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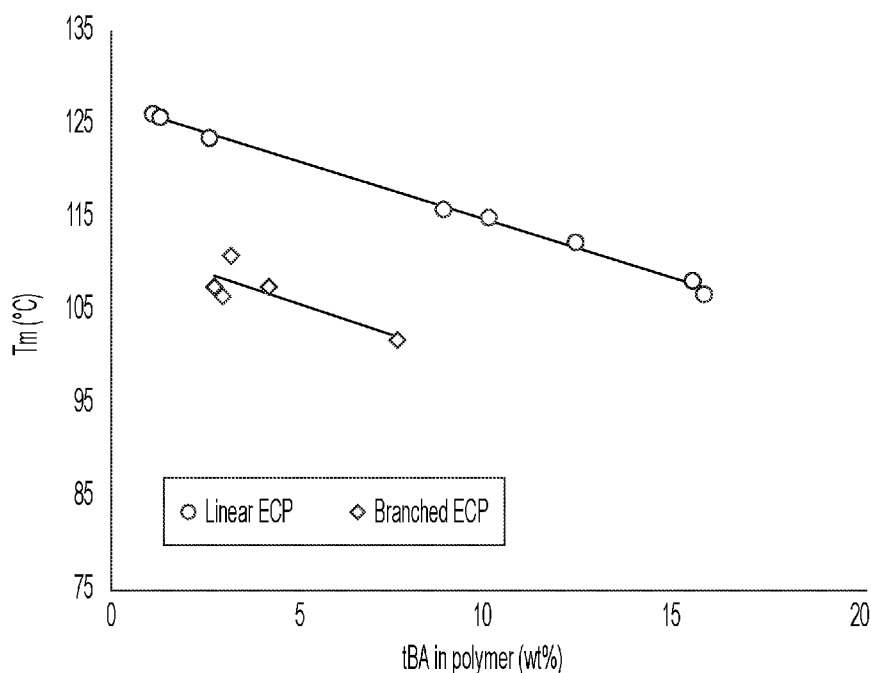
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(54) Title: USE OF TRANSITION METAL CATALYST TO PRODUCE LINEAR ETHYLENE/POLAR COPOLYMERS IN A HIGH PRESSURE PROCESS



(57) **Abstract:** Processes for polymerizing ethylene and one or more polar comonomers and optionally one or more (C₃-C₁₂) α -olefins, and optionally an aluminum compound, in the presence of the catalyst system to form an ethylene-based copolymer in a high pressure reactor at a pressure of greater than 1000 barg and a temperature of greater than 100°C, wherein the catalyst system comprises a transition metal catalyst.

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USE OF TRANSITION METAL CATALYST TO PRODUCE LINEAR ETHYLENE/POLAR COPOLYMERS IN A HIGH PRESSURE PROCESS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Serial No. 63/511,257 filed June 30, 2023, the contents of which are incorporated in their entirety herein.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure generally relate to ethylene and polar comonomer polymerization processes to produce linear ethylene copolymers, and, more specifically, to polymerization processes conducted at high temperatures and high pressures that incorporate catalyst systems having transition metal catalysts.

BACKGROUND

[0003] Commercially, ethylene/acrylate copolymers are formed through high-pressure and/or high-temperature radical processes and have a highly branched microstructure similar to that of low-density polyethylene (LDPE). Methods for copolymerizing ethylene and vinyl monomers containing a polar group, e.g. vinyl acetate and (meth)acrylates, by radical polymerization at high temperature ($> 100\text{ }^{\circ}\text{C}$) under high pressure ($> 1000\text{ barg}$) are well known. These methods, however, result in the production of copolymers with relatively low thermal resistance (low melting temperature due to their low crystallinity and high degree of long-chain branching).

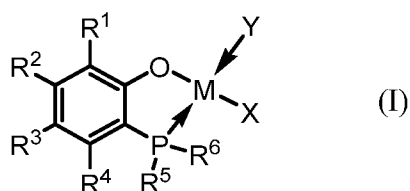
[0004] Coordination catalysis in solution provides routes to highly linear ethylene/acrylate copolymers with structures similar to that of linear low-density polyethylene (LLDPE). The linear ethylene/acrylate copolymers formed by coordination catalysis exhibit greater crystallinity and higher thermal resistance than those of the copolymers formed through the radical processes. Both Ni and Pd catalysts have been reported for the copolymerization of ethylene and acrylate monomers in solution at relatively low pressures of ethylene (10-50 barg); however, the reported catalyst efficiencies are typically quite low. The reported Ni and Pd catalysts also exhibit significant deactivation in solution at temperatures $> 120\text{ }^{\circ}\text{C}$ and the Mw of the copolymers decreases precipitously at temperatures above $90\text{ }^{\circ}\text{C}$.

SUMMARY

[0005] Ongoing needs exist to create an improved process for the copolymerization of ethylene and acrylate comonomers to give highly linear copolymers. This process should promote both high rates of ethylene copolymerization activity and high incorporation of the alkylacrylate comonomer to create highly linear copolymers. The linear ethylene/alkylacrylate copolymers may exhibit improved molecular weight distribution and increased melt temperatures. Solution-based processes with Ni and Pd catalysts produce highly linear copolymers, but at low rates. These rates can be improved by introducing the Ni or Pd catalyst to a high pressure (> 1000 barg) and high temperature (> 100 °C) reactor, where the copolymerization reaction occurs in super-critical ethylene. This leads to the production of highly linear copolymers at increased rates and higher molecular weights.

[0006] Embodiments of this disclosure includes a polymerization process. The process includes polymerizing ethylene, one or more polar comonomers, optionally one or more (C₃–C₁₂) α -olefins, and optionally an aluminum species in the presence of the catalyst system to form an ethylene-based copolymer in a high pressure reactor at a pressure of greater than 1000 barg and a temperature of greater than 100°C, wherein the catalyst system comprises a transition metal catalyst.

[0007] In one or more embodiments, the transition metal catalyst comprises nickel(II) or palladium(II). In some embodiments, the transition metal catalyst or transition metal procatalyst comprises nickel(II) or palladium(II), and has a structure according to formula (I).

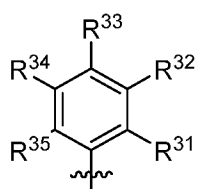


[0008] M is nickel(II) or palladium(II); X is a ligand chosen from (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –CH₂Si(R^C)_{3-Q}(OR^C)_Q, –Si(R^C)_{3-Q}(OR^C)_Q, –OSi(R^C)_{3-Q}(OR^C)_Q, –Ge(R^C)_{3-Q}(OR^C)_Q, –P(R^C)_{2-W}(OR^C)_W, –P(O)(R^C)_{2-W}(OR^C)_W, –N(R^C)₂, –NH(R^C), –N(Si(R^C)₃)₂, –NR^CSi(R^C)₃, –NHSi(R^C)₃, –OR^C, –SR^C, –NO₂, –CN, –CF₃, –OCF₃, –S(O)R^C, –S(O)₂R^C, –OS(O)₂R^C, –N=C(R^C)₂, –N=CH(R^C), –N=CH₂, –N=P(R^C)₃, –OC(O)R^C, –C(O)OR^C, –N(R^C)C(O)R^C, –N(R^C)C(O)H, –NHC(O)R^C, –C(O)N(R^C)₂, –C(O)NHR^C, –C(O)NH₂, a halogen, or a hydrogen, wherein each R^C is independently a substituted or unsubstituted (C₁–

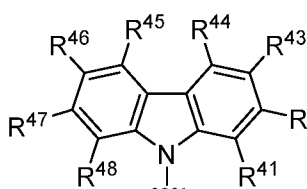
(C₃₀)hydrocarbyl, or a substituted or unsubstituted (C₁–C₃₀)heterohydrocarbyl, and Q is 0, 1, 2 or 3 and W is 0, 1, or 2.

[0009] In formula (I) each Y is a Lewis base, wherein X and Y are optionally linked. P is phosphorous.

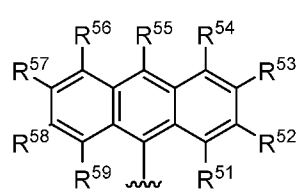
[0010] In formula (I), R¹ is independently selected from the group consisting of –H, (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –Si(R^C)_{3-Q}(OR^C)_Q, –OSi(R^C)_{3-Q}(OR^C)_Q, –Ge(R^C)_{3-Q}(OR^C)_Q, –P(=O)(R^P)₂, –P(R^C)_{2-W}(OR^C)_W, –P(O)(R^C)_{2-W}(OR^C)_W, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–, R^CS(O)₂–, –N=C(R^C)₂, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)₂NC(O)–, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

[0011] In formulas (II), (III), and (IV), each of R^{31–35}, R^{41–48}, and R^{51–59} is independently chosen from –H, (C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–, R^CS(O)₂–, (R^C)₂C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R^N)–, (R^C)₂NC(O)–, or halogen.

[0012] In formula (I), R², R³, and R⁴ are independently selected from a substituted (C₁–C₃₀)hydrocarbyl, unsubstituted (C₁–C₃₀)hydrocarbyl, substituted (C₁–C₃₀)heterohydrocarbyl, unsubstituted (C₁–C₃₀)heterohydrocarbyl, –Si(R^C)_{3-Q}(OR^C)_Q, –OSi(R^C)_{3-Q}(OR^C)_Q, –Ge(R^C)_{3-Q}(OR^C)_Q, –P(R^C)_{2-W}(OR^C)_W, –P(O)(R^C)_{2-W}(OR^C)_W, –N(R^C)₂, –NH(R^C)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, –OCF₃, –S(O)R^C, –S(O)₂R^C, –OS(O)₂R^C, –N=C(R^C)₂, –N=P(R^C)₃, –OC(O)R^C, –C(O)OR^C, –N(R)C(O)R^C, –C(O)N(R^C)₂, or a halogen, wherein each R^C is independently a substituted or unsubstituted (C₁–C₃₀)hydrocarbyl, or a substituted or unsubstituted (C₁–C₃₀) heterohydrocarbyl; Q is 0, 1, 2, or 3 and W is 0, 1, or 2.

[0013] In formula (I), R⁵ and R⁶ are independently selected from a substituted (C₁–C₃₀)hydrocarbyl, unsubstituted (C₁–C₃₀)hydrocarbyl, substituted (C₁–C₃₀)heterohydrocarbyl, or unsubstituted (C₁–C₃₀)heterohydrocarbyl.

[0014] In some embodiments, in formula (I), optionally, R⁵ and R⁶ are linked to form a ring structure; optionally, R² and R³ are linked to form a ring structure; or optionally, R³ and R⁴ are linked to form a ring structure.

BRIEF DESCRIPTION OF THE FIGURES

[0015] The FIGURE is a graph of the melt temperature of the acrylate/ethylene copolymers as a function of the weight percent (wt.%) of the polar comonomer.

DETAILED DESCRIPTION

[0016] Specific embodiments of catalyst systems will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the scope of the subject matter to those skilled in the art.

[0017] Common abbreviations are listed below:

[0018] **Me** : methyl; **Et** : ethyl; **Ph** : phenyl; **Bn** : benzyl; **i-Pr** : *iso*-propyl; **t-Bu** : *tert*-butyl; **t-Oct** : *tert*-octyl (2,4,4-trimethylpentan-2-yl); **THF** : tetrahydrofuran; **Et₂O** : diethyl ether; **CH₂Cl₂** : dichloromethane; **EtOAc** : ethyl acetate; **C₆D₆** : deuterated benzene or benzene-*d*₆; **CDCl₃** : deuterated chloroform; **Na₂SO₄** : sodium sulfate; **MgSO₄** : magnesium sulfate; **HCl** : hydrogen chloride; ***n*-BuLi** : butyllithium; ***t*-BuLi** : *tert*-butyl lithium; **K₂CO₃** : potassium carbonate; **N₂** : nitrogen gas; **PhMe** : toluene; **PPR** : parallel pressure reactor; **MAO** : methylaluminoxane; **MMAO** : modified methylaluminoxane; **GC** : gas chromatography; **LC** : liquid chromatography; **NMR** : nuclear magnetic resonance; **MS** : mass spectrometry; **mmol** : millimoles; **mL** : milliliters; **M** : molar; **min or mins** : minutes; **h or hrs** : hours; **d** : days; **R_f** : retention factor; **TLC** : thin-layer chromatography; **rpm** : revolutions per minute.

[0019] The term “independently selected” followed by multiple options is used herein to indicate that individual groups appearing before the term, such as R¹, R², R³, and R^C, can be identical or different, without dependency on the identity of any other group also appearing before the term.

[0020] The term “procatalyst” refers to a compound that has catalytic activity after activation, for example upon removal of the Lewis base coordinated to the Ni or Pd metal center.

[0021] When used to describe certain carbon atom-containing chemical groups, a parenthetical expression having the form “(C_x–C_y)” means that the unsubstituted form of the chemical group has from x carbon atoms to y carbon atoms, inclusive of x and y. For example, a (C₁–C₅₀)alkyl is an alkyl group having from 1 to 50 carbon atoms in its unsubstituted form. In

some embodiments and general structures, certain chemical groups may be substituted by one or more substituents such as R^S wherein R^S generically represents any substituent defined in this application. An R^S substituted version of a chemical group defined using the “(C_x–C_y)” parenthetical may contain more than y carbon atoms depending on the identity of any groups R^S . For example, a “(C₁–C₅₀)alkyl substituted with exactly one group R^S , where R^S is phenyl (–C₆H₅)” may contain from 7 to 56 carbon atoms. Thus, in general when a chemical group defined using the “(C_x–C_y)” parenthetical is substituted by one or more carbon atom-containing substituents R^S , the minimum and maximum total numbers of carbon atoms of the chemical group are determined by adding to both x and y, respectively, the combined sum of the number of carbon atoms from all of the carbon atom-containing substituents R^S .

[0022] The term “substitution” means that at least one hydrogen atom (–H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a substituent (e.g., R^S). The prefix “per” has its usual meaning of “thoroughly.” For example, the term “persubstitution” or “persubstituted” means that every hydrogen atom (H) bonded to a carbon atom or heteroatom of a corresponding unsubstituted compound or functional group is replaced by a substituent (e.g., R^S). Thus, a “perfluorinated alkyl” is an alkyl group in which every hydrogen atom is replaced by a fluorine atom. The term “polysubstitution” means that at least two, but fewer than all, hydrogen atoms bonded to carbon atoms or heteroatoms of a corresponding unsubstituted compound or functional group are replaced by a substituent. The term “–H” means a hydrogen or hydrogen radical that is covalently bonded to another atom. “Hydrogen” and “–H” are interchangeable, and unless clearly specified have identical meanings.

[0023] The term “(C₁–C₅₀)hydrocarbyl” means a hydrocarbon radical of from 1 to 50 carbon atoms and the term “(C₁–C₅₀)hydrocarbylene” means a hydrocarbon diradical of from 1 to 50 carbon atoms, in which each hydrocarbon radical and each hydrocarbon diradical is aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (having three carbons or more, and including mono- and poly-cyclic, fused and non-fused polycyclic, and bicyclic) or acyclic, and substituted by one or more R^S or unsubstituted.

[0024] In this disclosure, a (C₁–C₅₀)hydrocarbyl includes, without limitation, unsubstituted or substituted forms of the following groups: (C₁–C₅₀)alkyl, (C₃–C₅₀)cycloalkyl, (C₃–C₂₀)cycloalkyl-(C₁–C₂₀)alkylene, (C₆–C₄₀)aryl, or (C₆–C₂₀)aryl-(C₁–C₂₀)alkylene (such as benzyl (–CH₂–C₆H₅)).

[0025] The terms “(C₁–C₅₀)alkyl” and “(C₁–C₁₈)alkyl” mean a saturated straight or branched hydrocarbon radical of from 1 to 50 carbon atoms and a saturated straight or branched hydrocarbon radical of from 1 to 18 carbon atoms, respectively, that is unsubstituted or substituted by one or more R^S. The radical may be on any one carbon atom of the alkyl. Examples of unsubstituted (C₁–C₅₀)alkyl are unsubstituted (C₁–C₂₀)alkyl; unsubstituted (C₁–C₁₀)alkyl; unsubstituted (C₁–C₅)alkyl; methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2-butyl; 2-methylpropyl; 1,1-dimethylethyl; 1-pentyl; 2,2-dimethylpropyl; 1-hexyl; 1-heptyl; 1-nonyl; and 1-decyl. Examples of substituted (C₁–C₄₀)alkyl are substituted (C₁–C₂₀)alkyl, substituted (C₁–C₁₀)alkyl, trifluoromethyl, and [C_n]alkyl. The term “[C_n]alkyl” means the radical, including substituents, contains up to a maximum of n carbon atoms wherein n is an integer from 1 to 45. For example, a [C₄₅]alkyl is, for example, a (C₂₇–C₄₀)alkyl substituted by one R^S, which is a (C₁–C₅)alkyl, or is, for example a (C₁₅–C₂₅)alkyl substituted by two R^S groups, which are each a (C₁–C₁₀)alkyl. Examples of (C₁–C₅)alkyl include methyl, ethyl, 1-propyl, 1-methylethyl, 2,2-dimethylpropyl; or 1,1-dimethylethyl. 1,1-Dimethylethyl is a four-carbon alkyl having its radical on the tertiary carbon. The term “tertiary carbon atom” refers to a carbon atom that is covalently bonded to three other carbon atoms.

