .

[0098] The LS detector is a Wyatt Technology High Temperature DAWN HELEOS. The molecular weight, M , at each point in the chromatogram is determined by analyzing the
 25 LS output using the Zimm model for static light scattering (M.B. Huglin, **LIGHT SCATTERING FROM POLYMER SOLUTIONS**, Academic Press, 1971):

$$\frac{K_0 c}{AR(\Theta)} = \frac{1}{MP(\Theta)} + 2A_2 c$$

Here, $AR(\Theta)$ is the measured excess Rayleigh scattering intensity at scattering angle Θ , c is the polymer concentration determined from the DRI analysis, A_2 is the second virial
 30 coefficient. $P(\Theta)$ is the form factor for a monodisperse random coil, and K_0 is the optical constant for the system:

$$K_o = \frac{4\pi^2 n^2 (dn/dc)^2}{\lambda^4 N_A}$$

where N_A is Avogadro's number, and (dn/dc) is the refractive index increment for the system, which take the same value as the one obtained from DRI method. The refractive index, $n = 1.500$ for TCB at 145°C and $\lambda = 657$ nm.

5 [0099] A high temperature Viscotek Corporation viscometer, which has four capillaries arranged in a Wheatstone bridge configuration with two pressure transducers, is used to determine specific viscosity. One transducer measures the total pressure drop across the detector, and the other, positioned between the two sides of the bridge, measures a differential pressure. The specific viscosity, η_s , for the solution flowing through the
10 viscometer is calculated from their outputs. The intrinsic viscosity, $[\eta]$, at each point in the chromatogram is calculated from the following equation:

$$\eta_s = c[\eta] + 0.3(c[\eta])^2$$

where c is concentration and was determined from the DRI output.

[00100] The branching index $(g'_v i_s)$ is calculated using the output of the GPC-DRI-LS-VIS
15 method as follows. The average intrinsic viscosity, $[\eta]_{\text{avg}}$, of the sample is calculated by:

$$[\eta]_{\text{avg}} = \frac{\sum c_i [\eta]_i}{\sum c_i}$$

where the summations are over the chromatographic slices, i , between the integration limits.

The branching index $g'_v i_s$ is defined as:

$$g'_{vis} = \frac{[\eta]_{\text{avg}}}{kM_v^\alpha}$$

20 M_v is the viscosity-average molecular weight based on molecular weights determined by LS analysis. Z average branching index $(g'_{z,ave})$ is calculated using C_i = polymer concentration in the slice i in the polymer peak times the mass of the slice squared, M_i^2 .

[00101] All molecular weights are weight average unless otherwise noted. All molecular weights are reported in g/mol unless otherwise noted.

25 Molecular Weight and Comonomer Composition Determination with PolymerChar GPC-IR

[00102] The distribution and the moments of molecular weight (M_w , M_n , M_w/M_n , etc.) and the comonomer content (C_2 , C_3 , C_6 , etc.), are determined with a high temperature Gel Permeation Chromatography (PolymerChar GPC-IR) equipped with a multiple-channel band
30 filter based Infrared detector ensemble IR5, in which a broad-band channel is used to

measure the polymer concentration while two narrow-band channels are used for characterizing composition. Three Agilent PLgel 10 μ m Mixed-B LS columns are used to provide polymer separation. Aldrich reagent grade 1,2,4-trichlorobenzene (TCB) with 300 ppm antioxidant butylated hydroxytoluene (BHT) is used as the mobile phase. The TCB mixture is filtered through a 0.1 μ m Teflon filter and degassed with an online degasser before entering the GPC instrument. The nominal flow rate is 1.0 mL/min and the nominal injection volume is 200 μ L. The whole system including transfer lines, columns, detectors are contained in an oven maintained at 145°C. Given amount of polymer sample is weighed and sealed in a standard vial with 10 μ L flow marker (Heptane) added to it. After loading the vial in the autosampler, polymer is automatically dissolved in the instrument with 8 mL added TCB solvent. The polymer is dissolved at 160°C with continuous shaking for about 1 hour for most PE samples or 2 hour for PP samples. The TCB densities used in concentration calculation are 1.463 g/ml at room temperature and 1.284 g/ml at 145°C. The sample solution concentration is from 0.2 to 2.0 mg/ml, with lower concentrations being used for higher molecular weight samples.

[00103] The concentration, c , at each point in the chromatogram is calculated from the baseline-subtracted IR5 broadband signal, I , using the following equation:

$$c = \alpha I$$

where α is the mass constant determined with PE or PP standards. The mass recovery is calculated from the ratio of the integrated area of the concentration chromatography over elution volume and the injection mass which is equal to the pre-determined concentration multiplied by injection loop volume.

[00104] The molecular weight is determined by combining universal calibration relationship with the column calibration which is performed with a series of monodispersed polystyrene (PS) standards. The MW is calculated at each elution volume with following equation.

$$\log M_X = \frac{\log(K_X/K_{PS})}{a_X + 1} + \frac{a_{PS} + 1}{a_X + 1} \log M_{PS}$$

where the variables with subscript "X" stand for the test sample while those with subscript "PS" stand for PS. In this method, $a_{PS} = 0.67$ and $K_e = 0.000175$ while a_X and K_X are obtained from published literature. Specifically, $a/K = 0.695/0.000579$ for PE and $0.705/0.0002288$ for PP.

[00105] The comonomer composition is determined by the ratio of the IR detector

intensity corresponding to CH₂ and CH₃ channel calibrated with a series of PE and PP homo/copolymer standards whose nominal value are predetermined by NMR or FTIR.

[00106] CRC was performed according to the following procedure: Cross-fractionation chromatography (CFC) analysis was done using a CFC-2 instrument from Polymer Char, S.A., Valencia, Spain. The principles of CFC analysis and a general description of the particular apparatus used are given in the article Ortin, A.; Monrabal, B.; Sancho-Tello, J. *Macromol. Symp.* 2007, 257, 13. Fig. 1 of the article is an appropriate schematic of the particular apparatus used. Pertinent details of the analysis method and features of the apparatus used are as follows.

10 [00107] 1,2-Dichlorobenzene (ODCB) solvent stabilized with approximately 380 ppm of 2,6-bis(1,1-dimethylethyl)-4-methylphenol (butylated hydroxy toluene) was used for preparing the sample solution and for elution. The sample to be analyzed (approximately 50 mg) was dissolved in ODCB (25 ml metered at ambient temperature) by stirring (200 rpm) at 150°C for 75 min. A small volume (0.5 ml) of the solution was introduced into a TREF
15 column (stainless steel; o.d., 3/8"; length, 15 cm; packing, non-porous stainless steel micro-balls) at 150°C, and the column temperature was stabilized for 30 min at a temperature (120-125°C) approximately 20°C higher than the highest-temperature fraction for which the GPC analysis was included in obtaining the final bivariate distribution. The sample volume was then allowed to crystallize in the column by reducing the temperature to 30°C at a cooling
20 rate of 0.2°C/min. The low temperature was held for 10 min before injecting the solvent flow (1 ml/min) into the TREF column to elute the soluble fraction (SF) into the GPC columns (3 x PLgel 10 µm Mixed-B 300 x 7.5 mm, Varian, Inc.); the GPC oven was held at high temperature (140°C). The SF was eluted for 5 min from the TREF column and then the injection valve was put in the "load" position for 40 min to completely elute all of the SF
25 through the GPC columns (standard GPC injections). All subsequent higher-temperature fractions were analyzed using overlapped GPC injections wherein at each temperature step the polymer was allowed to dissolve for at least 16 min and then injected from the TREF column into the GPC column for 3 min. The IR4 (Polymer Char) infrared detector was used to generate an absorbance signal that is proportional to the concentration of polymer in the
30 eluting flow.

[00108] The universal calibration method was used for determining the molecular weight distribution (MWD) and molecular-weight averages (Mn, Mw, etc.) of eluting polymer fractions. Thirteen narrow molecular-weight distribution polystyrene standards (obtained

from Polymer Labs, UK) within the range of 1.5-8200 kg/mol were used to generate a universal calibration curve. Mark-Houwink parameters were obtained from Appendix I of Mori, S.; Barth, H. G. Size Exclusion Chromatography; Springer, 1999. For polystyrene $K = 1.38 \times 10^{-4}$ dl/g and $a = 0.7$; and for polyethylene $K = 5.05 \times 10^{-4}$ dl/g and $a = 0.693$ were used. For a polymer fraction, which eluted at a temperature step, that has a weight fraction (weight % recovery) of less than 0.5 %, the MWD and the molecular-weight averages were not computed; additionally, such polymer fractions were not included in computing the MWD and the molecular-weight averages of aggregates of fractions.

Example 1

10 **Preparation of Fluorided silica-1 via dry mixing.**

[00109] 50 g of Grace Davison D948™ silica and 2.3 g $(\text{NH}_4)_2\text{SiF}_6$ were combined in a plastic jar. The mixture was tumbled together for 1 hour. The solid mixture was transferred into a tube furnace, and was heated to 200°C under constant nitrogen flow (temperature program: 25°C/h ramped to 150°C; held at 150°C for 4 hours; 50°C/h ramped to 200°C; held at 200°C for 4 hours; cooled down to room temperature). 47 g of fluorided silica-1 was collected after the calcination.

Preparation of Fluorided silica-2 via wet mixing ;

[00110] 1.18 g $(\text{NH}_4)_2\text{SiF}_6$ was dissolved in 7.00 g water in a 20 ml glass vial. 50 g of Grace Davison D948™ silica and 200 g of toluene were combined in a 250 ml Wheaton Celstir™. Under vigorous stirring, the aqueous stock solution of $(\text{NH}_4)_2\text{SiF}_6$ was added via a syringe to the toluene slurry of silica. The mixture was allowed to stir at room temperature for 2.5 h. The slurry was filtered through a 110 ml Optichem™ disposable polyethylene frit, rinsed with 200 g pentane three times, then dried in air overnight to yield a white, free-flowing solid. The solid was transferred into a tube furnace, and was heated under constant nitrogen flow (temperature program: 25°C/h ramped to 150°C; held at 150°C for 4 hours; 50°C/h ramped to 200°C; held at 200°C for 4 hours; cooled down to room temperature). 46 g of fluorided silica-2 was collected after the calcination. The calculated "F" loading was 0.9 mmol/g.

Preparation of supported methylalumoxane (sMAO) from fluorided silica-1.

30 [00111] In a drybox, 36 g MAO toluene solution (Albermarle, 13.6 wt% Al) and 68 g of anhydrous toluene were combined in a 125 ml Wheaton Celstir™. The stirring rate was set to 450 rpm. Every 5 minutes, 5 g of fluorided silica-1 was slowly added to the Celstir™. A total amount of 26 g of fluorided silica-1 was added over a period of 30 minutes. The

resulting slurry was allowed to stir at room temperature for 15 minutes. Then the Celstir™ was placed in a sand bath heated to 100°C. The slurry was heated at 100°C for an additional 3 hours at a stirring rate of 215 rpm. The final slurry was filtered through a 110 ml Optichem disposable polyethylene frit. The solid collected in the frit was first rinsed with 30 g toluene for 2 times, then 30 g pentane for 3 times. The solid was dried in-vacuo for 3 hours. 34.9 g of sMAO-1 was obtained. Calculated Al loading: 4.2 mmol Al per gram of sMAO-1.

Preparation of supported methylalumoxane (sMAO) from fluorided silica-2.

