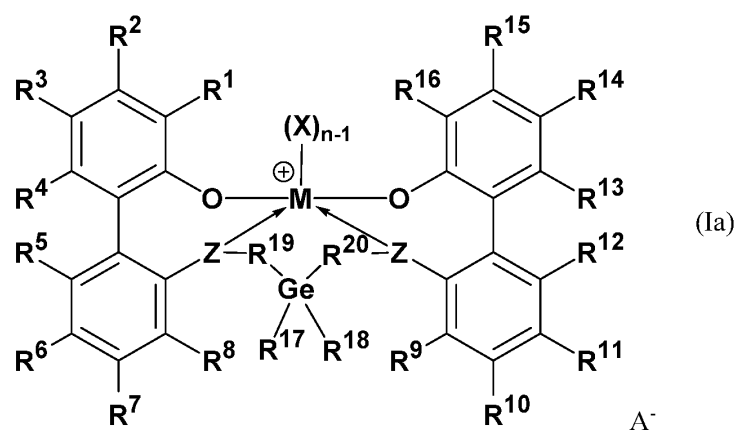


CLAIMS

1. A process for producing an ethylene-based copolymer having a reverse comonomer distribution, the process comprising polymerizing ethylene and one or more (C₃–C₁₂) α -olefin comonomers in the presence a catalyst system in a single gas-phase polymerization reactor at a reactor temperature of 60 °C to less than or equal to 150 °C and a molar feed ratio of less than or equal to 0.020 of the one or more (C₃–C₁₂) α -olefin comonomers to the ethylene, wherein:

the catalyst system comprises an activated metal-ligand complex disposed on one or more support materials; and the metal-ligand complex has a structure according to formula (Ia):



wherein:

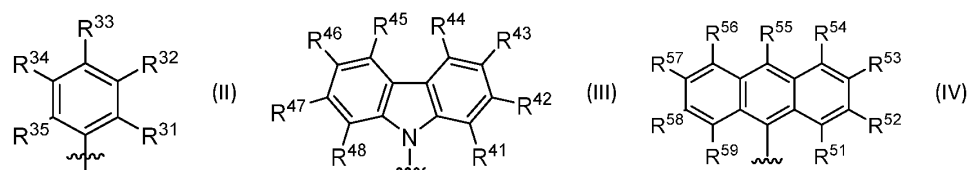
A⁻ is an anion;

M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

each X is a monodentate ligand independently chosen from unsaturated (C₂–C₅₀)hydrocarbon, unsaturated (C₂–C₅₀)heterohydrocarbon, (C₁–C₅₀)hydrocarbyl, (C₁–C₅₀)heterohydrocarbyl, (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, halogen, –N(R^N)₂, and –N(R^N)COR^C;

R¹ and R¹⁶ are independently chosen from (C₆–C₅₀)aryl, (C₄–C₅₀)heteroaryl, (C₁–C₄₀)alkyl, (C₃–C₄₀)heteroalkyl, radicals having formula (II), radicals having formula (III), and radicals having formula (IV):



wherein R³¹⁻³⁵, R⁴¹⁻⁴⁸, and R⁵¹⁻⁵⁹ are independently chosen from -H, (C₁-C₅₀)hydrocarbyl, (C₁-C₅₀)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, R⁴, R⁵, R⁶, R⁷, R⁸, R⁹, R¹⁰, R¹¹, R¹², R¹³, R¹⁴, and R¹⁵ are independently chosen from -H, (C₁-C₅₀)hydrocarbyl, (C₁-C₅₀)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)-, and halogen; R¹⁹ and R²⁰ are independently chosen from -(CR^C)_m-, wherein subscript m is from 1 or 2, and R^C is -H or (C₁-C₁₀)hydrocarbyl;

R¹⁷ and R¹⁸ are independently chosen from linear or branched (C₁-C₂₀)alkyl; and each R^C, R^P, and R^N are independently chosen from -H, (C₁-C₅₀)hydrocarbyl, and (C₁-C₅₀)heterohydrocarbyl; and

the ethylene-based copolymer has a unimodal molecular weight distribution as determined by gel permeation chromatography (GPC) and a molecular weight comonomer distribution index of greater than 0 as determined by determined by rapid Fourier Transform-Infrared (FT-IR) spectroscopy of the gel permeation chromatography (GPC) measurement.