[0026] The term “(C₆–C₅₀)aryl” means an unsubstituted or substituted (by one or more R^S) monocyclic, bicyclic, or tricyclic aromatic hydrocarbon radical of from 6 to 40 carbon atoms, of which at least from 6 to 14 of the carbon atoms are aromatic ring carbon atoms. A monocyclic aromatic hydrocarbon radical includes one aromatic ring; a bicyclic aromatic hydrocarbon radical has two rings; and a tricyclic aromatic hydrocarbon radical has three rings. When the bicyclic or tricyclic aromatic hydrocarbon radical is present, at least one of the rings of the radical is aromatic. The other ring or rings of the aromatic radical may be independently fused or non-fused and aromatic or non-aromatic. Examples of unsubstituted (C₆–C₅₀)aryl include: unsubstituted (C₆–C₂₀)aryl, unsubstituted (C₆–C₁₈)aryl; 2-(C₁–C₅)alkyl-phenyl; phenyl; fluorenyl; tetrahydrofluorenyl; indacenyl; hexahydroindacenyl; indenyl; dihydroindenyl; naphthyl; tetrahydronaphthyl; anthracenyl; and phenanthrenyl. Examples of substituted (C₆–C₄₀)aryl include: substituted (C₁–C₂₀)aryl; substituted (C₆–C₁₈)aryl; 2,4-bis([C₂₀]alkyl)-phenyl; 3,5-bis([C₂₀]alkyl)-phenyl; pentafluorophenyl; and fluoren-9-one-1-yl.

[0027] The term “(C₃–C₅₀)cycloalkyl” means a saturated cyclic hydrocarbon radical of from 3 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S. Other cycloalkyl groups (e.g., (C_x–C_y)cycloalkyl) are defined in an analogous manner as having from x to y carbon

atoms and being either unsubstituted or substituted with one or more R^S . Examples of unsubstituted (C_3-C_{40}) cycloalkyl are unsubstituted (C_3-C_{20}) cycloalkyl, unsubstituted (C_3-C_{10}) cycloalkyl, cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl, and cyclodecyl. Examples of substituted (C_3-C_{40}) cycloalkyl are substituted (C_3-C_{20}) cycloalkyl, substituted (C_3-C_{10}) cycloalkyl, cyclopentanone-2-yl, and 1-fluorocyclohexyl.

[0028] Examples of (C_1-C_{50}) hydrocarbylene include, without limitation, unsubstituted or substituted forms of groups such as (C_6-C_{50}) arylene, (C_3-C_{50}) cycloalkylene, and (C_1-C_{50}) alkylene (e.g., (C_1-C_{20}) alkylene). The diradicals may be on the same carbon atom (e.g., $-CH_2-$) or on adjacent carbon atoms (i.e., 1,2-diradicals), or are spaced apart by one, two, or more than two intervening carbon atoms (e.g., 1,3-diradicals, 1,4-diradicals, etc.). Some diradicals include 1,2-, 1,3-, 1,4-, or an α,ω -diradical, and others a 1,2-diradical. The α,ω -diradical is a diradical that has maximum carbon backbone spacing between the radical carbons. Some examples of (C_2-C_{20}) alkylene α,ω -diradicals include ethan-1,2-diyl (i.e., $-CH_2CH_2-$), propan-1,3-diyl (i.e., $-CH_2CH_2CH_2-$), 2-methylpropan-1,3-diyl (i.e., $-CH_2CH(CH_3)CH_2-$). Some examples of (C_6-C_{50}) arylene α,ω -diradicals include phenyl-1,4-diyl, naphthalen-2,6-diyl, or naphthalen-3,7-diyl.

[0029] The term “ (C_1-C_{50}) alkylene” means a saturated straight chain or branched chain diradical (i.e., the radicals are not on ring atoms) of from 1 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S . Examples of unsubstituted (C_1-C_{50}) alkylene are unsubstituted (C_1-C_{20}) alkylene, including unsubstituted $-CH_2CH_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$, $-(CH_2)_7-$, $-(CH_2)_8-$, $-CH_2C^*HCH_3$, and $-(CH_2)_4C^*(H)(CH_3)$, in which “ C^* ” denotes a carbon atom from which a hydrogen atom is removed to form a secondary or tertiary alkyl radical. Examples of substituted (C_1-C_{50}) alkylene are substituted (C_1-C_{20}) alkylene, $-CF_2-$, $-C(O)-$, and $-(CH_2)_{14}C(CH_3)_2(CH_2)_5-$ (i.e., a 6,6-dimethyl substituted 1,20-eicosylene). Examples of substituted (C_1-C_{50}) alkylene also include 1,2-cyclopentanediyldis(methylene), 1,2-cyclohexanediyldis(methylene), 7,7-dimethyl-bicyclo[2.2.1]heptane-2,3-diylbis(methylene), and bicyclo[2.2.2]octane-2,3-diylbis(methylene).

[0030] The term “ (C_3-C_{50}) cycloalkylene” means a cyclic diradical (i.e., the radicals are on ring atoms) of from 3 to 50 carbon atoms that is unsubstituted or substituted by one or more R^S .

[0031] The term “heteroatom,” refers to an atom other than hydrogen or carbon. Examples of groups containing one or more than one heteroatom include $-O-$, $-S-$, $-S(O)-$, $-S(O)_2-$, $-Si(R^C)_2-$, $-P(R^P)-$, $-P(R^P)_2-$, $-P(O)(R^P)_2-$, $-N(R^N)-$, $-N(R^N)_2-$, $-N=C(R^C)_2-$, $-N=C(NR^N_2)(R^C)$,

$-\text{Ge}(\text{R}^{\text{C}})_2-$, or $-\text{Si}(\text{R}^{\text{C}})_3$, where each R^{C} and each R^{P} is unsubstituted $(\text{C}_1-\text{C}_{18})$ hydrocarbyl or $-\text{H}$, and where each R^{N} is unsubstituted $(\text{C}_1-\text{C}_{18})$ hydrocarbyl or $-\text{H}$. The term “heterohydrocarbon” refers to a molecule or molecular framework in which one or more carbon atoms of a hydrocarbon are replaced with a heteroatom. The term “ $(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl” means a heterohydrocarbon radical of from 1 to 50 carbon atoms, and the term “ $(\text{C}_1-\text{C}_{50})$ heterohydrocarbylene” means a heterohydrocarbon diradical of from 1 to 50 carbon atoms. The heterohydrocarbon of the $(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl or the $(\text{C}_1-\text{C}_{50})$ heterohydrocarbylene has one or more heteroatoms. The radical of the heterohydrocarbyl may be on a carbon atom or a heteroatom. The two radicals of the heterohydrocarbylene may be on a single carbon atom or on a single heteroatom. Additionally, one of the two radicals of the diradical may be on a carbon atom and the other radical may be on a different carbon atom; one of the two radicals may be on a carbon atom and the other on a heteroatom; or one of the two radicals may be on a heteroatom and the other radical on a different heteroatom. Each $(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl and $(\text{C}_1-\text{C}_{50})$ heterohydrocarbylene may be unsubstituted or substituted (by one or more R^{S}), aromatic or non-aromatic, saturated or unsaturated, straight chain or branched chain, cyclic (including mono- and poly-cyclic, fused and non-fused polycyclic), or acyclic.

[0032] The $(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl may be unsubstituted or substituted. Non-limiting examples of the $(\text{C}_1-\text{C}_{50})$ heterohydrocarbyl include $(\text{C}_1-\text{C}_{50})$ heteroalkyl, $(\text{C}_1-\text{C}_{50})$ hydrocarbyl- $\text{O}-$, $(\text{C}_1-\text{C}_{50})$ hydrocarbyl- $\text{S}-$, $(\text{C}_1-\text{C}_{50})$ hydrocarbyl- $\text{S}(\text{O})-$, $(\text{C}_1-\text{C}_{50})$ hydrocarbyl- $\text{S}(\text{O})_2-$, $(\text{C}_1-\text{C}_{50})$ hydrocarbyl- $\text{Si}(\text{R}^{\text{C}})_2-$, $(\text{C}_1-\text{C}_{50})$ hydrocarbyl- $\text{N}(\text{R}^{\text{N}})-$, $(\text{C}_1-\text{C}_{50})$ hydrocarbyl- $\text{P}(\text{R}^{\text{P}})-$, $(\text{C}_2-\text{C}_{50})$ heterocycloalkyl, $(\text{C}_2-\text{C}_{19})$ heterocycloalkyl- $(\text{C}_1-\text{C}_{20})$ alkylene, $(\text{C}_3-\text{C}_{20})$ cycloalkyl- $(\text{C}_1-\text{C}_{19})$ heteroalkylene, $(\text{C}_2-\text{C}_{19})$ heterocycloalkyl- $(\text{C}_1-\text{C}_{20})$ heteroalkylene, $(\text{C}_1-\text{C}_{50})$ heteroaryl, $(\text{C}_1-\text{C}_{19})$ heteroaryl- $(\text{C}_1-\text{C}_{20})$ alkylene, $(\text{C}_6-\text{C}_{20})$ aryl- $(\text{C}_1-\text{C}_{19})$ heteroalkylene, or $(\text{C}_1-\text{C}_{19})$ heteroaryl- $(\text{C}_1-\text{C}_{20})$ heteroalkylene. Additional examples include, but are not limited to $-\text{Si}(\text{R}^{\text{C}})_{3-\text{Q}}(\text{OR}^{\text{C}})_{\text{Q}}$, $-\text{OSi}(\text{R}^{\text{C}})_{3-\text{Q}}(\text{OR}^{\text{C}})_{\text{Q}}$, $-\text{Ge}(\text{R}^{\text{C}})_{3-\text{Q}}(\text{OR}^{\text{C}})_{\text{Q}}$, $-\text{P}(\text{R}^{\text{C}})_{2-\text{W}}(\text{OR}^{\text{C}})_{\text{W}}$, $-\text{P}(\text{O})(\text{R}^{\text{C}})_{2-\text{W}}(\text{OR}^{\text{C}})_{\text{W}}$, $-\text{N}(\text{R}^{\text{C}})_2$, $-\text{NH}(\text{R}^{\text{C}})_2$, $-\text{OR}^{\text{C}}$, $-\text{SR}^{\text{C}}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{CF}_3$, $-\text{OCF}_3$, $-\text{S}(\text{O})\text{R}^{\text{C}}$, $-\text{S}(\text{O})_2\text{R}^{\text{C}}$, $-\text{OS}(\text{O})_2\text{R}^{\text{C}}$, $-\text{N}=\text{C}(\text{R}^{\text{C}})_2$, $-\text{N}=\text{P}(\text{R}^{\text{C}})_3$, $-\text{OC}(\text{O})\text{R}^{\text{C}}$, $-\text{C}(\text{O})\text{R}^{\text{C}}$, $-\text{C}(\text{O})\text{OR}^{\text{C}}$, $-\text{N}(\text{R}^{\text{C}})\text{C}(\text{O})\text{R}^{\text{C}}$, and $-\text{C}(\text{O})\text{N}(\text{R}^{\text{C}})_2$.

[0033] The term “ $(\text{C}_4-\text{C}_{50})$ heteroaryl” means an unsubstituted or substituted (by one or more R^{S}) monocyclic, bicyclic, or tricyclic heteroaromatic hydrocarbon radical of from 2 to 50 total carbon atoms and from 1 to 10 heteroatoms. The radical of the heteroaryl may be on a carbon

atom or a heteroatom. A monocyclic heteroaromatic hydrocarbon radical includes one heteroaromatic ring; a bicyclic heteroaromatic hydrocarbon radical has two rings; and a tricyclic heteroaromatic hydrocarbon radical has three rings. When the bicyclic or tricyclic heteroaromatic hydrocarbon radical is present, at least one of the rings in the radical is heteroaromatic. The other ring or rings of the heteroaromatic radical may be independently fused or non-fused and aromatic or non-aromatic. Other heteroaryl groups (e.g., (C_x–C_y)heteroaryl generally, such as (C₄–C₁₂)heteroaryl) are defined in an analogous manner as having from x to y carbon atoms (such as 4 to 12 carbon atoms) and being unsubstituted or substituted by one or more than one R^S. The monocyclic heteroaromatic hydrocarbon radical is a 5-membered ring or a 6-membered ring. The 5-membered ring has 5 minus h carbon atoms, wherein h is the number of heteroatoms and may be 1, 2, 3, or 4; and each heteroatom independently may be O, S, N, or P. Examples of 5-membered ring heteroaromatic hydrocarbon radicals include pyrrol-1-yl; pyrrol-2-yl; furan-3-yl; thiophen-2-yl; pyrazol-1-yl; isoxazol-2-yl; isothiazol-5-yl; imidazol-2-yl; oxazol-4-yl; thiazol-2-yl; 1,2,4-triazol-1-yl; 1,3,4-oxadiazol-2-yl; 1,3,4-thiadiazol-2-yl; tetrazol-1-yl; tetrazol-2-yl; and tetrazol-5-yl. The 6-membered ring has 6 minus h carbon atoms, wherein h is the number of heteroatoms and may be 1, 2 or 3 and the heteroatoms may be N or P. Examples of 6-membered ring heteroaromatic hydrocarbon radicals include pyridine-2-yl; pyrimidin-2-yl; pyrazin-2-yl; 1,3,5-triazin-2-yl. The bicyclic heteroaromatic hydrocarbon radical can be a fused 5,6- or 6,6-ring system. Examples of the fused 5,6-ring system bicyclic heteroaromatic hydrocarbon radical are indol-1-yl; and benzimidazol-1-yl. Examples of the fused 6,6-ring system bicyclic heteroaromatic hydrocarbon radical are quinolin-2-yl; and isoquinolin-1-yl. The tricyclic heteroaromatic hydrocarbon radical can be a fused 5,6,5-, 5,6,6-, 6,5,6-, or 6,6,6-ring system. An example of the fused 5,6,5-ring system is 1,7-dihydropyrrolo[3,2-f]indol-1-yl. An example of the fused 5,6,6-ring system is 1H-benzo[f]indol-1-yl. An example of the fused 6,5,6-ring system is 9H-carbazol-9-yl. An example of the fused 6,6,6-ring system is acrydin-9-yl.

[0034] The term “(C₁–C₅₀)heteroalkyl” means a saturated straight or branched chain radical containing 1 to 50 carbon atoms, and one or more than one heteroatom. The term “(C₁–C₅₀)heteroalkylene” means a saturated straight or branched chain diradical containing from 1 to 50 carbon atoms and one or more than one heteroatom. The heteroatoms of the heteroalkyls or the heteroalkylenes may include, but are not limited to Si(R^C)₃, Ge(R^C)₃, Si(R^C)₂, Ge(R^C)₂, P(R^P)₂, P(R^P), P(O)(R^P)₂, N(R^N)₂, N(R^N), N, O, OR^C, S, SR^C, S(O), and S(O)₂, wherein each of the heteroalkyl and heteroalkylene groups are unsubstituted or are substituted by one or more R^S.

[0035] Examples of unsubstituted (C₂–C₄₀)heterocycloalkyl include unsubstituted (C₂–C₂₀)heterocycloalkyl, unsubstituted (C₂–C₁₀)heterocycloalkyl, aziridin-1-yl, oxetan-2-yl, tetrahydrofuran-3-yl, pyrrolidin-1-yl, tetrahydrothiophen-S,S-dioxide-2-yl, morpholin-4-yl, 1,4-dioxan-2-yl, hexahydroazepin-4-yl, 3-oxa-cyclooctyl, 5-thio-cyclononyl, and 2-aza-cyclodecyl.

[0036] The term “halogen atom” or “halogen” means the radical of a fluorine atom (F), chlorine atom (Cl), bromine atom (Br), or iodine atom (I). The term “halide” means the anionic form of the halogen atom: fluoride (F[−]), chloride (Cl[−]), bromide (Br[−]), or iodide (I[−]).

