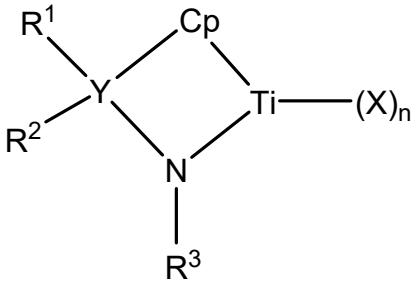
[0010] The disclosure includes processes of polymerizing olefin monomers. In one or more examples, the process includes reacting ethylene and optionally one or more olefin monomers in the presence of a catalyst system. The catalyst system includes hydrocarbyl-modified methylaluminoxane and a procatalyst. The hydrocarbyl-modified methylaluminoxane having less than 25 mole percent trihydrocarbyl aluminum compounds $AlR^{A1}R^{B1}R^{C1}$, based on the total moles of aluminum, where R^{A1}, R^{B1}, and R^{C1} are independently linear $(C_1–C_{40})$alkyl, branched $(C_1–C_{40})$alkyl, or $(C_6–C_{40})$aryl; and one or more procatalysts comprising a metal–ligand complex according to formula (I):



(I)

[0011] In formula (I), Ti is titanium. Subscript n of $(X)_n$ is 1, 2, or 3. Each X is a monodentate ligand or bidentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2–C_{50})$heterohydrocarbon, saturated $(C_2–C_{50})$heterohydrocarbon, $(C_1–C_{50})$hydrocarbyl, $(C_6–C_{50})$aryl, $(C_6–C_{50})$heteroaryl, cyclopentadienyl, substituted cyclopentadienyl, $(C_4–C_{12})$diene, halogen, $–N(R^N)_2$, and $–NCOR^C$. The metal–ligand complex is overall charge-neutral.

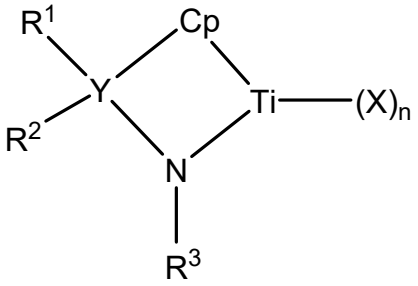
[0012] In formula (I), Cp is selected from the group consisting of cyclopentadienyl and R^S substituted cyclopentadienyl, the Cp being bound in an η^5 bonding mode to Ti, wherein R^S is independently selected from the group consisting of $(C_1–C_{20})$alkyl, $(C_1–C_{20})$heteroalkyl, $(C_1–C_{20})$aryl, or R^S substituent $(C_1–C_{20})$aryl, $(C_1–C_{20})$heteroaryl, or R^S substituent $(C_1–C_{20})$heteroaryl, wherein two adjacent R^S groups are optionally linked to form a ring.

[0013] In formula (I), N is nitrogen; Y is carbon or silicon; wherein Y is covalently bonded to Cp; and R^1 and R^2 are independently selected from −H, $(C_1–C_{40})$hydrocarbyl, and $(C_1–C_{40})$heterohydrocarbyl; and R^3 are independently selected from $(C_1–C_{40})$hydrocarbyl, and $(C_1–C_{40})$heterohydrocarbyl.

[0013a] In one aspect, there is provided a process of polymerizing olefin monomers, the process comprising reacting ethylene and optionally one or more C_3-C_{20} α-olefin monomers in the presence of a catalyst system, wherein the catalyst system comprises:

hydrocarbyl-modified methylaluminoxane having less than 25 mole percent active trihydrocarbyl aluminum compounds $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum, where R^{A1}, R^{B1}, and R^{C1} are independently linear $(C_1–C_{40})$alkyl, branched $(C_3–C_{40})$alkyl, or $(C_6–C_{40})$aryl; and

one or more procatalysts comprising a metal–ligand complex according to formula (I):



(I)

where:

Ti is titanium;

n is 1, 2, or 3;

each X is a monodentate ligand or bidentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2–C_{50})$heterohydrocarbon, saturated $(C_2–C_{50})$heterohydrocarbon, $(C_1–C_{50})$hydrocarbyl, and halogen;

the metal–ligand complex is overall charge-neutral;

Cp is selected from the group consisting of cyclopentadienyl and R^S substituted cyclopentadienyl, the Cp being bound in an η^5 bonding mode to Ti, wherein R^S is independently selected from the group consisting of $(C_1–C_{20})$alkyl, $(C_1–C_{20})$heteroalkyl, $(C_1–C_{20})$aryl, or $(C_1–C_{20})$heteroaryl, wherein two adjacent R^S groups are optionally linked to form a ring;

N is nitrogen;

Y is carbon or silicon and is covalently bonded to Cp; and

R^1 and R^2 are independently selected from −H, $(C_1–C_{40})$hydrocarbyl, and $(C_1–C_{40})$heterohydrocarbyl;

R^3 are independently selected from $(C_1–C_{40})$hydrocarbyl, and $(C_1–C_{40})$heterohydrocarbyl;

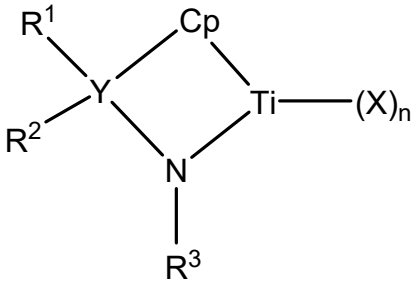
wherein the catalyst system does not contain a borate activator.

