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(54) **Title:** DOUBLE SHUTTLING OF POLYOLEFIN POLYMERYL CHAINS

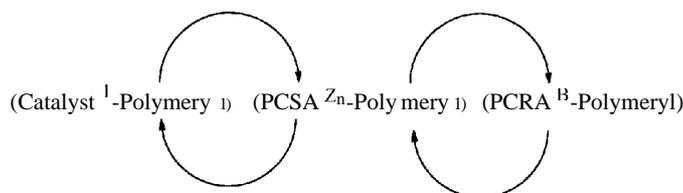


Fig. 2a

(57) **Abstract:** The invention generally relates to a process for preparing a metal-functionalized polyolefin and a composition useful therein, and to the metal-functionalized polyolefin prepared thereby and new non-metallic polymers prepared therefrom.

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Double Shuttling of Polyolefin Polymeryl Chains

Field of the Invention

The invention generally relates to a process for preparing a metal-functionalized polyolefin and a composition useful therein, and to the metal-functionalized polyolefin prepared thereby and
5 new non-metallic polymers prepared therefrom.

Introduction

Telechelic polymers comprise polymeryl chains that contain functional groups at their chain ends. Many types of telechelic polymers are known. Examples include polymers that contain a hydroxyl group at each polymeryl chain end. Telechelic polymers can be used, for example, as
10 rocket fuel binders and as ingredients in coatings, sealants, and adhesives.

Telechelic polymers have been prepared by a number of methods. U.S. Patent Number 5,247,023 mentions telechelic polymers prepared from certain metal-functionalized polyolefins, e.g., intermediate hydrocarbon-based polymers containing borane at polymeryl chain ends or in polymer backbones thereof. Such telechelic polymers have a statistical (i.e., essentially random) distribution
15 of terminal functional groups.

A chain shuttling agent can transfer polymer chains between two distinct catalysts with different olefin monomer selectivities in a single polymerization reactor. The resulting catalyst system produces polyolefins, including olefin block copolymers with alternating semicrystalline and amorphous segments and a number of desirable material properties. (see Arriola DJ, et al., *Catalytic
20 Production of Olefin Block Copolymers via Chain Shuttling Polymerization*, Science, 2006; 312: 714-719).

As a result, chain shuttling agents and polyolefins have recently been an important area of research. See, for example, PCT International Patent Application Publication Numbers WO 2005/073283 A1; WO 2005/090425 A1; WO 2005/090426 A1; WO 2005/090427 A2; WO
25 2006/101595 A1; WO 2007/035485 A1; WO 2007/035492 A1; and WO 2007/035493 A2. For example, WO 2005/090427 A2, page 19, defines the term "[chain] shuttling agent" as referring to a compound or mixture of compounds employed in the composition of WO 2005/090427 A2 that is capable of causing polymeryl chain exchange between at least two active catalyst sites of the catalysts included in the composition under the conditions of the polymerization. WO 2005/090427
30 A2 goes on to mention on page 20 that by selecting different combinations of catalysts having differing comonomer incorporation rates as well as differing reactivities, and by combining various shuttling agents or mixtures of agents with these catalyst combinations, polymer products having segments of different densities or comonomer concentrations, different block lengths, and different numbers of such segments or blocks in each copolymer can be prepared. WO 2005/090427 A2 goes

on to mention on page 22 that the mixtures of shuttling agents include the reaction product or mixture formed by combining a shuttling agent that is an organometal (hydrocarbyl metal) compound with less than a stoichiometric quantity (relative to the number of hydrocarbyl groups) of a secondary amine or a hydroxyl compound. WO 2005/090427 A2 does not specifically mention
5 combining two organometals comprising different metals.

Sita et al. in WO 2009/061499 and Sita et al., *Aufbaureaktion Redux: Scalable Production of Precision Hydrocarbons from AIR₃ (R = Et or iBu) by Dialkyl Zinc Mediated Ternary Living Coordinative Chain-Transfer Polymerization*, *Angew. Chem. Int. Ed.* 2010; 49:1768-1772, mention, among other things, a process for preparation of polyolefins via living coordinative chain transfer
10 polymerization with a metallocene-type catalyst that employs diethyl zinc (DEZ), triethyl aluminum (TEA), or triisobutylaluminum (TIBA). The Sita et al. process employs diethyl zinc as both a "secondary surrogate" and a chain-transfer mediator. Sita et al.'s use of DEZ is "mechanistically quite distinct from its role as a chain-shuttling agent for transferring a polymeryl group between two different active transition metal propagating species, as originally introduced by [the
15 aforementioned] Arriola and co-workers for the production of blocky poly(ethene-co-octene) by a non-living process" (page 1770). Sita et al. do not mention non-metallocene-type catalyst and require multiple molar equivalents of DEZ, TEA, TIBA, or certain combinations thereof, relative to the catalyst.

BRIEF SUMMARY OF THE INVENTION

20 The inventors discovered and the present invention generally provides, among other things, a composition and polymerization process capable of polymerizing olefin monomer(s) with a non-metallocene-type olefin polymerization catalyst (NMOP catalyst) in presence of a polymeryl chain shuttling agent (PCSA) and a repository compound, referred to herein as a polymeryl chain repository agent (PCRA), to give a useful metal-containing polyolefin polymeryl chain. The PCSA
25 and PCRA are matched based on their relative chain transfer constants C_{tr1} and C_{tr2} in such a way so as to advantageously enable the process to: metallate *in situ* in a facile, reversible manner the polyolefin polymeryl chain so as to give the metal-containing polyolefin polymeryl chain; reduce the amount of PCSA required relative to NMOP catalyst to sub-stoichiometric quantities, as the PCRA functions, in part, to reversibly store excess amount (quantity not immediately used by
30 NMOP catalyst) of the polyolefin polymeryl chain *in situ*; ultimately produce new polyolefins or telechelic polymers that have at least one improved property (e.g., enhanced melt flow rate (MFR), lower number average molecular weight (M_n), or both), as the PCRA also functions, in part, to reversibly functionalize the polyolefin polymeryl chain *in situ* in a form from which such polyolefins or telechelic polymers can be readily prepared; or a combination thereof.

In a first embodiment the present invention provides a polymerization process for preparing a metal-functionalized polyolefin, the process comprising contacting a first olefin monomer with a mixture comprising ingredients (a), (b), and (c), or a reaction product of any portion thereof:

Ingredient (a) a polymeryl chain repository effective amount of a first metal (Ci-C₂₀)hydrocarbyl

5 (the PCRA); Ingredient (b) a polymeryl chain shuttling effective amount of a second metal

(Ci-C₂₀)hydrocarbyl (the PCSA); and Ingredient (c) a catalytically-effective amount of a first non-

metallocene-type olefin polymerization catalyst (first NMOP catalyst) comprising a mixture of a

first non-metallocene-type precatalyst and at least one first co-catalyst, or a reaction product thereof;

10 wherein the contacting is performed under olefin polymerizing conditions (described later) in such a

way so as to polymerize the first olefin monomer and thereby prepare a metal-functionalized

polyolefin; Wherein the first metal (Ci-C₂₀)hydrocarbyl comprises a first metal cation and at least

one (Ci-C₂₀)hydrocarbyl (maximum number of (Ci-C₂₀)hydrocarbyl(s) therein preferably is equal to

the first metal cation's formal valence number), wherein the first metal cation is a Group 1, 2, 12, or

15 at least one (Ci-C₂₀)hydrocarbyl (maximum number of (Ci-C₂₀)hydrocarbyl(s) therein preferably is

equal to the second metal cation's formal valence number), wherein the second metal cation is a

Group 1, 2, 12, or 13 metal cation; Wherein the first and second metal cations are different from

each other; Wherein the first and second metal (Ci-C₂₀)hydrocarbyls are characterizable by chain

20 transfer constants C_{tr1} and C^{\wedge} , respectively, wherein chain transfer constant C_{tr2} is greater than chain

transfer constant C_{tri} (i.e., $C_{tr2} > C_{tr1}$) and C_{tr1} is greater than 0 (i.e., $C_{tr1} > 0$); and Wherein the metal-

functionalized polyolefin comprises a polyolefin polymeryl chain and a third metal cation, wherein a

majority of the third metal cation is the same as the first metal cation of or from the first metal

(Ci-C₂₀)hydrocarbyl. In the invention process, mole fraction of the second metal cation in a

combination of moles of the first and second metal cations is by definition from > 0.0 to < 1.0 .

25 In a second embodiment the present invention provides the metal-functionalized polyolefin prepared in the first embodiment.

In a third embodiment the present invention provides a composition comprising the mixture of the aforementioned ingredients (a), (b), and (c), or the reaction product of any portion thereof;

wherein the first non-metallocene-type olefin polymerization catalyst is characterizable as being

30 capable of catalytically polymerizing a first olefin monomer under olefin polymerizing conditions so

as to produce a metal-functionalized polyolefin that upon reacting with a quenching reagent

substantially releases the metal therefrom and prepares a polyolefin having an enhanced melt flow rate (i.e., melt flow index).

The invention process polymerizes olefin monomer(s), and thereby prepares the metal-functionalized polyolefin. The invention composition is useful in the invention process. As will be described later, the metal-functionalized polyolefin is especially useful for preparing known and, preferably, new polyolefins and telechelic polyolefins. In preferred embodiments the invention process enables facile synthesis of the metal-functionalized polyolefin without substantially decreasing catalyst efficiency of first NMOP catalyst (i.e., decreasing it by less than 10%) or, when two different non-metallocene-type olefin polymerization catalysts are employed, without preventing polymeryl chain shuttling between them, or both.

The telechelic polyolefins prepared by the invention process are especially useful as, for example, as rocket fuel binders and as ingredients in coatings, sealants, and adhesives. The polyolefins prepared by the invention process are especially useful as, for example, synthetic lubricants and, especially for the olefin block copolymers (OBCs), elastic films for hygiene applications (e.g., for diaper covers); flexible molded goods for appliances, tools, consumer goods (e.g., toothbrush handles), sporting goods, building and construction, automotive, and medical applications; flexible gaskets and profiles for appliance (e.g., refrigerator door gaskets and profiles), building and construction, and automotive applications; adhesives for packaging (e.g., for use in manufacturing corrugated cardboard boxes), hygiene applications, tapes, and labels; and foams for sporting goods (e.g., foam mats), packaging, consumer goods, and automotive applications.

BRIEF DESCRIPTION OF THE DRAWING(S)

Figure (Fig.) 1a shows a generic polymeryl chain shuttling scheme of the present invention employing a single catalyst.

Fig. 1b shows another generic polymeryl chain shuttling scheme of the present invention employing a single catalyst.

Fig. 1c shows a generic polymeryl chain shuttling scheme of the present invention that summarizes Figs. 1a and 1b.

Fig. 2a shows a version of Fig. 1c comprising a generic Zn-based PCSA/B-based PCRA polymeryl chain shuttling scheme employing a single catalyst.

Fig. 2b shows a version of Fig. 1c comprising a generic Zn-based PCSA/Al-based PCRA polymeryl chain shuttling scheme employing a single catalyst.

Fig. 3 shows a generic polymeryl chain shuttling scheme of the present invention employing two different catalysts.

Figs. 4a to 4g show different reactions for preparing various functionalized polymer from the boron-containing PCRA, all of the present invention.

Figs. 5a to 5c show different reactions for preparing various functionalized polymer from the aluminum-containing PCRA, all of the present invention.

Fig. 6 shows a continuous flow polymerization reactor system.

Fig. 7 is a graphical plot of results of MFR versus zinc cation mole fraction for non-
5 invention processes (0% and 100% mole fraction of zinc cation) and processes of Examples 11a to 12a to 12f.

DETAILED DESCRIPTION OF THE INVENTION

The invention relates to the process for preparing a metal-functionalized polyolefin and the
10 composition useful therein, and to the metal-functionalized polyolefin prepared thereby and new non-metallic polymers prepared therefrom, all as summarized previously.

Any lower limit of a range of numbers, or any preferred lower limit of the range, may be combined herein with any upper limit of the range, or any preferred upper limit of the range, to define a preferred aspect or embodiment of the range. Unless otherwise indicated, each range of
15 numbers includes all numbers, both rational and irrational numbers, subsumed within that range (e.g., the range from about 1 to about 5 includes, for example, 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5).

The word "optionally" means "with or without." For example, "optionally, an additive" means with or without an additive.

In any aspect or embodiment of the instant invention described herein, the term "about" in a
20 phrase referring to a numerical value may be deleted from the phrase to give another aspect or embodiment of the instant invention. Preferably "about" means from 90 percent to 100 percent of the numerical value, from 100 percent to 110 percent of the numerical value, or from 90 percent to 110 percent of the numerical value. In any aspect or embodiment of the instant invention described herein, the open-ended terms "comprising," "comprises," and the like (which are synonymous with
25 "including," "having," and "characterized by") may be replaced by the respective partially closed phrases "consisting essentially of," "consists essentially of," and the like or the respective closed phrases "consisting of," "consists of," and the like to give another aspect or embodiment of the instant invention. The term "characterizable" is open-ended and means distinguishable or capable of being distinguished. The term "plurality" means two or more, wherein each plurality is
30 independently selected unless indicated otherwise. The term "independently" means separately without regard for another. The terms "first," "second," etc. serve as a convenient means of distinguishing between two or more elements or limitations (e.g., a first chair and a second chair) and do not imply quantity or order unless specifically so indicated. Where the invention, or a portion thereof (e.g., element or step), is defined in the alternative by a Markush group having two or more

members, the invention contemplates preferred embodiments too numerous to recite each one herein. For convenience, such preferred embodiments can be readily determined by: (i) selecting any single member from the Markush group, thereby limiting scope of the Markush group to the selected single member thereof; or (ii) deleting any single member from the Markush group, thereby limiting the Markush group to any one of the remaining member(s) thereof. In some embodiments the member that is selected or deleted is based on one of the Examples or other species of the present invention described herein.

As used herein, the term "catalyst efficiency" means weight in grams of polymer produced divided by weight in grams of a catalytic metal of a metal-containing precatalyst (e.g., first non-metallocene precatalyst) employed. The catalytic metal is described later.

The term "catalytically effective amount" means a less-than-stoichiometric quantity sufficient for increasing rate of the polymerization of olefin monomer(s).

The term "chain repository effective amount" means a quantity that is sufficient to store a majority, and preferably at least 90 mole percent (mol%), of the polyolefin polymeryl chain as the metal-functionalized polyolefin.

The term "chain shuttling effective amount" means a quantity that is sufficient to transfer the polyolefin polymeryl chain between the first NMOP catalyst and the first metal (Ci-C₂₀)hydrocarbyl (PCRA).

The term "chain transfer constant" means a ratio of a chain transfer rate constant to a monomer propagation rate constant according to equation (a):

$$(a): \frac{1}{M_n} = B + \frac{C_{tr1} [PCRA]}{[M]} + \frac{C_{tr2} [PCSA]}{[M]}$$

wherein M_n is number average molecular weight of a test polyolefin prepared by quenching the metal-functionalized polyolefin, which is prepared according to the process of the first embodiment; B is $1/M_{n(native)}$, wherein $M_{n(native)}$ is number average molecular weight of a native polyolefin, wherein B is determined or calculated as described below; C_{tr1} is chain transfer constant for the first metal (Ci-C₂₀)hydrocarbyl; [PCRA] is concentration of the first metal (Ci-C₂₀)hydrocarbyl (the polymeryl chain repository agent); C_{tr2} is chain transfer constant for the second metal (Ci-C₂₀)hydrocarbyl; [PCSA] is molar concentration of the second metal (Ci-C₂₀)hydrocarbyl (the polymeryl chain shuttling agent); and [M] is molar concentration of olefin monomer. Solve equation (a) for C_{tr1} by varying [PCRA] at constant [PCSA]. Likewise, solve equation (a) for C_{tr2} by varying [PCSA] at constant [PCRA]. Determine B by running a control olefin polymerization reaction in the absence of any PCRA and PCSA under a same set of polymerization conditions to produce a native polyolefin, measuring M_n thereof by GPC as described later, and taking its inverse. Alternatively, calculate the

$M_{n(native)}$ by running a series of at least 3 olefin polymerization reactions under the same set of polymerization conditions and at various levels of the PCSA and with a fixed amount of, or preferably in absence of the PCRA so as to produce polyolefins therefrom, measuring M_n thereof by GPC as described later, and plotting $1/M_n$ versus the mole ratios of PCSA to olefin monomer,

5 wherein the resulting y-intercept of that plot would be equal to B . The same set of polymerization conditions comprises same reactor model and polymerization temperature or, preferably, same reactor model, polymerization temperature and catalyst efficiency (i.e., catalyst conversion). Preferably, the reactor model is Parr batch reactor model number 4532; polymerization temperature is 120 degrees Celsius ($^{\circ}C$); and catalyst conversion is 100,000 grams polyolefin per gram of metal

10 of the non-metallocene-type precatalyst. Equation (a) is particularly valuable for determining chain transfer constants for polymerizations conducted in continuous-flow stirred polymerization reactors with a constant olefin monomer conversion rate (e.g., about 90% conversion) and constant feed concentrations of the first and second metal (Ci-C₂₀)hydrocarbyl and olefin monomer, where [PCRA], [PCSA], and [M] are concentrations thereof in their respective feeds in an inert

15 hydrocarbon solvent such as, for example, a mixed alkanes solvent such as an isoparaffin fluid.