[0037] The term “saturated” means lacking carbon–carbon double bonds, carbon–carbon triple bonds, and (in heteroatom-containing groups) carbon–nitrogen, carbon–phosphorus, nitrogen–nitrogen, nitrogen–phosphorus, and carbon–silicon double or triple bonds. Where a saturated chemical group is substituted by one or more substituents R^S, one or more double and/or triple bonds optionally may or may not be present in substituents R^S. The term “unsaturated” means containing one or more carbon–carbon double bonds, carbon–carbon triple bonds, or (in heteroatom-containing groups) one or more carbon–nitrogen, carbon–phosphorus, nitrogen–nitrogen, nitrogen–phosphorus, or carbon–silicon double or triple bonds, not including double bonds that may be present in substituents R^S, if any, or in (hetero) aromatic rings, if any.

[0038] Embodiments of this disclosure include polymerization processes. The polymerization processes include polymerizing ethylene and one or more polar comonomers and optionally one or more (C₃–C₁₂) α -olefins in the presence of the catalyst system to form an ethylene-based copolymer in a high pressure reactor at a pressure of greater than 1000 barg and a temperature of greater than 100°C, wherein the catalyst system comprises a transition metal catalyst.

[0039] In one or more embodiments, the reactor temperature is from 100°C to 500°C. In some embodiments, the reactor temperature is from 120°C to 500°C, 140°C to 500°C, 150°C to 500°C, 160°C to 500°C, 120°C to 400°C, 130°C to 400°C, 140°C to 400°C, 150°C to 400°C, 120°C to 300°C, 130°C to 300°C, 140°C to 300°C, or 150°C to 300°C. In various embodiments, the reactor temperature is greater 150°C.

[0040] In one or more embodiments, the reactor pressure is from 1000 barg to 10,000 barg. In some embodiments, the reactor pressure is from 1000 barg to 5,000 barg, 1,100 barg to 5,000 barg, 1,200 barg to 5,000 barg, 1,300 barg to 5,000 barg, 1,400 barg to 5,000 barg, 1,500 barg to 5,000 barg, 1000 barg to 4,000 barg, 1,100 barg to 4,000 barg, 1,200 barg to 4,000 barg, 1,300 barg to 4,000 barg, 1,400 barg to 4,000 barg, 1,500 barg to 4,000 barg, 1000 barg to 3,000 barg,

1,100 barg to 3,000 barg, 1,200 barg to 3,000 barg, 1,300 barg to 3,000 barg, 1,400 barg to 3,000 barg, or 1,500 barg to 3,000 barg.

[0041] In some embodiments, the polar comonomer may include alkyl acrylate, glycidyl acrylate, vinyl acetate, $\text{CH}_2=\text{C}(\text{H})\text{C}(\text{O})(\text{OR}^{\text{X}})$, $\text{CH}_2=\text{C}(\text{H})(\text{CH}_2)_n\text{C}(\text{O})(\text{OR}^{\text{X}})$, $\text{CH}_2=\text{CHC}(\text{O})\text{R}^{\text{X}}$, $\text{CH}_2=\text{C}(\text{H})(\text{CH}_2)_n\text{C}(\text{O})\text{OR}^{\text{X}}$, $\text{CH}_2=\text{CH}(\text{OR}^{\text{X}})$, $\text{CH}_2=\text{CH}(\text{CH}_2)_n(\text{OR}^{\text{X}})$, $\text{CH}_2=\text{CHSi}(\text{R}^{\text{X}})_{3-\text{Y}}(\text{OR}^{\text{X}})_{\text{Y}}$, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{Si}(\text{R}^{\text{X}})_{3-\text{Y}}(\text{OR}^{\text{X}})_{\text{Y}}$, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{OSi}(\text{R}^{\text{X}})_{3-\text{Y}}(\text{OR}^{\text{X}})_{\text{Y}}$, or $\text{CH}_2=\text{CHCl}$, where R^{X} is chosen from $-\text{H}$, a substituted or unsubstituted $(\text{C}_1-\text{C}_{30})$ hydrocarbyl, or a substituted or unsubstituted $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl, and subscript Y is 0, 1, 2, or 3 (n is from 1 to 10). In various embodiments, the polar monomers comprise alkyl acrylate. In some embodiments, the alkyl acrylate is methyl acrylate, ethyl acrylate, n-butyl acrylate, or t-butyl acrylate.

[0042] Olefinic monomers, such as $(\text{C}_3-\text{C}_{12})\alpha$ -olefins, may include, but are not limited to, propylene, 1-butene, 1-hexene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 4-methyl-1-pentene, styrene, cyclobutene, cyclopentene, norbornene, ethylidene norbornene.

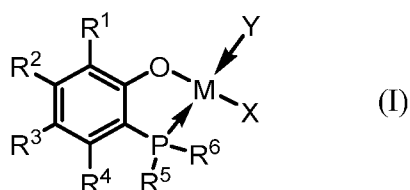
[0043] In various embodiments of the polymerization processes, the polar comonomer includes alkyl acrylates $\text{CH}_2=\text{CHC}(\text{O})(\text{OR})$, glycidyl acrylate, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{C}(\text{O})(\text{OR})$, $\text{CH}_2=\text{CHC}(\text{O})\text{R}$, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{C}(\text{O})\text{R}$, $\text{CH}_2=\text{CH}-\text{OC}(\text{O})\text{R}$, $\text{CH}_2=\text{CH}(\text{CH}_2)_n-\text{OC}(\text{O})\text{R}$, $\text{CH}_2=\text{CH}(\text{OR})$, $\text{CH}_2=\text{CH}(\text{CH}_2)_n(\text{OR})$, $\text{CH}_2=\text{CHSi}(\text{R})_{3-\text{T}}(\text{OR})_{\text{T}}$, $\text{CH}_2=\text{CH}(\text{CH}_2)_n\text{Si}(\text{R})_{3-\text{T}}(\text{OR})_{\text{T}}$, $\text{CH}_2=\text{CH}-\text{OSi}(\text{R})_{3-\text{T}}(\text{OR})_{\text{T}}$, $\text{CH}_2=\text{CH}(\text{CH}_2)_n-\text{OSi}(\text{R})_{3-\text{T}}(\text{OR})_{\text{T}}$ or $\text{CH}_2=\text{CHCl}$. Each R is chosen from $-\text{H}$, substituted $(\text{C}_1-\text{C}_{30})$ hydrocarbyl, unsubstituted $(\text{C}_1-\text{C}_{30})$ hydrocarbyl, substituted $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl, or unsubstituted $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl. Subscript T is 0, 1, 2, or 3. Subscript n is 1 to 10. In embodiments in which the polar monomer is an alkyl acrylate, substituted $(\text{C}_1-\text{C}_{30})$ hydrocarbyl acrylate, unsubstituted $(\text{C}_1-\text{C}_{30})$ hydrocarbyl acrylate, substituted $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl acrylate, or unsubstituted $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl acrylate, the polar ethylene-based copolymer may be de-esterified to form an acrylic acid/ethylene-based copolymer.

[0044] In some embodiments of the polymerization process, the alkyl acrylate monomer may be, by way of example and not limitation, methyl acrylate, ethyl acrylate, n-butyl acrylate, iso-butyl acrylate, t-butyl acrylate, or combinations thereof. In various embodiments, the alkyl acrylate has an alkyl group with from 1 to 8 carbons. This is designated a C_1-C_8 -alkyl acrylate. In particular embodiments, the alkyl acrylate is t-butyl acrylate or n-butyl acrylate.

[0045] In some embodiments of the polymerization process the optional α -olefin monomer may be, by way of example and not limitation, propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 4-methyl-1-pentene, styrene, or combinations thereof. In one or more embodiments of the polymerization process, the process may further include a cyclic olefin, such as cyclobutene, cyclopentene, norbornene, and norbornene derivatives that are substituted in the 5- and 6-positions with (C₁-C₂₀)hydrocarbyl groups.

[0046] The polymerization processes include polymerizing ethylene and one or more polar comonomers and optionally one or more (C₃-C₁₂) α -olefins, and optionally an aluminum species, in the presence of the catalyst system to form an ethylene-based copolymer in a high pressure reactor at a pressure of greater than 1000 barg and a temperature of greater than 100°C, wherein the catalyst system comprises a transition metal catalyst. In some embodiments, the transition metal catalyst comprises nickel(II) or palladium(II).

[0047] In various embodiments, the transition metal catalyst or transition metal procatalyst comprises nickel(II) or palladium(II), and has a structure according to formula (I).

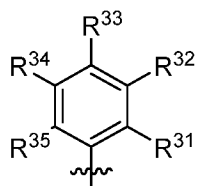


[0048] In formula (I), M is nickel(II) or palladium(II); and X is a ligand chosen from (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, -CH₂Si(R^C)_{3-Q}(OR^C)_Q, -Si(R^C)_{3-Q}(OR^C)_Q, -OSi(R^C)_{3-Q}(OR^C)_Q, -Ge(R^C)_{3-Q}(OR^C)_Q, -P(R^C)_{2-W}(OR^C)_W, -P(O)(R^C)_{2-W}(OR^C)_W, -N(R^C)₂, -NH(R^C), -N(Si(R^C)₃)₂, -NR^CSi(R^C)₃, -NHSi(R^C)₃, -OR^C, -SR^C, -NO₂, -CN, -CF₃, -OCF₃, -S(O)R^C, -S(O)₂R^C, -OS(O)₂R^C, -N=C(R^C)₂, -N=CH(R^C), -N=CH₂, -N=P(R^C)₃, -OC(O)R^C, -C(O)OR^C, -N(R^C)C(O)R^C, -N(R^C)C(O)H, -NHC(O)R^C, -C(O)N(R^C)₂, -C(O)NHR^C, -C(O)NH₂, a halogen, or a hydrogen, wherein each R^C is independently a substituted or unsubstituted (C₁-C₃₀)hydrocarbyl, or a substituted or unsubstituted (C₁-C₃₀)heterohydrocarbyl, and Q is 0, 1, 2 or 3 and W is 0, 1, or 2;

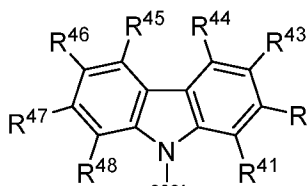
[0049] In formula (I), each Y is a Lewis base, wherein X and Y are optionally linked. P is phosphorous.

[0050] In formula (I), R¹ is independently selected from the group consisting of -H, (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, -Si(R^C)₃, -Si(R^C)_{3-Q}(OR^C)_Q, -

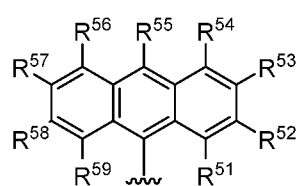
OSi(R^C)_{3-Q}(OR^C)_Q, -Ge(R^C)_{3-Q}(OR^C)_Q, -P(=O)(R^P)₂, -P(R^C)_{2-W}(OR^C)_W, -P(O)(R^C)_{2-W}(OR^C)_W, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-, -N=C(R^C)₂, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R)-, (R^C)₂NC(O)-, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

[0051] In formulas (II), (III), and (IV), each of R³¹⁻³⁵, R⁴¹⁻⁴⁸, and R⁵¹⁻⁵⁹ is independently chosen from -H, (C₁-C₄₀)hydrocarbyl, (C₁-C₄₀)heterohydrocarbyl, -Si(R^C)₃, -Ge(R^C)₃, -P(R^P)₂, -N(R^N)₂, -OR^C, -SR^C, -NO₂, -CN, -CF₃, R^CS(O)-, R^CS(O)₂-, (R^C)₂C=N-, R^CC(O)O-, R^COC(O)-, R^CC(O)N(R^N)-, (R^C)₂NC(O)-, or halogen.

[0052] In formula (I), R², R³, and R⁴ are independently selected from a substituted (C₁-C₃₀)hydrocarbyl, unsubstituted (C₁-C₃₀)hydrocarbyl, substituted (C₁-C₃₀)heterohydrocarbyl, unsubstituted (C₁-C₃₀)heterohydrocarbyl, -Si(R^C)_{3-Q}(OR^C)_Q, -OSi(R^C)_{3-Q}(OR^C)_Q, -Ge(R^C)_{3-Q}(OR^C)_Q, -P(R^C)_{2-W}(OR^C)_W, -P(O)(R^C)_{2-W}(OR^C)_W, -N(R^C)₂, -NH(R^C)₂, -OR^C, -SR^C, -NO₂, -CN, -CF₃, -OCF₃, -S(O)R^C, -S(O)₂R^C, -OS(O)₂R^C, -N=C(R^C)₂, -N=P(R^C)₃, -OC(O)R^C, -C(O)OR^C, -N(R)C(O)R^C, -C(O)N(R^C)₂, or a halogen, wherein each R^C is independently a substituted or unsubstituted (C₁-C₃₀)hydrocarbyl, or a substituted or unsubstituted (C₁-C₃₀) heterohydrocarbyl; Q is 0, 1, 2, or 3 and W is 0, 1, or 2.

[0053] In formula (I), R⁵ and R⁶ are independently selected from a substituted (C₁-C₃₀)hydrocarbyl, unsubstituted (C₁-C₃₀)hydrocarbyl, substituted (C₁-C₃₀)heterohydrocarbyl, or unsubstituted (C₁-C₃₀)heterohydrocarbyl.

[0054] In formula (I), R⁵ and R⁶ are optionally linked to form a ring structure and R² and R³ are optionally linked to form a ring structure. In some embodiments, R³ and R⁴ are optionally linked to form a ring structure.

[0055] In some embodiments, R⁵ and R⁶ are independently (C₁-C₂₀)alkyl or (C₆-C₂₀)aryl.

[0056] In some embodiments, R², R³, and R⁴ are (C₁-C₁₈)alkyl or -H.

[0057] In one or more embodiments, R¹ is a radical of formula (II), (III), or (IV). In some embodiments, R¹ is a radical of formula (I). In various embodiments, when R¹ is a radical of formula (III), then R⁴² and R⁴⁷ are (C₁-C₁₂)alkyl. In other embodiments, when R¹ is a radical of formula (III), then R⁴³ and R⁴⁶ are (C₁-C₁₂)alkyl.

[0058] In some embodiments, R⁵ and R⁶ are 2,6-dimethoxyphenyl, 2,6-diethoxyphenyl, 2,6-diphenoxyphenyl, 2,4,6-triethoxyphenyl, 2,4,6-trimethoxyphenyl, 2-phenylphenyl, or 2,6-diisopropoxyphenyl.

[0059] In the metal–ligand complex according to formula (I), each Y bonds with M through a dative bond or an ionic bond. In one or more embodiments, Y is a Lewis base. The Lewis base may be a compound or an ionic species, which can donate an electron pair to an acceptor moiety. For purposes of this description, the acceptor moiety is M, the metal of the metal–ligand complex of formula (I). In some embodiments, the Lewis base may be a heterohydrocarbon or a hydrocarbon. Examples of neutral heterohydrocarbon Lewis bases include, but are not limited to, amines, trialkylamines, ethers, cycloethers, or sulfides. Examples of neutral hydrocarbon Lewis bases include, but are not limited to, alkenes, alkynes, or arenes.

[0060] In one or more embodiments, Y is a neutral Lewis basic aprotic (C₂–C₄₀)heterohydrocarbon. Aprotic (C₂–C₄₀)heterohydrocarbons are (C₂–C₄₀)heterohydrocarbons as previously defined, for which every hydrogen atom of the (C₂–C₄₀)heterohydrocarbon has a pKa of greater than 30 wherein pKa is the negative base-10 logarithm of the acid dissociation constant (Ka). In some embodiments, Y is an organic Lewis base. Examples of organic Lewis bases include pyridine, or a substituted pyridine, a sulfoxide, a trialkyl or triaryl phosphine, a trialkyl or triaryl phosphine oxide, an olefin or cyclic olefin, a substituted or unsubstituted heterocycle, an alkyl ester of an aliphatic or aromatic carboxylic acid, an aliphatic ketone, an aliphatic amine, an alkyl or cycloalkyl ether, or mixtures thereof, each electron donor having 2 to 20 carbon atoms. In various embodiments, the organic Lewis base is selected from alkyl and cycloalkyl ethers having 2 to 20 carbon atoms; and dialkyl, diaryl, and alkylaryl ketones having 3 to 20 carbon atoms; and alkyl esters having 2 to 20 carbon atoms. Specific examples of an organic Lewis base include, but are not limited to: methyl formate, ethyl acetate, butyl acetate, ethyl ether, dioxane, di-n-propyl ether, dibutyl ether, ethyl formate, dimethylformamide, methyl acetate, ethyl anisate, ethylene carbonate, tetrahydropyran, tetrahydrofuran, ethyl propionate, lutidine, picoline, pyridine, dimethyl sulfoxide, trimethylphosphine, triethylphosphine, triphenylphosphine, cyclooctadiene, cyclopentene, ethylene, propylene, tert-butyl ethylene, trimethylamine, triethylamine, tributylamine, N,N-dimethylaniline, 1-methylimidazole, or 1-methylpyrazole.

