PROCESS FOR OLEFIN POLYMERIZATION

REFERENCE TO RELATED APPLICATIONS

The present application claims the benefit of U.S. Provisional Application No. 62/018,855, filed June 30, 2014, and incorporated herein by reference.

BACKGROUND

Olefin-based polymers such as ethylene-based polymers and/or propylene-based polymers are produced via various polymerization processes. Ethylene-based polymers, such as, polyethylene is known for use in the manufacture of a wide a variety of articles. The polyethylene polymerization process can be varied in a number of ways to produce a wide variety of resultant polyethylene resins, having different physical properties that render the various resins suitable for use in different applications. It is generally known that ethylene-based polymers can be produced in solution phase loop reactors, in which ethylene monomer, and optionally one or more alpha olefin comonomers, typically having from 3 to 10 carbon atoms, are circulated in the presence of one or more catalyst systems, under pressure, around a loop reactor, by a circulation pump. The ethylene monomers, and optionally one or more comonomers, are present in a liquid diluent, such as an alkane or isoalkane. Hydrogen may also be added to the reactor. The catalyst systems for producing ethylene-based polymers may typically comprise a chromium-based catalyst system, a Ziegler Natta catalyst system, and/or a molecular (either metallocene or non-metallocene) catalyst system. However, there is still a need for new polymerization processes, exhibiting high reactivity toward hydrogen, and capacity for producing higher molecular weight olefin-based polymers under optimum polymerization conditions. These needs have been met by the following invention.

SUMMARY

The instant disclosure provides a process to form an olefin-based polymer, said process comprising polymerizing at least one olefin, in the presence of at least one catalyst system comprising the reaction product of the following:

A) at least one cocatalyst; and

B) a procatalyst comprising a metal-ligand complex of Formula (I):

or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; and

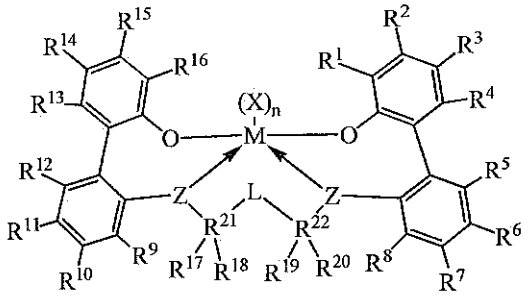
wherein, for Formula I, two or more of R^1 through R^{22}, optionally, may form one or more ring structures, and wherein each ring structure has from 3 to 50 atoms in the ring, excluding any hydrogen atoms; and

wherein, for Formula I, one or more hydrogen atoms may optionally be substituted with one or more deuterium atoms.

In one aspect, there is provided a process to form an olefin-based polymer, said process comprising polymerizing at least one olefin, in the presence of at least one catalyst system comprising the reaction product of the following:

A) at least one cocatalyst; and

B) a procatalyst comprising a metal-ligand complex of Formula (I):



(Formula I),

wherein:

M is titanium or zirconium, each independently being in a formal oxidation state of +2, +3, or +4; and n is an integer of from 0 to 3, and wherein when n is 0, X is absent; and

Each X, independently, is an (C_1-C_6)alkyl and wherein each X, independently, is a monodentate ligand that is neutral, monoanionic, or dianionic; or

wherein two Xs are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic; and

wherein X and n are chosen, in such a way, that the metal-ligand complex of Formula (I) is, overall, neutral; and

Each Z independently is an oxygen atom, a sulfur atom, -N[(C_1-C_{40})hydrocarbyl]-, or -P[(C_1-C_{40})hydrocarbyl]-; and

L is a substituted or unsubstituted (C_1-C_{40})hydrocarbylene, or a substituted or unsubstituted (C_1-C_{40})heterohydrocarbylene, and

wherein, for L, the (C_1-C_{40})hydrocarbylene has a portion that comprises a 1-carbon atom to 10-carbon atom linker backbone linking R^{21} and R^{22} in Formula (I) (to which L is bonded), or

wherein, for L, the $(C_1\text{-}C_{40})$heterohydrocarbylene has a portion that comprises a 1-atom to 10-atom linker backbone linking R^{21} and R^{22} in Formula (I), wherein each of the 1 to 10 atoms of the 1-atom to 10-atom linker backbone of the $(C_1\text{-}C_{40})$heterohydrocarbylene, independently, is one of the following: i) a carbon atom, ii) a heteroatom, wherein each heteroatom independently is –O– or –S–, or iii) a substituent selected from -S(O)-, $-S(O)_2$-, $-Si(R^C)_2$-, $-Ge(R^C)_2$-, $-P(R^C)$-, or $-N(R^C)$-, and wherein each R^C is, independently, a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarby; and