Certain unsubstituted chemical groups are described herein as having a maximum number of 20 carbon atoms (e.g., (Ci-C₂₀)hydrocarbyl) however number of carbon atoms is not critical. Twenty carbon atoms in such unsubstituted chemical groups is a practical upper limit; nevertheless in some embodiments the invention contemplates such unsubstituted groups having a maximum

20 number of carbon atoms that is higher than 20 (e.g., 40, 100, or more).

The term "(Ci-C₂₀)hydrocarbyl" (synonymous with the term "(Ci-C₂₀)hydrocarbyl group" when not used in a proper noun (e.g., "first metal (Ci-C₂₀)hydrocarbyl")) means a hydrocarbon radical of from 1 to 20 carbon atoms. Each hydrocarbon radical independently is aromatic (i.e., (C₆-C₂₀)aryl, e.g., phenyl) or non-aromatic (i.e., (Ci-C₂₀)aliphatic radical); saturated (i.e., (Ci-C₂₀)alkyl or (C₃-C₂₀)cycloalkyl) or unsaturated (i.e., (C₂-C₂₀)alkenyl, (C₂-C₂₀)alkynyl, or (C₃-C₂₀)cycloalkenyl); straight chain (i.e., normal-(Ci-C₂₀)alkyl) or branched chain (i.e., secondary-, iso-, or tertiary-(C₃-C₂₀)alkyl); cyclic (i.e., (C₆-C₂₀)aryl, (C₃-C₂₀)cycloalkenyl, or (C₃-C₂₀)cycloalkyl, including mono- and poly-cyclic, fused and non-fused polycyclic, including bicyclic;

25 at least 3 carbon atoms) or acyclic (i.e., (Ci-C₂₀)alkyl, (C₂-C₂₀)alkenyl, or (C₂-C₂₀)alkynyl); or a

30 combination of two or more thereof (e.g., (C₃-C₁₀)cycloalkyl-(Ci-C₁₀)alkyl or (C₆-C₁₀)aryl-(Ci-C₁₀)alkyl). Each hydrocarbon radical independently is the same as or different from another hydrocarbon radical and independently is unsubstituted or substituted by at least one halo. The term "halo" means fluoro, chloro, bromo, or iodo.

The term "enhanced melt flow rate" (enhanced MFR) is a discovery of the present invention and means an increase in number of grams of a melt of the polyolefin prepared by the invention process (invention process polyolefin) that moves through an orifice in a fixed period of time when under an applied force, compared to number of grams of a melt of a reference polyolefin that moves
5 through the same orifice under same MFR measurement conditions and using the MFR measurement method described later. The particular MFR measurement conditions used to demonstrate the enhanced MFR of the invention process polyolefin are not critical so long as they are the same for both the invention process and reference polyolefins. Preferred MFR measurement conditions comprise temperature of the melts is 190 °C; applied force is 2160-gram force; orifice is a
10 0.0825-inch (2.0955-millimeter) diameter orifice; and time period is 10 minutes. The reference polyolefin is prepared by a reference process that is the same as the invention process except the reference process lacks (does not employ) the second metal (Ci-C₂o)hydrocarbyl (i.e., the mole fraction of the first metal cation is 100% and the mole fraction of the second metal cation = 0.0% in the reference process). The increase in MFR (enhanced MFR) observed for the invention process
15 polyolefin demonstrates that the number average molecular weight (M_n) of the invention process polyolefin is lower than the M_n of the reference polyolefin, and this indicates a synergistic interaction occurs between the first and second metal (Ci-C₂o)hydrocarbyls, or reaction products thereof, in the invention process.

It is not critical how the invention process is conducted for demonstrating the enhanced
20 MFR. Preferably the enhanced MFR is measured for invention process polyolefins prepared from polymerizations conducted in continuous-flow stirred polymerization reactors with a constant olefin monomer conversion rate (e.g., about 90% conversion) and constant feed rates of the first and second metal (Ci-C₂o)hydrocarbyl and olefin monomer. The feed rates can be expressed as micromoles per minute. The increase in or enhancement of MFR of the invention process polyolefin
25 can, if desired, be visually observed by graphically plotting MFR on y-axis versus second metal cation mole fraction of 0.0%, 25%, 50%, and 100% (0.0, 0.25, 0.50, and 1.0 mole fraction, respectively) on x-axis. In absence of such a synergistic interaction, the MFR would plot as a flat horizontal line having MFR value equal to MFR for mole fraction of the second metal cation = 0.0, which flat horizontal line is expected for the reference polyolefin. The present synergistic
30 interaction, however, shows the increase of MFR of the invention process polyolefin as a point or line that plots above such a flat horizontal line at mole fraction of the second metal cation > 0.0% and < 100%. The difference between the point and line or two lines at any particular value of mole fraction of the second metal cation > 0.0% and < 100% equals the increase in or enhancement of MFR and demonstrates the aforementioned synergistic interaction in the invention process. In some

embodiments the invention process preferably is characterizable as being capable of producing the invention process polyolefin having the enhanced MFR.

The term "Group 1, 2, 12, or 13 metal cation" means a positive ionic form of an element of any one of Groups 1, 2, 12, and 13 of the Periodic Table of the Elements.

5 The term "metal-functionalized polyolefin" means a molecule or molecules comprising a polyolefin polymeryl chain bonded to a cation of an electropositive element (e.g., metal cation), preferably of Groups 1, 2, 12, or 13.

The term "metal (C_i-C₂O)hydrocarbyl" means a molecule or molecules comprising at least one (C_i-C₂O)hydrocarbyl bonded to a cation of an electropositive element.

10 The term "non-metallocene-type precatalyst" means a substance or molecule comprising the catalytic metal and at least one ligand bonded thereto, wherein each of the at least one ligand lacks an unsubstituted or substituted cyclopentadiene or anionic derivative thereof, wherein the substance or molecule is capable of increasing rate of a reaction of olefin monomer(s) to give the polyolefin polymeryl chain without the substance or molecule being changed. Substituted cyclopentadiene
15 includes benzo-fused cyclopentadiene. The catalytic metal has a positive formal oxidation state, i.e., formally is a cation. Examples of the catalytic metal are metals of Groups 3 to 9, preferably Groups 3 to 6, and more preferably Group 4, of the Periodic Table of the Elements. A preferred Group 4 metal is hafnium, zirconium, or titanium.

The term "non-metallocene-type olefin polymerization catalyst" means a substance of
20 molecule comprising, or a reaction product of, a mixture comprising the non-metallocene-type precatalyst and at least one activating co-catalyst. The NMOP catalyst lacks the unsubstituted or substituted cyclopentadiene or anionic derivative thereof.

The term "olefin monomer" means a molecule or molecules that can directly produce a
25 repeat unit of a polyolefin wherein each molecule independently contains a non-aromatic carbon-carbon triple bond or, preferably, a non-aromatic carbon-carbon double bond and can be polymerized to ultimately form a polyolefin.

The term "olefin polymerizing conditions" means a set of reaction parameters such as, for
30 example, temperature, pressure, time, rate of heating or cooling, type of reactor employed, and presence or absence of additional ingredients (e.g., solvent, molecular weight control agent, or a combination thereof). These conditions are described later.

The term "polyolefin polymeryl chain" means a radical or polyradical (i.e., at least two radicals) of a polymer comprising repeat units comprising residuals of olefin monomer(s).

The term "portion" referring to the mixture of ingredients means a structural part (e.g., metal cation part of metal (Ci-C₂o)hydrocarbyl) or whole of one of the ingredients, or a combination of any two or more structural parts or wholes of any two or more ingredients.

The term "reaction product" means a new substance resulting from a reversible or, preferably, irreversible chemical reaction between two or more reactant substances.

Fig. 1a shows an invention generic polymeryl chain shuttling scheme of the present invention employing a single catalyst, catalyst¹. The polymeryl chain ("Polymeryl") reversibly shuttles from catalyst¹ to a PCSA (Exchange 1), and from the PCSA to the PCRA (Exchange 2).

Fig. 1b shows another invention generic polymeryl chain shuttling scheme of the present invention employing a single catalyst. The polymeryl chain from the PCRA to the PCSA (Exchange 3), and from the PCSA to catalyst¹ (Exchange 4).

Figs. 2a and 2b show different versions of Fig. 1c comprising an invention embodiment of the shuttling scheme of Fig. 1c. Fig. 2a shows a generic Zn-based PCSA/B-based PCRA polymeryl chain shuttling scheme employs a single catalyst¹. Fig. 2b shows a generic Zn-based PCSA/Al-based PCRA polymeryl chain shuttling scheme employing a single catalyst¹.

Fig. 3 shows an invention polymeryl chain shuttling scheme employing two different catalysts, catalyst¹ and catalyst². In Fig. 3, the polymeryl chain reversibly shuttles between catalyst¹ and PCSA, and between the PCSA and either catalyst² or the PCRA.

Without wishing to be bound by theory, it is believed that in the contacting step of the invention process, the first NMOP catalyst is capable of polymerizing the first olefin monomer (or the first olefin monomer and at least one olefin comonomer, as the case may be) so as to produce a growing polyolefin polymeryl chain. Chain growth occurs when the polyolefin polymeryl chain is bonded to the catalytic metal of the first NMOP catalyst or catalytic metal of another catalyst, if any, as described later herein. It is believed that the first metal (Ci-C₂o)hydrocarbyl is capable of functioning as, or forming *in situ*, the polymeryl chain repository agent (PCRA) and the second metal (Ci-C₂o)hydrocarbyl is capable of functioning as, or forming *in situ*, the polymeryl chain shuttling agent (PCSA). The PCSA, PCRA, olefin monomer, and the first NMOP catalyst can unpredictably act together so as to synergistically increase (enhance) MFR and concomitantly lower M_n of the polyolefin polymeryl chain as demonstrated as described previously. It is believed that the amount of the polyolefin polymeryl chain that is reversibly stored and functionalized as the metal-functionalized polyolefin by the PCRA is at least an amount of the polyolefin polymeryl chain that is in excess of the combined bonding capacities of the second metal cation and catalyst metal of the first NMOP catalyst, and preferably is a majority of the polyolefin polymeryl chain.

Preferably the invention process prepares the metal-functionalized polyolefin via a non-living polymerization reaction. Non-living polymerization reaction is distinguishable from a living polymerization reaction by polydispersity index (PDI). As used herein, living polymerization means a reaction producing a polyolefin having a PDI of at most 1.80 and, in some cases, at most 1.40.

5 Preferably, the contacting step of the invention process does not employ, and the mixture does not contain, a metallocene-type catalyst (i.e., as an additional catalyst in the contacting step).

In some embodiments the mixture in the contacting step of the invention process is prepared with, and the invention process employs, only one non-metallocene-type precatalyst (i.e., and only the first NMOP catalyst). In other embodiments the mixture is prepared with, and the invention
10 process employs, only two non-metallocene-type precatalysts (i.e., prepared from the first non-metallocene-type precatalyst and a different second non-metallocene-type precatalyst) such that there are only the first and second NMOP catalysts. The PCSA would also shuttle the polyolefin polymeryl chain between the first and second NMOP catalysts

The invention process contemplates employing a batch or, preferably, continuous-flow
15 polymerization method and reactor for the contacting step.

The invention olefin polymerization reactions can be run in one reactor or multiple (two or more) reactors with one NMOP catalyst and optionally one or more other catalysts. For example in one embodiment, at least two catalysts are introduced into a single reactor and placed under the olefin polymerization conditions, wherein at least the first one of the catalysts is the first NMOP
20 catalyst and each catalyst inherently produces a mixture or blend of different polyolefins or polyolefin copolymers. As used herein, the term "copolymer" means a molecule comprising repeat units comprising residuals of at least two, preferably only two, different monomers. The terms "mixture" and "blend" as applied to the polyolefin and polyolefin copolymers are synonymous. In one embodiment, a relatively high molecular weight polyolefin (M_w from 100,000 g/mol to over
25 1,000,000 g/mol, more preferably 200,000 g/mol to 500,000 g/mol) is formed from one of the catalysts while a polyolefin of a relatively low molecular weight (M_w 2,000 g/mol to 300,000 g/mol) is formed from another of the catalysts. The at least two catalysts can have similar or different comonomer incorporation abilities, different polymer molecular weight producing capabilities, or a combination thereof. The resulting mixture or blend of different polyolefin copolymers will have
30 properties dependent, in part, on the ratio of the at least two catalysts that are employed in the single reactor. Suitable combinations of polyolefin molecular weight, comonomer incorporation ability, processes, and ratios of catalysts for such products are disclosed in U.S. Pat. No. 6,924,342.

Examples of suitable processes and systems employing multiple reactors include such processes and systems as are disclosed in U.S. Pat. No. 3,914,342. The multiple reactors, preferably

two reactors, can be operated in series or in parallel, with at least the first NMOP catalyst being employed in at least one of the reactors. Polyolefin products from these reactors can have similar or different densities. The final polyolefin polymer product is a mixture or blend of effluents of different polyolefins from the at least two reactors. The effluents of different polyolefins are preferably combined by mixing or blending prior to being subjected to devolatilization so as to more easily result in a uniform mixing or blending of the different polyolefins. In another embodiment, the molecular weight of the different polyolefins from the at least two reactors is nearly the same but the densities vary to the extent that one of the reactors produces a first polyolefin polymer with density in the range of 0.865-0.895, while another reactor produces a second polyolefin polymer with a different density in the range of 0.885-0.950. When two reactors and two catalysts, at least one of which is the first NMOP catalyst, are employed, such a dual reactor/dual catalyst process allows for the preparation of a mixture or blend of polyolefin polymers with tailored properties. In some embodiments employing the dual reactors, two reactors are connected in series, that is, the effluent from a first reactor is charged to a second reactor and, optionally, fresh monomer, solvent and hydrogen are added to the second reactor. The first NMOP catalyst can be employed in the first or second reactor or both. Olefin polymerization conditions are adjusted in the second reactor so that they are different from the olefin polymerization conditions that are employed in the first reactor such that a weight ratio of weight of the polyolefin polymer produced in the first reactor to weight of the polyolefin polymer produced in the second reactor is ideally in the range of from 20:80 to 80:20. This embodiment of a dual reactor process is capable of producing a mixture or blend of different polyolefin polymers having broadened molecular weight distribution or polydispersity index (PDI). In a more preferred embodiment, the invention process produces a mixture or blend of different polyolefin polymers that comprises high and low molecular weight polyolefin polymer components.

In some embodiments one of the two reactors of the dual reactor embodiment, including the first of two reactors operating in series, contains a heterogeneous Ziegler-Natta catalyst or a chromium containing catalyst, such as one of the numerous such catalysts known in the art. Examples of Ziegler-Natta catalysts include, but are not limited to, titanium-based catalysts supported on $MgCl_2$, and additionally comprise compounds of aluminum containing at least one aluminum-alkyl bond. Suitable Ziegler-Natta catalysts and their preparation include, but are not limited to, those disclosed in U.S. Pat. Nos. 4,612,300, 4,330,646, and 5,869,575. Suitable chromium based catalysts are those disclosed in U.S. Pat. Nos. 4,981,927, 4,835,219, 4,564,660, 4,173,548, 3,953,413, and elsewhere. The first NMOP catalyst is contained in the same or different one of the two reactors as the aforementioned catalysts.

The invention process employs olefin polymerizing conditions. Olefin polymerizing conditions independently refer to reaction conditions such as solvent(s), atmosphere(s), temperature(s), pressure(s), time(s), and the like that are preferred for giving, after 15 minutes reaction time, at least a 10 percent (%), more preferably at least 20%, and still more preferably at least 30% reaction yield of the metal-functionalized polyolefin from the invention process.