[0061] In one or more embodiments, the Lewis base may be a monodentate ligand that may be a neutral ligand. In some embodiments, the neutral ligand may contain a heteroatom. In

specific embodiments, the neutral ligand is a neutral group such as $R^TNR^KR^L$, R^KOR^L , R^KSR^L , or $R^TPR^KR^L$, where each R^T independently is $[(C_1-C_{10})\text{hydrocarbyl}]_3\text{Si}(C_1-C_{10})\text{hydrocarbylene}$, $(C_1-C_{40})\text{hydrocarbyl}$, $[(C_1-C_{10})\text{hydrocarbyl}]_3\text{Si}$, or $(C_1-C_{40})\text{heterohydrocarbyl}$ and each R^K and R^L independently is hydrogen, $(C_1-C_{40})\text{hydrocarbyl}$, or $(C_1-C_{40})\text{heterohydrocarbyl}$.

[0062] In some embodiments, the Lewis base is $(C_1-C_{20})\text{hydrocarbon}$. In some embodiments, the Lewis base is cyclopentadiene, 1,3-butadiene or cyclooctene.

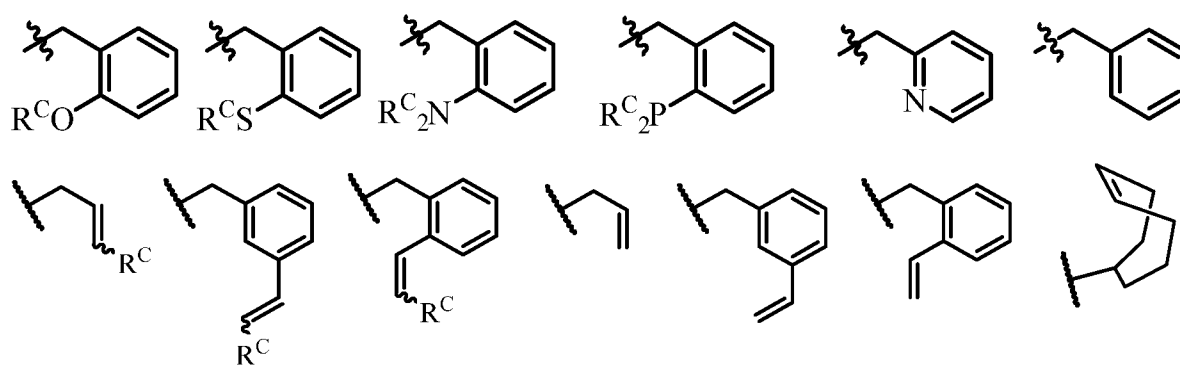
[0063] In various embodiments, the Lewis base is a $(C_1-C_{20})\text{heterohydrocarbon}$, wherein the heteroatom of the heterohydrocarbon is oxygen. In some embodiments, Y is tetrahydrofuran, pyrene, dioxane, diethyl ether, or methyl *tert*-butyl ether (MTBE).

[0064] In various embodiments, the Lewis base is a $(C_1-C_{20})\text{heterohydrocarbon}$, wherein the heteroatom of the heterohydrocarbon is nitrogen. In some embodiments, Y is pyridine, picoline, lutidine, trimethylamine, or triethylamine.

[0065] In various embodiments, the Lewis base is a $(C_1-C_{20})\text{heterohydrocarbon}$, wherein the heteroatom of the heterohydrocarbon is phosphorus. In some embodiments, Y is trimethylphosphine, triethylphosphine, triphenylphosphine, triethylphosphite, trimethylphosphite, triphenylphosphite, or triphenylphosphine oxide.

[0066] In some embodiments, X and Y are covalently linked. Specific examples of an organic Lewis base Y covalently linked together with an X group include, but are not limited to: 4-cycloocten-1-yl, 2-dimethylaminobenzyl, and 2-dimethylaminomethylphenyl.

[0067] In some embodiments, X and Y are linked and selected from the group consisting of:



where R^C is $-H$ or $(C_1-C_{30})\text{hydrocarbyl}$, $(C_1-C_{30})\text{heterohydrocarbyl}$, $(C_1-C_{20})\text{alkyl}$, or $(C_1-C_{12})\text{alkyl}$.

[0068] In the metal-ligand complex according to formula (I), X bonds with M through a covalent bond or an ionic bond. In some embodiments, X may be a monoanionic ligand having a net formal oxidation state of -1 . Each monoanionic ligand may independently be hydride,

(C₁–C₄₀)hydrocarbyl carbanion, (C₁–C₄₀)heterohydrocarbyl carbanion, halide, nitrate, hydrogencarbonate, dihydrogenphosphate, hydrogensulfate, HC(O)O[–], HC(O)N(H)[–], (C₁–C₄₀)hydrocarbylC(O)O[–], (C₁–C₄₀)hydrocarbylC(O)N((C₁–C₂₀)hydrocarbyl)[–], (C₁–C₄₀)hydrocarbylC(O)N(H)[–], R^KR^LB[–], R^KR^LN[–], R^KO[–], R^KS[–], R^KR^LP[–], or R^MR^KR^LSi[–], where each R^K, R^L, and R^M independently is hydrogen, (C₁–C₄₀)hydrocarbyl, or (C₁–C₄₀)heterohydrocarbyl, or R^K and R^L are taken together to form a (C₂–C₄₀)hydrocarbylene or (C₁–C₂₀)heterohydrocarbylene and R^M is as defined above.

[0069] In some embodiments, X is a halogen, (C₁–C₂₀)hydrocarbyl, (C₁–C₂₀)heterohydrocarbyl, (C₁–C₂₀)hydrocarbylC(O)O[–], or R^KR^LN[–], wherein each of R^K and R^L independently is an (C₁–C₂₀)hydrocarbyl. In some embodiments, each monodentate ligand X is a chlorine atom, (C₁–C₁₀)hydrocarbyl (e.g., (C₁–C₆)alkyl or benzyl), unsubstituted (C₁–C₁₀)hydrocarbylC(O)O[–], or R^KR^LN[–], wherein each of R^K and R^L independently is an unsubstituted (C₁–C₁₀)hydrocarbyl.

[0070] In various embodiments, X is a substituted or unsubstituted (C₁–C₃₀)hydrocarbyl, a substituted or unsubstituted (C₁–C₃₀)heterohydrocarbyl.

[0071] In further embodiments, X is selected from methyl; ethyl; 1-propyl; 2-propyl; 1-butyl; 2,2,-dimethylpropyl; trimethylsilylmethyl; dimethylphenylsilylmethyl; methyldiphenylsilylmethyl; triphenylsilylmethyl; benzyldimethylsilylmethyl; trimethylsilylmethyldimethylsilylmethyl; phenyl; benzyl; or chloro.

[0072] In one or more embodiments, X is –(CH₂)SiR^X₃, in which each R^X is independently a (C₁–C₃₀)alkyl or a (C₁–C₃₀)heteroalkyl and at least one R^X is (C₁–C₃₀)alkyl. In some embodiments, when one of R^X is a (C₁–C₃₀)heteroalkyl, the heteroatom is a silicon or oxygen atom. In some embodiments, R^X is methyl, ethyl, propyl, 2-propyl, butyl, 1,1-dimethylethyl (or *tert*-butyl), pentyl, hexyl, heptyl, n-octyl, *tert*-octyl, or nonyl.

[0073] In one or more embodiments X is –(CH₂)Si(CH₃)₃, –(CH₂)Si(CH₃)₂(C₆H₅), –(CH₂)Si(CH₃)(C₆H₅)₂, –(CH₂)Si(C₆H₅)₃, –(CH₂)Si(CH₃)₂(CH₂C₆H₅), –(CH₂)Si(CH₃)₂(CH₂CH₃); –(CH₂)Si(CH₃)(CH₂CH₃)₂, –(CH₂)Si(CH₂CH₃)₃, –(CH₂)Si(CH₃)₂(n-butyl), –(CH₂)Si(CH₃)₂(n-hexyl), –(CH₂)Si(CH₃)(n-oct)R^X, –(CH₂)Si(CH₃)₂R^X, –(CH₂)Si(n-oct)R^X₂, –(CH₂)Si(CH₃)₂(2-ethylhexyl), –(CH₂)Si(CH₃)₂(dodecyl), or –CH₂Si(CH₃)₂CH₂Si(CH₃)₃ (herein referred to as –CH₂Si(CH₃)₂(CH₂TMS)). Optionally, in some embodiments, in the metal–ligand complex according to formula (I), exactly two R^X are covalently linked or exactly three R^X are covalently linked.

[0074] In some embodiments, X is $-\text{CH}_2\text{Si}(\text{R}^{\text{C}})_{3-\text{Q}}(\text{OR}^{\text{C}})_{\text{Q}}$, $-\text{Si}(\text{R}^{\text{C}})_{3-\text{Q}}(\text{OR}^{\text{C}})_{\text{Q}}$, $-\text{OSi}(\text{R}^{\text{C}})_{3-\text{Q}}(\text{OR}^{\text{C}})_{\text{Q}}$, in which subscript Q is 0, 1, 2 or 3 and each R^{C} is independently a substituted or unsubstituted $(\text{C}_1-\text{C}_{30})$ hydrocarbyl, or a substituted or unsubstituted $(\text{C}_1-\text{C}_{30})$ heterohydrocarbyl. In some embodiments, X is $-\text{CH}_2\text{Si}(\text{CH}_3)_3$.

[0075] In various embodiments, X is methyl, 2,2-dimethylpropyl, trimethylsilylmethyl, (n-butyl)dimethylsilylmethyl, (n-hexyl)dimethylsilylmethyl, (n-octyl)dimethylsilylmethyl, or benzyl.

[0076] Aluminum species

[0077] In one or more embodiments, the aluminum species may 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). The term “alkyl aluminum” means a monoalkyl aluminum dihydride or monoalkylaluminum dihalide, a dialkyl aluminum hydride or dialkyl aluminum halide, or a trialkylaluminum. Examples of polymeric or oligomeric alumoxanes include methylalumoxane, triisobutylaluminum-modified methylalumoxane, and isobutylalumoxane.

[0078] In one or more embodiments, the aluminum species may include Group 13 metal compounds containing $(\text{C}_1-\text{C}_{20})$ hydrocarbyl substituents as described herein. In some embodiments, Group 13 metal compounds are tri $((\text{C}_1-\text{C}_{20})$ hydrocarbyl)-substituted-aluminum. In other embodiments, aluminum species may include tri(hydrocarbyl)-substituted-aluminum, tri $((\text{C}_1-\text{C}_{10})$ alkyl)aluminum, and halogenated (including perhalogenated) derivatives thereof.

[0079] In some embodiments, the aluminum species may include polymeric or oligomeric aluminoxanes, especially methyl aluminoxane, as well as inert, compatible, noncoordinating, ion forming compounds. Exemplary suitable co-catalysts include, but are not limited to modified methyl aluminoxane (MMAO).

[0080] The ratio of total number of moles of one or more metal-ligand complexes of formula (I) to total number of moles of aluminum species is from 1:10,000 to 100:1. In some embodiments, the ratio is at least 1:5000, in some other embodiments, at least 1:1000; and 10:1 or less, and in some other embodiments, 1:1 or less.

[0081] Ethylene/ Acrylate Copolymer

[0082] In various embodiments, the polymerization process of this disclosure may produce a polar ethylene-based copolymer, in which the polar ethylene-based copolymer contains at least 50 percent by weight (wt.%) ethylene based on the weight of the polar ethylene-based copolymer. In

some embodiments, the polar ethylene-based copolymer is the reaction product of 70 wt% to 99.9 wt.% ethylene units and 0.1 wt.% to 30 wt.% polar comonomer units based on the sum of the ethylene units and the polar comonomer units.

[0083] In one or more embodiments, the polymerization process of this disclosure may include ethylene monomers, alkyl acrylate monomers, and optionally one or more α -olefins. In some embodiments of the polymerization process which includes α -olefins, the α -olefins may be incorporated into the produced polymers in amounts of from 0.01 wt.% to 49.9 wt.% based on the weight of the ethylene-based copolymer.

[0084] In various embodiments, the polymerization process of this disclosure may produce ethylene-based copolymer with a molecular weight of from 2,000 g/mol to 1,000,000 g/mol. In some embodiments, the produced polymer has a molecular weight of from 25,000 g/mol to 900,000 g/mol, from 30,000 g/mol to 800,000 g/mol, or from 10,000 g/mol to 300,000 g/mol.

[0085] GPC Procedure

[0086] The chromatographic system consisted of a PolymerChar GPC-IR (Valencia, Spain) high temperature GPC chromatograph equipped with an internal IR5 infra-red detector (IR5). The autosampler oven compartment was set at 160° Celsius and the column compartment was set at 150° Celsius. The columns used were 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns. The chromatographic solvent used was 1,2,4 trichlorobenzene and contained 200 ppm of butylated hydroxytoluene (BHT). The solvent source was nitrogen sparged. The injection volume used was 200 microliters and the flow rate was 1.0 milliliters/minute.

[0087] Calibration of the GPC column set was performed with a series of narrow molecular weight distribution polystyrene standards with molecular weights ranging from 580 up to 8,400,000 g/mol. The standards were purchased from Agilent Technologies. The polystyrene standards were prepared at 0.025 grams in 50 milliliters of solvent for molecular weights equal to or greater than 1,000,000, and 0.05 grams in 50 milliliters of solvent for molecular weights less than 1,000,000. The polystyrene standards were pre-dissolved at 80 °C with gentle agitation for 30 minutes then cooled and the room temperature solution is transferred cooled into the autosampler dissolution oven at 160°C for 30 minutes. The polystyrene standard peak molecular weights were converted to polyethylene molecular weights using Equation 1 (as described in Williams and Ward, J. Polym. Sci., Polym. Let., 6, 621 (1968)).:

$$M_{polyethylene} = A \times (M_{polystyrene})^B \quad (EQ1)$$

where M is the molecular weight, A has a value of 0.4117 and B is equal to 1.0.

[0088] A fifth order polynomial was used to fit the respective polyethylene-equivalent calibration points.

[0089] The total plate count of the GPC column set was performed with decane which was introduced into blank sample via a micropump controlled with the PolymerChar GPC-IR system. The plate count for the chromatographic system should be greater than 18,000 for the 4 Agilent “Mixed A” 30cm 20-micron linear mixed-bed columns.

[0090] Samples were prepared in a semi-automatic manner with the PolymerChar “Instrument Control” Software, wherein the samples were weight-targeted at 2 mg/ml, and the solvent (contained 200ppm BHT) was added to a pre nitrogen-sparged septa-capped vial, via the PolymerChar high temperature autosampler. The samples were dissolved for 2 hours at 160° Celsius under “low speed” shaking.

[0091] The calculations of $Mn_{(GPC)}$, $Mw_{(GPC)}$, and $Mz_{(GPC)}$ were based on GPC results using the internal IR5 detector (measurement channel) of the PolymerChar GPC-IR chromatograph according to Equations 2-4, using PolymerChar GPCOne™ software, the baseline-subtracted IR chromatogram at each equally-spaced data collection point (i), and the polyethylene equivalent molecular weight obtained from the narrow standard calibration curve for the point (i) from Equation 1.

$$Mn_{(GPC)} = \frac{\sum_i IR_i}{\sum_i \left(IR_i / M_{polyethylene_i} \right)} \quad (EQ\ 2)$$

$$Mw_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i})}{\sum_i IR_i} \quad (EQ\ 3)$$

$$Mz_{(GPC)} = \frac{\sum_i (IR_i * M_{polyethylene_i}^2)}{\sum_i (IR_i * M_{polyethylene_i})} \quad (EQ\ 4)$$

[0092] In order to monitor the deviations over time, a flowrate marker (decane) was introduced into each sample via a micropump controlled with the PolymerChar GPC-IR system. This flowrate marker (FM) was used to linearly correct the pump flowrate (Flowrate(nominal)) for each sample by RV alignment of the respective decane peak within the sample (RV(FM Sample)) to that of the decane peak within the narrow standards calibration (RV(FM Calibrated)). Any changes in the time of the decane marker peak are then assumed to be related to a linear-shift in flowrate (Flowrate(effective)) for the entire run. After calibrating the system based on a flow marker peak, the effective flowrate (with respect to the narrow standards calibration) is calculated as Equation 5. Processing of the flow marker peak was done via the PolymerChar GPCOne™ Software. Acceptable flowrate correction is such that the effective flowrate should be within +/- 0.5% of the nominal flowrate.