CLAIMS

1. A process of polymerizing olefin monomers, the process comprising reacting ethylene and optionally one or more C_3-C_{20} α-olefin monomers in the presence of a catalyst system, wherein the catalyst system comprises:

hydrocarbyl-modified methylaluminoxane having less than 25 mole percent active trihydrocarbyl aluminum compounds $AlR^{A1}R^{B1}R^{C1}$ based on the total moles of aluminum, where R^{A1}, R^{B1}, and R^{C1} are independently linear $(C_1–C_{40})$alkyl, branched $(C_3–C_{40})$alkyl, or $(C_6–C_{40})$aryl; and

one or more procatalysts comprising a metal–ligand complex according to formula (I):



(I)

where:

Ti is titanium;

n is 1, 2, or 3;

each X is a monodentate ligand or bidentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2–C_{50})$heterohydrocarbon, saturated $(C_2–C_{50})$heterohydrocarbon, $(C_1–C_{50})$hydrocarbyl, and halogen;

the metal–ligand complex is overall charge-neutral;

Cp is selected from the group consisting of cyclopentadienyl and R^S substituted cyclopentadienyl, the Cp being bound in an η^5 bonding mode to Ti, wherein R^S is independently selected from the group consisting of $(C_1–C_{20})$alkyl, $(C_1–C_{20})$heteroalkyl, $(C_1–C_{20})$aryl, or $(C_1–C_{20})$heteroaryl, wherein two adjacent R^S groups are optionally linked to form a ring;

N is nitrogen;

Y is carbon or silicon and is covalently bonded to Cp; and

R^1 and R^2 are independently selected from −H, $(C_1–C_{40})$hydrocarbyl, and $(C_1–C_{40})$heterohydrocarbyl;

R^3 are independently selected from (C_1–C_{40})hydrocarbyl, and

(C_1–C_{40})heterohydrocarbyl;

wherein the catalyst system does not contain a borate activator.

2. The polymerization process according to claim 1, where the hydrocarbyl-modified methylaluminoxane has less than 20 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane.

3. The polymerization process according to claim 1 or claim 2, where the hydrocarbyl-modified methylaluminoxane has less than 15 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane.

4. The polymerization process according to claim 1 or claim 2, where the hydrocarbyl-modified methylaluminoxane has less than 10 mole percent of trihydrocarbyl aluminum based on the total moles of aluminum in the hydrocarbyl-modified methylaluminoxane.

5. The polymerization process according to any one of the preceding claims, where R^{A1}, R^{B1}, and R^{C1} are independently linear (C_1–C_{20})alkyl.

6. The polymerization process according to any one of the preceding claims, where R^{A1}, R^{B1}, and R^{C1} are methyl, ethyl, propyl, 2-propyl, butyl, *n*-octyl, nonyl, decyl, undecyl, or dodecyl

7. The polymerization process according to any one of claims, wherein the polyolefin has a density ranging from 0.865 to 0.890 g/cm^3.

8. The polymerization process according to any one of claims, wherein the polyolefin has a molecular weight ranging from 30,000 to 100,000 g/mol.

9. The polymerization process according to any one of the preceding claims, wherein R^1 and R^2 are independently (C_1–C_{12})alkyl or (C_6–C_{20})aryl.