5 Preferably, the invention process is independently run under an inert atmosphere (e.g., under an inert gas consisting essentially of, for example, nitrogen gas, argon gas, helium gas, or a mixture of any two or more thereof). Other atmospheres are contemplated, however, and these include sacrificial olefin in the form of a gas and hydrogen gas (e.g., as a polymerization termination agent or

10 molecular weight control agent). In some aspects, the invention process independently is run without any solvent, i.e., is a neat process that is run in a neat mixture of ingredients (e.g., ingredients (a) to (c)). In other aspects, the neat mixture further contains additional ingredients (e.g., catalyst stabilizer such as triphenylphosphine) other than solvent(s). Preferably, the invention process is run with a solvent or mixture of two or more solvents, i.e., is a solvent-based process that is run as a solvent-

15 containing mixture of ingredients, and at least one solvent, e.g., an aprotic solvent. Preferably, the neat process or solvent-based process is run at a temperature of the neat mixture or solvent-containing mixture of from -20 °C to about 300 °C. In some embodiments, the temperature is at least 30 °C, and more preferably at least 40 °C. In some embodiments, the temperature is at least 100 °C. In some embodiments, the temperature is 200 °C or lower. A convenient temperature is from about

20 130 °C to about 190 °C (e.g., 150 °C or 170 °C or 190 °C). Preferably the invention process independently is run under a pressure of from about 0.9 atmospheres (atm) to about 10 atm (from about 91 kiloPascals (kPa) to about 1010 kPa). More preferably, the pressure is about 101 kPa).

The olefin monomers useful in the invention process are those that are polymerizable under the conditions thereof. In some embodiments olefin monomers (including olefin comonomers when

25 there are at least two olefin monomers) useful in the invention process are olefinic (C_2 - C_{40})hydrocarbons consisting of carbon and hydrogen atoms and containing at least 1, and preferably no more than 3, and more preferably no more than 2, carbon-carbon double bonds. In some embodiments, from 1 to 4 hydrogen atoms of the (C_2 - C_{40})hydrocarbons are replaced, each by a halogen atom, preferably fluoro or chloro to give halogen atom-substituted olefinic (C_2 -

30 C_{40})hydrocarbons as the useful olefin monomers. The olefinic (C_2 - C_{40})hydrocarbons (not halogen atom-substituted) are preferred. Still more preferred olefin monomers are ethylene and (C_3 - C_{40})olefins. Examples of the (C_3 - C_{40})olefins are alpha-olefins, cyclic olefins, styrene, and cyclic or acyclic dienes. In some embodiments the invention process employs the first olefin monomer and at least one other olefin monomer (i.e., at least one olefin comonomer), wherein the at least one

other olefin monomer is the alpha-olefin, and more preferably a (C₃-C₄₀)alpha-olefin. In some embodiments the (C₃-C₄₀)alpha-olefin is a (C₄-C₄₀)alpha-olefin, more preferably a (C₆-C₄₀)alpha-olefin, still more preferably a (C₇-C₄₀)alpha-olefin, and even more preferably a (C₈-C₄₀)alpha-olefin.

5 Preferably, the (C₃-C₄₀)alpha-olefin comprises a branched chain (C₃-C₄₀)alpha-olefin; more preferably a linear-chain (C₃-C₄₀)alpha-olefin; even more preferably a linear chain (C₃-C₄₀)alpha-olefin of formula (A): CH₂=CH₂-(CH₂)_zCH₃ (A), wherein z is an integer of from 0 to 40; and yet even more preferably a linear-chain (C₃-C₄₀)alpha-olefin that is 1-propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, or a linear-chain
10 (C₂₀-C₂₄)alpha-olefin. Preferably the cyclic olefin is a (C₃-C₄₀)cyclic olefin. Preferably, the cyclic or acyclic diene is a (C₄-C₄₀)diene, preferably an acyclic diene, more preferably an acyclic conjugated (C₄-C₄₀)diene, more preferably an acyclic 1,3-conjugated (C₄-C₄₀)diene, and still more preferably 1,3-butadiene.

Polyolefins that can be made by an invention process include, for example, polyethylene
15 and copolymers (interpolymers) that comprise residuals of ethylene and at least one (C₃-C₄₀)olefin. Preferred homopolymers are polyethylene and polypropylene. Preferred copolymers are those prepared by co-polymerizing a mixture of at least two olefin monomers (i.e., a mixture of the first olefin monomer and at least one olefin comonomer) such as, for example, ethylene/propylene, ethylene/1-butene, ethylene/1-pentene, ethylene/1-hexene, ethylene/4-methyl-1-pentene, ethylene/1-
20 octene, ethylene/styrene, ethylene/propylene/butadiene and other EPDM terpolymers. Preferably, the polyolefin is an ethylene homopolymer (e.g., a high density polyethylene), an ethylene/alpha-olefin copolymer (i.e., poly(ethylene alpha-olefin) copolymer such as, for example, a poly(ethylene 1-octene)), or an ethylene/alpha-olefin/diene interpolymers (i.e., a poly(ethylene alpha-olefin diene) terpolymer such as, for example, a poly(ethylene 1-octene 1,3-butadiene).

25 Preferably, (C_i-C₂₀)hydrocarbyl is (C_i-C₂₀)alkyl, (C₃-C₂₀)cycloalkyl, (C₆-C₈)aryl, or a composite radical of at least two thereof. An example of the composite radical is (C₆)aryl-(C_i-C₂)alkyl. The term "(C_i-C₂₀)alkyl" means a straight or branched saturated hydrocarbon radical of from 1 to 20 carbon atoms (e.g., methyl, ethyl, 1-propyl, 2-propyl, 1-butyl, 2-butyl, 1,1-dimethylethyl, etc.). Any hydrocarbon radical can be unsubstituted or substituted with phenyl,
30 naphthyl, or halo. The term "(C₆-C₈)aryl" means a mono-, bi- or tricyclic aromatic hydrocarbon radical of from 6 to 18 carbon atoms, of which at least from 6 to 14 of the carbon atoms are aromatic ring carbon atoms, and the mono-, bi- or tricyclic radical comprises 1, 2 or 3 rings, respectively; wherein the 1 ring is aromatic and the 2 or 3 rings independently are fused or non-fused and at least one of the 2 or 3 rings is aromatic. "(C₃-C₂₀)cycloalkyl" means a saturated or unsaturated (but not

aromatic) cyclic hydrocarbon radical of from 3 to 20 carbon atoms (e.g., cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, etc.)

Compounds that can function as the polymeryl chain shuttling agents are known. As used herein, the term "polymeryl chain shuttling agent" or PCSA means the second metal (5 (Ci-C₂₀)hydrocarbyl. Without being bound by theory, the PCSA is a molecule characterizable, without limitation, as functioning in the invention process in such a way that polymer chains are transferred between the PCRA and the first NMOP catalyst in a single polymerization reactor. When two (or more) distinct NMOP catalysts with different monomer selectivities are employed in the invention process, the PCSA further transfers the polyolefin polymeryl chains in a single 10 polymerization reactor between the two (or more) distinct NMOP catalysts. Typically, PCSAs comprise a metal that is Al, B, or Ga, the second metal cation being in a formal oxidation state of +3; or, preferably, a second metal cation that is Zn or Mg in a formal oxidation state of +2. Preferred chain shuttling agents are described in U.S. Patent Application Publication Number US 2007/0167315. PCSAs suitable for use in the invention process include diethylzinc, di(i-butyl)zinc, 15 di(n-hexyl)zinc, triethylaluminum, trioctylaluminum, triethylgallium, i-butylaluminum bis(dimethyl(t-butyl)siloxane), i-butylaluminum bis(di(trimethylsilyl)amide), n-octylaluminum di(pyridine-2-methoxide), bis(n-octadecyl)i-butylaluminum, i-butylaluminum bis(di(n-pentyl)amide), n-octylaluminum bis(2,6-di-t-butylphenoxide), n-octylaluminum di(ethyl(1-naphthyl)amide), ethylaluminum bis(t-butyl)dimethylsiloxide), ethylaluminum 20 di(bis(trimethylsilyl)amide), ethylaluminum bis(2,3,6,7-dibenzo-1-azacycloheptaneamide), n-octylaluminum bis(2,3,6,7-dibenzo-1-azacycloheptaneamide), n-octylaluminum bis(dimethyl(t-butyl)siloxide), ethylzinc (2,6-diphenylphenoxide), and ethylzinc (t-butoxide).

Compounds that can function as the polymeryl chain repository agents are known, although their storage (repository) and functionalization characteristics, and aforementioned beneficial 25 interactions with PCSAs, are believed to be first discovered by the present inventors. The term "polymeryl chain repository agent" or PCRA means the first metal (Ci-C₂₀) hydrocarbyl. The PCRA is independently selected from the aforementioned list of PCSAs in accordance with the chain transfer constants C_{tr2} and C^{\wedge} , respectively, wherein $C_{tr2} > C_{tr1}$ and $C_{tr1} > 0$.

Preferably, the second metal (Ci-C₂₀)hydrocarbyl (PCSA) is a zinc (Ci-C₂₀)hydrocarbyl and 30 the first metal (Ci-C₂₀)hydrocarbyl (PCRA) is a boron (Ci-C₂₀)hydrocarbyl or, more preferably, an aluminum (Ci-C₂₀)hydrocarbyl. More preferably the PCSA is diethylzinc, di(i-butyl)zinc, di(n-hexyl)zinc, ethylzinc (2,6-diphenylphenoxide), or ethylzinc (t-butoxide); and the PCRA is triethylaluminum, trioctylaluminum, i-butylaluminum bis(dimethyl(t-butyl)siloxane), i-butylaluminum bis(di(trimethylsilyl)amide), n-octylaluminum di(pyridine-2-methoxide), bis(n-

octadecyl)j-butylaluminum, i-butylaluminum bis(di(n-pentyl)amide), n-octylaluminum bis(2,6-di-t-butylphenoxide, n-octylaluminum di(ethyl(1-naphthyl)amide), ethylaluminum bis(t-butyl)dimethylsiloxide), ethylaluminum di(bis(trimethylsilyl)amide), ethylaluminum bis(2,3,6,7-dibenzo-1-azacycloheptaneamide), n-octylaluminum bis(2,3,6,7-dibenzo-1-azacycloheptaneamide),
5 or n-octylaluminum bis(dimethyl(t-butyl)siloxide). Still more preferably, the PCSA and PCRA are as described in any one of the Examples described later.

When the first metal (Ci-C₂₀)hydrocarbyl (PCRA) is a boron (Ci-C₂₀)hydrocarbyl, preferably the contact step is carried out at low rates of propagation of polyolefin polymeryl chains and sufficiently long reactor residence time (e.g., in a continuous-flow reactor), such that a majority
10 of polyolefin polymeryl chain ends are functionalized with a boron species, as determined by nuclear magnetic resonance (NMR) spectroscopy. When the first metal (Ci-C₂₀)hydrocarbyl (PCRA) is an aluminum (Ci-C₂₀)hydrocarbyl, the rates of propagation can be higher and reactor residence times can be shorter than those for the boron (Ci-C₂₀)hydrocarbyl.

In some embodiments the first metal (Ci-C₂₀)hydrocarbyl, or any reaction product thereof,
15 (PCRA) does not substantially decrease (any decrease is less than 10%) catalyst efficiency of the first non-metallocene-type olefin polymerization catalyst in the contacting step compared to a reference catalyst efficiency of the first non-metallocene-type olefin polymerization catalyst when the first metal (Ci-C₂₀)hydrocarbyl is absent.

In some embodiments the contacting step comprises a continuous-flow polymerization
20 process step operating in a continuous-flow reactor (preferably a continuous-flow stirred reactor) and the process further comprises a preliminary step of feeding the first olefin monomer, polymeryl chain repository effective amount of the first metal (Ci-C₂₀)hydrocarbyl (PCRA), polymeryl chain shuttling effective amount of the second metal (Ci-C₂₀)hydrocarbyl (PCSA), and first non-metallocene-type olefin polymerization catalyst into the continuous-flow reactor and a subsequent
25 step of removing the metal-functionalized polyolefin from the continuous-flow reactor so as to provide a removed metal-functionalized polyolefin.

In some embodiments the polymeryl chain shuttling effective amount of the second metal (Ci-C₂₀)hydrocarbyl (PCSA) is less on a mole basis than the polymeryl chain repository effective amount of the first metal (Ci-C₂₀)hydrocarbyl (PCRA) and less on a mole basis than the
30 catalytically effective amount of the first non-metallocene-type precatalyst and any other precatalyst. In some embodiments a sum of the polymeryl chain repository effective amount plus the polymeryl chain shuttling effective amount is, on a mole basis, greater than the catalytically effective amount of the first non-metallocene-type precatalyst (and preferably any catalytically effective amount of any other precatalyst (e.g., second non-metallocene-type precatalyst)).

The C_{tr1} and C_{tr2} are determined as described later. In some embodiments $C_{tr2} \geq 5C_{tr1}$. In some embodiments $C_{tr2} \geq 10 C_{tr1}$. In some embodiments $C_{tr2} < 50C_m$ or $C_{tr2} < 30C_{tr1}$. In some embodiments $C_{tr1} > 1$. In some embodiments $C_m > 2$. In some embodiments $C_m > 3$. In some embodiments $C_m < 10$.

5 Preferred metal (Ci-C₂₀)hydrocarbyl for the PCSA and PCRA are aluminum (Ci-C₂₀)hydrocarbyl, boron (Ci-C₂₀)hydrocarbyl, gallium (Ci-C₂₀)hydrocarbyl, magnesium (Ci-C₂₀)hydrocarbyl, or zinc (Ci-C₂₀)hydrocarbyl. More preferred are aluminum (Ci-C₂₀)alkyl, boron (Ci-C₂₀)alkyl, gallium (Ci-C₂₀)alkyl, magnesium (Ci-C₂₀)alkyl, or zinc (Ci-C₂₀)alkyl.

The matching of the PCSA and PCRA based on their relative chain transfer constants C_m and C_{tr2} so as to preferably achieve the enhancement of MFR and concomitant lower M_n . In some
10 embodiments the first metal (Ci-C₂₀)hydrocarbyl (PCRA) is a boron (Ci-C₂₀)hydrocarbyl. In some such embodiments the second metal (Ci-C₂₀)hydrocarbyl (PCSA) is aluminum (Ci-C₂₀)hydrocarbyl. In other such embodiments the second metal (Ci-C₂₀)hydrocarbyl is gallium (Ci-C₂₀)hydrocarbyl. In still other such embodiments the second metal (Ci-C₂₀)hydrocarbyl is
15 magnesium (Ci-C₂₀)hydrocarbyl. In still other such embodiments the second metal (C₁-C₂₀)hydrocarbyl is zinc (Ci-C₂₀)hydrocarbyl. In still other such embodiments the second metal (C₁-C₂₀)hydrocarbyl is a mixture of any two of the foregoing aluminum, gallium, magnesium, and zinc (Ci-C₂₀)hydrocarbyls. Preferably each such (Ci-C₂₀)hydrocarbyl independently is a (Ci-C₂₀)alkyl, and in some embodiments (Ci-C₁₀)alkyl or (Ci-C₅)alkyl.

20 In some embodiments the first metal (Ci-C₂₀)hydrocarbyl (PCRA) is an aluminum (Ci-C₂₀)hydrocarbyl. In some such embodiments the second metal (Ci-C₂₀)hydrocarbyl (PCSA) is gallium (Ci-C₂₀)hydrocarbyl. In other such embodiments the second metal (Ci-C₂₀)hydrocarbyl is magnesium (Ci-C₂₀)hydrocarbyl. In still other such embodiments the second metal (C₁-C₂₀)hydrocarbyl is zinc (Ci-C₂₀)hydrocarbyl. In still other such embodiments the second metal (C₁-C₂₀)hydrocarbyl is a mixture of any two of the foregoing gallium, magnesium, and zinc (d-
25 C₂₀)hydrocarbyls. Preferably each such (Ci-C₂₀)hydrocarbyl independently is a (Ci-C₂₀)alkyl, and in some embodiments (Ci-C₁₀)alkyl or (Ci-C₅)alkyl.

In some embodiments the second metal (Ci-C₂₀)hydrocarbyl (PCSA) is a zinc (Ci-C₂₀)hydrocarbyl. In some such embodiments the first metal (Ci-C₂₀)hydrocarbyl (PCRA) is
30 boron (Ci-C₂₀)hydrocarbyl. In other such embodiments the first metal (Ci-C₂₀)hydrocarbyl is aluminum (Ci-C₂₀)hydrocarbyl. In still other such embodiments the first metal (Ci-C₂₀)hydrocarbyl is gallium (Ci-C₂₀)hydrocarbyl. In still other such embodiments the first metal (Ci-C₂₀)hydrocarbyl is magnesium (Ci-C₂₀)hydrocarbyl. In still other such embodiments the first metal (C₁-C₂₀)hydrocarbyl is a mixture of any two of the foregoing boron, aluminum, gallium, and

magnesium (Ci-C₂₀)hydrocarbyls. Preferably each such (Ci-C₂₀)hydrocarbyl independently is a (Ci-C₂₀)alkyl, and in some embodiments (Ci-C₁₀)alkyl or (Ci-C₅)alkyl.