[0093]
$$\text{Flowrate(effective)} = \text{Flowrate(nominal)} * (\text{RV(FM Calibrated)} / \text{RV(FM Sample)}) \quad (\text{EQ5})$$

[0094] **FT-IR Procedure**

[0095] *Tert*-butyl acrylate (tBA) incorporation was quantified by Fourier transform infrared spectroscopy (FTIR). Samples with varying concentrations of tBA (~8 to 28 wt.%) were produced at the high pressure miniplants and the tBA content was measured by NMR. The samples were compression molded into thin (~10 mil) films using a Carver press with heated platens at 190C. IR spectra were collected from the films using a Thermo Nicolet 6700 FT-IR equipped with a DTGS KBr detector from 4000-400 cm⁻¹ utilizing 64 scans with a resolution of 4 cm⁻¹. Ratio of tBA (C=O overtone at 3438 cm⁻¹) to ethylene combination band (CH₂: 4253 cm⁻¹) peak heights were calculated and fit to a linear calibration curve to determine total tBA.

[0096] **¹³C Nuclear Magnetic Resonance Spectroscopy for Measuring tBA Content**

[0097] Samples for ¹³C NMR were prepared by adding approximately 3g of 1,1,2,2-tetrachloroethane (TCE) containing 25 wt% TCE-d₂ and 0.025 M Cr(AcAc)₃, to about 0.30 g polymer sample, in a 10 mm NMR tube. The samples were dissolved and homogenized by heating the tube and its contents to 115 °C using a heating block and vortex mixer. Each dissolved sample was visually inspected to ensure homogeneity. Samples were thoroughly mixed immediately prior to analysis and were not allowed to cool before insertion into the heated NMR sample holders.

[0098] All data were collected using a Bruker 600 MHz spectrometer equipped with a 10 mm high temperature cryoprobe. The ¹³C data was acquired using a 7.8 second pulse repetition delay, 90-degree flip angles, and inverse gated decoupling, with a sample temperature of 100 or 120 °C.

All measurements were made on non-spinning samples in locked mode. Samples were allowed to thermally equilibrate prior to data acquisition. The ^{13}C NMR chemical shifts were internally referenced to the EEE triad at 30.0 ppm.

[0099] *t*-Butylacrylate comonomer was quantitated using four peak areas, corresponding to the carbonyls at about 176 ppm, the $\text{CH}_2\text{-O-}$ at about 80 ppm, the quaternary carbon at about 47 ppm and the *t*-butyl methyls at about 28.5 ppm.

[00100] DSC Procedure

[00101] In preparation for Differential Scanning Calorimetry (DSC) testing, pellet-form samples are first loaded into a 1 in. diameter chase of 0.13 mm thickness and compression molded into a film under 25,000 lbs of pressure at 190°C for approximately 10 seconds. The resulting film is then cooled to room temperature. The film is then subjected to a punch press in order to extract a disk that will fit the aluminum DSC test pan. The sample weight is approximately 5-6mg. The disk is then weighed individually, placed into the aluminum pan, and sealed before being inserted into the DSC test chamber.

[00102] In reference to ASTM standard D3418, the DSC test is conducted using a heat-cool-heat cycle. First, the sample is equilibrated at 180°C and held isothermally for 5min. to remove thermal and process history. The sample is then quenched to below -40°C at a rate of 10°C/min. and held isothermally once again for 5min. Lastly, the sample is heated at a rate of 10 °C/min. to 150°C for the second heating cycle. For data analysis, the melting temperatures and enthalpy of fusion is extracted from the second heating curve, whereas the enthalpy of crystallization is determined from the cooling curve. The enthalpy of fusion and crystallization are obtained by integrating the DSC thermogram from -20°C to the end of melting and crystallization, respectively. The heat of fusion of 100% crystalline polyethylene is taken to be 292 J/g to calculate wt% crystallinity. The DSC tests are performed using the TA Instruments Discovery DSCs, and data analyses are conducted via TA Instruments Universal Analysis.

[00103] Catalyst Efficiency Calculation

[00104] Catalyst efficiency ($\text{g}_{\text{poly}}/\text{g}_{\text{metal}}$) was calculated by analyzing polymer samples using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The samples were weighed into quartz crucibles and approximately 2 mL of sulfuric acid was added. Duplicates of each sample were ashed in a muffle furnace at 550° C until all of the organic components were removed. The ash was then dissolved in aqua regia on a hotplate. The samples were diluted to weight with deionized water and analyzed using ICP-AES.

<u>Operational Parameters</u>	(Optima 8300DV: PerkinElmer, Shelton, CT)	
Power:	1500	Watts
Plasma Gas:	15	L/minute (argon)
Auxiliary Gas:	0.2	L/minute (argon)
Nebulizer Flow:	0.6	L/minute (argon)
Sample uptake:	1.5	mL/minute

EXAMPLES

[00105] Example 1 is the synthetic procedures for ligand intermediates, ligands, nickel precursors, and nickel precatalysts. Examples IE1 to IE8 are high pressure copolymerization reactions of Ni Catalyst 1, which are tabulated and discussed. Examples CE1 to CE7 are comparative examples. One or more features of the present disclosure are illustrated in view of the examples as follows:

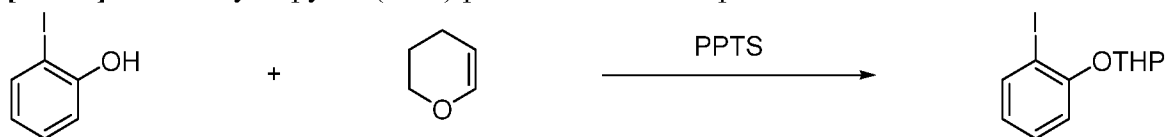
[00106] General Synthesis Considerations

[00107] All synthetic reactions were performed in a nitrogen-purged glove box unless otherwise noted. All solvents and reagents were obtained from commercial sources and used as received unless otherwise noted. Anhydrous toluene, hexanes, tetrahydrofuran, and diethyl ether were purified *via* passage through activated alumina and, in some cases, Q-5 reactant. Alumina for solvent purification was activated by passing a stream of nitrogen through the alumina for 8 hours at 300 °C. Q-5 reactant was activated by heating at 200 °C under a stream of nitrogen for 4 hours, followed by a stream of 5% hydrogen in nitrogen at 200 °C for 3 hours, and finally flushing with nitrogen gas. Solvents used for experiments performed in a nitrogen-filled glovebox were further dried by storage over activated 4Å molecular sieves. Glassware for moisture-sensitive reactions was dried in an oven overnight prior to use. HRMS analyses were performed using an Agilent 1290 Infinity LC with a Zorbax Eclipse Plus C18 1.8 µm 2.1x50 mm column coupled with an Agilent 6230 TOF Mass Spectrometer with electrospray ionization. NMR spectra were recorded on Varian 400-MR and VNMR5-500 spectrometers. ¹H NMR data are reported as follows: chemical shift (multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, sept = septet and m = multiplet), integration, and assignment). Chemical shifts for ¹H NMR data are reported in ppm downfield from tetramethylsilane (TMS, δ scale) using residual protons in the deuterated solvent as references. ¹³C NMR data were determined with ¹H decoupling, and the chemical shifts are reported in ppm versus tetramethylsilane. ¹³C NMR spectra of phosphines were complex due to C-P coupling. Chemical shifts for ³¹P NMR data

are reported in ppm relative to external neat H_3PO_4 . Deuterated solvents for NMR analyses were purchased from Cambridge Isotope Laboratories and stored over activated 4Å molecular sieves in a nitrogen-purged glove box.

[00108] Example 1 – Synthesis of Ni catalyst:

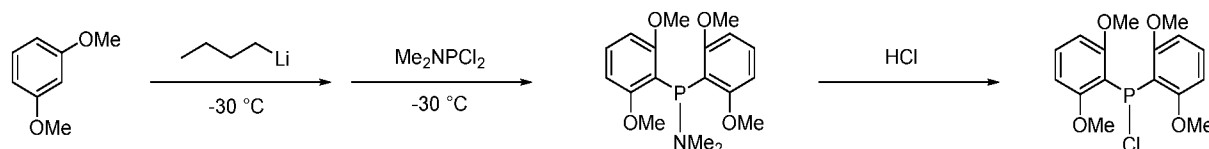
[00109] Tetrahydropyran (THP) protection of 2-iodophenol



[00110] Reaction was set up in a nitrogen atmosphere glovebox. An oven-dried 500 mL 3-necked round bottom flask with a stir bar was charged with 2-iodophenol (98.87 g, 449.38 mmol), pyridinium p-toluenesulfonate (11.29 g, 44.94 mmol), and anhydrous degassed methylene chloride (250 mL). The 3,4-dihydropyran (DHP, 102.50 mL, 1123.44 mmol) was loaded into an addition funnel, capped, and fitted to the middle neck of the flask. The other flask necks were capped with rubber septa and the set-up was moved to the fume hood. The flask was put under a nitrogen purge and the DHP was added dropwise over 45 minutes. An exotherm (from 16.6 to 40.4 °C) was observed while the temperature peaked when the addition was approximately 75% complete, after which the temperature began to fall. The reaction solution was sampled immediately after the DHP addition was complete (temperature was 28.4 °C) to check for reaction completion by GC/MS and ^1H NMR. Once reaction was determined to be complete (20 minutes later), the reaction solution was transferred to a separatory funnel and washed with brine (2 X 135 mL). The organic phase was dried over MgSO_4 then filtered. The solvent was removed by rotovap, resulting in 136.77 g of gold-colored oil. Analysis (NMR and GC/MS) showed traces of the starting phenol, so the product oil was moved to a glovebox, dissolved in 500 mL dry THF, followed by the addition of sodium methoxide (13.11 g, 242.66 mmol) to the solution. After stirring for 10 minutes, the flask was capped and transferred to the fume hood and passed through a short column of basic alumina. The column was pre-wetted with 10% EtOAc/hexane, and after the product solution was passed through the column, it was further rinsed with a total of 300 mL of the 10% EtOAc/hexane. The solvent was removed in vacuo, resulting in 135.55 g of a gold oil. After analysis by ^1H NMR, residual THF was removed by dissolving in dry dichloromethane (DCM), followed by drying under reduced pressure. Final product analysis of the 135.20 g (98.9%) of gold oil showed desired product (GC/MS and NMR).

[00111] ^1H NMR (400 MHz, Chloroform- d) δ 7.77 (dd, J = 7.8, 1.6 Hz, 1H), 7.27 (ddd, J = 8.3, 7.3, 1.6 Hz, 1H), 7.08 (dd, J = 8.3, 1.4 Hz, 1H), 6.73 (td, J = 7.6, 1.4 Hz, 1H), 5.54 (t, J = 2.9 Hz, 1H), 3.87 (td, J = 11.1, 2.9 Hz, 1H), 3.60 (dddd, J = 11.4, 4.5, 3.0, 1.6 Hz, 1H), 2.26 – 2.09 (m, 1H), 2.05 – 1.95 (m, 1H), 1.87 (dddd, J = 13.5, 11.9, 4.2, 3.1 Hz, 1H), 1.81 – 1.46 (m, 3H). ^{13}C NMR (101 MHz, Chloroform- d) δ 155.55, 139.29, 129.36, 123.28, 115.17, 96.50, 87.45, 61.72, 30.21, 25.25, 18.30.

[00112] Synthesis of chlorobis(2,6-dimethoxyphenyl)phosphine



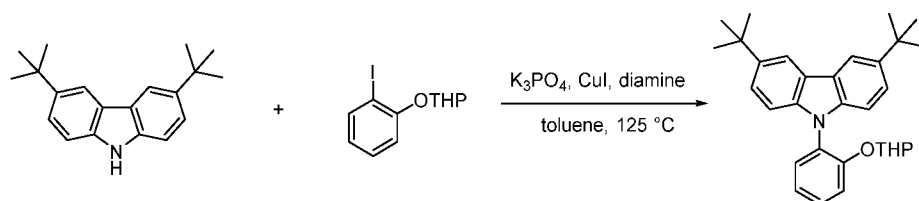
[00113] The reaction was carried out in a nitrogen atmosphere glovebox. n-BuLi was titrated prior to the reaction to check the solution concentration, and all glassware was oven-dried prior to use.

[00114] n-BuLi in hexanes (93.23 mL, 2.69 M, 250.79 mmol) was added to a 1 L jar (with stirbar) containing a -35 °C solution of 1,3-dimethoxybenzene (35.00 g, 253.32 mmol) in 400 mL THF. The solution was allowed to warm to ambient temperature and was stirred for 4 hours. The solution was cooled to -35 °C and dimethylphosphoramidous dichloride (18.32 g, 125.52 mmol) in 33 mL THF was slowly added dropwise. The reaction mixture was allowed to warm to room temperature while stirring overnight to give a yellow solution containing some precipitate. An aliquot was removed for ^{31}P NMR analysis which showed the starting Me₂NPCl₂ had been consumed. HCl in diethyl ether solution (146.93 mL, 2.0 M, 293.85 mmol) was added via syringe over the course of 10-15 minutes. Precipitate began to form immediately upon HCl addition. The reaction mixture was stirred overnight.

[00115] Volatiles were removed under reduced pressure. The residue was extracted with toluene (800 mL with vigorous stirring), filtered to produce a slightly cloudy solution, and toluene was removed under reduced pressure. Another 800 mL toluene was added, the mixture was filtered through Celite® to form a clear filtrate, and the toluene was removed under reduced pressure. The resulting white solid was triturated with 200-300 mL hexanes, filtered, washed with hexanes, and the resulting white solids were dried under reduced pressure and isolated to yield 32.60 g (75.6%) of the desired product.

[00116] ^1H NMR (400 MHz, Benzene- d_6) δ 7.05 (td, J = 8.3, 1.3 Hz, 2H), 6.23 (dd, J = 8.3, 2.8 Hz, 4H), 3.26 (s, 12H). ^{13}C NMR (101 MHz, Benzene- d_6) δ 162.34, 162.22, 131.06, 116.92, 116.40, 104.31, 55.32. ^{31}P NMR (162 MHz, Benzene- d_6) δ 60.33.

[00117] Synthesis of 3,6-di-tert-butyl-9-(2-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)-9H-carbazole

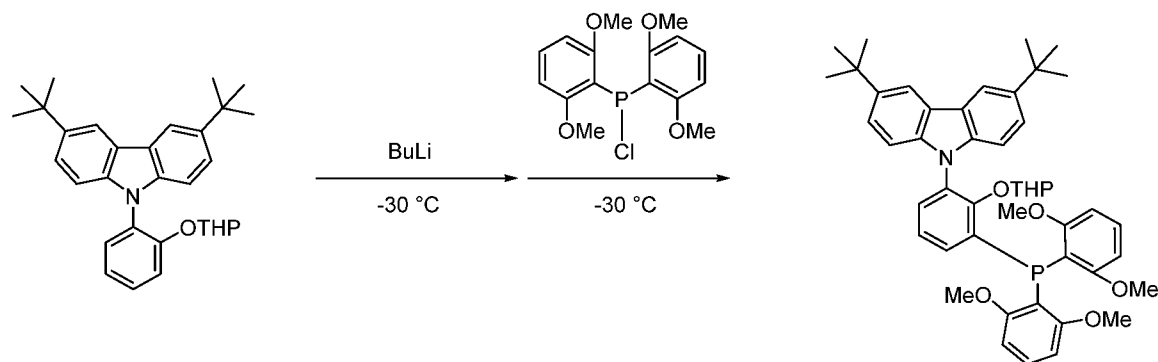


[00118] An oven-dried 2 L 2-necked round bottom flask with stir bar was transferred to a glove box. The flask was charged with 3,6-di-tert-butyl-9-(2-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)-9H-carbazole (69.40 g, 246.6 mmol), 2-(2-iodophenoxy)tetrahydro-2H-pyran (112.49 g, 369.88 mmol), K_3PO_4 (179.01 g, 843.33 mmol) and anhydrous degassed toluene (560 mL). Copper (I) iodide (2.02 g, 10.6 mmol) and $\text{N,N}'$ -dimethylethylenediamine (4.04 mL, 37.0 mmol) were weighed into a jar along with 65 mL toluene. This mixture was added to the carbazole solution, using a small amount of toluene to make sure the slurry was completely transferred. After the CuI solution was added, the solution turned olive green. The flask was fitted with a condenser (with rubber septum) and a rubber septum to close the other neck. The flask was transferred to a fume hood and put under a nitrogen sweep. The reaction solution was heated (heating block temperature set to $125\text{ }^\circ\text{C}$) for a total of 19 hours, sampling at 18 hours and analyzing by GC/MS to check for reaction completion. The solution was cooled to room temperature and filtered through a short silica plug (pre-washed with THF). The silica plug was rinsed with THF (4 X 400 mL) to ensure the product was flushed through. The filtrate was concentrated by rotovap resulting in a dark oil. Acetonitrile (1 L) was added and the mixture was stirred vigorously using an overhead stirrer until solids formed (which was almost immediately). Vigorous stirring for 30 minutes resulted in a solution that looked uniform and creamy. The slurry was filtered, and the solids rinsed with additional cold acetonitrile (3 X 300 mL). Volatiles were removed by rotovap, followed by addition of several hundred mL of methylene chloride and removal of all volatiles by rotovap. After drying further under reduced pressure, the resulting off-white solids (80.23 g, 71.1%) were analyzed by ^1H and ^{13}C NMR.