[00112] In a drybox, 34.5 g MAO toluene solution (Albermarle, 13.6 wt% Al) and 100 g of anhydrous toluene were combined in a 250 ml Wheaton Celstir™. The stir rate was set to 450 rpm. Every 5 minutes, 5 g of fluorided silica-2 was slowly added to the Celstir™. A total amount of 27.6 g of fluorided silica-2 was added over a period of 30 minutes. The resulting slurry was allowed to stir at room temperature for 15 minutes. Then the Celstir™ was placed in a sand bath heated to 100°C. The slurry was heated at 100°C for an additional 3 hours at a stirring rate of 215 rpm. The final slurry was filtered through a 110 ml Optichem disposable polyethylene frit. The solid collected in the frit was first rinsed with 80 g toluene for 2 times, then 60 g pentane for 3 times. The solid was dried in-vacuo for 12 hours. 37.4 g of free-flowing sMAO-2 was obtained. The calculated Al loading was 4.4 mmol Al per gram of sMAO-2.

Comparison of physical properties of fluorided supports.

Support	Surface Area* (m ² /g)	Pore volume* (cm ³ /g)	Pore Diameter* (Å)	Particle size Distribution**	
				Mean (µm)	S.D. (µm)
Silica-1	241	1.68	280	60.28	18.28
Silica-2	231	1.57	271	59.11	21.10
sMAO-1	353	0.96	109	58.21	18.23
sMAO-2	377	1.00	104	52.41	21.38

* BET surface area and porosity analysis were carried out with ASAP 2420 Accelerated Surface Area and Porosimetry Systems from Micromeritics.

** Particle size distribution (PSD) was measured with LS 13 320 Laser Diffraction Particle Size Analyzer.

Chemical properties of fluorided supports.

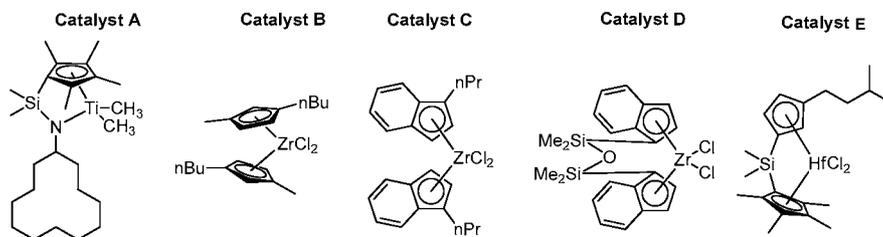
[00113] The chemical composition of fluorided silica supports was studied by NMR experiments. A representative procedure is as follows: In a 20 ml glass vial in the drybox, combined 0.203 g silica-2, 26.5 mg NMR internal standard Bis(4-fluorophenyl)methane (0.13 mmol), 0.80 g MAO/toluene solution (30wt%, Albemarle) and 0.20 g of toluene. The

mixture was vortexed at room temperature for 90 min and was allowed to sit still for 20 min. A small sample of the supernatant liquid was dissolved in THF-d8 in an NMR tube and the ^1H NMR spectrum was taken on Bruker 400 MHz NMR spectrometer (Figure 9).

[00114] An important difference noted between the middle spectrum in Fig. 9 (from reaction with silica-1) and bottom spectrum in Fig. 9 (from reaction with silica-2) is the presence of trimethylsilane (TMS), which originated from the reaction between the fluorinating agent $(\text{NH}_4)_2\text{SiF}_6$ and MAO (see top spectrum in Fig. 9 for reference). This observation suggests the presence of residual $(\text{NH}_4)_2\text{SiF}_6$ (estimated to be greater than 0.05 mmol $(\text{NH}_4)_2\text{SiF}_6$ per gram based on NMR integration) in fluorided silica-1 prepared through the dry-mixing method. Fluorided silica-2 prepared through the wet-mixing method contains no detectable amount of residual $(\text{NH}_4)_2\text{SiF}_6$.

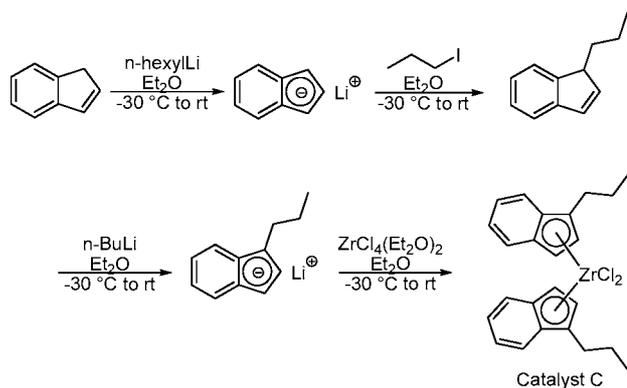
[00115] The significance of this observation is two-fold. First, the improved fluorided silica preparation (e.g., silica-2, wet-mixing) can be chemically differentiated from silica-1, dry-mixed materials (such as those described in US 2002/0123582). Secondly, since there are no residual fluorinating agents in silica-2, the possibility of in-situ generation of fluorinated MAO with fluorinating agent (organic or inorganic fluorine-containing compounds, as described in US 7,355,058) can be ruled out in the preparation of sMAO-2.

Synthesis of catalysts



[00116] Catalyst A was synthesized according to preparation described in patent WO 93/19103. Catalyst B was purchased from Boulder and used as received. Catalyst D was synthesized according to US 7,141,632.

Synthesis of Catalyst C;



[00117] Lithium salt of indene: Indene (25.1 g, 0.216 mol, 1.0 equiv.) was dissolved in 250 ml pentane in a 500 ml round bottom flask. Hexyl lithium/toluene solution (2.30 mol/L, 94 ml, 0.216 mol, 1.0 equiv.) was added to the flask via a syringe. The mixture was allowed to stir at room temperature for 16 h. The mixture was filtered and the collected white fine solid was washed with 50 ml pentane for 3 times. After drying in vacuo for 1 h., 26.0 g lithium salt was obtained (98% yield).

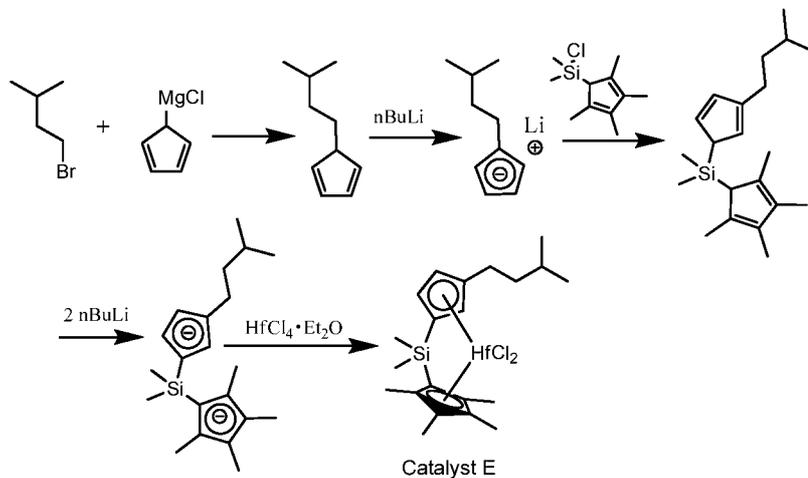
[00118] 1-Propyl indene: In a 100 ml round bottom flask kept at -30°C was added 1-iodopropane (6.80 g, 40 mmol, 1.0 equiv.) and 50 ml ether. Indene lithium salt (5.368 g, 44 mmol, 1.1 equiv.) was added to the flask in portion. The reaction mixture was stirred at -30°C for 30 min, then was brought to room temperature to stir for another 16 h. The solvent was removed in vacuo. 35 ml pentane was added to the residue to extract the product. A pale yellow oil was obtained after removing pentane in vacuo (5.0 g, 79% yield).

[00119] Lithium salt of 1-propyl indene: In a 100 ml round bottom flask chilled to -30°C was added 1-propyl indene (5.0 g, 31.6 mmol, 1.0 equiv.) and 50 ml ether. Dropwisely added n-butyl lithium/hexane solution (2.62 mol/L, 12.06 ml, 31.6 mmol, 1.0 equiv.) via a syringe. The mixture was stirred at -30°C for 20 min then warmed up to room temperature. The solvent was removed in vacuo. The solid was washed with 20 ml pentane for 2 times, and was dried in vacuo. White solid was obtained (4.59 g, 88% yield).

[00120] Catalyst C: In a 250 ml round bottom flask chilled to -30°C combined 1-propyl indene lithium salt (6.378 g, 38.9 mmol, 2.0 equiv.) and 100 ml ether. $ZrCl_4(Et_2O)_2$ (7.417g, 19.5 mmol, 1.0 equiv.) was added to the flask in portion. The mixture was stirred at -30°C for 20 min then warmed up to room temperature for 30 min. The solvent was removed in vacuo. To the solid residue was added dichloromethane (30 ml). The resulting slurry was filtered through Celite™ to yield a red solution. The dichloromethane solvent was then removed in vacuo to yield an orange solid. The solid was washed with 5 ml pentane for 3

times, and then dried in vacuo for 2 h. Final product is orange/yellow solid (6.81 g, 73% yield).

Synthesis of Catalyst E;



5 [00121] All reactions in the synthesis of Catalyst E were carried out in the dry-box under nitrogen atmosphere. 5-isopentylcyclopenta-1,3-diene (1): 1-bromo-3-methylbutane (7.93mL, 10.000g, 66.21mmol, 1.00eq) was added to cyclopenta-2,4-dienylmagnesium chloride (93.38mL of 0.934M sol., 88.06mmol, 1.33eq) in a 500mL round bottom flask and stirred at 60°C for 4hours. The mixture was brought to room temperature and concentrated under a stream of nitrogen. Pentane was added and the suspension was put under vacuum to remove the pentane and any remaining THF. The resulting residue was taken up in pentane and the solid impurities removed via vacuum filtration. The filtrate was concentrated to give light yellow oil, 1 (8.12g, 59.60mmol, 90.02%yield). Used in synthesis of 2 without further analysis.

15 [00122] Lithium salt of 5-isopentylcyclopenta-1,3-diene (2): Immediately following removal of the solvent, the 5-isopentylcyclopenta-1,3-diene, 1, (8.12g, 59.60mmol, 1.00eq) was taken up in tetrahydrofuran (100mL). n-Butyllithium (25.0mL of a 2.5M sol., 59.60mmol, 1.00eq) was added to the stirring solution and the reaction was allowed to stir at room temperature overnight. The solvent was removed under nitrogen and pentane was added to slurry up the solid. The white solid, 2, was collected via vacuum filtration and rinsed with additional pentane. Residual solvent was removed under vacuum giving 4.513g (31.74mmol, 53.25% yield) of the white solid, 2.

[00123] (3-isopentylcyclopenta-2,4-dienyl)dimethyl(2,3,4,5-tetramethylcyclopenta-2,4-dienyl)silane (3): Chlorodimethyl(2,3,4,5-tetramethylcyclopenta-2,4-dienyl)silane (6.818g, 18.58mmol, 1.00eq) was added to 2 in 20mL of tetrahydrofuran. The reaction mixture was

stirred overnight at room temperature. Pentane was added and solvent was removed under vacuum. The residue was taken up into pentane, filtered through Celite™ then removed solvent under reduced pressure. This gave yellow oil, 3, (6.430g, 20.44mmol, 64.40% yield).