In some embodiments the first metal cation of or from the first metal (Ci-C₂₀)hydrocarbyl (PCRA) is a Group 13 metal cation and the second metal cation of or from the second metal (Q-C₂₀)hydrocarbyl (PCSA) is a zinc cation. In some embodiments the first metal (Ci-C₂₀)hydrocarbyl is an aluminum (Ci-C₂₀)alkyl, which comprises an aluminum cation and from 1 to 3 (Ci-C₂₀)alkyl; or a boron (Ci-C₂₀)alkyl, which comprises a boron cation and from 1 to 3 (Ci-C₂₀)alkyl; and the second metal (Ci-C₂₀)hydrocarbyl is a zinc (Ci-C₂₀)alkyl, which comprises a zinc cation and 1 or 2 (Ci-C₂₀)alkyl. In some embodiments the first metal (Ci-C₂₀)hydrocarbyl is the aluminum (C₁-C₂₀)alkyl, which is an aluminum (Ci-C₆)alkyl; and the zinc (Ci-C₂₀)alkyl is a zinc (Ci-C₆)alkyl.

The aluminum (Ci-C₂₀)hydrocarbyl (e.g., ((Ci-C₂₀)alkyl)₃Al) can be obtained from commercial sources or are readily prepared by contacting an aluminum halide (e.g., AlCl₃) with 3 mole equivalents of a (Ci-C₂₀)hydrocarbyl Grignard reagent or, preferably, a (Ci-C₂₀)hydrocarbyl lithium.

The boron (Ci-C₂₀)hydrocarbyl (e.g., ((Ci-C₂₀)alkyl)₃B) can be obtained from commercial sources or are readily prepared by contacting triethylborate (B(OCH₂CH₃)₃) with the aluminum (Ci-C₂₀)hydrocarbyl. If desired, the product boron (Ci-C₂₀)hydrocarbyl can be evaporated *in vacuo* from aluminum ethoxide byproduct and collected so as to give an isolated and purified boron (Ci-C₂₀)hydrocarbyl.

The gallium (Ci-C₂₀)hydrocarbyl (e.g., ((Ci-C₂₀)alkyl)₃Ga) can be obtained from commercial sources or are readily prepared by contacting a gallium halide (e.g., GaCl₃) with 3 mole equivalents of a (Ci-C₂₀)hydrocarbyl Grignard reagent or, preferably, a (Ci-C₂₀)hydrocarbyl lithium.

The magnesium (Ci-C₂₀)hydrocarbyl (e.g., ((Ci-C₂₀)alkyl)₂Mg) can be obtained from commercial sources or are readily prepared by contacting magnesium metal with 3 mole equivalents of a (Ci-C₂₀)hydrocarbyl-bromide or (Ci-C₂₀)hydrocarbyl-iodide.

The zinc (Ci-C₂₀)hydrocarbyl (e.g., ((Ci-C₂₀)alkyl)₂Zn) can be obtained from commercial sources or are readily prepared by contacting a zinc-copper couple with 3 mole equivalents of a (Ci-C₂₀)hydrocarbyl-bromide or (Ci-C₂₀)hydrocarbyl-iodide.

In the aforementioned preparations of aluminum, boron, gallium, magnesium, and zinc (Ci-C₂₀)hydrocarbyl, the contacting can be performed in an aprotic solvent such as, for example, tetrahydrofuran or toluene under an inert gas atmosphere such as, for example, an atmosphere of nitrogen gas, helium, or argon gas, at a temperature of from about -80 °C to about 50 °C.

In some embodiments the majority of the third metal cation is a boron cation or, more preferably, an aluminum cation.

In some embodiments the process further comprises, in a preliminary step, mixing together the first non-metallocene-type precatalyst and at least one first co-catalyst in such a way so as to prepare the first NMOP catalyst before employing the first NMOP catalyst in the contacting step.

In some embodiments the contacting step further employs at least one second olefin monomer (i.e., olefin comonomer(s)) and copolymerizes the first and second olefin monomers, and thereby prepares the metal-functionalized polyolefin as a metal-functionalized olefin copolymer. In some embodiments the contacting step further employs the at least one second olefin monomer and the mixture in the contacting step further contains an ingredient (d): a catalytically effective amount of a second non-metallocene-type olefin polymerization (NMOP) catalyst, wherein the second non-metallocene-type olefin polymerization catalyst comprises a second non-metallocene-type precatalyst and at least one second co-catalyst, or a reaction product thereof; wherein the first and second co-catalysts are the same as or different than each other; the first and second non-metallocene-type precatalysts are different from each other; and the first and second NMOP catalysts are different from each other and are both catalytically active in the contacting step; and wherein the contacting step copolymerizes the first and second olefin monomers, and thereby prepares the metal-functionalized polyolefin as a metal-functionalized olefin block copolymer (which in some embodiments can be converted to an OBC). The second NMOP catalyst has a different monomer selectivity than that of the first NMOP catalyst. In such embodiments the process further employs at least three, preferably at most four, different olefin monomers, which includes the first olefin monomer. In some embodiments the olefin copolymer is an olefin block copolymer.

The metal-functionalized polyolefin contains at least one type of metal cation. As mentioned previously, a majority of the metal cation of the metal-functionalized polyolefin is the third metal cation. Preferably, at least 70 mol%, more preferably at least 80 mol%, and still more preferably at least 90 mol% of the metal cation of the metal-functionalized polyolefin is the third metal cation. As mentioned previously, the third metal cation is the same element as the first metal cation of the first metal (C_i-C₂o)hydrocarbyl (PCRA). The third metal cation can be exchanged for a fourth metal cation if desired.

In some embodiments the metal-functionalized polyolefin contains one metal cation per molecule and is useful for preparing the polyolefin. In other embodiments the metal-functionalized polyolefin contains two metal cations per molecule and is useful for preparing the polyolefin or telechelic polyolefin. In a branched polyolefin polymeryl chain, the metal-functionalized polyolefin contains at least three metal cations per molecule and is useful for preparing the polyolefin or functionalized polyolefins containing at least three functional groups per molecule.

Since the third (and first) metal cation typically has a formal valence of +2 or +3 and thus capability for coordinating to up to two or three ligands, respectively, the metal-functionalized polyolefin can further comprise additional ligands so as to satisfy the coordinating capacity of the third metal cation. Examples of such additional ligands are the (Ci-C₂₀)hydrocarbyl,
5 (Ci-C₂₀)alkoxide, and hydroxide. The (Ci-C₂₀)alkoxide and hydroxide can originate from, for example, quenching the mixture in the contacting step with a (Ci-C₂₀)alcohol or water after polymerization.

Preferably, the invention process further comprises contacting the metal-functionalized polyolefin (preferably the removed metal-functionalized polyolefin) with a quenching or
10 functionalization reagent in such a way so as to substantially release the metal therefrom and thereby respectively prepare the polyolefin or non-metallic functional group-containing polyolefin (e.g., telechelic polyolefin). In preparing the polyolefin, preferably, the quenching reagent is a protic solvent such as 2-propanol. Simultaneously or later, stabilize the resulting quenched mixture against further polymerization by contacting the quenched mixture with a toluene solution containing an
15 antioxidant effective amount of a hindered phenol antioxidant (e.g., IRGANOX™ 1010 from Ciba Geigy Corporation) and a stabilizing effective amount of a phosphorus stabilizer (e.g., IRGAFOS™ 168 from Ciba Geigy Corporation). In some embodiments the polyolefin is characterizable by an enhanced melt flow rate (i.e., melt flow index); a polydispersity index of 1.90 or greater; or a combination thereof.

In some embodiments melt flow rate (MFR) of the polyolefin produced from the metal-functionalized polyolefin prepared by the invention process is enhanced, i.e., increased. Since it is known that MFR and number average molecular weight (M_n) are inversely correlated, the M_n of the invention polyolefin is lower. The enhanced MFR and decreased M_n are compared to reference
20 MFR and M_n of a reference polyolefin prepared by a non-invention process employing the first metal (Ci-C₂₀)hydrocarbyl (PCRA) or second metal(Ci-C₂₀)hydrocarbyl (PCSA), but not both. More preferably, the invention process produces the invention polyolefin wherein the MFR thereof is at least 20%, more preferably at least 50%, still more preferably at least 90%, and even more preferably at least 100% greater than the reference MFR of the reference polyolefin. In some
25 embodiments, the enhanced MFR is greater than 1.20 grams per 10 minutes (g/10 min.), more preferably greater than 1.60 g/10 min., and still more preferably greater than 2.0 g/10 min., whereas the reference MFR is 1.1 g/10 mi. or less.

Preferably, the polyolefin produced by the invention process has a polydispersity index (PDI) of at least 1.90, more preferably at least 2.0, in some embodiments at least 2.40, in some embodiments at least 3.0, in some embodiments at least 4.0, and in some embodiments at least 5.0.

In some embodiments the PDI is at most 7.5, in some embodiments at most 6.0, in some embodiments at most 5.0, in some embodiments at most 4.0, and in some embodiments at most 3.0. In some embodiments the PDI is from 2.0 to 3.0 and in other embodiments from 2.0 to 2.2.

In some embodiments the process further comprises contacting the metal-functionalized polyolefin (preferably the removed metal-functionalized polyolefin) with the functionalization reagent in such a way so as to prepare a non-metallic functional group-containing polyolefin (i.e., a polyolefin containing at least one functional group, wherein the at least one functional group does not contain a metal). This polyolefin contains non-metallic functional groups in place of the metallic functional groups of the metal-functionalized polyolefin. In some embodiments the non-metallic functional group-containing polyolefin is a telechelic polyolefin that contains at least two non-metallic functional groups that each contains at least one oxygen, nitrogen, or halogen atom. Preferably each non-metallic functional group independently comprises a vinyl group (i.e., -CH=CH₂); hydroxyl group (i.e., -OH (e.g., -CH₂OH), by reaction of aqueous NaOH and H₂O₂), or a metal salt thereof; amino group (e.g., -NH₂ or -CH₂NH₂); silyl group (e.g., -Si((Ci-Ci₀)alkyl)₃); epoxy group (i.e., cyclic -C₂H₃O); halo group (i.e., fluoro, chloro, bromo, or iodo); formyl group (i.e., -C(=O)H); carboxyl group (i.e., -CO₂H), or a metal salt thereof; carboxylic ester group (e.g., -CO₂(Ci-Ci₀)alkyl); or ionomeric functional group (e.g., -[N((Ci-Ci₀)alkyl)₃]⁺) (the ionomeric functional group being a portion of an ionomer, that is a polymer that comprises repeat units of both electrically neutral repeat units and a fraction (usually no more than 15 percent) of ionized units).

The functionalization reagent is useful for synthesizing such non-metallic functional groups. For example, when the third metal cation is boron cation, preferably quench the boron-functionalized polyolefin with one of the following functionalization reagents (a) to (e): (a) quenching with bromine (Br₂)/sodium methoxide yields a bromo-substituted polyolefin; (b) quenching with a bis(hydrocarbyl) disulfide in presence of ultraviolet (UV) light yields a hydrocarbyl-S- substituted polyolefin; (c) quenching with ammonia/NaClO yields an amino- (H₂N-) substituted polyolefin; (d) quenching with a sacrificial olefin (e.g., ethylene) and a displacement catalyst (described later) yields a polyolefin containing a terminal carbon-carbon double bond; and (e) quenching with hydrogen peroxide yields a hydroxyl- (HO-) substituted polyolefin. Examples of such boron-based reactions are illustrated in Schemes 4a to 4g.

Fig. 4a shows an invention reaction for preparing at least one product comprising a polymer (i.e., polymeryl-H), wherein the at least one product is prepared from the B-based PCRA-polymeryl chain complex by contacting the latter with molecular hydrogen in presence of a hydrogenolysis catalyst (e.g., Pd/C).

Fig. 4b shows an invention reaction for preparing at least one product comprising a mono- or bis-vinyl-terminated polymer (i.e., polymeryl-CH=CH₂ or H₂C=CH-polymerylene-CH=CH₂), wherein the at least one product is prepared from the B-based PCRA-polymeryl chain complex by contacting the latter with the first olefin monomer (e.g., ethylene) in presence of a displacement catalyst (e.g., Ni(O₂CCH₃)₂). As used herein, the terms "polymerylene" and "polymerylene chain" are synonymous and mean a diradical of a polyolefin.

Fig. 4c shows an invention reaction for preparing at least one product comprising a mono- or bis-hydroxyl-terminated polymer (i.e., polymeryl-OH or HO-polymerylene-OH), wherein the at least one product is prepared from the B-based PCRA-polymeryl chain complex by contacting the latter with an oxidant such as hydrogen peroxide in presence of sodium hydroxide.

Fig. 4d shows an invention reaction for preparing at least one product comprising a mono- or bis-amino-terminated polymer (i.e., polymeryl-NH₂ or H₂N-polymerylene-NH₂), wherein the at least one product is prepared from the B-based PCRA-polymeryl chain complex by contacting the latter with a source of ammonia and a mild oxidant such as sodium hypochlorite.

Fig. 4e shows an invention reaction for preparing at least one product comprising a mono- or bis-RS-terminated polymer (i.e., polymeryl-SR or RS-polymerylene-SR, wherein R is (Ci-C₂₀)hydrocarbyl), wherein the at least one product is prepared from the B-based PCRA-polymeryl chain complex by contacting the latter with disulfide (R₂S-SR₂) in presence of ultraviolet light.

Fig. 4f shows an invention reaction for preparing at least one product comprising a mono- or bis-bromo-terminated polymer (i.e., polymeryl-Br or Br-polymerylene-Br), wherein the at least one product is prepared from the B-based PCRA-polymeryl chain complex by contacting the latter with molecular bromine or equivalent in presence of a Group 1 or 2 metal alkoxide such as sodium methoxide.

Fig. 4g shows an invention reaction for preparing at least one product comprising a mono-, di-, or tri-polymeryl-substituted methanol or bis-functionalized polymerylene analogs thereof, wherein R is (Ci-C₂₀)hydrocarbyl, wherein the at least one product is prepared from the B-based PCRA-polymeryl chain complex by contacting the latter with carbon monoxide.

When the third metal cation is aluminum cation, employ a functionalization reagent useful for synthesizing non-metallic functional groups therefrom. For example, when the third metal cation is aluminum cation, preferably quench the aluminum-functionalized polyolefin with one of the following functionalization reagents (a) to (c): (a) molecular oxygen; (b) sacrificial olefin and heat or displacement catalyst; or (c) aluminum alkoxide (e.g., Al(OR)₃, wherein R is (Ci-C₂₀)hydrocarbyl) in water. In (b), the contacting step is a displacement step that comprises the

heat, i.e., is a thermal displacement reaction or displacement catalyst. The thermal displacement reaction preferably is run without the displacement catalyst at elevated temperature and elevated pressure and with short residence time (i.e., time of contact) in the presence of excess of a sacrificial 1-olefin to generate the carbon-carbon double bond-substituted polyolefin. A preferred thermal displacement reaction is similar to the thermal displacement reaction described in U.S. Patent Number US 3,391,219 (e.g., see portion of Example 1 at column 7, lines 30-70). Preferably the elevated temperature is at least 140 °C, elevated pressure is greater than ambient pressure (i.e., greater than 15 pounds per square inch (psi; 101 kiloPascals (kPa)). For example, the elevated temperature is 280 °C and the elevated pressure is 150 psi (1010 kPa). The residence time is appropriate under the circumstances and readily determined. The displacement catalyst preferably is colloidal Ni, Pt, or Co, nickel acetylacetonate, a cobalt carboxylate (e.g., cobalt 1-naphthoate or cobalt acetate), nickel bis-1,5-cyclooctadiene (Ni(COD)₂) or a nickel carboxylate (e.g., nickel 1-naphthoate). The displacement catalyst optionally may be stabilized by combining it with a trivalent phosphorous ligand (e.g., triphenylphosphine). Preferably, the sacrificial olefin contains from 3 to 10 carbon atoms. Examples of sacrificial olefins are ethene, propene, and 1-butene.

Examples of such aluminum-based reactions are illustrated in Schemes 5a to 5c. Fig. 5a an invention reaction for preparing at least one product comprising a polymer (i.e., polymeryl-H), wherein the at least one product is prepared from the Al-based PCRA-polymeryl chain complex by contacting the latter with molecular oxygen (e.g., air). In some embodiments the contacting gives, after addition of water, a hydroxyl-substituted polyolefin (e.g., a hydroxy-telechelic polyolefin).

Fig. 5b shows an invention reaction for preparing at least one product comprising a mono- or bis-vinyl-terminated polymer (i.e., polymeryl-CH=CH₂ or H₂C=CH-polymerylene-CH=CH₂), wherein the at least one product is prepared from the Al-based PCRA-polymeryl chain complex by contacting the latter with the first olefin monomer (e.g., ethylene) in presence of displacement condition (e.g., heat or a displacement catalyst, e.g., Ni(O₂CCH₃)₂).