[00119] ^1H NMR (400 MHz, Chloroform- d) δ 8.13 (d, J = 1.9 Hz, 2H), 7.49 (dt, J = 7.7, 1.0 Hz, 1H), 7.46 – 7.38 (m, 4H), 7.20 – 7.14 (m, 2H), 7.10 (dd, J = 8.6, 0.6 Hz, 1H), 5.28 (t, J = 2.9

Hz, 1H), 3.71 (td, $J = 11.2, 2.9$ Hz, 1H), 3.54 – 3.45 (m, 1H), 1.46 (s, 18H), 1.43 – 1.36 (m, 1H), 1.33 – 1.00 (m, 5H). ^{13}C NMR (101 MHz, Chloroform- d) δ 153.86, 142.71, 140.40, 130.01, 129.41, 127.91, 123.66, 123.61, 123.60, 123.51, 122.55, 117.55, 116.34, 116.21, 110.69, 110.07, 97.31, 62.03, 35.16, 32.51, 30.40, 25.46, 17.94.

[00120] Synthesis of 9-(3-(bis(2,6-dimethoxyphenyl)phosphanyl)-2-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)-3,6-di-tert-butyl-9H-carbazole

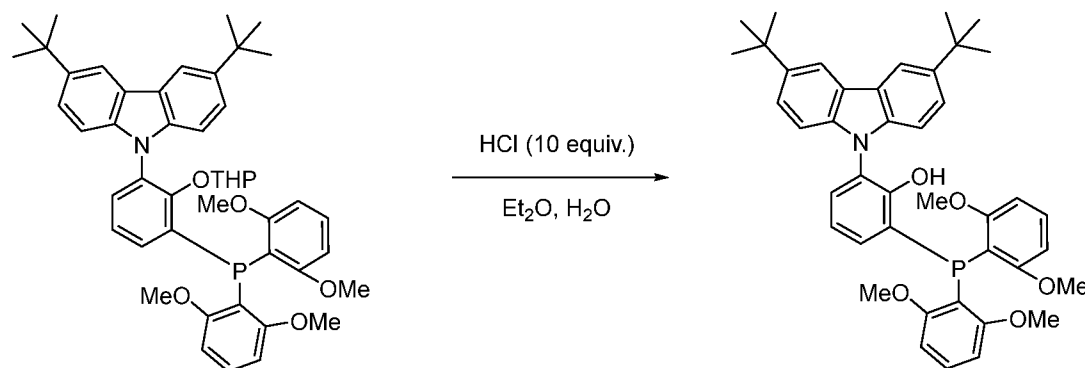


[00121] $n\text{-BuLi}$ was titrated prior to the reaction to check the solution concentration, and all glassware was oven-dried prior to use. In a nitrogen atmosphere glove box, a glass jar with stirbar was charged with 3,6-di-tert-butyl-9-(2-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)-9H-carbazole (36.50 g, 80.11 mmol) and 215 mL anhydrous THF. The solution was cooled in the dry box freezer ($-35\text{ }^{\circ}\text{C}$) for 60 min. The solution was removed from the freezer and the $n\text{-BuLi}$ (28.2 mL, 81.2 mmol, 2.29 M) was added dropwise over 9 minutes. The solution was allowed to warm up to room temperature and sampled at 180 min to determine reaction completion. To prepare the reaction aliquot, a small amount of the solution was quenched with CD_3OD , and the THF layer was analyzed by GC/MS. During the reaction time, the chlorobis(2,6-dimethoxyphenyl)phosphine (24.59 g, 72.10 mmol) was added to a jar along with 135 mL anhydrous THF and placed in the $-35\text{ }^{\circ}\text{C}$ freezer for approximately one hour. Once the lithiation was determined to be complete by GC/MS, the solution was returned to the freezer for 55 minutes. The reaction solution was moved out of the freezer and the chlorophosphine solution added dropwise to the reaction solution. The resulting solution was allowed to warm up to room temperature overnight. ^{31}P NMR analysis (C_6D_6) showed the reaction was complete with all the chlorophosphine starting material consumed. The solvents were removed in vacuo to produce a dark oily residue. To help remove the residual THF, 275 mL of hexanes were added to the product material and stirred vigorously, then the solvents removed under vacuum. A second round of hexane (275 mL) was added and the slurry was filtered. The filtered solids were rinsed with more

hexane, and then dried under vacuum overnight resulting in 52 g of solids. The solids were mixed with ~175 mL toluene, then filtered through Celite®. More toluene was used to rinse the solids and combined with the original filtrate. The filtrate was dried under vacuum at 50 °C overnight. Hexanes were added and volatiles removed under reduced pressure to remove any residual toluene. The product was dried under vacuum overnight resulting in 48.44 g (88.3%) product verified by NMR.

[00122] ¹H NMR (400 MHz, Benzene-d₆) δ 8.38 (d, J = 1.9 Hz, 2H), 7.58 – 7.49 (m, 3H), 7.43 (d, J = 8.7 Hz, 1H), 7.35 (d, J = 8.6 Hz, 1H), 7.17 (d, J = 0.9 Hz, 1H), 6.86 (td, J = 7.7, 0.8 Hz, 1H), 6.37 (dt, J = 8.3, 2.8 Hz, 4H), 5.37 (s, 1H), 4.01 – 3.79 (m, 1H), 3.19 (d, J = 2.2 Hz, 12H), 3.12 – 3.02 (m, 1H), 1.79 (dd, J = 14.4, 10.2 Hz, 1H), 1.61 – 1.51 (m, 1H), 1.43 (s, 18H), 1.33 – 0.82 (m, 6H). ¹³C NMR (101 MHz, Benzene-d₆) δ 163.43, 163.37, 163.33, 163.28, 155.49, 155.28, 142.43, 142.38, 140.24, 140.19, 137.04, 136.87, 133.50, 130.34, 130.30, 130.00, 129.94, 124.15, 124.02, 123.89, 123.70, 122.74, 116.30, 116.25, 115.35, 115.09, 114.80, 114.53, 111.34, 104.70, 104.53, 100.21, 100.14, 61.51, 61.41, 55.59, 55.55, 34.79, 32.21, 30.29, 25.53, 17.88, 17.86. ³¹P NMR (162 MHz, Benzene-d₆) δ -52.45.

[00123] Synthesis of 2-(bis(2,6-dimethoxyphenyl)phosphanyl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenol

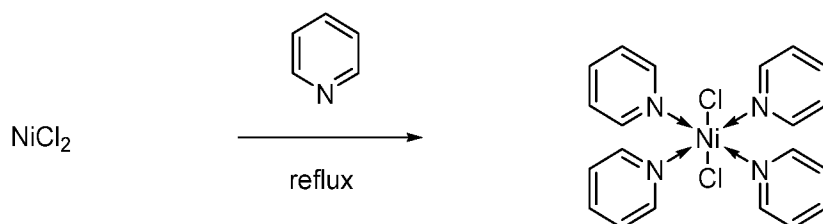


[00124] The glassware was oven dried. In a nitrogen atmosphere glovebox, a multi-neck 2 L round bottom flask equipped with a magnetic stir bar was charged with 9-(3-(bis(2,6-dimethoxyphenyl)phosphanyl)-2-((tetrahydro-2H-pyran-2-yl)oxy)phenyl)-3,6-di-tert-butyl-9H-carbazole (60.00 g, 78.96 mmol) and diethyl ether (550 mL) and stirred to produce a yellow, slightly cloudy solution. The middle neck of the flask was fitted with an addition funnel (500 mL) and the others sealed with rubber septa. The HCl in ether (394.78 mL, 789.55 mmol) was loaded into the addition funnel and it was also sealed with a rubber septum. The reaction mixture was removed from the glovebox and transferred to the fume hood and put under a nitrogen pad.

Degassed water (170 mL) was added which resulted in two phases that were light brown in color. The solution of HCl in diethyl ether was added dropwise to the reaction mixture over 55 minutes. There appeared to be white solids that crashed out of solution in the bottom phase upon HCl addition. The reaction was heated at 40 °C (heating block temperature) overnight. The organic layer was sampled and dried and then analyzed by ^1H and ^{31}P NMR spectroscopy. Upon determination of reaction completion, the reaction was allowed to cool to room temperature and water (360 mL) was added to the reaction mixture. Sodium bicarbonate (1.1 equiv. with respect to HCl) was cautiously added in portions to the reaction mixture. After allowing to stir briefly, the ether was mostly removed under reduced pressure. To the residue was added dichloromethane (650 mL) until the solids dissolved into solution. The solution was stirred well, then transferred to a separatory funnel and the phases were separated. A saturated solution of sodium bicarbonate (1.4 L) was added to the organic phase and the mixture was shaken vigorously for less than 1 minute. The phases were separated. The organic phase was dried over sodium sulfate, filtered, and concentrated under vacuum to afford a light brown solid. NMR analysis showed product with some impurities (51.87 g). The solids were triturated in ~250 mL hot methanol (~40 °C), filtered, and washed with more hot methanol. After drying several hours with the hood vacuum, the white solids (37.8 g, 70.8%) were isolated and the product analyzed by NMR.

[00125] ^1H NMR (400 MHz, Benzene- d_6) δ 8.36 (dd, J = 2.0, 0.6 Hz, 2H), 8.07 (ddd, J = 11.6, 7.6, 1.7 Hz, 1H), 7.49 – 7.37 (m, 3H), 7.25 (dt, J = 8.0, 1.1 Hz, 3H), 7.01 (td, J = 8.3, 1.1 Hz, 2H), 6.83 (td, J = 7.7, 1.4 Hz, 1H), 6.21 (dd, J = 8.3, 2.9 Hz, 4H), 3.12 (s, 12H), 1.42 (s, 18H). ^{13}C NMR (101 MHz, Benzene- d_6) δ 161.86, 161.78, 155.84, 155.78, 141.76, 140.27, 135.51, 135.15, 129.66, 129.49, 127.91, 127.67, 127.43, 123.97, 123.66, 123.32, 119.19, 119.06, 116.02, 113.00, 112.78, 110.26, 104.09, 55.09, 34.41, 31.88. ^{31}P NMR (162 MHz, Benzene- d_6) δ -58.87.

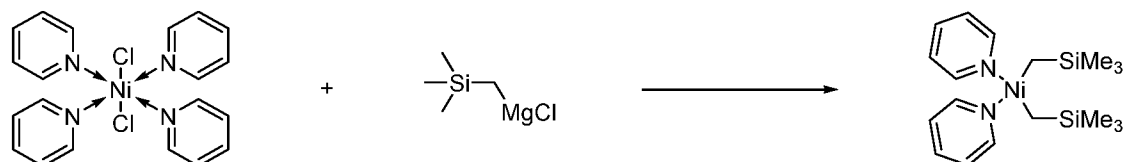
[00126] Synthesis of tetrakis(pyridine)nickel dichloride



[00127] In a nitrogen atmosphere glovebox, a 500 mL round bottom flask with stir bar was charged with NiCl_2 (25.318 g, 195.37 mmol) and anhydrous pyridine (253.2 mL, 3143.5 mmol). The flask was equipped with a Stevens condenser and moved to a fume hood. The reaction was heated to reflux for 3 hrs (boiling point of pyridine is 115 °C). The yellow/orange NiCl_2 was not

appreciably soluble in room temperature pyridine. After refluxing briefly, a turquoise precipitate was observed. After 3 hrs, a bright blue precipitate was observed. The hot plate was turned off and the solution allowed to cool overnight. The suspension was filtered, washed with hexane, and dried in vacuo to afford the product as a bright blue powder (83.09 g, 95.8%). The material was used without purification or characterization.

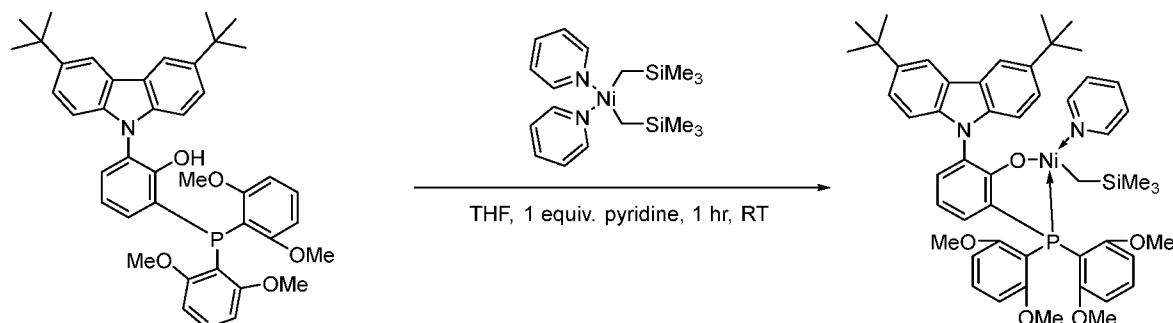
[00128] Synthesis of bis(pyridine)bis((trimethylsilyl)methyl)nickel



[00129] In a nitrogen atmosphere glovebox, a 32 ounce jar with stir bar was charged with tetrakis(pyridine)nickel dichloride (34.67 g, 77.74 mmol), anhydrous pyridine (19.1 mL, 237.1 mmol), and 630 mL diethyl ether. The jar was cooled in a $-30\text{ }^{\circ}\text{C}$ freezer for 2 hours. ((Trimethylsilyl)methyl)magnesium chloride solution in diethyl ether (1.03 M, 150.94 mL, 155.47 mmol) was added using an addition funnel over 1 hr. Upon addition completion, the reaction was stirred for 25 minutes. The solution was concentrated in vacuo, resulting in a thick slurry. A mixture of pentane (875 mL) and pyridine (21 mL) was prepared. Some of the pentane/pyridine solution was stirred into the product slurry, then filtered through Celite®. The remaining solution was used to rinse the solids. An additional pentane/pyridine solution as well as hexane was used for the rinsing. Filtration was slow. The filtrate was reduced during the vacuum filtration resulting in the precipitation of a solid. The filtrate was transferred to a 32 oz jar and hexane/pentane was used to rinse out the filter frit. The jar was capped and moved to the glove box freezer. After several days, the solution was decanted off and the solids lightly rinsed with cold hexane. The crystalline solids (brown needles) were dried under vacuum at room temperature overnight (resulting in 20.72 g), then analyzed by NMR. The decant and rinses were dried in vacuo, then enough hexane was added to mostly dissolve the solids. The solution was moved to the dry box freezer for recrystallization and after several days resulted in 4.85 g solids. The decant and rinses were again dried down and after some time in the freezer with fresh Hexane, the 3rd crop (1.04 g) was obtained. Yield = 87.5%.

[00130] ^1H NMR (400 MHz, Benzene- d_6) δ 8.63 – 8.18 (m, 4H), 6.64 (t, J = 7.6 Hz, 2H), 6.22 (s, 4H), 0.65 – 0.25 (m, 18H), -0.59 (s, 4H). ^{13}C NMR (101 MHz, Benzene- d_6) δ 150.16, 134.26, 122.99, 3.52, 0.22.