[00124] Lithium salt of (3-isopentylcyclopenta-2,4-dienyl)dimethyl(2,3,4,5-tetramethylcyclopenta-2,4-dienyl)silane (4): n-Butyllithium (17.2mL of a 2.5M sol., 42.92mmol, 2.1eq) was added drop-wise to a solution of 3 in 100mL of tetrahydrofuran. The reaction was stirred 24h at room temperature. The mixture was concentrated under a stream of nitrogen. Pentane was added and solvents were removed in vacuo. The residue was slurried up in pentane and the solid was collected via vacuum filtration giving white solid, 4
10 (3.832g, 11.73mmol, 57.4%).

[00125] Catalyst E: Hafnium tetrachloride-bis-etherate (5.49g, 11.73mmol, 1.00eq) was added to 4 (3.832g, 11.73mmol, 1.00eq) in 100mL of tetrahydrofuran/diethyl ether (1:1) at -35°C. The solution was stirred overnight at room temperature. The mixture was concentrated under a stream of nitrogen and pentane was added and solvents removed in vacuo. The residue was taken up in pentane and filtered through Celite™. The filtrate was concentrated in vacuo giving yellow oil, Catalyst E (5.633g, 5.05mmol, 43.1%).
15

Preparation of supported dual-metallocene catalyst systems.

[00126] **Supported catalyst a-1:** In a 20 ml glass vial in a dry box was added 1 g of the sMAO-1 obtained above. 3 g Toluene was added to the vial, followed by 1 g toluene solution containing Catalyst A (35 μπιοϊ) and Catalyst B (6 μπιοϊ). The vial was fitted with a cap and then vortexed at room temperature for 90 min. The resulting slurry was filtered through a 25 ml Optichem disposable polyethylene frit and rinsed with 3 g toluene for 2 times and 3 g pentane for 3 times. The supported catalyst was dried in-vacuo. 0.997 g of supported catalyst a-1 (Catalyst A/Catalyst B ratio = 5.8) was obtained.
20

[00127] **Supported catalyst b-1:** In a 20 ml glass vial in the dry box was added 1 g sMAO-1 obtained above. 3 g Toluene was added to the vial, followed by 1 g toluene solution containing metallocene Catalyst A (35 μπιοϊ) and Catalyst C (6 μπιοϊ). The vial was fitted with a cap and then vortexed at room temperature for 90 min. The resulting slurry was filtered through a 25 ml Optichem disposable polyethylene frit and rinsed with 3 g toluene for 2 times and 3 g pentane for 3 times. The supported catalyst was dried in-vacuo. 0.997 g of supported catalyst b-1 (Catalyst A/Catalyst C ratio = 5.8) was obtained.
25
30

[00128] **Supported catalyst c-1:** In a 20 ml glass vial in the dry box was added 1 g sMAO-1 obtained above. 3 g Toluene was added to the vial, followed by 1 g toluene solution

containing metallocene Catalyst A (29 μmol) and Catalyst D (9 μmol). The vial was fitted with a cap and then vortexed at room temperature for 90 min. The resulting slurry was filtered through a 25 ml Optichem disposable polyethylene frit and rinsed with 3 g toluene for 2 times and 3 g pentane for 3 times. The supported catalyst was dried in-vacuo. 1.001 g of supported catalyst **c-1** (Catalyst A/Catalyst D ratio = 3.2) was obtained.

[00129] Supported catalyst d-1: In a 20 ml glass vial in the dry box was added 1 g sMAO-1 obtained above. 3 g Toluene was added to the vial, followed by 1 g toluene solution containing metallocene Catalyst C (35 μmol) and Catalyst E (6 μmol). The vial was fitted with a cap and then vortexed at room temperature for 90 min. The resulting slurry was filtered through a 25 ml Optichem disposable polyethylene frit and rinsed with 3 g toluene for 2 times and 3 g pentane for 3 times. The supported catalyst was dried in-vacuo. 1.001 g of supported catalyst **d-1** (Catalyst A/Catalyst E ratio = 5.8) was obtained.

[00130] Supported catalyst e-1: In a dry box, 44.1 g sMAO-1 and 120 g anhydrous toluene were combined in a 250 ml Wheaton Celstir™. The stir rate was set to 450 rpm. A 60 g toluene stock solution containing Catalyst A (1.29 mmol) and Catalyst B (0.44 mmol) was added to the Celstir™ dropwisely with a pipette. The resulting yellow-orange slurry was allowed to stir at room temperature for 60 min. The resulting slurry was filtered through a 110 ml Optichem disposable polyethylene frit, and rinsed with 60 g toluene for 2 times, followed by 45 g pentane for 3 times. The orange solid was dried in-vacuo for 12 hours. 43.9 g of supported catalyst 6 was obtained (Catalyst A/Catalyst B mole ratio = 2.9).

[00131] Supported catalyst e-2: In a dry box, 51.7 g MAO toluene solution (Albermarle, 13.6 wt% Al) and 160 g anhydrous toluene were combined in a 250 ml Wheaton Celstir™. The stir rate was set to 450 rpm. Every 5 minutes, 5 g of fluorided silica-2 was slowly added to the Celstir™. A total amount of 40.5 g of fluorided silica-2 was added over a period of 40 minutes. The resulting slurry was allowed to stir at room temperature for 15 minutes. Then the Celstir™ was placed in a sand bath heated to 100°C. The slurry was heated at 100°C for an additional 3 hours at a stirring rate of 200 rpm. The final slurry was filtered through a 110 ml Optichem disposable polyethylene frit. The solid collected in the frit was first rinsed with 80 g toluene for 2 times. The collected solid was transferred back to the Celstir™ and slurried with 120 g anhydrous toluene. Set stir rate to 450 rpm. A 60 g toluene stock solution containing Catalyst A (1.56 mmol) and Catalyst B (0.52 mmol) was added to the Celstir™ dropwisely with a pipette. The resulting yellow-orange slurry was allowed to stir at room temperature for 60 min. The resulting slurry was filtered through a 110 ml Optichem

disposable polyethylene frit, and rinsed with 80 g toluene for 2 times, followed by 60 g pentane for 3 times. The orange solid was dried in-vacuo for 12 hours. 56.1 g of supported catalyst e-2 was obtained (Catalyst A/Catalyst B mole ratio = 3).

5 [00132] Supported catalyst f-1: In a dry box, 40.3 g MAO toluene solution (Albermarle, 13.6 wt% Al) and 70 g anhydrous toluene were combined in a 250 ml Wheaton Celstir™. The stir rate was set to 450 rpm. Every 5 minutes, 5 g of fluorided silica-1 was slowly added to the Celstir™. A total amount of 28.9 g of fluorided silica-1 was added over a period of 30 minutes. The resulting slurry was allowed to stir at room temperature for 15 minutes. Then the Celstir™ was placed in a sand bath heated to 80°C. The slurry was heated at 80°C for an additional 3 hours at a stirring rate of 200 rpm. The final slurry was filtered through a 110 ml Optichem disposable polyethylene frit. The solid collected in the frit was first rinsed with 30 g toluene for 3 times. The collected solid was transferred back to the Celstir™ and slurried with 50 g anhydrous toluene. Set stir rate to 450 rpm. A 70 g toluene stock solution containing Catalyst A (1.44 mmol) and Catalyst B (0.24 mmol) was added to the Celstir™
10 dropwisely with a pipette. The resulting yellow-orange slurry was allowed to stir at room temperature for 60 min. The resulting slurry was filtered through a 110 ml Optichem disposable polyethylene frit, and rinsed with 30 g toluene for 2 times, followed by 30 g pentane for 3 times. The orange solid was dried in-vacuo for 1 hour. 40.4 g of supported catalyst f-1 was obtained (Catalyst A/Catalyst B mole ratio = 6).

20 [00133] Supported catalyst g-2: In a dry box, 50.0 g MAO toluene solution (Albermarle, 13.6 wt% Al) and 160 g anhydrous toluene were combined in a 250 ml Wheaton Celstir™. The stir rate was set to 450 rpm. Every 5 minutes, 5 g of fluorided silica-2 was slowly added to the Celstir™. A total amount of 40.1 g of fluorided silica-2 was added over a period of 40 minutes. The resulting slurry was allowed to stir at room temperature for 35 minutes. Then
25 the Celstir™ was placed in a sand bath heated to 100°C. The slurry was heated at 100°C for an additional 3 hours at a stirring rate of 230 rpm. The final slurry was filtered through a 110 ml Optichem disposable polyethylene frit. The solid collected in the frit was first rinsed with 80 g toluene for 2 times. The collected solid was transferred back to the Celstir™ and slurried with 120 g anhydrous toluene. Set stir rate to 450 rpm. A 65 g toluene stock solution
30 containing Catalyst A (1.96 mmol) and Catalyst B (0.17 mmol) was added to the Celstir™ dropwisely with a pipette. The resulting yellow-orange slurry was allowed to stir at room temperature for 80 min. The resulting slurry was filtered through a 110 ml Optichem disposable polyethylene frit, and rinsed with 80 g toluene for 2 times, followed by 70 g

pentane for 3 times. The orange solid was dried in-vacuo for 3 hours. 57.0 g of supported catalyst **g-2** was obtained (Catalyst A/Catalyst B mole ratio = 12).

5 **[00134] Supported catalyst h-1:** In a dry box, 34.2 g sMAO-1 obtained above was weighed into a 125 ml Wheaton Celstir™. 70 g of toluene was added to the Celstir™. The stir rate was set to 450 rpm. 70 g toluene stock solution containing Catalyst A (1.69 mmol) and Catalyst C (0.60 mmol) was added to the Celstir™ dropwisely with a pipette. The resulting yellow-orange slurry was allowed to stir at room temperature for 90 min. The resulting slurry was filtered through a 110 ml Optichem disposable polyethylene frit, and rinsed with 30 g toluene for 2 times, followed by 30 g pentane for 3 times. The orange solid
10 was dried in-vacuo for 3 hours (Catalyst A/Catalyst C ratio = 2.8).

[00135] Supported catalyst h-2: In the dry box, 47.5 g sMAO-2 and 150 ml anhydrous toluene were combined in a 250 ml Celstir™. The stir rate was set to 450 rpm. A 60 ml toluene stock solution containing Catalyst A (1.43 mmol) and Catalyst C (0.48 mmol) was added to the Celstir™ dropwisely with a pipette. The resulting yellow-orange slurry was
15 allowed to stir at room temperature for 60 min. The resulting slurry was filtered through a frit, and rinsed with 60 g toluene for 2 times, followed by 45 g pentane for 3 times. The orange solid was dried in vacuo for 12 hours. 47.7 g of supported catalyst was obtained (Catalyst A/Catalyst C ratio = 3.0).

[00136] Supported catalyst i-1: In a 20 ml glass vial in the dry box was added 1 g sMAO-
20 2. 3 g Toluene was added to the vial, followed by 1 g toluene solution containing Catalyst B (40 μπιιοϊ). The vial was fitted with a cap and then vortexed at room temperature for 90 min. The resulting slurry was filtered through a 25 ml Optichem disposable polyethylene frit and rinsed with 3 g toluene for 2 times and 3 g pentane for 3 times. The supported catalyst was dried in-vacuo.

25 **[00137] Supported catalyst i-2:** In a 20 ml glass vial in the dry box was added 1 g sMAO-2. 3 g Toluene was added to the vial, followed by 1 g toluene solution containing Catalyst B (40 μπιιοϊ). The vial was fitted with a cap and then vortexed at room temperature for 90 min. The resulting slurry was filtered through a 25 ml Optichem disposable polyethylene frit and rinsed with 3 g toluene for 2 times and 3 g pentane for 3 times. The supported catalyst was
30 dried in-vacuo.