Fig. 5c shows an invention reaction for preparing at least one product comprising a mono- or bis-hydroxyl-terminated polymer (i.e., polymeryl-OH or HO-polymerylene-OH), wherein the at least one product is prepared from the Al-based PCRA-polymeryl chain complex by contacting the latter with an aluminum alkoxide (e.g., Al(OR)₃, wherein R is (C₁-C₂₀)hydrocarbyl) in water.

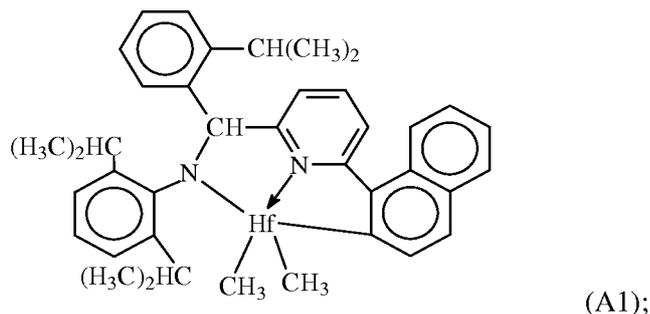
The invention process employs catalytic amounts of the NMOP catalyst(s). When more than one catalyst is employed in the invention process, each catalyst independently will be employed in a catalytic amount. The term "catalytic amount" means less than a stoichiometric quantity based on number of moles of a product-limiting stoichiometric reactant employed in the invention process. The catalytic amount is also equal to or greater than a minimum amount of the catalyst that is

necessary for at least some product of the catalyzed reaction to be formed and detected (e.g., by mass spectrometry). The minimum catalytic amount preferably is 0.0001 mole percent of the number of moles of a product-limiting stoichiometric reactant. In the invention process the product-limiting stoichiometric reactant for the invention catalyst typically will be an olefin monomer.

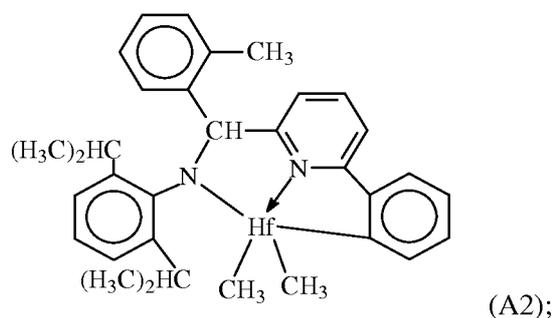
5 Preferably, the catalytic amount of the non-metallocene-type precatalyst used to prepare the NMOP catalyst is from 0.001 mol % to 50 mol % of the moles of the first olefin monomer, more preferably at least 0.01 mol%, still more preferably at least 0.05 mol %, and even more preferably at least 0.1 mol%. Also more preferably, the catalytic amount is 40 mol % or less, and still more preferably 35 mol % or less.

10 Representative non-metallocene-type precatalysts useful for preparing, and non-metallocene-type catalysts prepared therefrom and useful as, the NMOP catalyst(s) are disclosed in US 2006/0199930 A1; US 2007/0167578 A1; US 2008/0311812 A1; US 7,355,089 B2; or WO 2009/012215 A2 and include the precatalysts of formulas (A1) to (A5), (B1), and (B2):

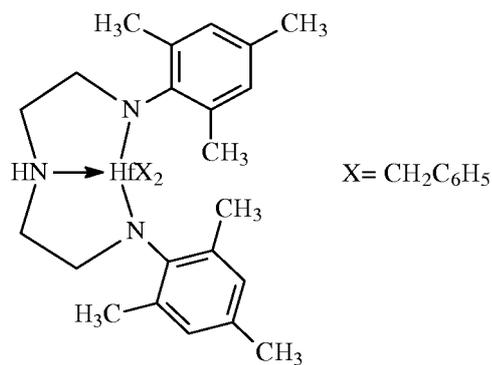
15 Precatalyst (A1) is [N-(2,6-di(1-methylethyl)phenyl)amido)(2-isopropylphenyl)(a-naphthalen-2-diyl(6-pyridin-2-diyl)methane)]hafnium dimethyl, prepared according to the teachings of WO 03/40195, US 6,953,764 B2, and WO 04/24740, and having the structure:



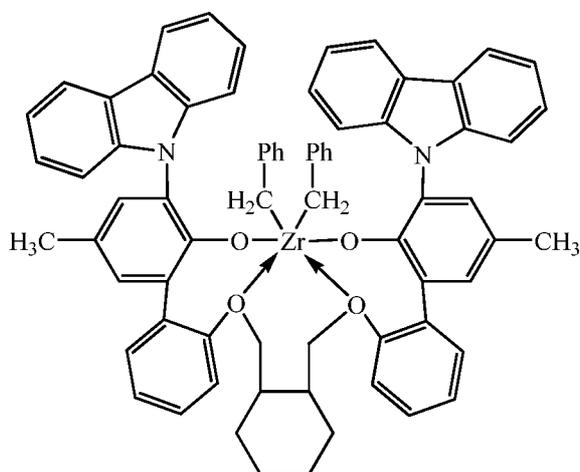
20 Precatalyst (A2) is [N-(2,6-di(1-methylethyl)phenyl)amido)(2-methylphenyl)(1,2-phenylene-(6-pyridin-2-diyl)methane)]hafnium dimethyl, prepared according to the teachings of WO 03/40195, US 6,953,764 B2, and WO 04/24740, and having the structure:



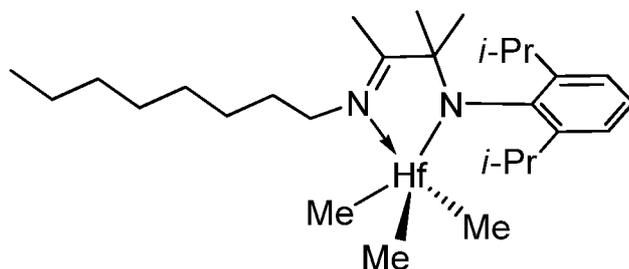
Precatalyst (A3) is bis[*N,N''*-(2,4,6-tri(methylphenyl)amido)ethylenediamine]hafnium dibenzyl, and having the structure:



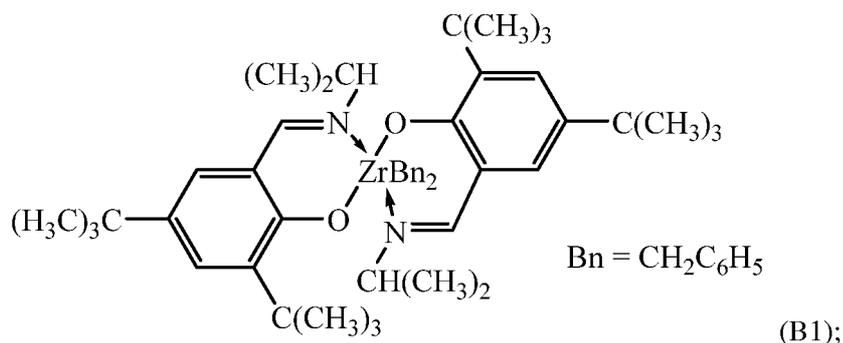
Precatalyst (A4) is bis((2-oxoyl-3-(dibenzo-1H-pyrrole-1-yl)-5-(methyl)phenyl)-2-phenoxy)methyl)cyclohexane-1,2-diyl zirconium (IV) dibenzyl, prepared substantially according to the teachings of US-A-2004/0010103, and having the structure:



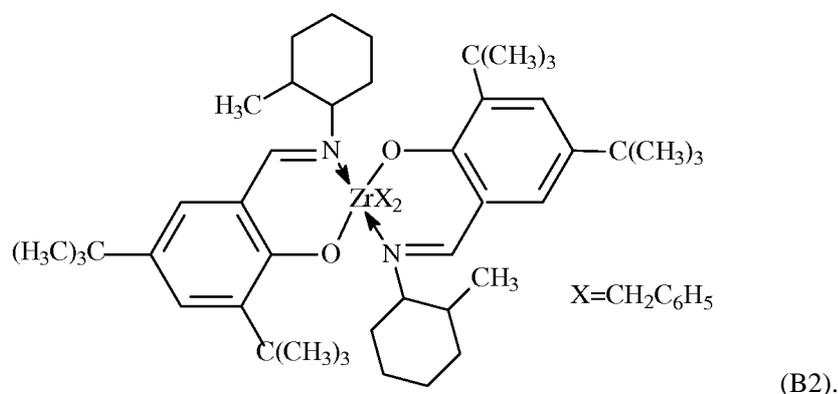
Precatalyst (A5) is [\wedge -2,6-diisopropyl-N-(2-methyl-3-(octylimino)butan-2-yl)benzeneamide]trimethylhafnium, prepared substantially according to the teachings of WO 2003/051935, and having the structure:



Precatalyst (B1) is 1,2-bis-(3,5-di-t-butylphenylene)(1-(N-(1-methylethyl)imino)methyl)(2-oxoyl) zirconium dibenzyl, and having the structure:



Precatalyst (B2) is 1,2-bis-(3,5-di-t-butylphenylene)(1-(N-(2-methylcyclohexyl)imino)methyl)(2-oxoyl) zirconium dibenzyl, and having the structure:



Preferably, each non-metallocene-type precatalyst preferably is rendered catalytically active, and thus prepares the corresponding NMOP catalyst, by contacting it to, or combining it with, the activating co-catalyst or by using an activating technique such as those that are known in the art for use with metal-based olefin polymerization reactions. Suitable activating co-catalysts for use herein include alkyl aluminums; polymeric or oligomeric alumoxanes (also known as aluminoxanes); neutral Lewis acids; and non-polymeric, non-coordinating, ion-forming compounds (including the use of such compounds under oxidizing conditions). A suitable activating technique is bulk electrolysis (explained in more detail hereinafter). Combinations of at least one each of the foregoing activating co-catalysts and techniques are also contemplated. The term "alkyl aluminum" means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a trialkylaluminum. Aluminoxanes and their preparations are known at, for example, United States Patent Number (USPN) US 6,103,657. Examples of preferred polymeric or oligomeric alumoxanes are methylalumoxane, triisobutylaluminum-modified methylalumoxane, and isobutylalumoxane.

Preferred Lewis acid activating co-catalysts are Group 13 metal compounds containing from 1 to 3 hydrocarbyl substituents as described herein. More preferred Group 13 metal compounds are tri(hydrocarbyl)-substituted-aluminum or tri(hydrocarbyl)-boron compounds, still more preferred are tri((Ci-Cio)alkyl)aluminum or tri((C₆-C₈)aryl)boron compounds and halogenated (including
5 perhalogenated) derivatives thereof, even more especially tris(fluoro-substituted phenyl)boranes, still even more especially tris(pentafluorophenyl)borane. In some embodiments, the activating co-catalyst is a tris((Ci-C₂₀)hydrocarbyl) borate (e.g., trityl tetrafluoroborate) or a tri((Ci-C₂₀)hydrocarbyl)ammonium tetra((Ci-C₂₀)hydrocarbyl)borane (e.g., bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borane). As used herein, the term
10 "ammonium" means a nitrogen cation that is a ((Ci-C₂₀)hydrocarbyl)₄N⁺, a ((Ci-C₂₀)hydrocarbyl)₃N(H)⁺, a ((Ci-C₂₀)hydrocarbyl)₂N(H)₂⁺, (Ci-C₂₀)hydrocarbylN(H)₃⁺, or N(H)₄⁺, wherein each (Ci-C₂₀)hydrocarbyl may be the same or different.

Preferred combinations of neutral Lewis acid activating co-catalysts include mixtures comprising a combination of a tri((Ci-C₄)alkyl)aluminum and a halogenated tri((C₆-C₈)aryl)boron
15 compound, especially a tris(pentafluorophenyl)borane. Also preferred are combinations of such neutral Lewis acid mixtures with a polymeric or oligomeric alumoxane, and combinations of a single neutral Lewis acid, especially tris(pentafluorophenyl)borane with a polymeric or oligomeric alumoxane. Preferred ratios of numbers of moles of (metal-ligand complex):(tris(pentafluoro-phenylborane): (alumoxane) [e.g., (Group 4 metal-ligand complex):(tris(pentafluoro-phenylborane):(alumoxane)] are from 1:1:1 to 1:10:30, more preferably from 1:1:1.5 to 1:5:10.
20

Many activating co-catalysts and activating techniques have been previously taught with respect to different non-metallocene-type (pre)catalysts in the following USPNs: US 5,064,802; US 5,153,157; US 5,296,433; US 5,321,106; US 5,350,723; US 5,425,872; US 5,625,087; US 5,721,185; US 5,783,512; US 5,883,204; US 5,919,983; US 6,696,379; and US 7,163,907.
25 Examples of suitable hydrocarbyloxides are disclosed in US 5,296,433. Examples of suitable Bronsted acid salts for addition polymerization (pre)catalysts are disclosed in US 5,064,802; US 5,919,983; US 5,783,512. Examples of suitable salts of a cationic oxidizing agent and a non-coordinating, compatible anion as activating co-catalysts for addition polymerization (pre)catalysts are disclosed in US 5,321,106. Examples of suitable carbenium salts as activating co-catalysts for
30 addition polymerization (pre)catalysts are disclosed in US 5,350,723. Examples of suitable silylium salts as activating co-catalysts for addition polymerization (pre)catalysts are disclosed in US 5,625,087. Examples of suitable complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are disclosed in US 5,296,433. Some of these (pre)catalysts are also

described in a portion of US 6,515,155 B1 beginning at column 50, at line 39, and going through column 56, at line 55, only the portion of which is incorporated by reference herein.

In some embodiments at least two of the foregoing activating co-catalysts are used in combination with each other. An especially preferred combination is a mixture of a tri((Cr
5 C₄)hydrocarbyl)aluminum, tri((C_i-C₄)hydrocarbyl)borane, or an ammonium borate with an oligomeric or polymeric alumoxane compound.

The ratio of total number of moles of each non-metallocene-type precatalyst to total number of moles of the at least one of the activating co-catalyst independently is from 1:10,000 to 100:1. Preferably, the ratio is at least 1:5000, more preferably at least 1:1000; and 10:1 or less, more
10 preferably 1:1 or less. When an alumoxane alone is used as the activating co-catalyst, preferably the number of moles of the alumoxane that are employed is at least 100 times the number of moles of the non-metallocene-type precatalyst. When tris(pentafluorophenyl)borane alone is used as the activating co-catalyst, preferably the number of moles of the tris(pentafluorophenyl)borane that are employed to the total number of moles of non-metallocene-type precatalyst is from 0.5:1 to 10:1,
15 more preferably from 1:1 to 6:1, still more preferably from 1:1 to 5:1. The remaining activating co-catalysts are generally employed in approximately mole quantities equal to the total mole quantities of the non-metallocene-type precatalyst.

In some embodiments the invention process further employs a molecular weight control agent. In these molecular weight control embodiments of the invention process the molecular weight
20 control agent is an ingredient (e). Examples of molecular weight control agents are trialkyl aluminum compounds and, preferably, hydrogen (H₂) gas.

Materials and Methods

Bis(diisobutylaluminum)oxide (BDAO); bis(octadecyl)methylammonium tetrakis(pentafluorophenyl)borate ([HNMe(C₈H₁₇)₂][B(C₆F₅)₄], abbreviated as BTB); Precatalyst
25 (A) (a non-metallocene-type precatalyst); diethylmagnesium (Et₂Mg, DEM); diethylzinc (Et₂Zn, DEZ); ethylene (C₂H₂); IRGAFOS™ 168 (CAS No. 31570-04-4); IRGANOX™ 1010 (CAS No. 98584-37-3); ISOPAR E (CAS No. 64741-66-8; ExxonMobil Corporation, Houston, Texas, USA; hereinafter referred to as "Isoparaffin Fluid"); 1-octene; triethyl aluminum (Et₃Al, TEA); triethylborane (Et₃B, TEB); triethylgallium (Et₃Ga, TEG); triisobutylaluminum-modified
30 methylalumoxane-3A (MMAO-3A); tri(1-octyl)aluminum (octyl₃Al, TOA); tri(1-octyl)borane (octyl₃B, TOB); and tritylborate (TB; B(OPh)₃ wherein Ph is phenyl). Obtain TEB from Aldrich Chemical Company (St. Louis, Missouri, USA); diethylzinc from Aldrich Chemical or Strem Chemicals (Newburyport, Massachusetts, USA); and TOA from Akzo-Nobel in Sure-Pac™ or steel cylinders and stored under dry nitrogen gas. Obtain all other chemicals from Aldrich Chemical. Pass

1-octene, toluene, ethylene and Isoparaffin Fluid through two columns, the first containing A2 alumina, and the second containing Q5 reactant. Pass the nitrogen gas used for transfers through a single column containing A204 alumina, 4 Angstrom (\AA) mole sieves, and Q5 reactant. Prior to use, filter neat DEZ through a 0.45 micron glass-fiber disposable filter.