[00131] Synthesis of (2-bis((2,6-dimethoxyphenyl)phosphanyl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenolate)nickel(pyridine)trimethylsilylmethyl (Metallation)

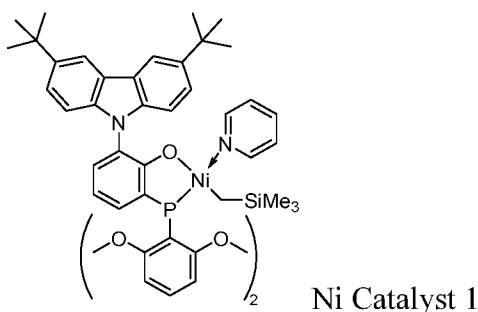


[00132] In a nitrogen atmosphere glovebox, a solution of 2-(bis(2,6-dimethoxyphenyl)phosphanyl)-6-(3,6-di-tert-butyl-9H-carbazol-9-yl)phenol (75.00 g, 111.0 mmol) in 1.13 L THF was prepared. Separately in the glovebox, a solution of bis(pyridine)bis(trimethylsilylmethyl)nickel (43.43 g, 111.0 mmol) in 563 mL THF containing 1 equiv. pyridine was prepared and added to the 6 L jacketed glass reactor. The ligand solution was added (in batches) to a 500 mL addition funnel and the ligand was added to the Ni precursor solution over the course of 25-30 minutes give a dark red-brown solution which was stirred at ambient temperature. An aliquot was dried and the reaction was monitored by ^{31}P NMR. After 60 minutes reaction time ($t = 0$ when ligand solution was completely added into reactor), the reaction was complete based on disappearance of the starting material peak in the ^{31}P NMR spectrum. The volatiles were removed under reduced pressure. The residue was triturated with 1 L of pentane and collected by filtration to yield an orange/rust colored solid that was analyzed by ^1H , ^{13}C , and ^{31}P NMR. To remove residual THF, the solids were transferred back into the (clean) 6 L reactor and ~1 L of toluene was added. Volatiles were removed overnight under reduced pressure at 35 °C. The resulting dried orange solid was collected and analyzed by NMR which showed the desired product (77.0 g) in quantitative yield.

[00133] ^1H NMR (400 MHz, Benzene- d_6) δ 8.75 – 8.59 (m, 2H), 8.39 (d, $J = 1.9$ Hz, 2H), 7.91 (ddd, $J = 10.5, 7.6, 1.7$ Hz, 1H), 7.65 (d, $J = 8.6$ Hz, 2H), 7.50 (dd, $J = 8.6, 2.0$ Hz, 2H), 7.43 (dd, $J = 7.4, 1.7$ Hz, 1H), 7.12 (t, $J = 8.1$ Hz, 3H), 6.65 (tt, $J = 7.6, 1.6$ Hz, 1H), 6.55 (td, $J = 7.5, 2.1$ Hz, 1H), 6.29 (dt, $J = 7.2, 2.7$ Hz, 6H), 3.30 (s, 12H), 1.47 (s, 18H), -0.11 (s, 9H), -0.66 (d, $J = 9.3$ Hz, 2H). ^{13}C NMR (101 MHz, Benzene- d_6) δ 159.70, 149.33, 139.00, 138.44, 133.97, 128.58, 121.51, 121.01, 113.76, 109.97, 102.66, 102.62, 53.26, 32.70, 30.34, 0.22. ^{31}P NMR (162 MHz, Benzene- d_6) δ -7.17.

[00134] Examples IE1 to IE8 and CE1 – Polymerization Process for the high pressure reactor.

[00135] In Table 1, the polymerization processes to produce linear ethylene copolymers was tabulated. Experiments were conducted in an outdoor miniplant. The procedure for the high pressure reactor campaign included feeding purified ethylene at 7 pph that was mixed with purified tert-butyl acrylate. Tert-butyl acrylate was supplied with 10-20 mass ppm methyl hydroquinone to prevent self-polymerization. As part of sample preparation, 100 mass ppm of 4-hydroxy TEMPO was added to the tert-butyl acrylate and then the tert-butyl acrylate was nitrogen purged to remove residual oxygen. The tert-butyl acrylate was then purified across an AZ-300 absorption bed as it was fed to the process, primarily to remove the methyl hydroquinone and 4-hydroxy TEMPO as well as other impurities. The feed of ethylene and tert-butyl acrylate was then compressed and pressurized to 2000 barg in two stages creating a supercritical ethylene stream. The supercritical ethylene stream was then fed to a 300 mL continuously stirred tank reactor. Reactor temperature was controlled to target temperature using 4 electric heating bands on the wall of the reactor. Separately, a mixture of Ni catalyst 1 diluted in toluene at varying concentrations (abbreviated “conc.” in the Tables) was fed to the reactor. The feed was controlled to target a set concentration of Ni in the reactor. In some cases, a mixture of MMAO-3A diluted in Isopar E at varying concentrations was additionally separately fed. After exiting the reactor, the stream was rapidly depressurized across a valve to 1 barg to separate the ethylene from the polymerized material. An oxygen/nitrogen mixture was added to the stream to neutralize the catalyst and freeze the polymer.



[00136] Example CE2 Low Pressure Solution Batch Reactor Polymerization Process to produce linear polar ethylene copolymers

[00137] Polymerization reactions were conducted in a 2 L Parr batch reactor. The reactor was heated by an electrical heating mantle and was cooled by an internal serpentine cooling coil containing cooling water. The water was pre-treated by passing through an Evoqua water

purification system. Both the reactor and the heating/cooling system were controlled and monitored by a Camile TG process computer. The bottom of the reactor was fitted with a dump valve, which emptied the reactor contents into a lidded dump pot. The dump pot was prefilled with a catalyst kill solution (typically 5 mL of an Irgafos / Irganox / toluene mixture). The lidded dump pot was vented to a 15 gal. blow-down tank, with both the pot and the tank being N₂-purged. All chemicals used for polymerization or catalyst makeup were run through purification columns in order to remove any impurities that may affect polymerization. The toluene was passed through two columns, the first containing A2 alumina and the second containing Q5 reactant. The *tert*-butyl acrylate was filtered through activated alumina. The ethylene was passed through two columns, the first containing A204 alumina and 4Å molecular sieves and the second containing Q5 reactant. The N₂, used for transfers, was passed through a single column containing A204 alumina, 4Å molecular sieves, and Q5 reactant.

[00138] The reactor was loaded first from a shot tank that contained toluene and *tert*-butyl acrylate. The shot tank was filled to the load set points by use of a differential pressure transducer. After solvent/acrylate addition, the shot tank was rinsed twice with toluene and the rinses were transferred to the reactor (total mass of toluene = 605 g, total mass *tert*-butyl acrylate = 9.28 g). The reactor was then heated to the desired polymerization temperature set point (150 °C). Upon reaching the temperature set point, ethylene was added to the reactor in order to reach the desired pressure set point (600 psi). The amount of ethylene added to the reactor was monitored by a micro-motion flow meter (initial ethylene loading = 89 g).

[00139] The catalyst, Ni Catalyst 1, was handled in an inert atmosphere glove box and introduced to the reactor as a solution in toluene. The catalyst solution was drawn into a syringe and pressure transferred into the catalyst shot tank (59.2 µmol catalyst added). This was followed by 3 rinses of toluene, 5 mL each. Catalyst was only added after the reactor pressure set point was achieved.

[00140] Immediately after catalyst addition, the run timer began. Ethylene was then fed (*via* Camile control) to the reactor in order to maintain the pressure set point. The ethylene/*tert*-butyl acrylate copolymerization reaction was run for 45 minutes, but ethylene uptake curves showed that the catalyst was only active during the first 3 minutes of the reaction. After 45 minutes, the agitator was stopped, and the bottom dump valve opened to empty reactor contents to the lidded dump pot. The valves on the lidded dump pot were closed and the sealed dump pot was disconnected from the reactor and taken to a fume hood. Once in the fume hood, the lid was

removed from the dump pot and the contents were poured into trays. The trays were left in the hood for a minimum of 36 hours to allow solvent and *tert*-butyl acrylate (tBA) to evaporate. The trays containing the remaining polymer were then transferred to a vacuum oven (note: 4-methoxyphenol was added to the trap to prevent spontaneous polymerization of *tert*-butyl acrylate), where they were heated up to 140°C under vacuum to remove any residual volatile materials. After the trays cooled to ambient temperature, the polymers were weighed for yield/efficiencies, and submitted for polymer testing. In this experiment, 14.6 g of copolymer was obtained.

Table 1: Summary of Reactor Conditions to produce Ni-catalyzed linear polyethylene and ethylene/*tert*-butylacrylate (copolymer in high pressure reactor)

Run Number	Unit	CE1	IE1	IE2	IE3	IE4
Average Reactor Temperature	°C	169.7	156	171.8	150.5	147.2
Reactor Pressure	barg	1962.5	2004.3	1987.7	2016	2058
Ethylene Flow	g/hr	3187.3	3214.6	3190.6	3100	3084
tBA Flow	g/hr	0	45.7	66.9	90	308
Ni Catalyst Flow	g Ni/hr	6.00E-03	2.17E-02	2.98E-02	2.11E-02	2.68E-02
Toluene Flow	g/hr	37.4	135.4	185.7	253	322
Propylene Flow	g/hr	98.6	0	0	0	0
tBA Reactor Concentration in Ethylene	g tBA/g ethylene	0	0.0142	0.021	0.03	0.10
MMAO-3A Flow	g Al/hr	0	0	0	7.96E-03	1.28E-02
Propylene Reactor Conc. in Ethylene	g propylene/g ethylene	0.0309	0	0	0	0
Ni Catalyst Reactor Conc. in Ethylene	µg Ni/g ethylene	1.88	6.75	9.34	6.80	8.68
Ni Catalyst Premixture Conc. in Toluene	µg Ni/g toluene	160.43	160.27	160.47	83.2	83.21
MMAO-3A Reactor Conc. in Ethylene	µg Al/g ethylene	0	0	0	2.57	4.16
MMAO-3A Premixture Conc. in Isopar E	µg Al/g Isopar E	0	0	0	400	378.65
Total Isopar E flow	g/hr	0	0	0	20	34

Table 1 Continued:

Run Number	Unit	IE5	IE6	IE7	IE8
Average Reactor Temperature	°C	152.7	147.8	139.4	144.8
Reactor Pressure	barg	2002	2000	2124	2026
Ethylene Flow	g/hr	3252	3069	2516	3213
tBA Flow	g/hr	439	453	699	647
Ni Catalyst Flow	g Ni/hr	5.69E-02	5.68E-02	5.69E-02	5.68E-02
Toluene Flow	g/hr	355	355	356	355
Propylene Flow	g/hr	0	0	0	0
tBA Reactor Concentration in Ethylene	g tBA/g ethylene	0.13	0.15	0.28	0.09
MMAO-3A Flow	g Al/hr	3.05E-02	4.49E-02	4.48E-02	4.55E-02
Propylene Reactor Conc. in Ethylene	g propylene/g ethylene	0	0	0	0
Ni Catalyst Reactor Conc. in Ethylene	µg Ni/g ethylene	17.5	18.52	22.61	17.68
Ni Catalyst Premixture Conc. in Toluene	µg Ni/g toluene	160.03	160.03	160.03	160.03
MMAO-3A Reactor Conc. in Ethylene	µg Al/g ethylene	9.37	14.62	17.82	14.15
MMAO-3A Premixture Conc. in Isopar E	µg Al/g Isopar E	358.12	381.09	367.73	398.04
Total Isopar E flow	g/hr	85	118	122	114

[00141] Run 1 in Table 1 (CE1) is a comparative example. The polymerization process did not include a polar comonomer.

Table 2 – Catalyst Efficiency for Ni-catalyzed linear polyethylene and linear ethylene/tert-butyl acrylate (E/t-BA) prepared in high pressure reactor.

Example	Description	Purification Bed Run Time (hr)	Efficiency (g _{polymer} /g _{Ni})
CE7	PE Homopolymer	n/a	82,645
IE1	E/t-BA Linear copolymer	Not measured	20,161
IE2	E/t-BA Linear copolymer	Not measured	8,621
IE3	E/t-BA Linear copolymer	11	25,445

IE4	E/t-BA Linear copolymer	24	17,575
IE5	E/t-BA Linear copolymer	49	8,264
IE6	E/t-BA Linear copolymer	59	5,051
IE7	E/t-BA Linear copolymer	61	4,673
IE8	E/t-BA Linear copolymer	63	5,650

Table 3 – Analytical characterization of Ni-catalyzed linear polyethylene and linear ethylene/tert-butyl acrylate (E/t-BA)

	DSC	GPC				¹³ CNMR			FTIR
Example	T _m (2nd heat)	MI	M _n	M _w	PDI	wt% tBA	mol% tBA	C1/1000C	wt% tBA
CE1	129.31	>100	13,010	34,571	2.66	-	-	2.47	-
CE2	109.9		4,573	10,973	2.4				11.7
IE1	126.19	49	19,718	43,942	2.23	1.1	0.25	1.69	1.85
IE2	125.82	55	13,742	40,450	2.94	1.3	0.29	1.9	1.31
IE3	123.6	68	19,578	39,569	2.02	2.6	0.58	1.76	3.72
IE4	115.92	>100	16,705	31,455	1.88	8.8	2.07	1.49	7.94
IE5	115.05	226	15,052	28,285	1.88	10	2.37	1.53	8.89
IE6	112.4	137	17,355	31,869	1.84	12.3	2.98	1.28	10.61
IE7	106.81	134	16,760	30,937	1.85	15.7	3.92	1.29	13.17
IE8	108.26	201	15,494	28,091	1.81	15.4	3.83	1.34	13.00

[00142] The polymer produced from CE1 has a high melt index and a high melt temperature when compared to the other inventive examples of Table 3. However, the polymer of CE1 is a linear polymer that lacks the polar comonomer, and is not an illustrative embodiment of this disclosure.

[00143] In Example CE2, the Ni-catalyzed copolymerization of ethylene and tert-butyl acrylate was conducted in solution at low pressure. The MW of the copolymer of example CE2 was significantly lower than that achieved in IE1 to IE8. When the linear ethylene/tert-butyl acrylate copolymers produced from the polymerization processes of IE1 to IE8 were compared to ethylene/tert-butyl acrylate copolymers that are highly branched (CE3 to CE7, Table 5), the polymers of IE1 to IE8 had a higher melt temperature (T_m) and a higher molecular weight (M_w).

[00144] The process condition to produce the comparative branched polymers (CE3 to CE7) were recorded in Table 4.

[00145] **Comparative examples CE3-CE7**

[00146] In Table 4, the polymerization processes to produce comparative highly branched ethylene copolymers (CE3 to CE7) was tabulated. These copolymers were prepared without adding a nickel catalyst to the reactor. The procedure to produce the branched polyethylene copolymers included feeding purified ethylene at 7 pph that was mixed with purified *tert*-butyl acrylate and Isopar E. The ethylene/*tert*-butyl acrylate mixture was compressed and pressurized to 2000 barg to create a supercritical ethylene stream. The supercritical ethylene stream was then fed to a 300 mL continuously stirred tank reactor. Reactor temperature was controlled to target temperature using 4 electric heating bands on the wall of the reactor. Separately, a mixture of *tert*-butyl peroctoate and Isopar E was fed to the reactor to initiate free radical polymerization. The feed was controlled so that ethylene conversion in the reactor, as measured based on total polymer collected, remained 12 +/- 2%. After exiting the reactor, the stream was rapidly depressurized across a valve to 1 barg to separate the ethylene from the polymerized material. Nitrogen was added to the stream to freeze the polymer.

Table 4 – Reactor Conditions for Comparative Branched ECP

	Units	CE3	CE4	CE5	CE6	CE7
Average Reactor Temp	°C	200.4	198.3	198.1	199.1	200.7
Reactor Pressure	Barg	1888	1738	1775	1733	1618
Ethylene Flow	g/hr	3200	3090	3083	3047	3193
t-Butyl Acrylate Flow	g/hr	38.43	166.36	188.00	34.11	29.19
Ni Catalyst Flow	g Ni/hr	0	0	0	0	0
Toluene Flow	g/hr	0	0	0	0	0
Propylene Flow	g/hr	0	0	0	0	0
MMAO-3A Flow	g Al/hr	0	0	0	0	0
tert-butyl peroctoate Flow	g/hr	0.64	0.65	0.66	0.69	0.57
Total Isopar E flow	g/hr	479.32	519.06	459.98	470.39	587.90
tBA Reactor Conc. in Ethylene	g tBA/g ethylene	0.0120	0.0538	0.0610	0.0112	0.0091
Propylene Reactor Conc. in Ethylene	g propylene/g ethylene	0	0	0	0	0
Ni Catalyst Reactor Conc. in Ethylene	µg Ni/ g ethylene	0	0	0	0	0
Ni Catalyst Premixture Conc in Toluene	µg Ni/g toluene	0	0	0	0	0
MMAO-3A Reactor Conc. in Ethylene (	µg Al/g ethylene	0	0	0	0	0
MMAO-3A Premixture Conc. in Isopar E	µg Al/g Isopar E	0	0	0	0	0
tert-butyl Peroctoate Conc. in Ethylene	g TBPO/g ethylene	200.5	209.8	214.9	225.9	179.8
tert-butyl Peroctoate Premixture Conc. in Isopar E	µg TBPO/g Isopar E	5000	5001	5002	5003	5004
Residual tBA	ppmw	ND	10	10	ND	ND

[00147] In Table 5, the reactor conditions were very similar to the reactor conditions as tabulated in Tables 1 and 2. However, the reactor conditions reported in Table 4 did not include a transition metal catalyst. Polymerization was initiated using a radical initiator, tert-butyl peroctoate.

