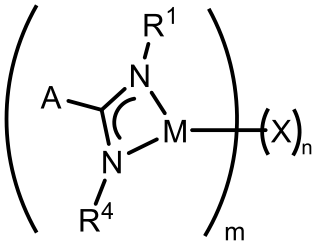
may be processed to remove the polyethylene product from the diluent and the unreacted reactants, with the diluent and unreacted reactants typically being recycled back into the reactor. Alternatively, the reaction mixture may be sent to a second reactor, serially connected to the first reactor, where a second polyethylene fraction may be produced.

[0005] Despite the number of currently available homogeneous solution olefin polymerization catalyst systems, there is a need for high temperature polymerization catalysts that have improved molecular properties facilitating the production of high molecular weight (Mw) polymers having narrow polydispersities (PDIs), and/or high molecular weight (Mw) ethylene/comonomer copolymers having a range of comonomer incorporation (i.e. 0 – 20 mol% of 1-hexene or 1-octene, etc), and/or high molecular weight (Mw) polymers that can undergo chain transfer with chain transfer agents (CSAs) to produce olefin block copolymers (OBCs).

SUMMARY

[0006] This disclosure relates to polymerization processes. These polymerization processes produce ethylene-based polymers. The polymerization process comprising contacting ethylene and optionally one or more (C_3−C_{12})α-olefin in the presence of a catalyst system, wherein the catalyst system comprises a metal−ligand complex having a structure according to formula (I):



(I)

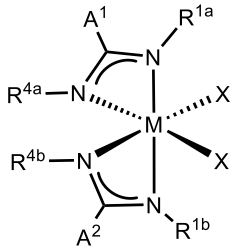
[0007] In formula (I), M is titanium, zirconium, or hafnium. Each X is a monodentate or bidentate ligand independently chosen from unsaturated (C_2−C_{20})hydrocarbon, unsaturated (C_2−C_{50})heterohydrocarbon, (C_1−C_{50})hydrocarbyl, (C_1−C_{50})heterohydrocarbyl, (C_6−C_{50})aryl, (C_6−C_{50})heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, (C_4−C_{12})diene, halogen, −OR^X, −$N(R^X)_2$, or –$NCOR^X$, wherein each R^X is (C_1−C_{30})hydrocarbyl or –H. Subscript n of $(X)_n$ is 1, 2, or 3. Subscript m is 1 or 2; and m plus n equals 3 or 4 (m + n = 3 or 4).

[0008] In formula (I), each R^1 is R^{1a} or R^{1b}; each R^4 is R^{4a} or R^{4b}; and R^{1a}, R^{1b}, R^{4a}, and R^{4b} are independently chosen from –H, (C_2–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, −$Si(R^C)_3$,

$-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, $-NO_2$, $-CN$, $-CF_3$, $R^CS(O)-$, $R^CS(O)_2-$, $(R^C)_2C=N-$, $R^CC(O)O-$, $R^COC(O)-$, $R^CC(O)N(R)-$, $(R^C)_2NC(O)-$, or halogen.

[0009] In formula (I), each A is independently $-NR^2R^3$; each R^2 is R^{2a} or R^{2b}; each R^3 is R^{3a} or R^{3b}; R^{2a}, R^{2b}, R^{3a}, and R^{3b} are independently –H or (C_1-C_{40})hydrocarbyl; provided that when (1) m is 2 and (2) all of R^{2a}, R^{2b}, R^{3a}, and R^{3b} are methyl, at least one of R^{1a}, R^{1b}, R^{4a}, and R^{4b} is not 2-propyl; when m is 1, each X is identical; and any of R^1 and R^2, or R^2 and R^3, or R^3 and R^4 optionally may be connected to form a ring.

[0009a] In one aspect, there is provided a process for polymerizing polyolefin, the process comprising contacting ethylene and optionally one or more (C_3-C_{12})α-olefin in the presence of a catalyst system, wherein the catalyst systems comprises a metal−ligand structure according to formula (II):



(II)

where:

M is a metal chosen from zirconium or hafnium, the metal having a formal oxidation state of +2, +3, or +4;

X is a monodentate or bidentate ligand independently chosen from (C_1-C_{20})alkyl, (C_1-C_{20})heteroalkyl, (C_6-C_{20})aryl, (C_4-C_{20})heteroaryl;

n is 2 or 3;

m is 2;

m + n = 3 or 4;