5 Precatalyst (A) (a preferred non-metallocene-type precatalyst): is prepared according to the procedure of Example 7 of US 6,953,764 B2.

Method (A) FT-IR spectroscopy: dissolve a polymer sample in 1,2,4-trichlorobenzene at 160 °C for 1 hr while shaking to give a solution having a concentration of 30 milligrams polymer per milliliter 1,2,4-trichlorobenzene (mg/mL). Deposit some of the 160 °C solution into individual
10 cells on a silicon wafer, evaporate the 1,2,4-trichlorobenzene, and cool the polymer to room temperature. Analyze the resulting wafer using a Nicolet Nexus 670 FT-IR ESP infrared spectrometer to determine mole percent of octene within each sample.

Method (B) GPC: determine weight average molecular weight (M_w), M_n , and polydispersity index (PDI) values by analysis of a polymer sample on a SYMYX™ High-Throughput Gel
15 Permeation Chromatographer. Utilize three Polymer Labs PLgel 10 $\mu\eta$ MIXED-B columns (300 millimeters (mm) x 10 mm) at a flow rate of 2.5 mL/minute in 1,2,4-trichlorobenzene at 160 °C. The molecular weight determination is deduced by using ten narrow molecular weight distribution polystyrene standards (from Polymer Laboratories, EasiCal PSI ranging from 580 g/mol to 7,500,000 g/mole) in conjunction with their elution volumes. The equivalent propylene-ethylene
20 copolymer molecular weights are determined by using appropriate Mark-Houwink coefficients for polypropylene (as described by Th. G. Scholte, N. L. J. Meijerink, H. M. Schoffeleers, and A. M. G. Brands, Journal of Applied Polymer Science, 29, 3763-3782 (1984)) and polystyrene (as described by E. P. Otocka, R. J. Roe, N. Y. Hellman, P. M. Muglia, Macromolecules, 4, 507 (1971)) in the Mark-Houwink equation: $\{N\}=KMa$, where $K_{pp}=1.90E-04$, $a_{pp}=0.725$ and $K_{pa}=1.26E-04$, $a_{ps}=0.702$.

25 Method (C) DSC: measure melting and crystallization temperatures of the polymer with a differential scanning calorimeter model DSC 2910, TA Instruments, Inc. Prepare polymer sample by pressing some polymer into a thin film, cut from about 3 milligrams (mg) to 10 mg portions of the film into a 6 mm diameter disks, accurately weigh them (about 50 mg total), placed in a light aluminum pan, which is then crimped shut. Sequentially process the prepared polymer sample as
30 follows: heat from room temperature to 210 °C at a heating rate of 10 °C/minute; hold at 210 °C for 4 minutes; cool to -40 °C at a cooling rate of 10 °C/minute; hold at -40 °C for 4 minutes; and heat to 215 °C at a heating rate of 10 °C/minute. Determine at least one of glass transition temperature (T_g), melting temperature (T_m), peak crystallization temperature (T_c), and percent crystallinity using the standard TA Instruments DSC software.

Method (D) Melt Flow Rates (MFR, also known as Melt Flow Indices) (I_{10} and I_2): Obtain MFR I_{10} and I_2 data using a Melt Flow Jr. instrument from CEAST according to ASTM D 1238 Methods A and B. The instrument comprises a barrel and piston. Calibrate the instrument using Dowlex 2045. 11G, which has a known MFR. Cut polymer samples into slices, and place the slices
5 into the barrel of the Melt Flow Jr. Insert the piston into the barrel, and heat the placed samples to 190 °C for two minutes. Place a 2.16 kilogram (kg) weight on the top of the piston and allow the samples to heat for an additional five minutes while expelling polymer. Cut strands of expelled polymer at precise time intervals.

EXAMPLE(S) OF THE PRESENT INVENTION

10

Example A

General Procedure for Laboratory-scale Batch Reactor-Based Copolymerization of Ethylene/ 1-octene to prepare a metal-functionalized poly(ethylene-co-1-octene) *in situ*, and quenching same to give a poly(ethylene-co- 1-octene) copolymer:

(1) Employ a 2 liter (L) batch mode, stirred tank reactor (model no. 4532 manufactured by
15 Parr Instrument company, Moline Illinois, USA) fitted with a bottom dump valve and containing an agitator and an internal serpentine cooling coil containing circulating ethylene glycol/water for cooling and in fluid communication with a shot tank and ethylene source (via a MICRO MOTION™ flow meter). Control and monitor the reactor, addition of ethylene thereto, and the heating/cooling thereof using a Camile TG process computer (Camile). The dump valve operates to
20 empty (void) contents of the reactor into a nitrogen gas-purged stainless steel (SS) dump pot that is vented to a nitrogen gas-purged 30 gallon (114 L) blowdown tank.

(2) SS Dump Pot terminator/stabilizer Packages: for runs with triethylborane ($B(CH_2CH_3)_3$ or TEB), add into the SS dump pot a TEB antioxidant package that comprises 5 milliliters (mL) ethanol, 0.5 mL 5 Normal aqueous sodium hydroxide (5N NaOH), and 0.5 mL 30 weight percent
25 hydrogen peroxide in water (30 wt% H_2O_2). In runs that do not use TEB, add into the SS dump pot a standard antioxidant/stabilizer package that comprises 5 mL of a toluene solution containing dissolved therein approximately 33 milligrams (mg) of the hindered phenol antioxidant IRGANOX™ 1010 and 67 mg of the phosphorus stabilizer IRGAFOS™ 168. Also, prepare stabilizer package comprising a solution of 1.6 g IRGAFOS™ 168 in toluene.

(3) Load the reactor with either 533 grams (g), 595 g, or 741 g Isoparaffin Fluid and
30 respectively either 250 g, 188 g, or 42 g 1-octene (actual amounts are listed later). Optionally as listed later, add 45 psig (0.31 MPa) hydrogen gas by differential pressure expansion from a 75 mL volume addition tank at 300 psi (2070 kPa). Then stir/agitate and heat the contents of the reactor up to the desired polymerization temperature set-point (120 °C for later Examples 1a to 10b). During

heat-up (and before ethylene addition), separately add effective amounts of at least one PCRA and at least one PCSA into the reactor (actual amounts are listed later). In some runs (in later Examples 2b, 4b, 5b, 7b, 8b, and 9b), also add 5 μmol tritylborate (an activator). After contents of the reactor reach the desired temperature set-point, add ethylene and establish therein a desired ethylene
5 pressure set point of either 460 pounds per square inch gauge (psig, 3.4 megapascals (MPa), 350 psig (2.6 MPa), or 100 psig (0.74 MPa). Each of the amounts of ethylene is respectively for each aforementioned amounts of 1-octene and Isoparaffin Fluid.

(4) In a flask in a glovebox mix 1.2 micromoles (μmol) or 2.4 μmol of the non-metallocene-type precatalyst (the aforementioned Precatalyst (Al) in later Examples 1a to 10b), respectively 1.0
10 μmol or 2.0 μmol BTB (in later Examples 1a to 10b) and respectively 10 μmol or 20 μmol MMAO-3A (in later Examples 1a to 10b) with toluene to give the catalyst solution. Pressure-transfer the catalyst solution via syringe into the catalyst shot tank. Rinse the flask 3 times with 5 mL each toluene, and pressure-transfer the rinses to the catalyst shot tank.

(5) Add the catalyst solution/rinses from the catalyst shot tank into the reactor, and
15 immediately start a run timer. Observe an exotherm, typically from 0.2 °C to 2.3 °C, as the copolymerization proceeds. As needed, add controlled amount of ethylene into the reactor so as to maintain the ethylene pressure set-point. Record total weight of ethylene added.

(6) When the polymerization time set-point (i.e., period of polymerization reaction) is reached (10 minutes or 30 minutes for later Examples 1a to 10b), promptly open the bottom dump
20 valve to empty the reactor contents into the SS dump pot containing either the TEB or standard antioxidant/stabilizer package. For runs with TEB, then add the standard antioxidant/stabilizer package into the SS dump pot. In all runs, also add thereinto the stabilizer package comprising the solution of 1.6 g IRGAFOS™ 168 in toluene.

(7) Pour the SS dump pot contents into trays placed in a lab hood, and allow the solvent to
25 evaporate off overnight, dry the residue at 140 °C under vacuum to remove any remaining solvent, cool to ambient (room) temperature, and weigh the resulting product polymer. Characterize polymer samples by at least one of Fourier Transform Infrared (FT-IR) spectroscopy, proton or carbon-13 nuclear magnetic resonance ($^1\text{H-NMR}$ or $^{13}\text{C-NMR}$), differential scanning calorimetry (DSC), or gel permeation chromatographer (GPC).

30 Invention Examples 1a to 10b

Batch reactor-based copolymerizations of ethylene and 1-octene to give metal-functionalized poly(ethylene 1-octene) *in situ*, and quenching same to give a poly(ethylene 1-octene) copolymer.

Perform 24 runs using the batch procedure of Example A so as to prepare poly(ethylene 1-octene) copolymers. Use 533 g Isoparaffin Fluid in Examples 1a to 1b; 595 g Isoparaffin Fluid in

Examples 2a to 9b; and 741 g Isoparaffin Fluid in Examples 10a to 10b. Also use the other starting materials, amounts, and run times shown below in Table 1 of Fig. 8. In Table 1, Ex. No. means Example Number; PCSA (or PCRA) means believed to be acting as polymeryl chain shuttling agent, i.e., the second metal (Ci-C₂₀)hydrocarbyl but could be acting as polymeryl chain repository agent, i.e., the first metal (Ci-C₂₀)hydrocarbyl; PCRA (or PCSA) means the opposite of PCSA (or PCRA); Cat. (A) means the Precatalyst (A); and min. means minutes.

Table 1: starting materials, amounts and run times

Ex. No.	PCSA (or PCRA) (μmol)	PCRA (or PCSA) (μmol)	TB (μmol)	Cat. (A) (μmol)	BTB (μmol)	MMAO-3A (μmol)	1-octene (g)	C ₂ H ₂ (g)	Run Time (min.)
1a	Et ₂ Zn (50)	Et ₃ B (200)	None	1.0	1.2	10	250	6.6	10
1b	Et ₂ Zn (50)	Et ₃ B (400)	None	1.0	1.2	10	250	7.0	10
1c	Et ₂ Zn (10)	Et ₃ B (400)	None	1.0	1.2	10	250	5.8	10
2a	octyl ₃ Al (50)	Et ₃ B (200)	None	1.0	1.2	10	188	12.4	10
2b	octyl ₃ Al (50)	Et ₃ B (400)	5	1.0	1.2	10	188	9.5	10
2c	octyl ₃ Al (10)	Et ₃ B (400)	None	1.0	1.2	10	188	7.2	10
3	Et ₂ Zn (400)	octyl ₃ B (400)	None	1.0	1.2	10	188	6.7	10
4a	BDAO (50)	Et ₃ B (200)	None	1.0	1.2	10	188	4.8	10
4b	BDAO (50)	Et ₃ B (400)	5	1.0	1.2	10	188	4.0	10
4c	BDAO (10)	Et ₃ B (400)	None	1.0	1.2	10	188	3.7	10
5a	Et ₃ Ga (50)	Et ₃ B (200)	None	1.0	1.2	10	188	14.2	10
5b	Et ₃ Ga (50)	Et ₃ B (400)	5	1.0	1.2	10	188	11.3	10
5c	Et ₃ Ga (50)	Et ₃ B (400)	None	1.0	1.2	10	188	5.2	10
6a	Et ₂ Mg (1)	octyl ₃ B (10) and Et ₃ B (390)	None	1.0	1.2	10	188	3.2	10
6b	Et ₂ Mg (2)	octyl ₃ B (20) and Et ₃ B (380)	None	1.0	1.2	10	188	3.7	10
6c	Et ₂ Mg	octyl ₃ B	None	1.0	1.2	10	188	1.2	10

	(10)	(100) and Et ₃ B (300)							
7a	octyl ₃ Al (50)	Et ₃ B (400)	None	1.0	1.2	10	188	19.7	30
7b	octyl ₃ Al (50)	Et ₃ B (400)	5	1.0	1.2	10	188	14.2	30
8a	octyl ₃ Al (100)	Et ₃ B (800)	None	1.0	1.2	10	188	19.9	30
8b	octyl ₃ Al (100)	Et ₃ B (800)	5	1.0	1.2	10	188	17.0	30
9a	octyl ₃ Al (200)	Et ₃ B (1600)	None	2.0	2.4	20	188	12.5	30
9b	octyl ₃ Al (200)	Et ₃ B (1600)	5	2.0	2.4	20	188	9.6	30
10a	Et ₃ Ga (50)	Et ₃ B (400)	None	1.0	1.2	10	42	7.4	10
10b	Et ₃ Ga (50)	Et ₃ B (400)	None	1.0	1.2	10	42	6.2	10

Obtain the poly(ethylene 1-octene) copolymers described later in Table 2. In Table 2, Ex. No.-Example Number; min. -minutes; gP/gM-grams of polymer produced per gram of metal of the non-metallocene-type precatalyst used; PEO-poly(ethylene-co- 1-octene); T_m -melting temperature; 5 M_w (g/mol) -weight average molecular weight in grams per mole determined by GPC; M_n (g/mol) - number average molecular weight in grams per mole determined by GPC; PDI-polydispersity index; g/mL- grams per milliliter; Mol% octene (FT-IR) -mole percent of 1-octene incorporated into the PEO as determined by FT-IR spectroscopy; and n.d. - not determined.

Table 2: Catalyst efficiency and certain characterizations of poly(ethylene-co- 1-octene).

Ex. No.	Catalyst efficiency (gP/gM)	Yield PEO (g)	T _m (°C)	M _w (g/mol)	M _n (g/mol)	PDI (M _w / M _n)	Density (g/mL)	Mol% octene (FT-IR)
1a	136,000	24.3	53.6	724,000	191,000	3.79	0.867	12.1
1b	147,000	26.3	52.3	658,000	135,000	4.89	0.868	12.0
1c	131,000	23.3	49.5	684,000	158,000	4.33	0.858	14.3
2a	132,000	23.6	48.9	414,000	128,000	3.24	0.878	9.95
2b	112,000	20.0	45.4	373,000	65,200	5.71	0.869	11.7
2c	142,000	25.4	46.2	623,000	185,000	3.37	0.857	14.4
3	94,000	16.8	52.3	92,800	30,600	3.03	0.877	10.1

4a	140,000	24.9	45.5	669,000	126,000	5.31	0.861	13.5
4b	121,000	21.6	46.5	662,000	115,100	5.75	0.864	12.7
4c	111,000	19.8	45.7	706,000	124,000	5.70	0.868	11.8
5a	167,000	29.8	51.5/117.3/122.0	519,000	69,700	7.45	0.876	10.2
5b	123,000	22.0	47.4/117.7/121.9	627,000	167,000	3.75	0.877	10.1
5c	130,000	23.2	48.4/117.5/122.0	789,000	152,000	5.19	0.892	7.34
6a	90,800	16.2	49.4/117.6/122.0	856,000	190,000	4.50	0.893	7.24
6b	109,000	19.4	51.0/117.6/121.8	885,000	185,000	4.78	0.88	9.46
6c	34,700	6.2	46.2/117.7/121.7	796,000	235,000	3.39	0.947	n.d.
7a	173,000	30.8	56.1/117.6/122.0	460,000	83,100	5.53	0.875	10.4
7b	177,000	31.6	54.4/117.6/121.9	450,000	86,500	5.21	0.870	11.4
8a	202,000	36.0	58.2/117.5/121.9	254,000	63,700	3.99	0.871	11.1
8b	182,000	32.5	56.1/121.9	276,000	67,300	4.10	0.870	11.5
9a	75,100	26.8	103.3/121.9	53,200	21,500	2.47	0.865	12.5
9b	60,800	21.7	103.9/121.7	47,800	19,700	2.43	0.869	11.7
10a	90,800	16.2	48.4	535,000	90,200	5.93	0.876	10.2
10b	77,300	13.8	6.5/47.0	584,000	126,000	4.65	0.877	10.1

Example B

General Procedure For Laboratory-scale Continuous Reactor-Based Continuous-flow Copolymerization Procedure of Ethylene/ 1-octene to prepare a metal-functionalized poly(ethylene-co-1-octene) *in situ*, and quenching same to give a poly(ethylene -co- 1-octene) copolymer:

(1) Use continuous flow reactor system 10 shown in Fig. 6. In Fig. 6, continuous flow reactor system 10 comprises feed conduits 11 and 12, outlet conduit 13, and transfer conduits 14 and 15; reactor 30 (a 100 mL volumed EZE-Seal Reactor from the Autoclave Engineers division of Snap-tite, Inc., Erie, Pennsylvania, USA); oil bath jacket 40; agitator motor 50; FT-NIR cell 60; pressure control valve 70 (from Badger Meter Inc); three-way valve 72; air-actuated valve controller 73; prime receiver 80; and off-grade receiver 90. Reactor 30 defines enclosed volumetric space 38 having a 100 mL volume. Reactor 30 and agitator motor 50 are sealably in operative contact with stir shaft 35, which is in operative connection to a four-blade pitched impeller 36. Separate containers ((not shown; sources of Feed Groups A and B and terminator and antioxidant/stabilizer packages) are in independent fluid communication with enclosed volumetric space 38 of reactor 30 via inlet conduits 11 and 12 as indicated by arrows 21 and 22, respectively. Enclosed volumetric

space 38 of reactor 30 is in sequential fluid communication with FT-NIR cell 60, pressure control valve 70, three-way valve 72 and air-actuated valve controller 73 via outlet conduit 13. Three-way valve 72 is also in fluid communication with prime receiver 80 via conduit 14 and off-grade receiver 90 via transfer conduit 15. Outlet conduit 13 is electrically heat traced, insulated, and defines a
5 chemical package inlet (not shown) where indicated at point 71.