R^{21} and R^{22} are each, independently, C or Si; and

R^1 through R^{20} are each, independently, selected from the group consisting of the following: a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$hetero-hydrocarbyl, $-OR^C$, $-SR^C$,CF_3, a halogen atom, and a hydrogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; and

wherein, when R^{17} is a hydrogen atom, then R^{18} is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, OR^C, $-SR^C$,CF_3,a halogen atom, or a hydrogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; or

wherein, when R^{18} is a hydrogen atom, then R^{17} is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, OR^C, $-SR^C$, CF_3, a halogen atom, or a hydrogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; and/or

wherein, when R^{19} is a hydrogen atom, then R^{20} is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, OR^C, $-SR^C$, CF_3, a halogen atom, or a

hydrogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; or

wherein, when R^{20} is a hydrogen atom, then R^{19} is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, OR^C, $-SR^C$, CF_3, , a halogen atom, or a hydrogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; and

wherein, for Formula I, two or more of R^1 through R^{22}, optionally, may form one or more ring structures, and wherein each ring structure has from 3 to 50 atoms in the ring, excluding any hydrogen atoms; and

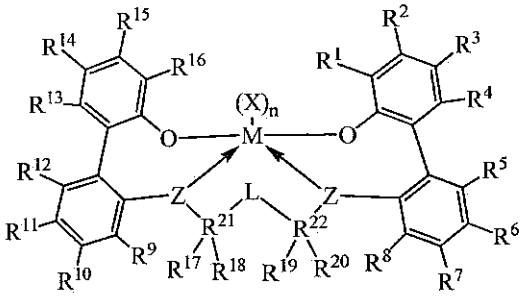
wherein, for Formula I, one or more hydrogen atoms may optionally be substituted with one or more deuterium atoms.

DETAILED DESCRIPTION OF THE INVENTION

The instant invention provides a process to form an olefin-based polymer, said process comprising polymerizing at least one olefin, further ethylene or propylene, and further ethylene, in the presence of at least one catalyst system comprising the reaction product of the following:

A) at least one cocatalyst; and

B) a procatalyst comprising a metal-ligand complex of Formula (I):



(Formula I),

wherein, Formula I is described above.

An inventive process may comprise a combination of two or more embodiments as described herein.

The procatalyst may comprise a combination of two or more embodiments as described herein.

As used herein, R1 = R^1, R2 = R^2, R3 = R^3, and so forth. As known in the art, O is oxygen, S is sulfur, Si is silicon, and so forth.

In one embodiment, for Formula I, when R^{17} is a hydrogen atom, then R^{18} is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^C)_2$, $-N(R^C)_2$, $-OR^C$, $-SR^C$, $-NO_2$, -CN,

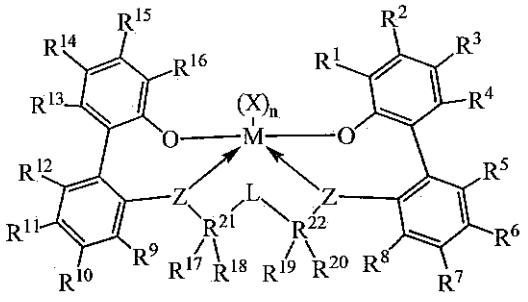
$-CF_3$, $-S(O)R^C$, $-S(O)_2R^C$, $-N{=}C(R^C)_2$, $-OC(O)R^C$, $-C(O)OR^C$, $-N(R)C(O)R^C$, $-C(O)N(R^C)_2$, or a halogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; or

CLAIMS:

1. A process to form an olefin-based polymer, said process comprising polymerizing at least one olefin, in the presence of at least one catalyst system comprising the reaction product of the following:

A) at least one cocatalyst; and

B) a procatalyst comprising a metal-ligand complex of Formula (I):



(Formula I),

wherein:

M is titanium or zirconium, each independently being in a formal oxidation state of +2, +3, or +4; and n is an integer of from 0 to 3, and wherein when n is 0, X is absent; and

Each X, independently, is an $(C_1\text{-}C_6)$alkyl and wherein each X, independently, is a monodentate ligand that is neutral, monoanionic, or dianionic; or

wherein two Xs are taken together to form a bidentate ligand that is neutral, monoanionic, or dianionic; and

wherein X and n are chosen, in such a way, that the metal-ligand complex of Formula (I) is, overall, neutral; and

Each Z independently is an oxygen atom, a sulfur atom, -N[$(C_1\text{-}C_{40})$hydrocarbyl]-, or -P[$(C_1\text{-}C_{40})$hydrocarbyl]-; and