[00138] Supported catalyst j-1: In a 20 ml glass vial in the dry box was added 1 g sMAO-1. 3 g Toluene was added to the vial, followed by 1 g toluene solution containing Catalyst A (40 μπιιοϊ). The vial was fitted with a cap and then vortexed at room temperature for 90 min.

The resulting slurry was filtered through a 25 ml Optichem disposable polyethylene frit and rinsed with 3 g toluene for 2 times and 3 g pentane for 3 times. The supported catalyst was dried in-vacuo.

[00139] Supported catalyst j-2: In a 20 ml glass vial in the dry box was added 1 g sMAO-
5 2. 3 g Toluene was added to the vial, followed by 1 g toluene solution containing Catalyst A (40 μm). The vial was fitted with a cap and then vortexed at room temperature for 90 min. The resulting slurry was filtered through a 25 ml Optichem disposable polyethylene frit and rinsed with 3 g toluene for 2 times and 3 g pentane for 3 times. The supported catalyst was dried in-vacuo.

10 Example 2: High Throughput Ethylene- 1-hexene Copolymerization.

[00140] Supported catalysts **a-1** to **d-1** were tested in a high throughput unit in slurry ethylene- 1-hexene copolymerization.

[00141] Preparation of catalyst slurry for high throughput run: In a dry box, 45 mg of supported catalyst was weighed into a 20 ml glass vial. 15 ml of toluene was added to the
15 vial to make a slurry that contained 3 mg supported catalyst/ml slurry. The resulting mixture was vortexed prior to injection.

High Throughput - Polymerizations;

[00142] Transition metal compounds were supported as detailed in the examples above. Solvents, polymerization grade toluene and isohexane were supplied by ExxonMobil
20 Chemical Company and thoroughly dried and degassed prior to use. Polymerization grade ethylene was used and further purified by passing it through a series of columns: 500 cc Oxyclear cylinder from Labclear (Oakland, CA) followed by a 500 cc column packed with dried 3A mole sieves purchased from Aldrich Chemical Company, and a 500 cc column packed with dried 5A mole sieves purchased from Aldrich Chemical Company. TnOAl (tri-
25 ft-octylaluminum, neat) was used as a 2 mmol/L solution in toluene.

[00143] Reactor Description and Preparation: Polymerizations were conducted in an inert atmosphere (N_2) drybox using autoclaves equipped with an external heater for temperature control, glass inserts (internal volume of reactor = 22.5 mL), septum inlets, regulated supply of nitrogen, ethylene and hexene, and equipped with disposable PEEK mechanical stirrers
30 (800 RPM). The autoclaves were prepared by purging with dry nitrogen prior to use.

[00144] Ethylene/1-hexene Copolymerization: The reactor was prepared as described above, and then purged with ethylene. Isohexane, 1-hexene and TnOAl were added via syringe at room temperature and atmospheric pressure. The reactor was then brought to

process temperature (85 °C) and charged with ethylene to process pressure (130 psig = 896 kPa) while stirring at 800 RPM. The transition metal compound (100 μL of a 3 mg/mL toluene slurry, unless indicated otherwise) was added via syringe with the reactor at process conditions. TnOAl was used as 200 μL of a 20 mmol/L in isohexane solution. Ethylene was allowed to enter (through the use of computer controlled solenoid valves) the autoclaves during polymerization to maintain reactor gauge pressure (+/- 2 psig). Reactor temperature was monitored and typically maintained within +/- 1°C. Polymerizations were halted by addition of approximately 50 psi 0 2/Ar (5 mole% O₂) gas mixture to the autoclaves for approximately 30 seconds. The polymerizations were quenched after a predetermined cumulative amount of ethylene had been added or for a maximum of 45 minutes polymerization time. The final conversion (in psi) of ethylene added/consumed is reported in Table 1, in addition to the quench time for each run. The reactors were cooled and vented. The polymer was isolated after the solvent was removed in-vacuo. Yields reported include total weight of polymer and residual catalyst. Catalyst activity is reported as kilograms of polymer per mol transition metal compound per hour of reaction time (kg/mol•hr). Characterization data for polymers produced are shown in Figures 1 to 4.

Table 1. Ethylene Hexene Polymerization. Run condition: isohexane as solvent, 85°C, 130 psi ethylene pressure, 30 μl of 1-hexene, 300 ppm hydrogen.

Supported Catalyst	mol ratio of Catalysts	Final Ethylene Uptake (psi)	Activity (kg/mol *h)	Mw (g/mol)	Mw/Mn
a-1	A/B = 5.8	55	28,092	161,000	3.6
b-1	A/C = 5.8	55	14,076	189,000	5.4
c-1	A/D = 3.2	55	13,705	204,000	6.3
d-1	A/E = 5.8	55	12,334	180,000	2.9

Table 2. Ethylene Hexene Polymerization. Run condition: isohexane as solvent, 85°C, 130 psi ethylene pressure, 30 μl of 1-hexene, 0 ppm hydrogen.

Supported Catalyst	Support	Averaged Activity (kg/mol*h)
i-1	Fluorided silica-1 (dry-mix)	24371
i-2	Fluorided silica-2 (wet-mix)	21990
j-1	Fluorided silica-1 (dry-mix)	7481
j-2	Fluorided silica-2 (wet-mix)	9532

Example 3: Polymerization of Ethylene and Hexene:

- [00145] Polymerization was performed in a gas-phase fluidized bed reactor with a 6" body and a 10" expanded section. Cycle and feed gases were fed into the reactor body through a perforated distributor plate, and the reactor was controlled at 300 psi and 70 mol% ethylene.
- 5 Reactor temperature was maintained by heating the cycle gas. Supported catalyst was fed as a 10 wt% slurry in Sono Jell ® from Sonneborn (Parsippany, NJ). The slurry was thinned and delivered to the reactor by nitrogen and isopentane feeds in the cat probe. Products were collected from the reactor as necessary to maintain the desired bed weight. Average process conditions are listed in Tables 3 and 4.

10 **Table 3.** Average process conditions for supported catalysts **e-1** and **e-2**.

Supported catalyst	e-1*	e-2
Catalyst composition	Catalyst A/Catalyst B=2.9	Catalyst A/Catalyst B=3
Support	Fluoride silica-1 (dry-	Fluoride silica-2 (wet-mix)
Temperature (°C)	185	185
Pressure (psi)	300	300
Ethylene (mole %)	69.8	70.0
Hydrogen (ppm)	264	270
Hexene (mole %)	1.32	1.31
Bed Weight (g)	2000	2000
Residence Time (hr)	6.5	5.0
Cycle Gas Velocity (ft/s)	1.48	1.52
Production Rate (g/hr)	310	399
Activity ($g_{poly}/g_{supported\ cat}$)	1100	2260
Catalyst Slurry Feed (cc/hr)	3.2	2.0
MI I2.1 (g/10min)	1.50	1.07
HLMI I21 (g/10min)	34.04	26.15
MIR (I21/I2.1)	22.69	24.37
Density (g/cm^3)	0.9156	0.9185
Bulk Density (g/cc)	0.2428	0.3344
N₂ Cat. Probe Feed (cc/min)	6000	6000
iC₅ Cat. Probe Feed (g/min)	1	1

*Values are averaged over the run including catalyst probe plugging issue.

*No operability issue was encountered with supported catalyst **e-2**. Good activity (2260 g PE/g supported catalyst) was obtained.

*Catalyst feed line was repeatedly plugged when running supported catalyst **e-1**.

Table 4. Average process conditions for the supported catalysts **f-1** and **f-2**.

Supported catalyst	h-1	h-2
Catalyst composition	Catalyst A/Catalyst C=2.8	Catalyst A/Catalyst C=3
Support	Fluoride silica-1 (dry-)	Fluoride silica-2 (wet-mix)
Temperature (°C)	185	185
Pressure (psi)	300	300
Ethylene (mole %)	70.0	70.0
Hydrogen (ppm)	180	180
Hexene (mole %)	2.71	2.14
Bed Weight (g)	2000	2000
Residence Time (hr)	4.8	4.8
Cycle Gas Velocity (ft/s)	1.53	1.52
Production Rate (g/hr)	414	416
Activity ($\frac{g_{poly}}{g_{supported\ cat}}$)	2380	2277
Catalyst Slurry Feed	2.0	2.1
MI I2.1 (g/10min)	1.07	0.98
HLMI I21 (g/10min)	41.2	40.1
MIR (I21/I2.1)	38.4	40.9
Density (g/cm^3)	0.9206	0.9174
Bulk Density (g/cc)	0.3872	0.3793
N ₂ Cat. Probe Feed	6000	6000
iC ₅ Cat. Probe Feed (g/min)	1	1

Table 5. Average process conditions for the supported catalysts **e-2**, **f-1** and **g-2**.

Supported Catalyst	e-2	f-1	g-2
Catalyst composition	Catalyst A/Catalyst	Catalyst A/Catalyst	Catalyst A/Catalyst B=12
Support	Fluoride silica-2	Fluoride silica-1	Fluoride silica-2
Temperature (°C)	185	185	185
Pressure (psi)	300	300	300
Ethylene (mole %)	70.0	70.0	70.1
Hydrogen (ppm)	270	327	601
Hexene (mole %)	1.31	1.12	0.97
Bed Weight (g)	2000	2000	2000
Residence Time (hr)	5.0		4.6
Cycle Gas Velocity	1.52	1.62	1.49
Production Rate (g/hr)	399	454	431
Activity ($\frac{g_{poly}}{g_{supported}}$)	2260	1870	2070
Catalyst Slurry Feed	2.0	2.8	2.4
MI I2.1 (g/10min)	1.07	1.04	0.93
HLMI I21 (g/10min)	26.15	32.71	60.36
MIR (I21/I2.1)	24.37	31.53	64.64
Density (g/cm^3)	0.9185	0.917	0.9170
Bulk Density (g/cc)	0.3344	0.3444	0.3216
N ₂ Cat. Probe Feed	6000	6000	6000
iC ₅ Cat. Probe Feed	1		1

[00146] Melt index (MI) also referred to as I2, reported in g/10 min, is determined according to ASTM 1238, 190°C, 2.16 kg load.

5 [00147] High load melt index (HLMI) also referred to as I21, reported in g/10 min, is determined according to ASTM 1238, 190°C, 21.6 kg load.

[00148] Melt index ratio (MIR) is MI divided by HLMI is determined by ASTM 1238. Density is determined according to ASTM D 1505.

[00149] The MI, HLMI, MIR and density data in Tables 3, 4 and 5 are averaged numbers based on several measurements.

[00150] All documents described herein are incorporated by reference herein, including any priority documents and/or testing procedures to the extent they are not inconsistent with
5 this text.