(2) Reaction ingredients comprise Feed Groups A and B and terminator and the terminator/stabilizer packages. Feed Group A comprises separate feeds of ethylene, 1-octene, and hydrogen gas. Ethylene and hydrogen gas are separately metered into conduit 11 using mass flow controllers (Brooks Instrument, Hatfield, Pennsylvania, USA). Ratio of ethylene to 1-octene in Feed
10 A is from 1/1 (100%) to 1/6th (17%) or 1/8 (14%) of the ratios of ethylene/ 1-octene used in Example A. Feed Group B comprises separate feeds of catalyst solution in toluene, PCRA solution, PCSA solution, and, optionally, an activator solution using Isoparaffin Fluid as solvent. Introduce feed streams into enclosed volumetric space 38 of reactor 30 via dip tubes as shown in Fig. 6. Liquid feeds (1-octene and the solutions) are separately fed from syringe pumps (Isco, Inc., a Teledyne
15 Technologies Company, Lincoln, Nebraska, USA). Preferred mole ratios of catalyst:PCSA:ethylene are 1:20:20,000. A source (not shown) of a polymerization terminator package (small amount of water/propanol in toluene) and polymerization antioxidant/stabilizer package is in fluid communication with outlet conduit 13 at point 71.

(3) Start flow of reaction ingredients except catalyst solution. Fill enclosed volumetric space
20 38 of reactor 30 with liquid contents to starting proportions thereof. Run reactor 30 liquid full with vigorous stirring. Oil bath jacket 40 contains hot oil that circulates through from a source (not shown) of hot oil into oil batch jacket 40 via conduit 24 and out via conduit 25 so as to maintain contents of the reactor 30 at a desired temperature set-point of 120 °C.

(4) Start flow of catalyst solution. Adjust flow rates of component feeds in Feed Groups A
25 and B so as to maintain an average concentration of 0.3 g to 0.6 g ethylene in reactor 30 and an average residence time of contents in reactor 30 of about 6 minutes. Ethylene feed rate is 0.700 gram per minute (g/min). In continuous flow operation, remove about 1 gram of metal-functionalized poly(ethylene-co- 1-octene) per minute out of top of reactor 30 via outlet conduit 13. Monitor in real-time produced metal-functionalized poly(ethylene-co-1-octene)-containing effluent from reactor 30
30 with FT-NIR cell 60. Start flow of termination package comprising water and propanol and antioxidant/stabilizer package into outlet conduit 13 at point 71.

(5) Collect resulting poly(ethylene -co- 1-octene) in open pan, and dry it up to a drying temperature setpoint of 140 °C to 150 °C and characterize same as described in Example A. Find it has 86 weight percent ethylene residuals and 14 wt% 1-octene residuals.

Invention Examples 11a to 11e

Continuous flow reactor copolymerizations of ethylene and 1-octene using PCSA and PCRA feeds that together feed a constant rate of ethyls from PCSA + PCRA to give metal-functionalized poly(ethylene 1-octene) *in situ*, and quenching same to give poly(ethylene 1-octene) copolymer; and comparison with 0% and 100% mole fraction of PCSA (0% and 100% mole fractions are prepared in comparative non-invention examples). See Examples 12a to 12f below.

Invention Examples 12a to 12f

Continuous flow reactor copolymerizations of ethylene and 1-octene using PCSA and PCRA feeds that together feed a constant total moles of PCSA + PCRA to give metal-functionalized poly(ethylene 1-octene) *in situ*, and quenching same to give poly(ethylene 1-octene) copolymer; and comparison with 0% and 100% mole fraction of PCSA (0% and 100% mole fractions are prepared in comparative non-invention examples)

For Examples 11a to 12f, perform continuous-flow polymerization processes according to the procedure of Example B with Et_2Zn as PCSA (i.e., second metal (C_i-C₂₀)hydrocarbyl) and Et_3Al as PCRA (i.e., first metal (C_i-C₂₀)hydrocarbyl) at constant monomer conversion (about 91%) and various relative feed levels of Et_3Al and Et_2Zn . It is found that identical molar feed rates of Et_2Zn and Et_3Al each gave identical MFR values. For the expected narrow molecular weight distribution, samples with the same MFR should have the same M_n and M_w . Feed rates (a) to (d):

(a) Non-invention 0% mole fraction of Zn cation: Et_3Al feed rate = 6 micromoles/minute (6 $\mu\text{mole/minute}$) and Et_2Zn feed rate = 0 $\mu\text{mole/minute}$. After quenching, MFR of resulting polyolefin = 1.1 grams/10 minutes (g/10 min.). Results are shown in Fig. 7 (0.0 Zinc fraction).

(b) Non-invention 100% mole fraction of Zn cation: Et_3Al feed rate = 0 micromoles/minute (0 $\mu\text{mole/minute}$) and Et_2Zn feed rate = 6 $\mu\text{mole/minute}$. After quenching, MFR of resulting polyolefin = 1.1 g/10 min. Results are shown in Fig. 7 (1.0 Zinc fraction).

(c) Examples 11a to 11e: Invention > 0% mole fraction Zn cation to < 100% mole fraction Zn cation: A range of Et_2Zn and Et_3Al feed rates of 5% (Example 11a), 10% (Example 11b), 15% (Example 11c), 25% (Example 11d), and 50% (Example 11e) mole fraction of Zn cation are tried in the reactor, all the while keeping the total of sum of Et_2Zn and Et_3Al feed rates constant at 6 $\mu\text{mole/minute}$. After quenching, MFR of resulting polyolefins are shown in Fig. 7 for at 0.05 zinc fraction, 0.1 zinc fraction, 0.15 zinc fraction, 0.25 zinc fraction, and 0.5 zinc fraction, respectively.

(d) Examples 12a to 12f: Invention > 0% mole fraction Zn cation to < 100% mole fraction Zn cation: A range of Et_2Zn and Et_3Al feed rates of 7% (Examples 12a and 12b), 14% (Example 12c), 22% (Example 12d), 34% (Example 12e), and 61% (Example 12f) mole fraction of Zn cation are tried in the reactor, all the while keeping the total of sum of Et_2Zn and Et_3Al feed rates constant

at 6 μmole/minute After quenching, MFR of resulting polyolefins are shown in Fig. 7 for at 0.07 zinc fraction, 0.14 zinc fraction, 0.22 zinc fraction, 0.34 zinc fraction, and 0.61 zinc fraction, respectively.

Results of MFR versus zinc cation ratio from (a) to (d) are graphically plotted in Fig. 7.

5 Instead of each PCSA and PCRA operating independently, as would be expected in the art, and thus all MFR values equaling the 100% mole fraction of zinc cation MFR value of 0.11 g/minute, as also would be expected in the art, surprising increases in MFR are observed in Fig. 7 for (c) and (d) in the range > 0% mole fraction zinc cation to < 100% mole fraction zinc cation for the invention of Examples 11a to 12f. Since it is known in the art that an increase in MFR is correlated to a decrease
10 in M_n , therefore, M_n of the polyolefin of the invention Examples 11a to 12f are unexpectedly decreased, which indicate a synergistic interaction occurs between the PCSA (e.g., Et_2Zn) and PCRA (e.g., Et_3Al) in the invention polymerization process.

As shown by the Examples, the invention composition and process are useful for and capable of (co)polymerizing olefin monomer(s) with a non-metallocene-type olefin polymerization
15 catalyst (NMOP catalyst) in presence of the PCSA and PCRA to give a polyolefin-type (co)polymeryl chain. The PCSA reversibly shuttles the polyolefin-type (co)polymeryl chain between the NMOP catalyst and the PCRA. The PCRA is effective for reversibly storing and functionalizing the polyolefin-type (co)polymeryl chain *in situ* as the metal-functionalized polyolefin in presence of the PCSA and NMOP catalyst Once a desired degree of polymerization is achieved, the metal-
20 functionalized polyolefin is useful for preparing a polyolefin-type polymer product that substantially lacks the metal (i.e., has less than 10 mole percent of initial amount of the metal) such as, for example, a polyolefin or telechelic polyolefin. In some embodiments the invention process enables facile synthesis of the metal-functionalized polyolefin without substantially decreasing (i.e., decreasing by less than 10%) catalyst efficiency of the NMOP catalyst used therein. The Examples
25 also show that MFR of a polyolefin product is increased, and thus the M_n of the polyolefin product is decreased compared to M_n of a reference polyolefin product that has been prepared by a non-invention process employing the PCRA or PCSA, but not both.

WHAT IS CLAIMED IS:

1. A polymerization process for preparing a metal-functionalized polyolefin, the process comprising contacting a first olefin monomer with a mixture comprising ingredients (a), (b), and (c), or a reaction product of any portion thereof:

5 Ingredient (a) a polymeryl chain repository effective amount of a first metal (Ci-C₂₀)hydrocarbyl;

 Ingredient (b) a polymeryl chain shuttling effective amount of a second metal (Ci-C₂₀)hydrocarbyl; and

10 Ingredient (c) a catalytically-effective amount of a first non-metallocene-type olefin polymerization catalyst comprising a mixture of a first non-metallocene-type precatalyst and at least one first co-catalyst, or a reaction product thereof;

 Wherein the contacting is performed under olefin polymerizing conditions in such a way so as to polymerize the first olefin monomer and thereby prepare a metal-functionalized polyolefin;

15 Wherein the first metal (Ci-C₂₀)hydrocarbyl comprises a first metal cation and at least one (Ci-C₂₀)hydrocarbyl (up to the first metal cation's formal valence number of (Ci-C₂₀)hydrocarbyl), wherein the first metal cation is a Group 1, 2, 12, or 13 metal cation;

20 Wherein the second metal (Ci-C₂₀)hydrocarbyl comprises a second metal cation and at least one (Ci-C₂₀)hydrocarbyl (up to the second metal cation's formal valence number of (Ci-C₂₀)hydrocarbyl), wherein the second metal cation is a Group 1, 2, 12, or 13 metal cation;

 Wherein the first and second metal cations are different from each other;

25 Wherein the first and second metal (Ci-C₂₀)hydrocarbyls are characterizable by chain transfer constants C_{tr1} and C[^], respectively, wherein chain transfer constant C_{tr2} is greater than chain transfer constant C_{tr1} and C_{tr1} is greater than 0; and

 Wherein the metal-functionalized polyolefin comprises a polyolefin polymeryl chain and a third metal cation, wherein a majority of the third metal cation is the same as the first metal cation of or from the first metal (Ci-C₂₀)hydrocarbyl.

- 30 2. The process as in claim 1, wherein the polymeryl chain shuttling effective amount of the second metal (Ci-C₂₀)hydrocarbyl (PCSA) is less on a mole basis than the polymeryl chain repository effective amount of the first metal (Ci-C₂₀)hydrocarbyl (PCRA) and less on a mole basis than the catalytically effective amount of the first non-metallocene-type precatalyst and any other precatalyst.

3. The process as in claim 1 or 2, wherein the contacting step comprises a continuous-flow polymerization process step operating in a continuous-flow reactor and the process further comprises a preliminary step of feeding the first olefin monomer, polymeryl chain repository effective amount of the first metal (Ci-C₂₀)hydrocarbyl, polymeryl chain shuttling effective amount of the second metal (Ci-C₂₀)hydrocarbyl, and first non-metallocene-type olefin polymerization catalyst into the continuous-flow reactor and a subsequent step of removing the metal-functionalized polyolefin from the continuous-flow reactor so as to provide a removed metal-functionalized polyolefin.
- 5
4. The process as in any one of the preceding claims, wherein the chain transfer constant C_{tr2} is at least 5 times greater than chain transfer constant C_{tr1}.
- 10
5. The process as in any one of the preceding claims, wherein the first metal cation of or from the first metal (Ci-C₂₀)hydrocarbyl is a Group 13 metal cation and the second metal cation of or from the second metal (Ci-C₂₀)hydrocarbyl is a zinc cation.
6. The process as in claim 7, wherein the first metal (Ci-C₂₀)hydrocarbyl is an aluminum (Ci-C₂₀)alkyl, which comprises an aluminum cation and from 1 to 3 (Ci-C₂₀)alkyl; or a boron (Ci-C₂₀)alkyl, which comprises a boron cation and from 1 to 3 (Ci-C₂₀)alkyl; and the second metal (Ci-C₂₀)hydrocarbyl is a zinc (Ci-C₂₀)alkyl, which comprises a zinc cation and 1 or 2 (Ci-C₂₀)alkyl.
- 15
7. The process as in claim 8, wherein the first metal (Ci-C₂₀)hydrocarbyl is the aluminum (Ci-C₂₀)alkyl, which is an aluminum (Ci-C₆)alkyl; and the zinc (Ci-C₂₀)alkyl is a zinc (Ci-C₆)alkyl; and wherein the majority of the third metal cation is an aluminum cation.
- 20
8. The process as in any one of the preceding claims, the process further comprising contacting the metal-functionalized polyolefin with a quenching reagent in such a way so as to substantially release the metal therefrom and thereby prepare a polyolefin.
- 25
9. The process as in claim 10, wherein the polyolefin is characterizable by an enhanced melt flow rate; a polydispersity index of 1.90 or greater; or a combination thereof.
10. The process as in any one of claims 1 to 9, the process further comprising contacting the metal-functionalized polyolefin with a functionalization reagent in such a way so as to prepare a non-metallic functional group-containing polyolefin.

11. The process as in claim 12, wherein the non-metallic functional group-containing polyolefin is a telechelic polyolefin that contains at least two non-metallic functional groups that each contain at least one oxygen, nitrogen, or halogen atom.
- 5 12. The process as in any one of the preceding claims, wherein the contacting step further employs a second olefin monomer and copolymerizes the first and second olefin monomers, and thereby prepares the metal-functionalized polyolefin as a metal-functionalized olefin copolymer.
- 10 13. The process as in any one of the preceding claims, wherein the contacting step further employs a second olefin monomer and the mixture in the contacting step further contains an Ingredient (d): a catalytically effective amount of a second non-metallocene-type olefin polymerization catalyst, wherein the second non-metallocene-type olefin polymerization catalyst comprises a second non-metallocene-type precatalyst and at least one second co-catalyst, or a reaction product thereof; wherein the first and second co-catalysts are the same as or different than each other; the first and second non-metallocene-type precatalysts are
15 different from each other; and the first and second non-metallocene-type olefin polymerization catalysts are different from each other and are both catalytically active in the contacting step; and wherein the contacting step copolymerizes the first and second olefin monomers, and thereby prepares the metal-functionalized polyolefin as a metal-functionalized olefin block copolymer (which can be converted to an OBC).
- 20 14. A metal-functionalized polyolefin prepared as in any one of the preceding claims.
- 25 15. A composition comprising the mixture of ingredients (a), (b), and (c), or the reaction product of any portion thereof, as in any one of claims 1 to 15; wherein the first non-metallocene-type olefin polymerization catalyst is characterizable as being capable of catalytically polymerizing a first olefin monomer under olefin polymerizing conditions so as to produce a metal-functionalized polyolefin that upon reacting with a quenching reagent substantially releases the metal therefrom and prepares a polyolefin having an enhanced melt flow rate.