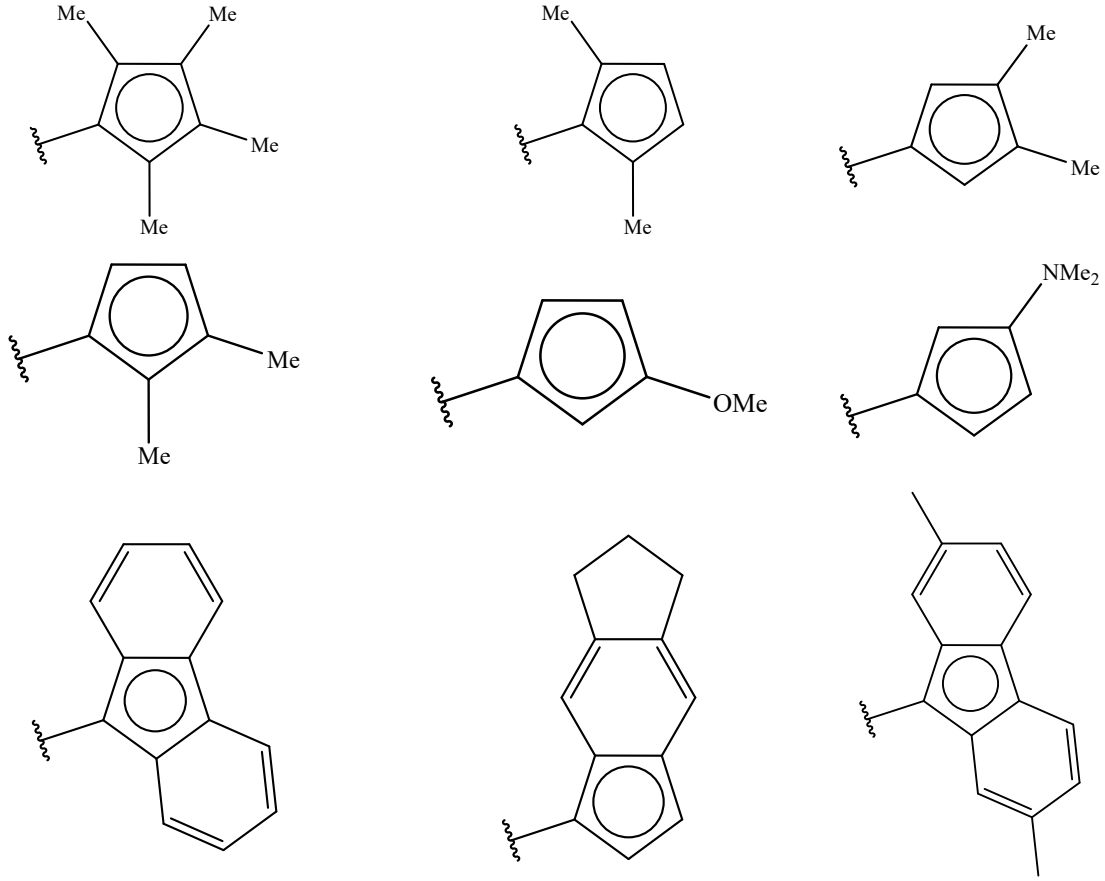
10. The polymerization process according to any one of the preceding claims, wherein R^1 and R^2 are methyl, ethyl, propyl, or phenyl.

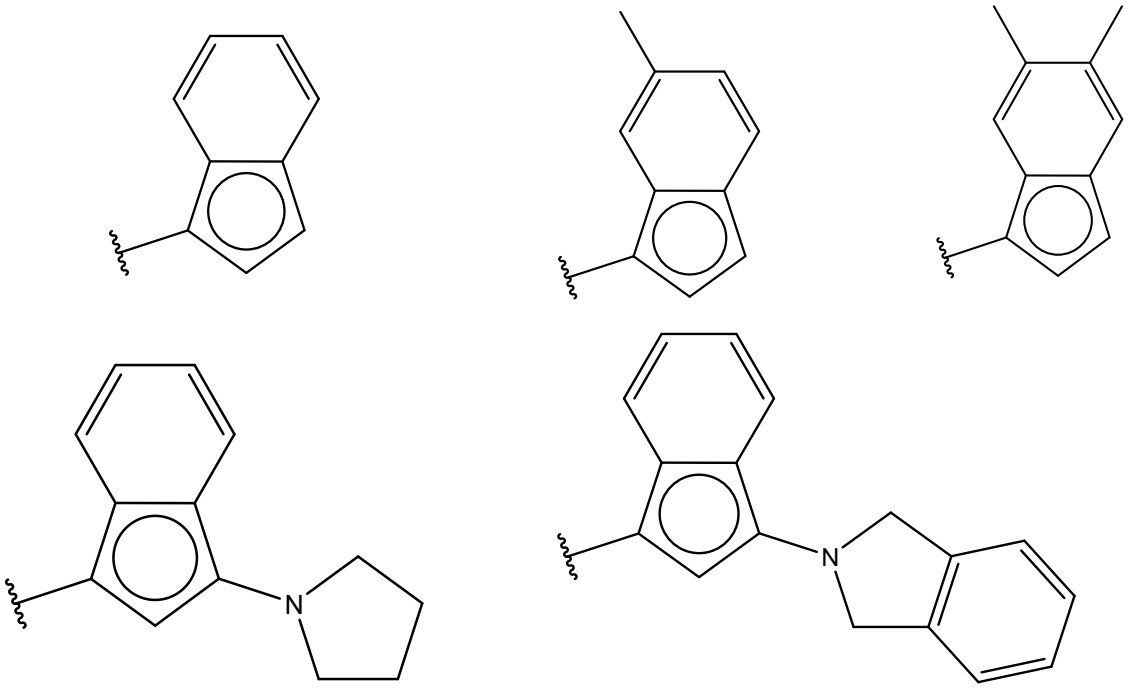
11. The polymerization process according to any one of the preceding claims, wherein R^3 is independently (C_1-C_{12})alkyl.

12. The polymerization process according to any one of the preceding claims, wherein R^3 is independently *tert*-butyl, *tert*-octyl, or *n*-octyl.

13. The polymerization process according to any one of the preceding claims, wherein Cp is independently tetramethylcyclopentadienyl.

14. The polymerization process according to any one of the preceding claims, wherein Cp is selected from:





15. The polymerization process according to any one of the preceding claims, wherein the polymerization process is a solution polymerization reaction.