2. The process of claim 1, wherein R¹ and R¹⁶ are the same.
3. The process of claim 2 or claim 3, wherein at least one of R¹ and R¹⁶ is a radical having formula (II) and at least one of R³² and R³⁴ is *tert*-butyl.
4. The process of any one of the preceding claims, wherein at least one of R¹ and R¹⁶ is a radical having formula (III).
5. The process of claim 4, wherein at least one of R⁴², R⁴³, R⁴⁶, and R⁴⁷ is *tert*-butyl.
6. The process of claim 5, wherein R⁴¹-R⁴⁸ are -H.
7. The process of any one of the preceding claims, wherein the one or more support materials comprise fumed silica.

8. The process of any one of the preceding claims, wherein the catalyst system is in the form of spray-dried particles, wherein the spray-dried particles are made by spray-drying the metal-ligand complex onto the one or more support materials.
9. The process of any one of the preceding claims, wherein the process produces greater than or equal to 2,500 grams of the ethylene-based copolymer per gram of the catalyst system per hour.
10. The process of any one of the preceding claims, wherein a ratio of a weight average molecular weight of the ethylene-based copolymer to a comonomer weight percent (wt %) of the ethylene-based copolymer is greater than or equal to 10,000; or is greater than or equal to 20,000; or is greater than or equal to 30,000.
11. The process of any one of the preceding claims, wherein the molecular weight comonomer distribution is greater than 0 when the weight molecular weight average is greater than 200,000 g/mol.
12. The process of any one of the preceding claims, wherein the ethylene-based polymer further comprises a weight molecular weight average of greater than 500,000 g/mol.
13. A process for producing an ethylene-based copolymer having a reverse comonomer distribution, the process comprising polymerizing ethylene and one or more (C₃–C₁₂) α -olefin comonomers in the presence a catalyst system in a single gas-phase polymerization reactor at a reactor temperature of less than or equal to 150 °C and a molar feed ratio of less than or equal to 0.020 of the one or more (C₃–C₁₂) α -olefin comonomers to the ethylene, wherein:
the catalyst system comprises an activated metal–ligand complex having a Group IV metal center and at least one dianionic heterohydrocarbyl ligand and one or more monoanionic hydrocarbyl ligand provided that the ligand is not cyclopentadienyl; wherein the catalyst system does not contain a support material; and
the ethylene-based copolymer has a unimodal molecular weight distribution and a molecular weight comonomer distribution index of greater than 0.
14. The process of claim 13, wherein the catalyst system further comprises one or more activators.
15. The process of claim 13 or 14, wherein the one or more activators comprises methylalumoxane (MAO).

16. The process of any one of claims 13 to 15, wherein the catalyst system is fed to the gas-phase polymerization reactor in neat form, as a solution, as a slurry, or a combination thereof.
17. The process of any one of claims 13 to 16, wherein the reactor temperature is less than or equal to 120°C; or wherein the reactor temperature is 75°C to 105°C; or wherein the reactor temperature is 80°C to 100°C; or wherein the reactor temperature is 85°C to 95°C.
18. The process of any one of claims 13 to 17, wherein the molecular weight average of the ethylene-based copolymer is greater than 200,000 g/mol; or wherein the ethylene-based copolymer comprises a molecular weight average of greater than 500,000 g/mol.
19. The process of any one of claims 13 to 18, wherein the ethylene-based copolymer further comprises a comonomer incorporation of less than 30 wt.% as determined by Rapid FT-IR spectroscopy on dissolved polymer or a GPC measurement.