CLAIMS;

What is claimed is:

1. A catalyst system comprising the reaction product of fluorided silica support, alkylaluminum activator and at least two metallocene catalyst compounds, where the first
5 metallocene is a bridged monocyclopentadienyl group 4 transition metal compound and the second metallocene is a biscyclopentadienyl group 4 transition metal compound where the fluorided silica support has not been calcined at a temperature of 400°C or more.
2. The catalyst system of claim 1, wherein the metallocenes are represented by the
10 formula:
- $$T_y Cp_m MG_n X_q$$
- wherein each Cp is, independently, a cyclopentadienyl group which may be substituted or unsubstituted, M is a group 4 transition metal, G is a heteroatom group represented by the formula JR^*_z where J is N, P, O or S, and R* is a linear branched or cyclic hydrocarbyl group
15 having from one to twenty carbon atoms and z is 1 or 2, T is a bridging group, and y is 0 or 1, X is a leaving group, and m=1 or 2, n=0, 1, 2 or 3, q=0, 1, 2 or 3, and the sum of m+n+q is equal to the oxidation state of the transition metal; wherein m = 1, n = 1 and y = 1 in the first metallocene catalyst compound; and n = 0 and m = 2 in the second metallocene catalyst
20 compound.
3. The catalyst system of claim 2, wherein y is one in the second metallocene compound and at least one Cp in the second metallocene compound is not a substituted or unsubstituted indene group.
- 25 4. The catalyst system of claim 2 or claim 3, wherein each Cp is a cyclopentadiene, indene or fluorene, which may be substituted or unsubstituted, each M is titanium, zirconium, or hafnium, and each X is, independently, a halide, a hydride, an alkyl group, an alkenyl group or an arylalkyl group.
- 30 5. The catalyst system of any one of the preceding claims, wherein the activator comprises an alkylaluminum and a non-coordinating anion.
6. The catalyst system of any one of the preceding claims, wherein the activator

comprises methylalumoxane.

7. The catalyst system of any one of the preceding claims, wherein for the bridged monocyclopentadienyl transition metal compound m is one, n is one, where J is N , and R^* is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, cyclooctyl, cyclododecyl, decyl, undecyl, dodecyl, adamantyl or an isomer thereof.

8. The catalyst system of any one of the preceding claims, wherein the bridged monocyclopentadienyl transition metal compound comprises one or more of:

10 dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)titanium dimethyl;
dimethylsilyl (tetramethylcyclopentadienyl)(cyclododecylamido)titanium dichloride;
dimethylsilyl (tetramethylcyclopentadienyl)(*t*-butylamido)titanium dimethyl;
dimethylsilyl (tetramethylcyclopentadienyl)(*t*-butylamido)titanium dichloride;
 μ -(CH₃)₂Si(cyclopentadienyl)(1-adamantylamido)M(R)₂;
15 μ -(CH₃)₂Si(3-*tert*butylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂C(tetramethylcyclopentadienyl)(1-adamantylamido)M(R)₂;
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-*tert*butylamido)M(R)₂;
20 μ -(CH₃)₂Si(fluorenyl)(1-*tert*butylamido)M(R)₂;
 μ -(CH₃)₂Si(tetramethylcyclopentadienyl)(1-cyclododecylamido)M(R)₂;
 μ -(C₆H₅)₂C(tetramethylcyclopentadienyl)(1-cyclododecylamido)M(R)₂;
 μ -(CH₃)₂Si(η^5 -2,6,6-trimethyl-1,5,6,7-tetrahydro-5H-indacen-1-yl)(*tert*butylamido)M(R)₂;
where M is selected from a group consisting of Ti, Zr, and Hf and R is selected from halogen
25 or C₁ to C₅ alkyl.

9. The catalyst system of any one of the preceding claims, wherein the second metallocene compound comprises one or more of: Bis(tetrahydroindenyl)Hf Me₂; Bis(1-butyl,3-methylcyclopentadienyl)ZrCl₂; Bis(*n*-butylcyclopentadienyl)ZrCl₂; (Dimethylsilyl)²O bis(indenyl)ZrCl₂; Dimethylsilyl(3-(3-methylbutyl)cyclopentadienyl)(2,3,4,5-tetramethylcyclopentadienyl)ZrCl₂; Dimethylsilylbis(tetrahydroindenyl)ZrCl₂; Dimethylsilyl(3-phenyl-indenyl)(tetramethylcyclopentadienyl)ZrCl₂; Dimethylsilyl(3-neopentylcyclopentadienyl)(tetramethylcyclopentadienyl)HfCl₂; Tetramethyldisilylene bis(4-

- (3,5-di-tert-butylphenyl)-indenyl)ZrCl₂; Cyclopentadienyl(1,3-diphenylcyclopentadienyl)ZrCl₂; bis(cyclopentadienyl)zirconium dichloride; bis(pentamethylcyclopentadienyl)zirconium dichloride; bis(pentamethylcyclopentadienyl)zirconium dimethyl;
- 5 is(pentamethylcyclopentadienyl)hafnium dichloride; bis(pentamethylcyclopentadienyl)zirconium dimethyl; bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dichloride; bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dimethyl; bis(1-methyl-3-n-butylcyclopentadienyl)hafnium dichloride; bis(1-methyl-3-n-butylcyclopentadienyl)zirconium dimethyl;
- 10 bis(indenyl)zirconium dichloride; bis(indenyl)zirconium dimethyl; bis(tetrahydro-1-indenyl)zirconium dichloride; bis(tetrahydro-1-indenyl)zirconium dimethyl; dimethylsilylbis(tetrahydroindenyl)zirconium dichloride; dimethylsilylbis(tetrahydroindenyl)zirconium dimethyl; dimethylsilylbis(indenyl)zirconium dichloride; dimethylsilyl(bisindenyl)zirconium dimethyl;
- 15 dimethylsilylbis(cyclopentadienyl)zirconium dichloride; and dimethylsilylbis(cyclopentadienyl)zirconium dimethyl.

10. The catalyst system of any one of the preceding claims, wherein the first and second metallocene compounds comprise one or more of:
- 20 SiMe₂(Me₄Cp)(cCi2N)TiMe₂ and bis(1-Bu,3-Me-Cp) ZrCl₂;
 SiMe₂(Me₄Cp)(cCi2N)TiMe₂ and (SiMe₂) bis(indenyl)ZrCl₂;
 SiMe₂(Me₄Cp)(cCi2N)TiMe₂ and (SiMe₂)₂0 bis(indenyl)ZrCl₂;
 SiMe₂(Me₄Cp)(cCi2N)TiMe₂ and (SiMe₂)₂0 bis(indenyl)ZrMe₂;
 SiMe₂(Me₄Cp)(cCi2N)TiMe₂ and SiMe₂(3-neopentylCp)((Me₄Cp)HfCl₂);
- 25 SiMe₂(Me₄Cp)(cCi2N)TiMe₂ and SiMe₂(3-neopentylcyclopentadienyl)(Me₄Cp)HfMe₂;
 SiMe₂(Me₄Cp)(1-adamantylamido)TiMe₂ and bis(1-Bu,3-MeCp)ZrCl₂; and
 SiMe₂(Me₄Cp)(1-t-butylainido)TiMe₂ and bis(1-Bu,3-MeCp)ZrCl₂.

11. The catalyst system of any one of the preceding claims, wherein the fluorided support
 30 has been calcined at a temperature of 100 to less than 400°C.

12. A process to produce ethylene polymer comprising: i) contacting, in the gas phase or slurry phase, ethylene and, optionally C₃ to C₂₀ comonomer, with the catalyst system of any

of claims 1 to 11, and ii) obtaining an ethylene polymer comprising at least 50 mol% ethylene.

13. The process of claim 12, wherein the ethylene polymer comprises ethylene and at least one C₃ to C₂₀ comonomer, and has a bi-modal composition distribution.

14. The process of claim 12 or claim 13, wherein the ethylene polymer has a multimodal molecular weight distribution as determined by Gel Permeation Chromatography.

15. The process of any one of claims 12-14, wherein the activator comprises methylalumoxane.

16. The process of claim 15, wherein the activator further comprises a non-coordinating anion activator.

15

17. The process of any one of claims 12-16, wherein the process occurs at a temperature of from about 0°C to about 300°C, at a pressure in the range of from about 0.35 MPa to about 10 MPa, and at a time up to 300 minutes.

18. The process of any one of claims 12-17, wherein the comonomer is present and is selected from propylene, butene, pentene, hexene, heptene, octene, nonene, decene, undecene, dodecene or a mixtures thereof.

19. The process of any one of claims 12-18, wherein the fluorided supported catalyst systems is prepared by the method comprising combining a fluoride compound with a non-polar solvent, then combining with a slurry of a non-polar solvent and support, removing the non-polar solvent, thereafter combining the calcined support with a second solvent, which may be the same as or different from the non-polar solvent, and two catalyst compounds and activator, wherein the fluorided support is calcined at a temperature from 100 to less than 400°C, before or after combination with the activator and/or catalyst compounds.

20. The process of claim 19, wherein the ratio (by weight) of non-polar solvent to non-polar solvent is between 1:10 to 1:1000.

21. The process of claim 19 or claim 20, wherein the non-polar solvent is toluene, pentane, hexane, benzene, or chloroform.

5 22. The process of any one of claims 19-21, wherein the fluoride compound is one or more of NH_4BF_4 , $(\text{NH}_4)_2\text{SiF}_6$, NH_4PF_6 , NH_4F , $(\text{NH}_4)_2\text{TaF}_7$, NH_4NbF_4 , $(\text{NH}_4)_2\text{GeF}_6$, $(\text{NH}_4)_2\text{SmF}_6$, $(\text{NH}_4)_2\text{TiF}_6$, $(\text{NH}_4)_2\text{ZrF}_6$, MoF_6 , ReF_6 , GaF_3 , SO_2ClF , F_2 , SiF_4 , SF_6 , ClF_3 , ClF_5 , BrF_5 , IF_7 , NF_3 , HF , BF_3 , NHF_2 and NH_4HF_2 .

10

23. The process of any one of claims 19-22, wherein the fluoride compound comprises ammonium hexafluorosilicate, ammonium tetrafluoroborate or a mixture thereof.

15 24. The process of any one of claims 19-23, wherein the non-polar solvent is water, the ratio (by weight) of water to non-polar solvent is between 1:10 to 1:1000; the non-polar solvent is toluene, pentane, hexane, benzene, or chloroform; and the fluoride compound is one or more of NH_4BF_4 , $(\text{NH}_4)_2\text{SiF}_6$, NH_4PF_6 , NH_4F , $(\text{NH}_4)_2\text{TaF}_7$, NH_4NbF_4 , $(\text{NH}_4)_2\text{GeF}_6$, $(\text{NH}_4)_2\text{SmF}_6$, $(\text{NH}_4)_2\text{TiF}_6$, $(\text{NH}_4)_2\text{ZrF}_6$, MoF_6 , ReF_6 , GaF_3 , SO_2ClF , F_2 , SiF_4 , SF_6 , ClF_3 , ClF_5 , BrF_5 , IF_7 , NF_3 , HF , BF_3 , NHF_2 and NH_4HF_2 .

20

25 25. A process of preparing fluorided supported catalyst systems comprising combining a fluoride compound with water, then combining with a slurry of non-polar solvent and support, removing the non-polar solvent, thereafter combining the calcined support with a second solvent, which may be the same or different from the non-polar solvent, and two catalyst compounds and alkylalumoxane activator, wherein the fluorided support is calcined at a temperature from 100 to less than 400°C, before or after combination with the activator and/or catalyst compounds.

Figure 1a. GPC-3D Characterization of PE produced with supported catalyst a-1.