R^{1a}, R^{1b}, R^{4a}, and R^{4b} are independently chosen from –H, (C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, (C_1-C_{40})aryl, (C_1-C_{40})heteroaryl, $-P(R^P)_2$, $-N(R^N)_2$, $R^CS(O)-$, $R^CS(O)_2-$, or $(R^C)_2C=N-$;

A^1 and A^2 are independently $-NR^2R^3$; where each R^2 is R^{2a} or R^{2b}; each R^3 is R^{3a} or R^{3b}; and R^{2a}, R^{2b}, R^{3a}, and R^{3b} are independently –H, (C_1-C_{40})hydrocarbyl, (C_1-C_{40})heterohydrocarbyl, (C_1-C_{40})aryl, or (C_1-C_{40})heteroaryl;

provided that

when all of R^{2a}, R^{2b}, R^{3a}, and R^{3b} are methyl, at least one of R^{1a}, R^{1b}, R^{4a}, and R^{4b} is not 2-propyl;

when m is 1, each X is identical; and

any of R^1 and R^2, or R^2 and R^3, or R^3 and R^4 optionally may be connected to form a ring.

BRIEF SUMMARY OF THE DRAWINGS

[0010] FIG. 1 is a general synthetic scheme that may be used to synthesize the ligand.

[0011] FIG. 2 is the synthetic scheme for the synthesis of Ligand 1.

[0012] FIGS. 3 – 5 are structures of the ligand of this disclosure.

DETAILED DESCRIPTION

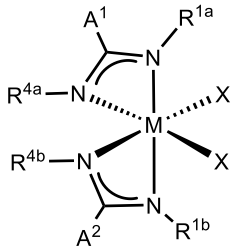
[0013] Specific embodiments of catalyst systems will now be described. It should be understood that the catalyst systems of this disclosure may be embodied in different forms and should not be construed as limited to the specific embodiments set forth in this disclosure. Rather, embodiments are provided 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.

[0014] Common abbreviations are listed below:

[0015] **R, Z, M, X and n**: as defined above; **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); **Tf** : trifluoromethane sulfonate; **THF** : tetrahydrofuran; **Et_2O** : diethyl ether; **CH_2Cl_2** : dichloromethane; **CV** : column volume (used in column chromatography); **EtOAc** : ethyl acetate; **C_6D_6 :** deuterated benzene or benzene-*d*6 : **$CDCl_3$** : deuterated chloroform; **Na_2SO_4** : sodium sulfate; **$MgSO_4$** : magnesium sulfate; **HCl** : hydrogen chloride; ***n*-BuLi:** butyllithium; ***t*-BuLi** : *tert*-butyllithium; **Cu_2O :** Copper (I) Oxide; ***N,N'*-DMEDA:** *N,N'*-dimethylethylenediamine; **K_3PO_4:** Potassium phosphate tribasic; **Pd(AmPhos)Cl_2:** Bis(di-tert-butyl(4-dimethylaminophenyl)phosphine)dichloropalladium(II); **Pd(dppf)Cl_2:** [1,1'-Bis(diphenylphosphino)ferrocene]palladium(II) dichloride; **$AgNO_3$:** Silver nitrate; **K_2CO_3:**

CLAIMS

1. A process for polymerizing polyolefin, the process comprising contacting ethylene and optionally one or more (C_3–C_{12})α-olefin in the presence of a catalyst system, wherein the catalyst systems comprises a metal–ligand structure according to formula (II):



(II)

where:

M is a metal chosen from zirconium or hafnium, the metal having a formal oxidation state of +2, +3, or +4;

X is a monodentate or bidentate ligand independently chosen from (C_1–C_{20})alkyl, (C_1–C_{20})heteroalkyl, (C_6–C_{20})aryl, (C_4–C_{20})heteroaryl;

n is 2 or 3;

m is 2;

m + n = 3 or 4;

R^{1a}, R^{1b}, R^{4a}, and R^{4b} are independently chosen from –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, (C_1-C_{40})aryl, (C_1-C_{40})heteroaryl, $-P(R^P)_2$, $-N(R^N)_2$, $R^CS(O)-$, $R^CS(O)_2-$, or $(R^C)_2C=N-$;

A^1 and A^2 are independently $-NR^2R^3$; where each R^2 is R^{2a} or R^{2b}; each R^3 is R^{3a} or R^{3b}; and R^{2a}, R^{2b}, R^{3a}, and R^{3b} are independently –H, (C_1–C_{40})hydrocarbyl, (C_1–C_{40})heterohydrocarbyl, (C_1-C_{40})aryl, or (C_1-C_{40})heteroaryl;

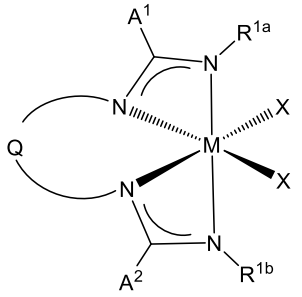
provided that

when all of R^{2a}, R^{2b}, R^{3a}, and R^{3b} are methyl, at least one of R^{1a}, R^{1b}, R^{4a}, and R^{4b} is not 2-propyl;

when m is 1, each X is identical; and

any of R^1 and R^2, or R^2 and R^3, or R^3 and R^4 optionally may be connected to form a ring.