Table 5 – Polymer Analysis of Comparative Branched ethylene/tert-butyl acrylate copolymers CE3 to CE7

	DSC		GPC			FTIR
Example	T _m (2nd heat)	MI	M _n	M _w	PDI	wt% tBA
CE3	107.6	47	13,239	52,752	3.98	4.17
CE4	107.6	49	9,386	39,764	4.24	2.73
CE5	101.9	44	13,548	54,619	4.03	7.57
CE6	111.0	51	12,483	58,472	4.68	3.17
CE7	106.6	268	8,897	34,565	3.89	2.96

[00148] The copolymers recorded in Table 5 are highly branched and have a significantly lower melt temperature when compared with the linear copolymers produced by the polymerization conditions recorded in Table 1 (IE1 to IE8). The FIGURE graphically depicts that branched polymers have a lower melt temperature than the linear polymers. In general, for the same level (wt%) of acrylate incorporation, the linear copolymers (IE1-IE8) have an increase in T_m of at least 10 °C over the branched copolymers (CE3-CE7).

Table 6 – Catalyst Efficiency as a Function of Ethylene Concentration

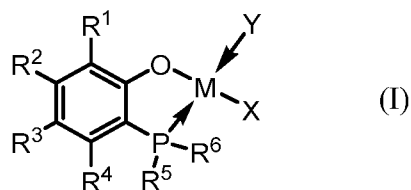
Conditions	Low Batch CE2	Pressure Reactor,	High Pressure Reactor, IE3	High Pressure Reactor, IE4
Temperature, °C	150		150	150
[C ₂], mol/L	2.7		19.4	18.2
Reactor Pressure (barg)	41		2016	2058
C ₂ /tBA, mol/mol	45		162	46
Reaction Time	2-3 minutes		2-3 minutes	2-3 minutes
Efficiency, g poly/g Ni	4,202		25,000	17,241
GPC	M _w 10,973		M _w 37,970	M _w 30,130
	M _n 4,573		M _n 16,760	M _n 14,120
	PDI 2.40		PDI 2.27	PDI 2.13
tBA in polymer, wt%	11.7		2.6	8.8

[00149] The results tabulated in Table 6 can demonstrate the increased efficiency of the catalyst when the ethylene concentration in the reactor is greatly increased at a given reaction time, temperature, and C₂/tBA ratio. The reaction process for CE2 was a solution polymerization process at lower pressure (41 barg), and the efficiency of Ni Catalyst 1 was significantly lower when compared to high pressure experiments IE3 and IE4 (> 2000 barg). For instance, CE2 and

IE4 were run at the same C2/tBA ratio, same temperature, and same reaction time, but the ethylene concentration in the reactor in IE4 is nearly 7 times higher than in CE2. This leads to a nearly 4X improvement in catalyst efficiency for IE4, accompanied by a nearly 3X improvement in copolymer MW (high t-BA incorporation maintained).

CLAIMS

1. A polymerization process comprising:
polymerizing ethylene, one or more polar comonomers, optionally one or more (C₃–C₁₂) α -olefins, and optionally an aluminum species in the presence of the catalyst system to form an ethylene-based copolymer in a high pressure reactor at a pressure of greater than 1000 barg and a temperature of greater than 100°C, wherein the catalyst system comprises a transition metal catalyst.
2. The polymerization process according to claim 1, wherein the aluminum species comprises aluminoxane or alkyl aluminum, or combinations of aluminoxane and alkyl aluminum.
3. The polymerization process of claim 1 or claim 2, wherein the transition metal catalyst comprises nickel(II) or palladium(II).
4. The polymerization process of any one of the preceding claims, wherein the transition metal catalyst or transition metal procatalyst comprises nickel(II) or palladium(II), and has a structure according to formula (I).



where:

M is nickel(II) or palladium(II);

X is a ligand chosen from (C₁–C₄₀)hydrocarbyl,

(C₁–C₄₀)heterohydrocarbyl, -CH₂Si(R^C)_{3-Q}(OR^C)_Q,
 -Si(R^C)_{3-Q}(OR^C)_Q, -OSi(R^C)_{3-Q}(OR^C)_Q, -Ge(R^C)_{3-Q}(OR^C)_Q,
 -P(R^C)_{2-W}(OR^C)_W, -P(O)(R^C)_{2-W}(OR^C)_W, -N(R^C)₂, -NH(R^C),
 -N(Si(R^C)₃)₂, -NR^CSi(R^C)₃, -NHSi(R^C)₃, -OR^C, -SR^C, -NO₂, -CN,
 -CF₃, -OCF₃, -S(O)R^C, -S(O)₂R^C, -OS(O)₂R^C, -N=C(R^C)₂,
 -N=CH(R^C), -N=CH₂, -N=P(R^C)₃, -OC(O)R^C, -C(O)OR^C,
 -N(R^C)C(O)R^C, -N(R^C)C(O)H, -NHC(O)R^C, -C(O)N(R^C)₂,
 -C(O)NHR^C, -C(O)NH₂, a halogen, or a hydrogen, wherein each R^C is independently a substituted or unsubstituted (C₁–C₃₀)hydrocarbyl, or a

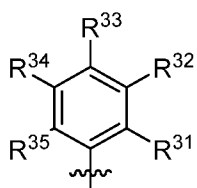
substituted or unsubstituted (C₁–C₃₀)heterohydrocarbyl, and Q is 0, 1, 2 or 3 and W is 0, 1, or 2;

each Y is a Lewis base, wherein X and Y are optionally linked;

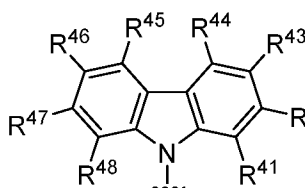
P is phosphorous;

R¹ is independently selected from the group consisting of –H,

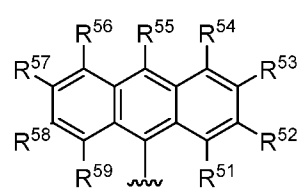
(C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –Si(R^C)₃-Q(OR^C)_Q, –OSi(R^C)₃-Q(OR^C)_Q, –Ge(R^C)₃-Q(OR^C)_Q, –P(=O)(R^P)₂, –P(R^C)₂-w(OR^C)_w, –P(O)(R^C)₂-w(OR^C)_w, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–, R^CS(O)₂–, –N=C(R^C)₂, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R)–, (R^C)₂NC(O)–, halogen, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



(II)



(III)



(IV)

where each of R^{31–35}, R^{41–48}, and R^{51–59} is independently chosen from –H,

(C₁–C₄₀)hydrocarbyl, (C₁–C₄₀)heterohydrocarbyl, –Si(R^C)₃, –Ge(R^C)₃, –P(R^P)₂, –N(R^N)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, R^CS(O)–, R^CS(O)₂–, (R^C)₂C=N–, R^CC(O)O–, R^COC(O)–, R^CC(O)N(R^N)–, (R^C)₂NC(O)–, or halogen;

R², R³, and R⁴ are independently selected from a substituted

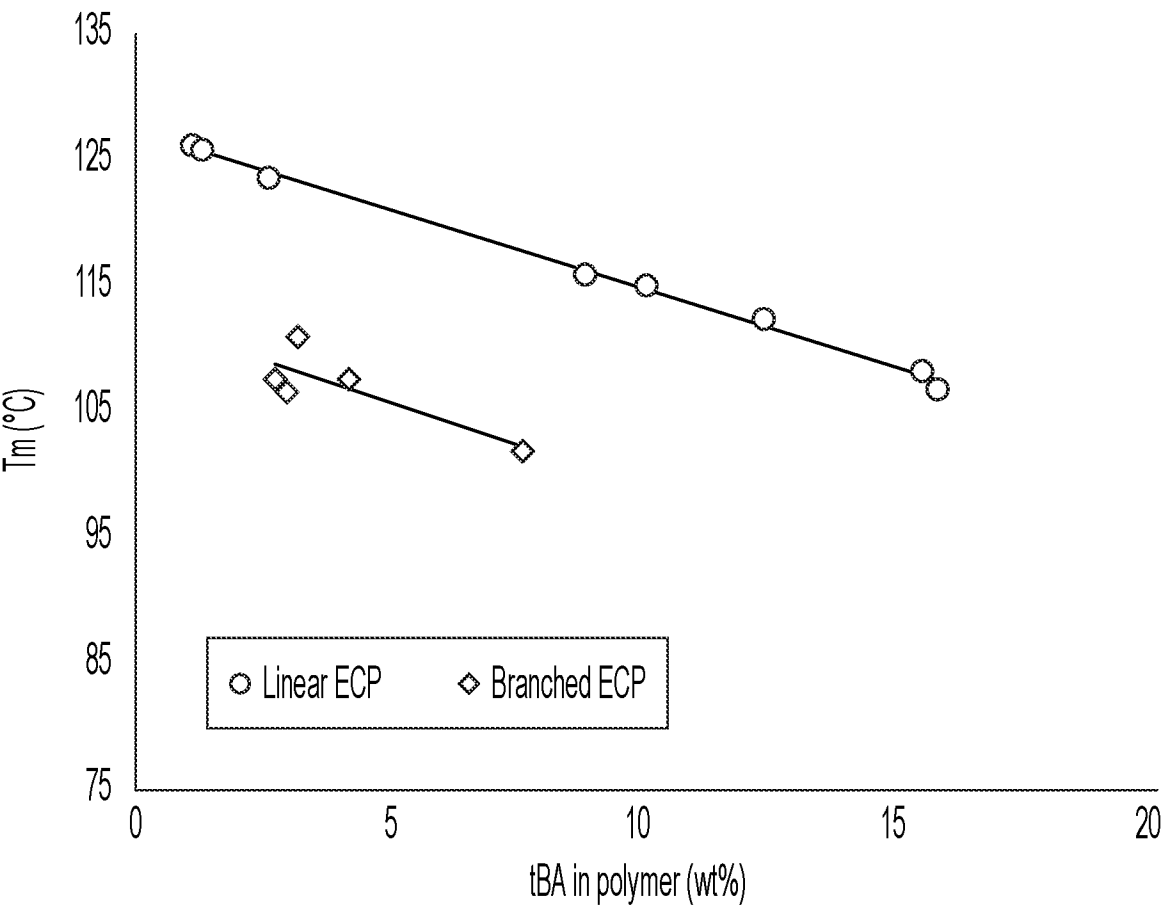
(C₁–C₃₀)hydrocarbyl, unsubstituted (C₁–C₃₀)hydrocarbyl, substituted (C₁–C₃₀)heterohydrocarbyl, unsubstituted (C₁–C₃₀)heterohydrocarbyl, –Si(R^C)₃-Q(OR^C)_Q, –OSi(R^C)₃-Q(OR^C)_Q, –Ge(R^C)₃-Q(OR^C)_Q, –P(R^C)₂-w(OR^C)_w, –P(O)(R^C)₂-w(OR^C)_w, –N(R^C)₂, –NH(R^C)₂, –OR^C, –SR^C, –NO₂, –CN, –CF₃, –OCF₃, –S(O)R^C, –S(O)₂R^C, –OS(O)₂R^C, –N=C(R^C)₂, –N=P(R^C)₃, –OC(O)R^C, –C(O)OR^C, –N(R)C(O)R^C, –C(O)N(R^C)₂, or a halogen, wherein each R^C is independently a substituted or unsubstituted (C₁–C₃₀)hydrocarbyl, or a substituted or unsubstituted (C₁–C₃₀)heterohydrocarbyl; Q is 0, 1, 2, or 3 and W is 0, 1, or 2; and

R⁵ and R⁶ are independently selected from a substituted (C₁–C₃₀)hydrocarbyl, unsubstituted (C₁–C₃₀)hydrocarbyl, substituted (C₁–C₃₀)heterohydrocarbyl, or unsubstituted (C₁–C₃₀)heterohydrocarbyl; and

where:

optionally, R⁵ and R⁶ are linked to form a ring structure;
optionally, R² and R³ are linked to form a ring structure; or
optionally, R³ and R⁴ are linked to form a ring structure.

5. The polymerization process claim 4, wherein R⁵ and R⁶ are independently (C₁–C₂₀)alkyl, (C₆–C₂₀)aryl, or substituted (C₆–C₂₀)aryl.
6. The polymerization process any one of claim 4 or claim 5, wherein Y is pyridine, substituted pyridine, sulfoxide, trialkyl, triaryl phosphine, trialkyl, triaryl phosphine oxide, substituted heterocycle, unsubstituted heterocycle, aliphatic ketone, aliphatic amine, alkyl ether, or cycloalkyl ether.
7. The polymerization process any one of claims 4 to 6, wherein R², R³, and R⁴ are (C₁–C₁₈)alkyl or –H.
8. The polymerization process any one of claims 4 to 7, wherein R¹ is a radical of formula (II), (III), or (IV).
9. The polymerization process of any one of claims 4 to 8, wherein X is a substituted or unsubstituted (C₁–C₃₀)hydrocarbyl, a substituted or unsubstituted (C₁–C₃₀)heterohydrocarbyl.
10. The polymerization process of any one or the preceding claims, wherein the polar monomers comprise one or more alkyl acrylate monomers.
11. The polymerization process of any one or the preceding claims, wherein the alkyl acrylate is methyl acrylate, ethyl acrylate, n-butyl acrylate, or t-butyl acrylate.
12. The polymerization process of any one or the preceding claims, wherein temperature is from greater than 100°C to 250°C.
13. The polymerization process of any one or the preceding claims, wherein pressure is from greater than 1000 barg to 5000 barg.
14. An ethylene-based polymer produced from the polymerization process of either of claims 9 to 12.
15. A procatalyst according to any structure of this disclosure.



FIGURE

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2024/035545

A. CLASSIFICATION OF SUBJECT MATTER INV. C07F9/50 C07F15/04 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) C07F		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, CHEM ABS Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2019/188499 A1 (JAPAN POLYETHYLENE CORP [JP]; JAPAN POLYPROPYLENE CORP [JP]) 3 October 2019 (2019-10-03) paragraph [0079] example 9 claims 1-6 -----	1 - 15
X	WO 2018/021446 A1 (UNIV TOKYO [JP]; JAPAN POLYCHEM CORP [JP]) 1 February 2018 (2018-02-01) examples 3-2 claims 1-34 -----	1 - 15
X	US 2017/002120 A1 (SATO NAOMASA [JP] ET AL) 5 January 2017 (2017-01-05) examples 1, 2 claims 1-10 ----- - / - -	1 - 15
☒ Further documents are listed in the continuation of Box C. ☒ 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 application or patent 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 7 October 2024		Date of mailing of the international search report 16/10/2024
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 Neumeier, Michael

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2024/035545

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	YANPING ZHANG ET AL: "Elaborate Tuning in Ligand Makes a Big Difference in Catalytic Performance: Bulky Nickel Catalysts for (Co)polymerization of Ethylene with Promising Vinyl Polar Monomers", CHEMCATCHEM, JOHN WILEY & SONS, INC, HOBOKEN, USA, vol. 11, no. 9, 10 April 2019 (2019-04-10), pages 2329-2340, XP072435192, ISSN: 1867-3880, DOI: 10.1002/CCTC.201900265 Scheme 1 -----	15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2024/035545

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2019188499 A1	03-10-2019	CN 111971310 A	20-11-2020
		EP 3800207 A1	07-04-2021
		JP 7329937 B2	21-08-2023
		JP 2019172983 A	10-10-2019
		US 2021122853 A1	29-04-2021
		WO 2019188499 A1	03-10-2019
WO 2018021446 A1	01-02-2018	CN 109601002 A	09-04-2019
		EP 3476858 A1	01-05-2019
		US 2019263945 A1	29-08-2019
		WO 2018021446 A1	01-02-2018
US 2017002120 A1	05-01-2017	CN 105940016 A	14-09-2016
		EP 3101040 A1	07-12-2016
		JP 6594628 B2	23-10-2019
		JP 2015163691 A	10-09-2015
		US 2017002120 A1	05-01-2017
		US 2018201704 A1	19-07-2018
		WO 2015115378 A1	06-08-2015