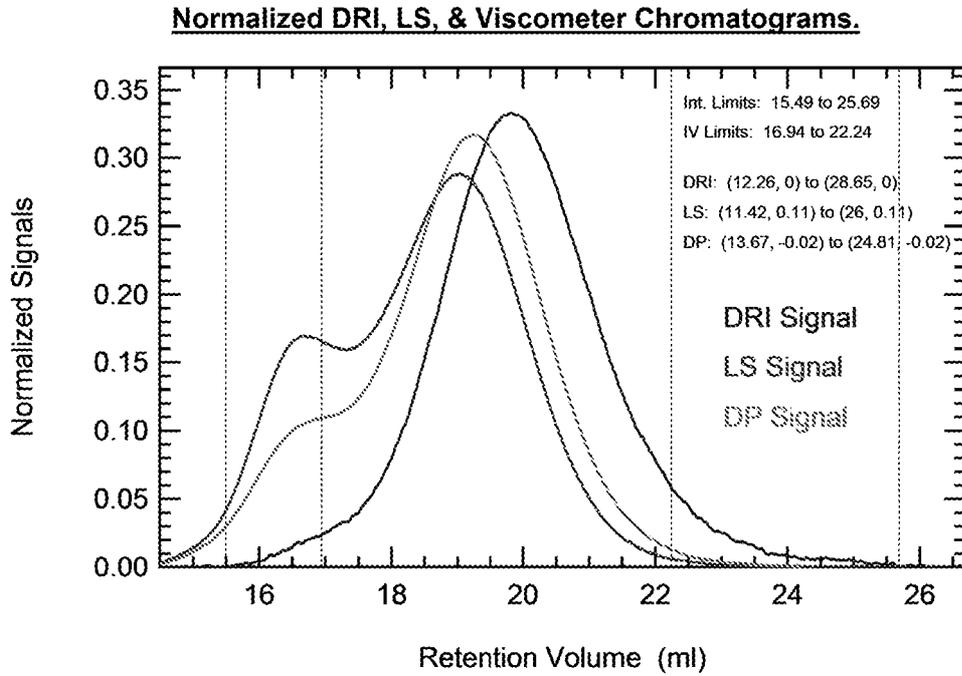


Figure 1b. GPC-IR Characterization of PE produced with supported catalyst a-1

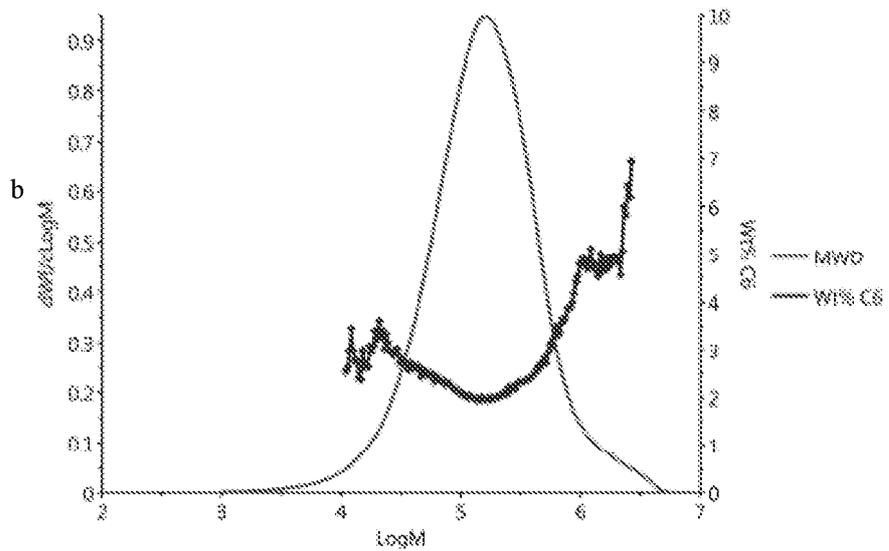


Figure 2a. GPC-3D Characterization of PE produced with catalyst **b-1**.

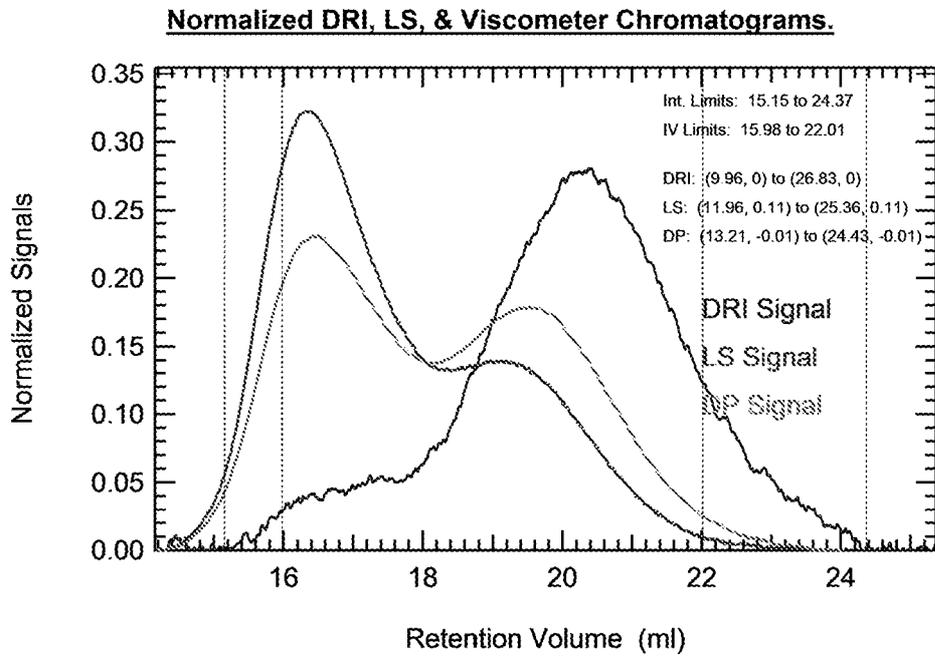


Figure 2b. GPC-4D Characterization of PE produced with catalyst **b-1**.

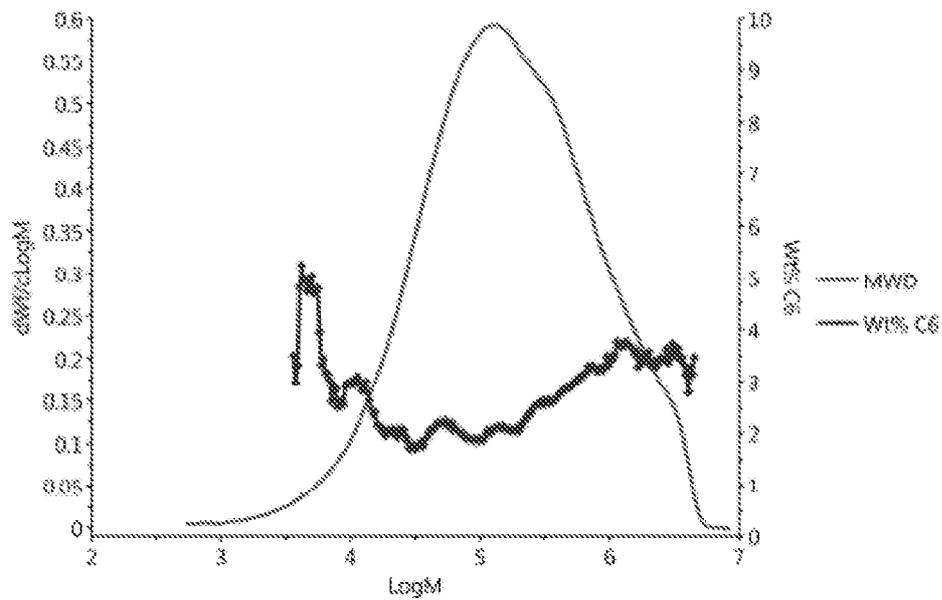


Figure 3a. GPC-3D Characterization of PE produced with catalyst c-1.

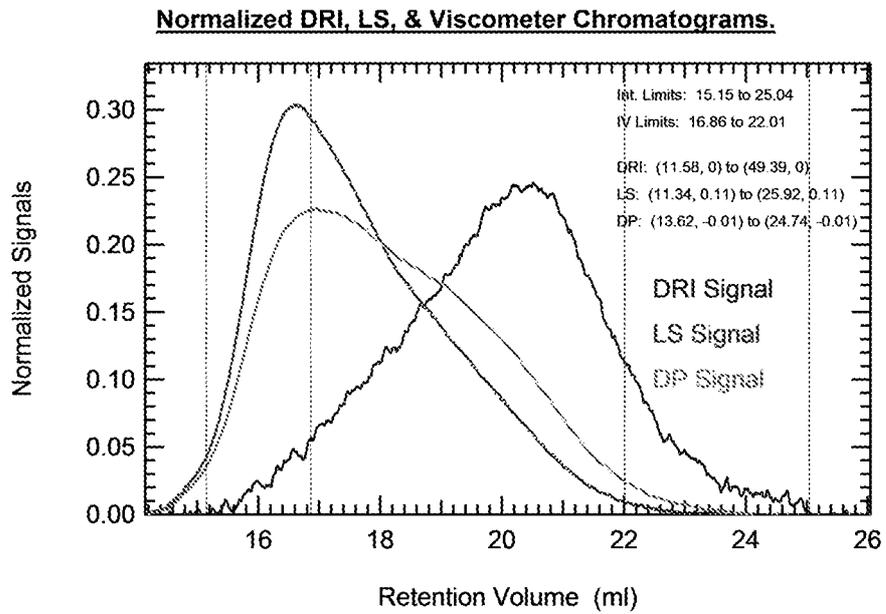


Figure 3b. GPC-4D Characterization of PE produced with catalyst c-1.

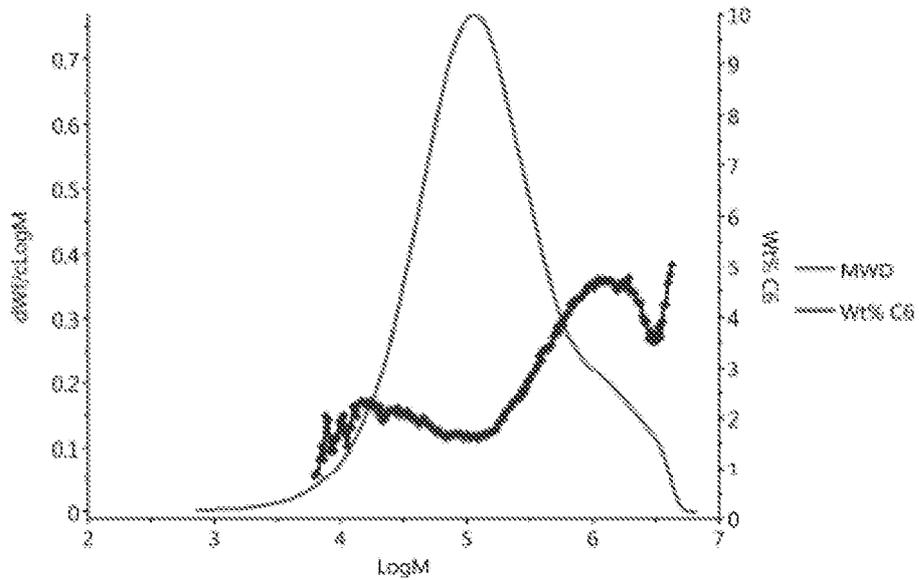


Figure 4 GPC-3D Characterization of PE produced with catalyst d-1.