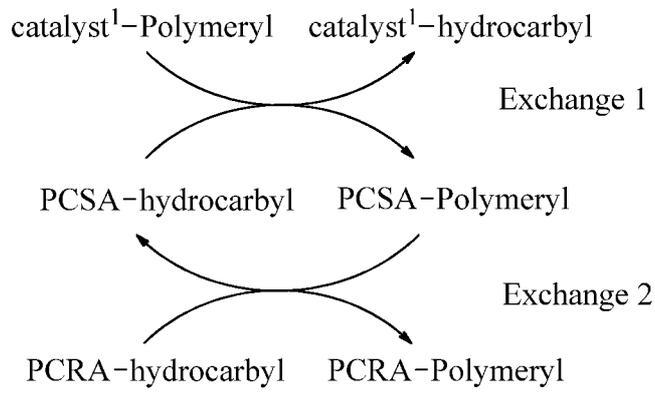


Fig. 1a

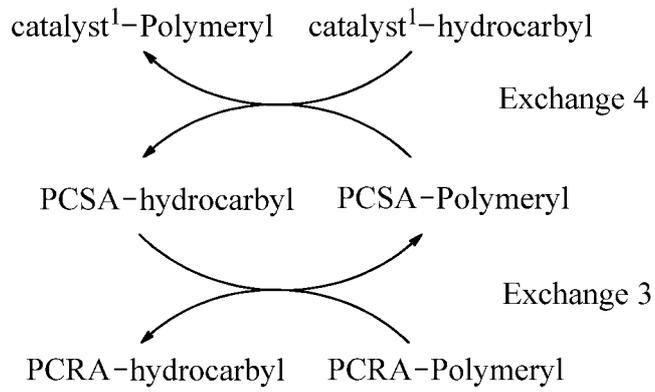


Fig. 1b

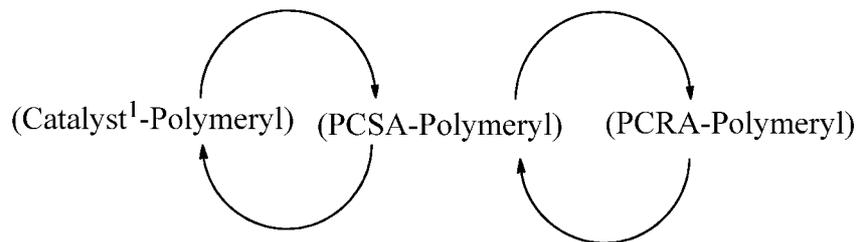


Fig. 1c

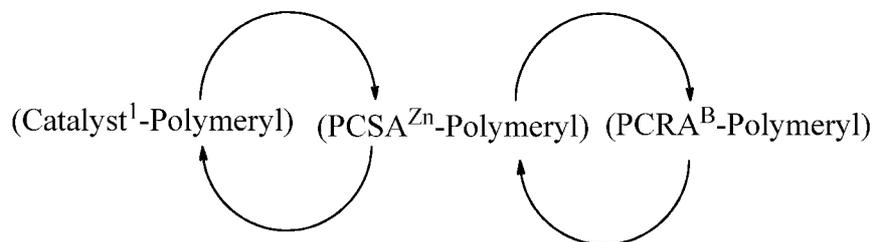


Fig. 2a

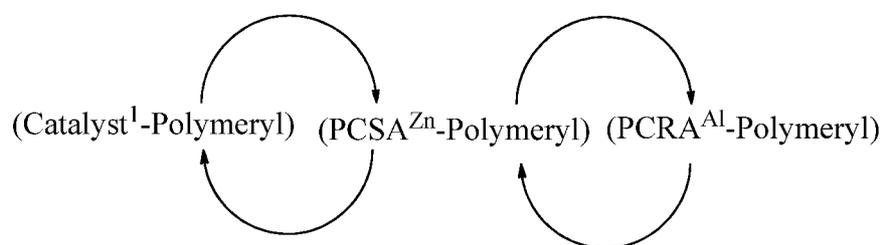


Fig. 2b

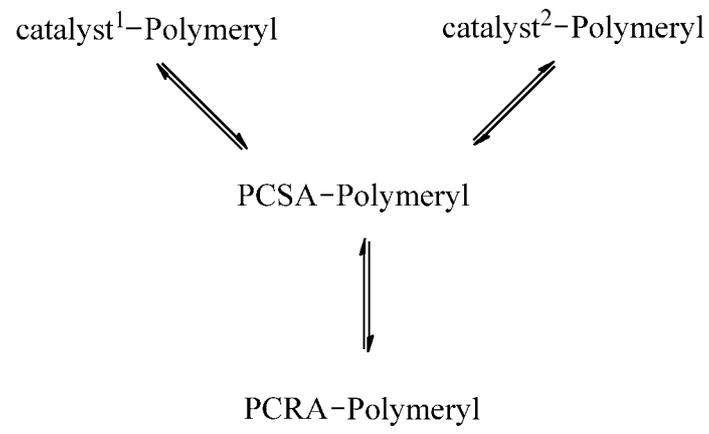
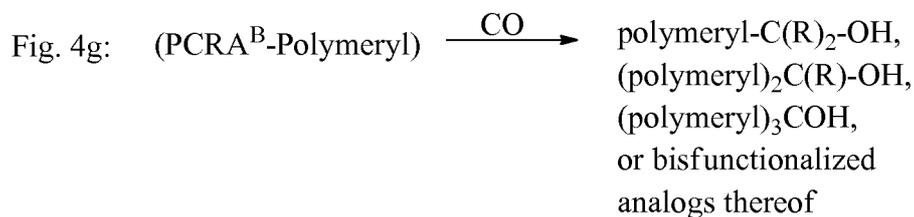
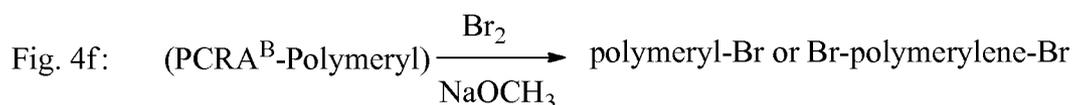
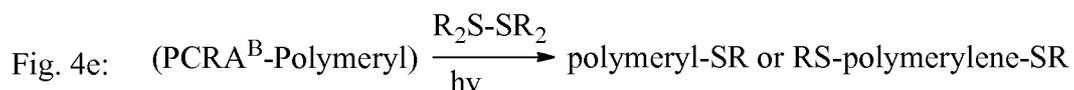
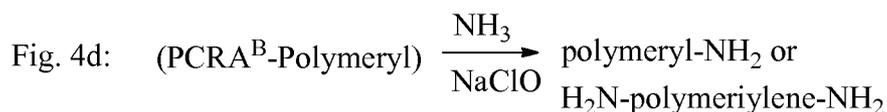
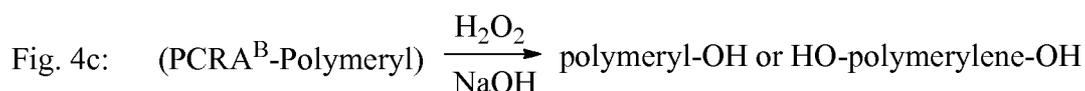
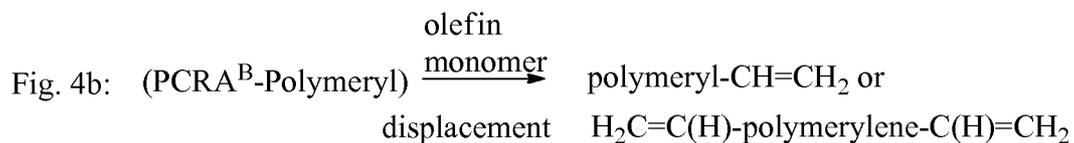
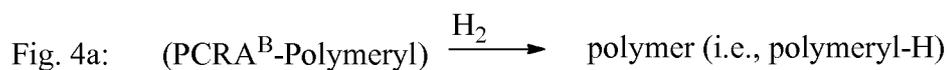
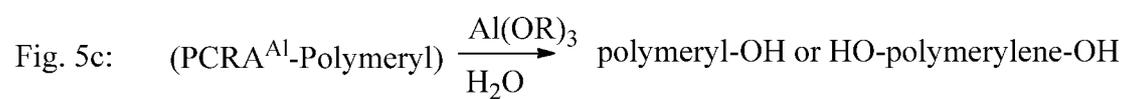
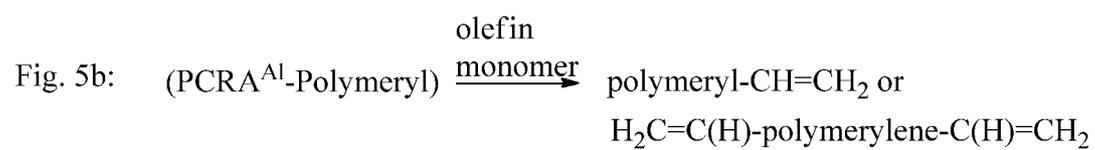
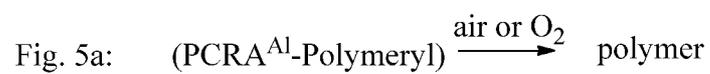


Fig. 3





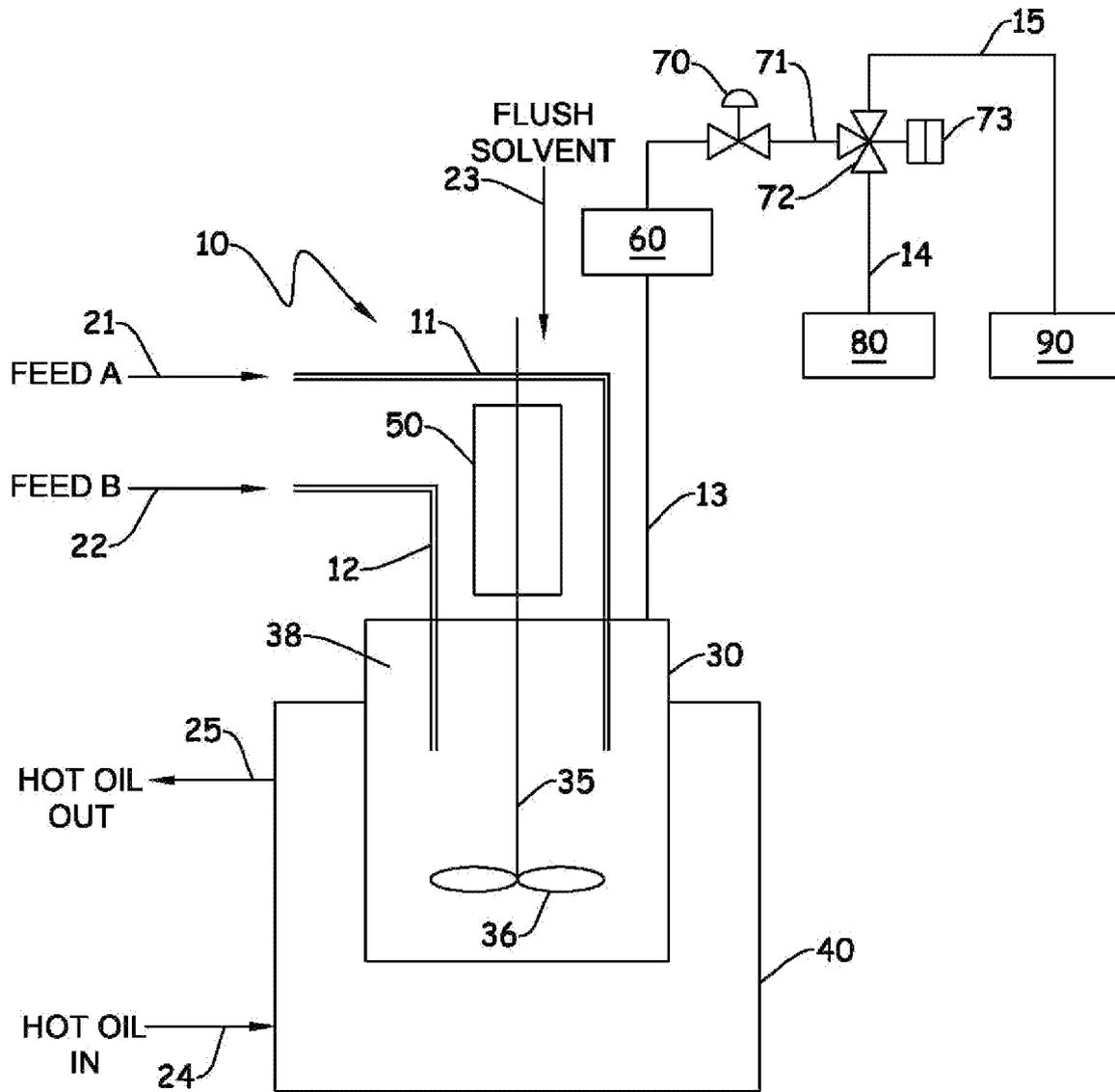


Fig. 6

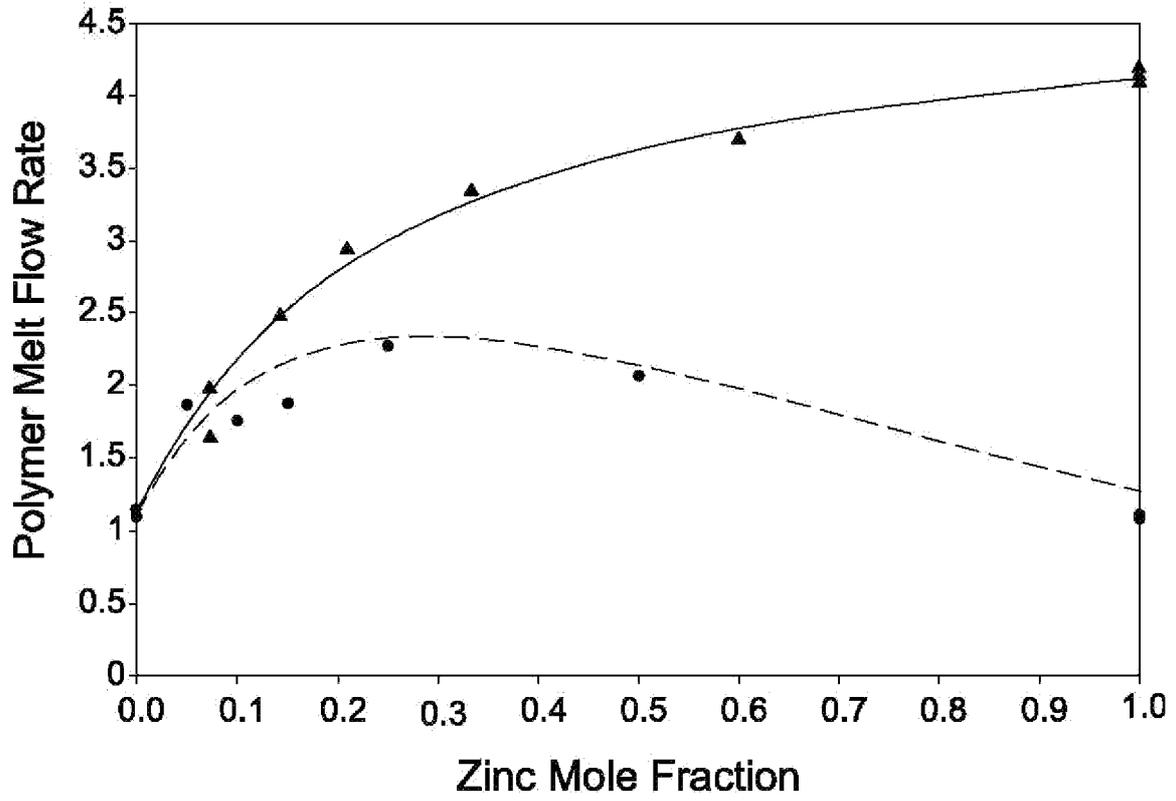


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/059326

A. CLASSIFICATION OF SUBJECT MATTER INV. C08F21Q/16 C08F4/659 C08F2/38 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 practical, search terms used) EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GEORGE J. P. BRITOVSEK ET AL: " Iron Catalyzed Polyethylene Chain Growth on Zinc: A Study of the Factors Delineating Chain Transfer versus Catalyzed Chain Growth in Zinc and Related Metal Alkyl Systems" , JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, vol . 126, no. 34, 1 September 2004 (2004-09-01) , pages 10701-10712, XP55017990, ISSN : 0002-7863, DOI : 10. 1021/ja0485560 page 1074, col umn 2, l ine 5 - l ine 46 table 2 <p align="center">-----</p>	1,4-10, 14, 15
<input type="checkbox"/>	Further documents are listed in the continuation of Box C.	<input type="checkbox"/>
		See patent family annex.
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. "&" document member of the same patent family	
Date of the actual completion of the international search <p align="center">31 January 2012</p>		Date of mailing of the international search report <p align="center">07/02/2012</p>
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 <p align="center">Thomas , Domi nik</p>