2. The process according to claim 1, wherein m is 2, n is 2, and R^{4a} and R^{4b} are covalently linked, whereby the metal−ligand complex comprises a divalent radical Q consisting of the two covalently linked groups R^{4a} and R^{4b} and the metal−ligand complex has a structure according to formula (III):



(III)

where:

Q is (C_2–C_{12})alkylene, (C_2–C_{12})heteroalkylene, (C_6–C_{50})arylene, (C_4–C_{50})heteroarylene, (–$CH_2Si(R^C)_2CH_2$–), (–$CH_2CH_2Si(R^C)_2CH_2CH_2$–), (–$CH_2Ge(R^C)_2CH_2$–), or (–$CH_2CH_2Ge(R^C)_2CH_2CH_2$–); and

R^{1a}, R^{1b}, R^{2a}, R^{2b}, R^{3a}, R^{3b}, R^{4a}, R^{4b}, M, and X are as defined in formula (I) and A^1 and A^2 are as defined in formula (II).

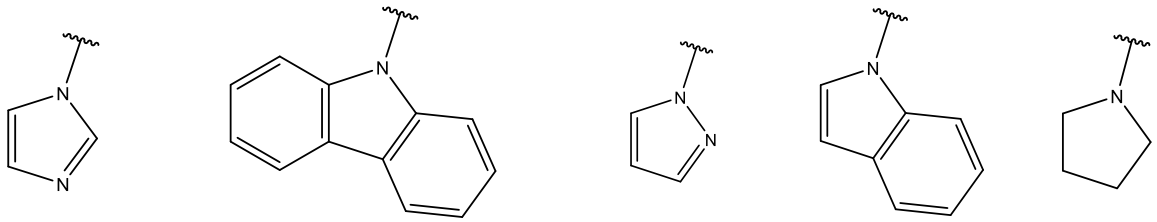
3. The process of any one of the preceding claims, wherein each X is benzyl, chloro, −CH_2SiMe_3, or phenyl.

4. The process of any one of the preceding claims, wherein each R^1, R^{1a}, or R^{1b} and each R^4, R^{4a}, or R^{4b} are independently (C_1–C_{20})alkyl or (C_1-C_{20})aryl.

5. The process of any one of the preceding claims, wherein each R^1 and each R^4 are independently benzyl, cyclohexyl, 2,6-dimethylphenyl, *tert*-butyl, or ethyl.

6. The process of claim 2, wherein R^{1a} and R^{1b} are 2-propyl.

7. The process of any one of the preceding claims, wherein each A has one of the following structures:



8. The process of any one of claims 1 to 7, wherein R^{2a}, R^{2b}, R^{3a}, and R^{3b} are $(C_1–C_{12})$alkyl.

9. The process of claim 8, wherein R^{2a}, R^{2b}, R^{3a}, and R^{3b} are methyl, ethyl, 1-propyl, 2-propyl, n-butyl, *tert*-butyl, 2-methylpropyl (*iso*-butyl), n-butyl, n-hexyl, cyclohexyl, *n*-octyl, or *tert*-octyl.

10. The process of any one of claims 1 to 3, wherein R^{1a}, R^{1b}, R^{4a}, and R^{4b} are independently chosen from 3,5-di-*tert*-butylphenyl; 2,4,6-trimethylphenyl; 2,6-dimethylphenyl; 2,4,6-triisopropylphenyl; 2,6-di-*iso*-propylphenyl; benzyl, cyclohexyl, or 2-propyl..

11. The catalyst system according to claim 2, wherein Q is chosen from $–(CH_2)_x–$, where x is from 2 to 5.

12. The catalyst system according to claim 2, wherein Q is $–(CH_2)_4–$.

13. The catalyst system of any one of the preceding claims, wherein the catalyst system further comprises a chain transfer agent.

14. The catalyst system according to claim 13, wherein the chain transfer agent is diethylzinc.