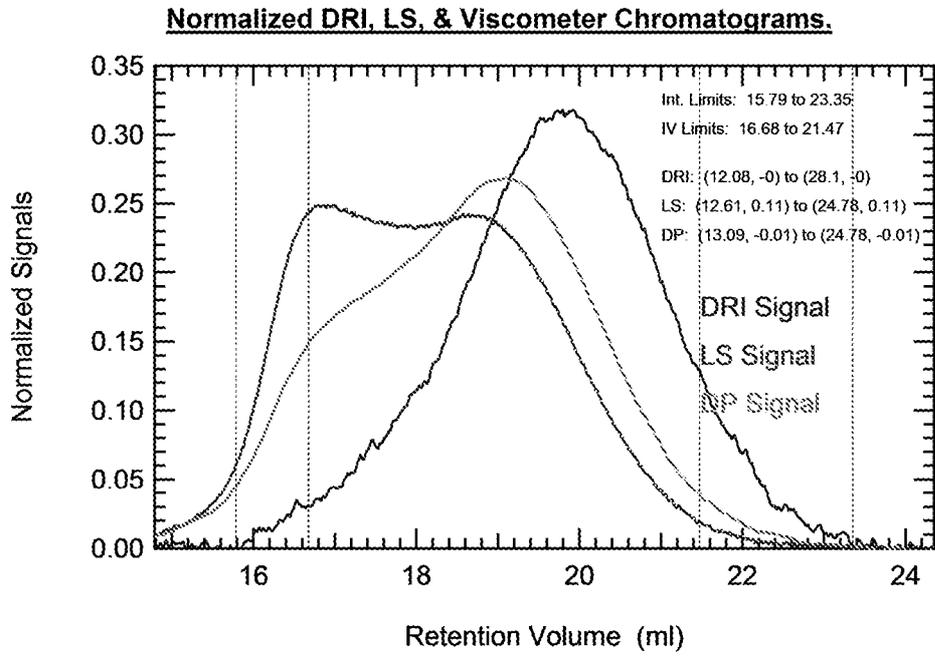


Figure 5a: GPC-3D Characterization of PE produced with catalyst e-1.

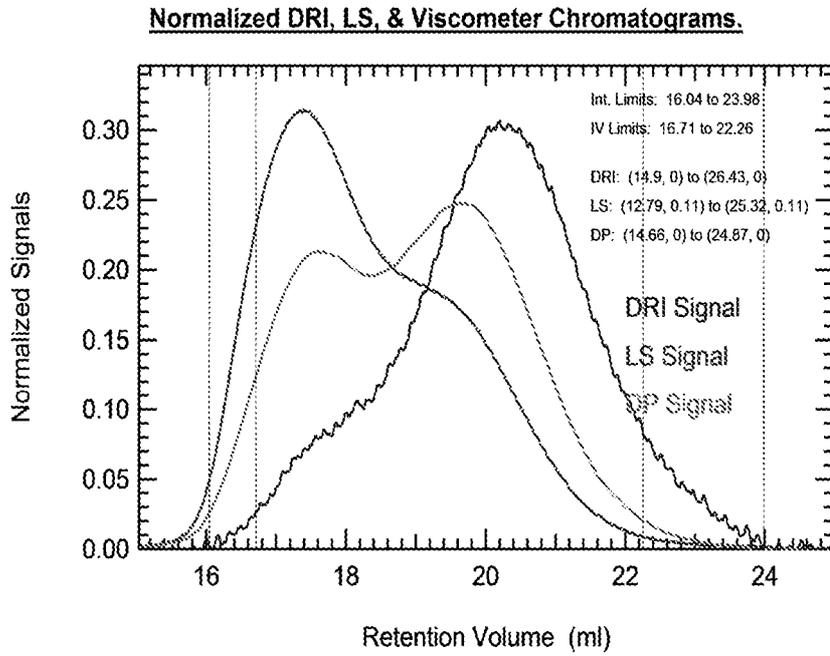
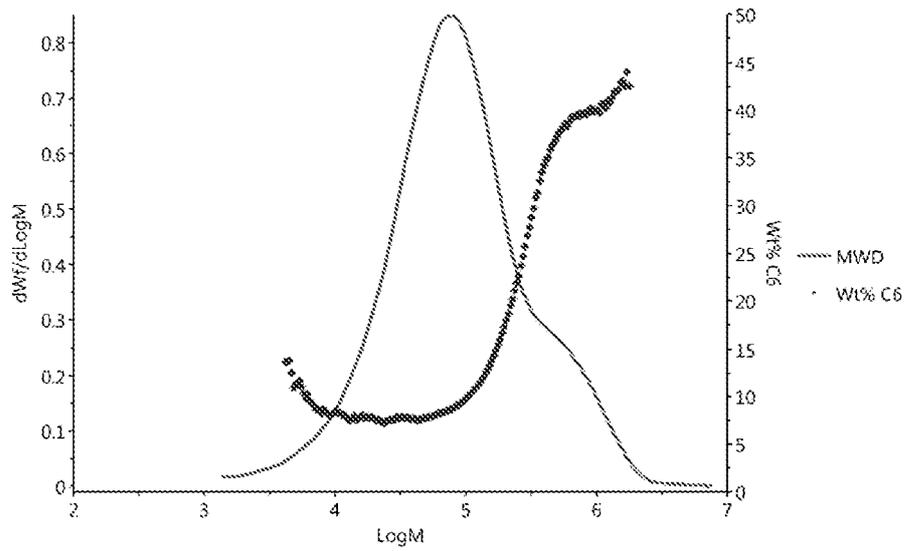


Figure 5b: GPC-4D of PE produced produced with supported catalyst e-1.



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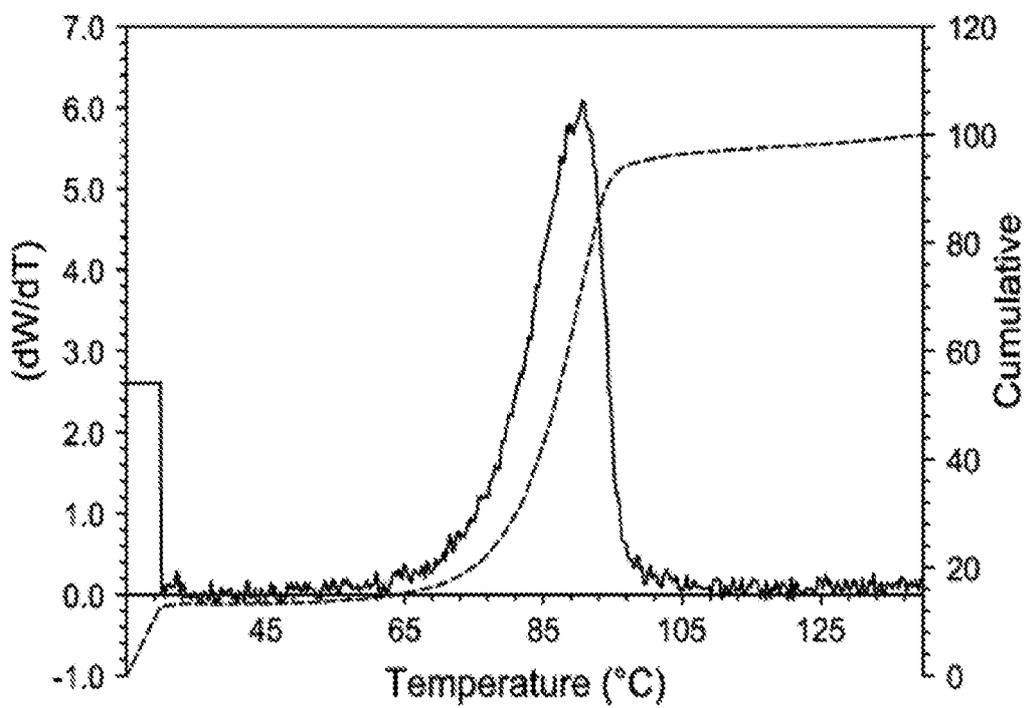