L is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbylene, or a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbylene, and

wherein, for L, the $(C_1\text{-}C_{40})$hydrocarbylene has a portion that comprises a 1-carbon atom to 10-carbon atom linker backbone linking R^{21} and R^{22} in Formula (I) (to which L is bonded), or

wherein, for L, the $(C_1\text{-}C_{40})$heterohydrocarbylene has a portion that comprises a 1-atom to 10-atom linker backbone linking R^{21} and R^{22} in Formula (I), wherein each of the 1 to 10 atoms of the 1-atom to 10-atom linker backbone of the $(C_1\text{-}C_{40})$heterohydrocarbylene, independently,

is one of the following: i) a carbon atom, ii) a heteroatom, wherein each heteroatom independently is –O– or –S–, or iii) a substituent selected from -S(O)-, -$S(O)_2$-, -$Si(R^C)_2$-, -$Ge(R^C)_2$-, -$P(R^C)$-, or -$N(R^C)$-, and wherein each R^C is, independently, a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; and

R^{21} and R^{22} are each, independently, C or Si; and

R^1 through R^{20} are each, independently, selected from the group consisting of the following: a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})hetero-hydrocarbyl, -OR^C, -SR^C,CF_3, a halogen atom, and a hydrogen atom; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; and

wherein, when R^{17} is a hydrogen atom, then R^{18} is a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, OR^C, -SR^C,CF_3,a halogen atom, or a hydrogen atom; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; or

wherein, when R^{18} is a hydrogen atom, then R^{17} is a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, OR^C, -SR^C, CF_3, a halogen atom, or a hydrogen atom; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; and/or

wherein, when R^{19} is a hydrogen atom, then R^{20} is a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, OR^C, -SR^C, CF_3, a halogen atom, or a

hydrogen atom; and wherein each R^C is independently a substituted or unsubstituted

$(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; or

wherein, when R^{20} is a hydrogen atom, then R^{19} is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, OR^C, $-SR^C$, CF_3, , a halogen atom, or a hydrogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; and

wherein, for Formula I, two or more of R^1 through R^{22}, optionally, may form one or more ring structures, and wherein each ring structure has from 3 to 50 atoms in the ring, excluding any hydrogen atoms; and

wherein, for Formula I, one or more hydrogen atoms may optionally be substituted with one or more deuterium atoms.

2. The process of claim 1, wherein of claim 1, wherein, for Formula I, wherin when R^{17} is a hydrogen atom, then R^{18} is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, OR^C, $-SR^C$, CF_3or a halogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; or

wherein, when R^{18} is a hydrogen atom, then R^{17} is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, OR^C, $-SR^C$, CF_3or a halogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a substituted or unsubstituted $(C_1\text{-}C_{30})$ heterohydrocarbyl; and/or

wherein, when R^{19} is a hydrogen atom, then R^{20} is a substituted or unsubstituted $(C_1\text{-}C_{40})$hydrocarbyl, a substituted or unsubstituted $(C_1\text{-}C_{40})$heterohydrocarbyl, OR^C, $-SR^C$, CF_3or a halogen atom; and wherein each R^C is independently a substituted or unsubstituted $(C_1\text{-}C_{30})$hydrocarbyl, or a

substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl; or

wherein, when R^{20} is a hydrogen atom, then R^{19} is a substituted or unsubstituted (C_1-C_{40})hydrocarbyl, a substituted or unsubstituted (C_1-C_{40})heterohydrocarbyl, OR^C, -SR^C, CF_3or a halogen atom; and wherein each R^C is independently a substituted or unsubstituted (C_1-C_{30})hydrocarbyl, or a substituted or unsubstituted (C_1-C_{30}) heterohydrocarbyl.

3. The process of claim 1 or claim 2, wherein the polymerization is a solution polymerization.

4. The process of any one of the previous claims, wherein the cocatalyst is selected from a borate, an alkyl aluminum, or an aluminoxane.

5. The process of any one of the previous claims, wherein the polymerization takes place at a temperature from 25°C to 250°C.

6. The process of any one of the previous claims, wherein the polymerization takes place at a pressure from 10 psi to 2000 psi.

7. The process of any one of the previous claims, wherein the olefin-based polymer is an ethylene-based polymer.

8. The process of any one of claims 1-6, wherein the olefin-based polymer is a propylene-based polymer.

9. The process of any one of the previous claims, wherein for Formula I, each Z is an oxygen atom.

10. The process of any one of the previous claims, wherein for Formula I, R^{21} and R^{22} are each C (carbon).

11. The process of any one of the previous claims, wherein for Formula I, L is selected from the following: –CH2CH2CH2–, –CH2CH2– or –CH2–.

12. The process of any one of the previous claims, wherein for Formula I, each (C_1-C_{40})-hydrocarbyl, and each (C_1-C_{40})heterohydrocarbyl is not substituted.

13. The process of any one of the previous claims, wherein for Formula I, M is zirconium or hafnium; n is 2; each X, independently, is a (C_1-C_6)alkyl; and R^2, R^4, R^5, R^7, R^8, R^9, R^{10}, R^{12}, R^{13} and R^{15} are each hydrogen.

14. The process of any one of the previous claims, wherein for Formula I, M is zirconium; and each Z is an oxygen atom.