FIG. 5c

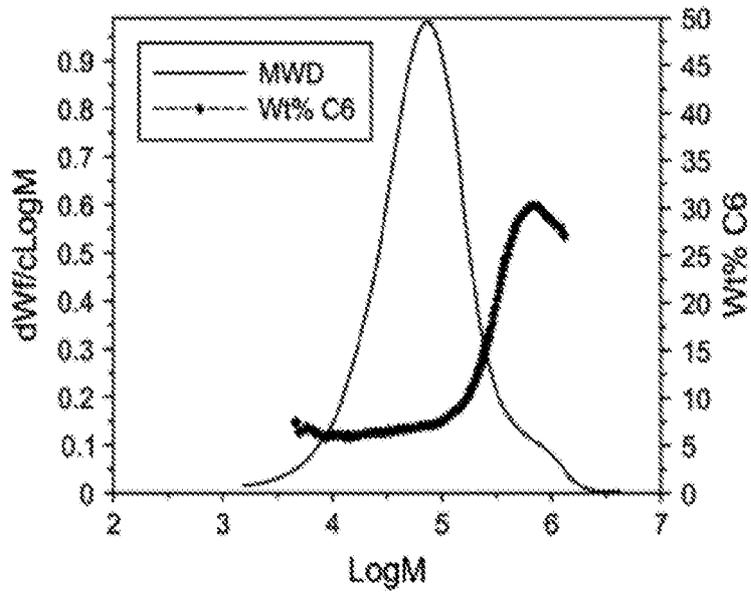


FIG. 6a

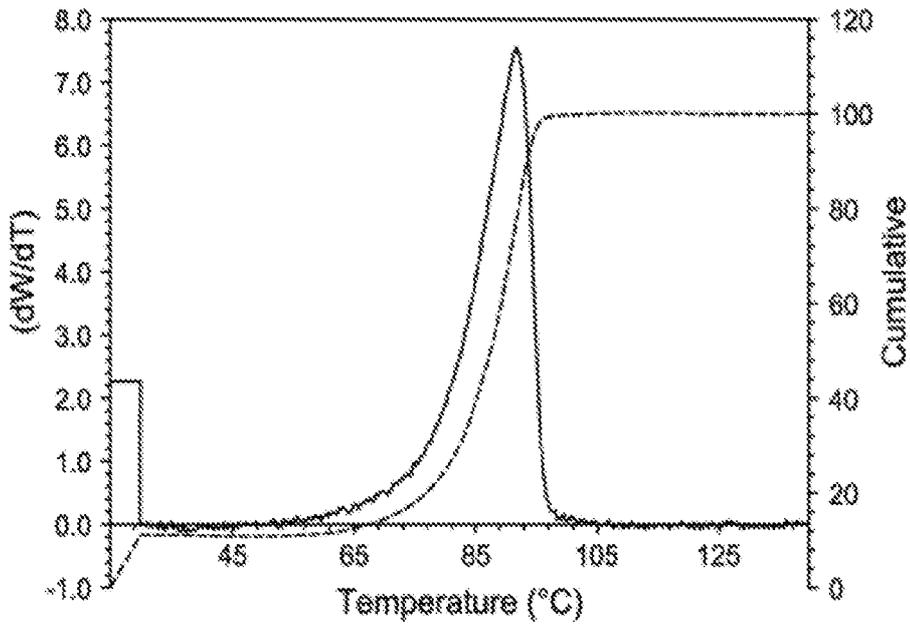


FIG. 6b

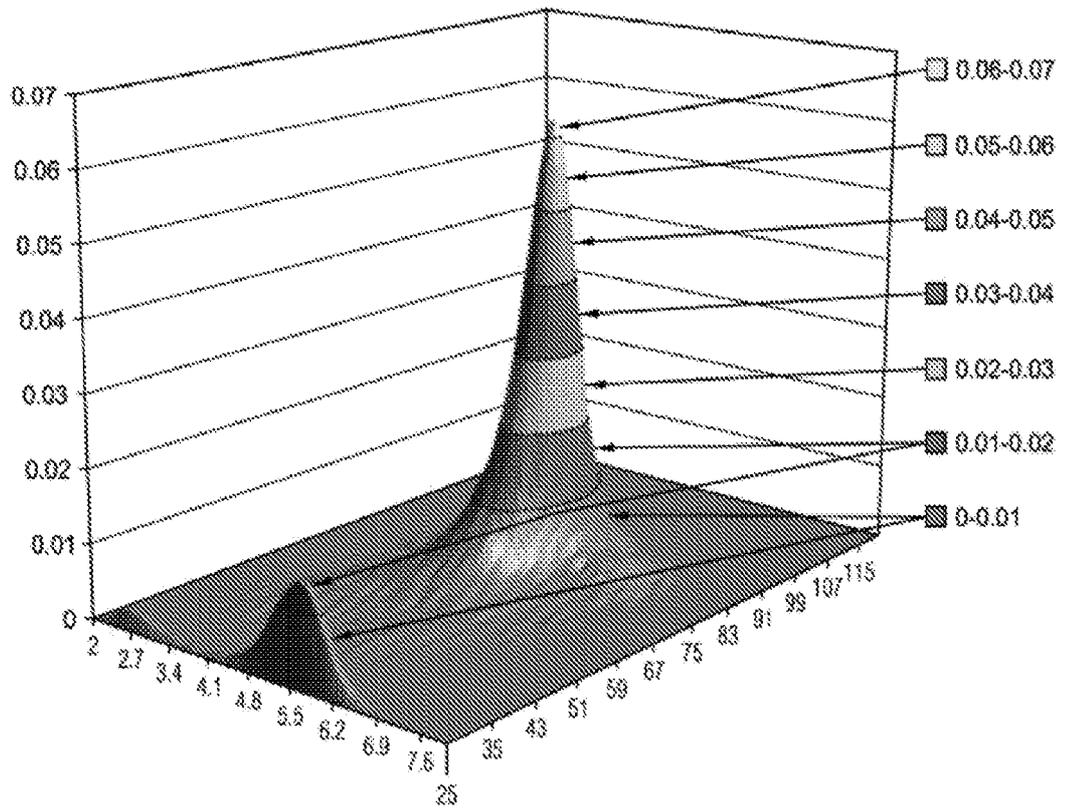


FIG. 6c

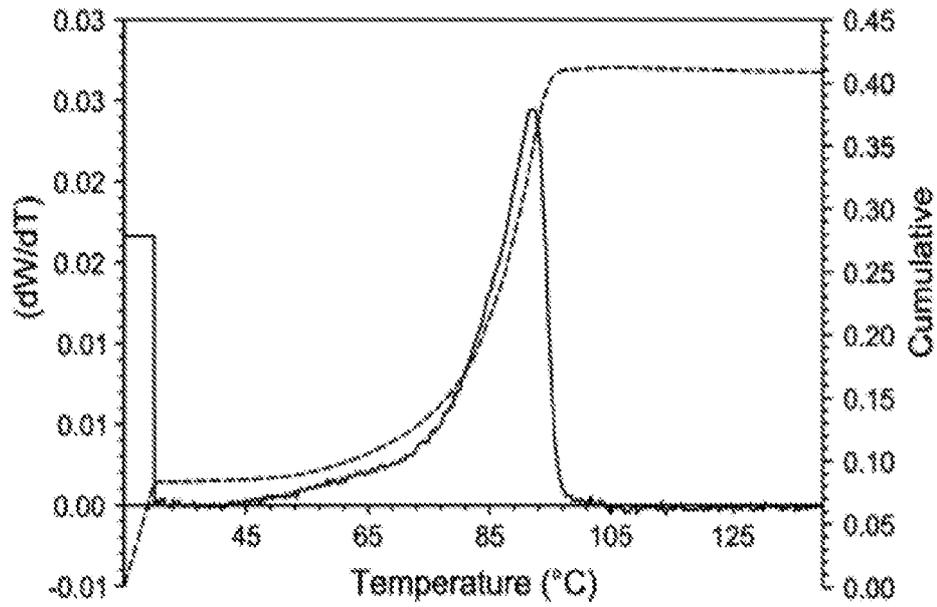


FIG. 7

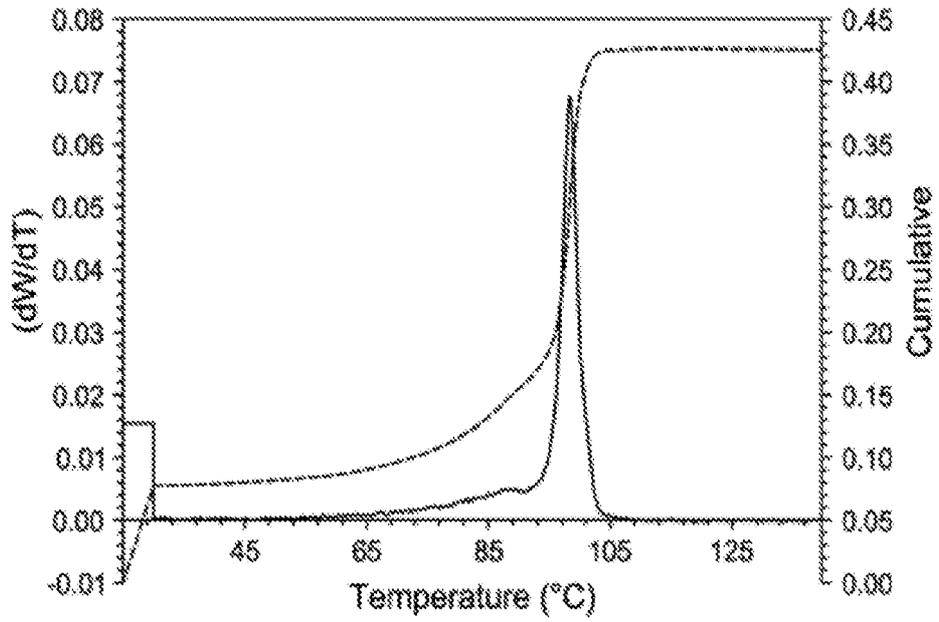


FIG. 8a

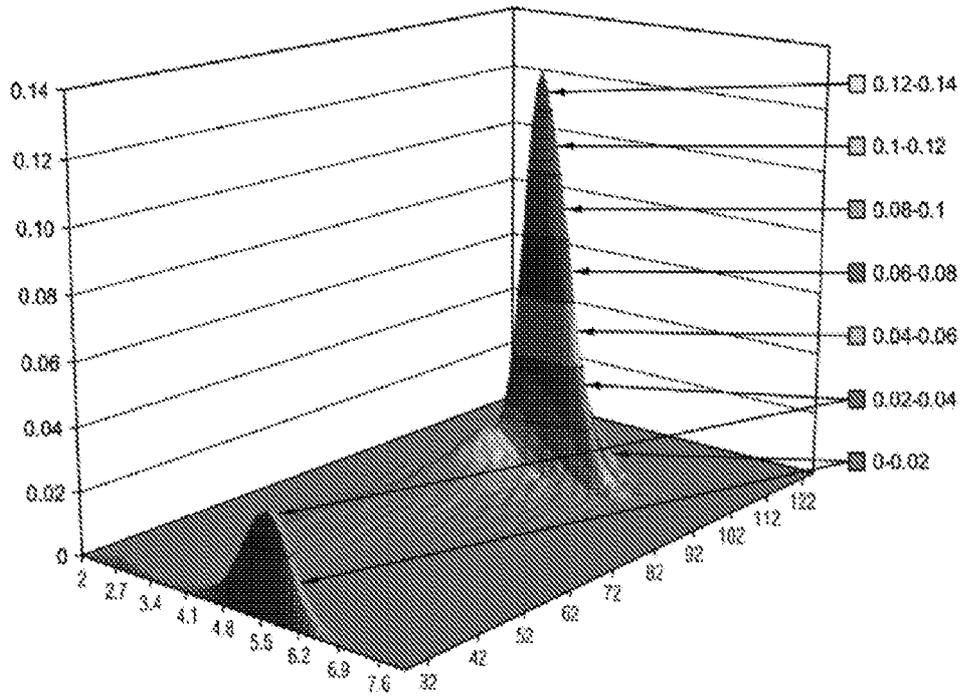


FIG. 8b

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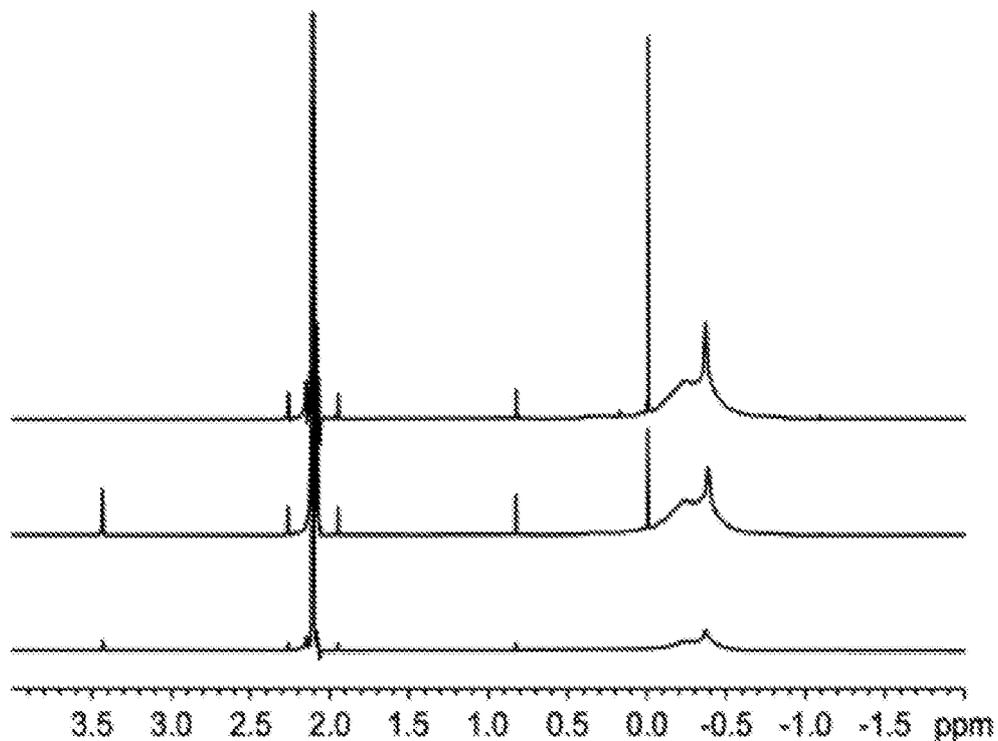


FIG. 9

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/021748

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C08F110/02 C08F210/16 C08F4/6592
 ADD.
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
 Minimum documentation searched (classification system followed by classification symbols)
 C08F
 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 2 374 822 A2 (LG CHEMICAL LTD [KR]) 12 October 2011 (2011-10-12) paragraph [0013] examples	I - 6, II- 15
Y	Wo 2009/146167 A2 (FINA TECHNOLOGY [US] ; MARIN VLADIMIR [US]) 3 December 2009 (2009-12-03) paragraph [0001] paragraph [0005] paragraph [0021] paragraph [0052] "or combinations thereof" ; paragraph [0036]	I - 6, II- 15
A	US 2004/259722 A1 (WANG SHAOTIAN [US]) 23 December 2004 (2004-12-23) comparative example 4	1-15
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Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search 23 June 2016	Date of mailing of the international search report 29/06/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Thomas , Domini k

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/021748

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