CATALYST SYSTEMS AND PROCESSES FOR PRODUCING POLYETHYLENE USING THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to U.S. Provisional Patent Application No. 63/031,638 filed May 29, 2020, U.S. Provisional Patent Application No. 63/143,324 filed January 29, 2021, and U.S. Provisional Patent Application No. 63/143,333 filed January 29, 2021, each of which is incorporated by reference in its entirety.

TECHNICAL FIELD

[0002] Embodiments of the present disclosure are generally directed to processes for producing polyethylene and, in particular, contacting ethylene and, optionally, one or more (C_3−C_{12})α-olefin comonomers with silyl-bridged bis-phenylphenoxy catalyst systems in a gas-phase polymerization reactor.

BACKGROUND

[0003] Since the discovery of Ziegler and Natta on heterogeneous olefin polymerizations, global polyolefin production reached approximately 150 million tons per year in 2015, and continues to increase due to market demand. The catalyst systems in the polyolefin polymerization process may contribute to the characteristics and properties of such polyolefins. For example, catalyst systems that include bis-phenylphenoxy (BPP) metal-ligand complexes may produce polyolefins that have flat or reverse short-chain branching distributions (SCBD), relatively high levels of comonomer incorporation, high native molecular weights, and/or narrow-medium molecular weight distributions (MWD).

[0004] However, when utilized in some polymerization processes, such as gas-phase polymerization, catalyst systems that include BPP metal-ligand complexes may exhibit generally poor productivity. That is, catalyst systems that include BPP metal-ligand complexes may generally produce less polymer relative to the amount of the catalyst system used. Therefore, the use of catalyst systems that include BPP metal-ligand complexes may not be commercially viable in gas-phase polymerization processes.

SUMMARY

[0005] Accordingly, ongoing needs exist for catalyst systems that are suitable for use in gas-phase reactors and have improved productivity when utilized in gas-phase polymerization processes. The present disclosure addresses these needs by providing catalyst systems that may be utilized in gas-phase polymerization processes, exhibit a greatly increased

productivity when compared to similar catalyst systems including BPP metal-ligand complexes without silicon-containing bridges.

[0006] Furthermore, ethylene-based copolymer (also called poly(ethylene-co-1-alkene)) resins generally have the short chain branching distribution (SCBD) or comonomer distribution. Many ethylene-based copolymers have a reverse SCBD or reverse comonomer distribution, in which the weight percent comonomer decreases as the molecular weight of the ethylene-based copolymer increases. However, producing copolymers with an increase in the weight percent (wt%) comonomer as the molecular weight (MW) of the polymer chains increases improves performances in many applications.

[0007] A reverse comonomer distribution is usually achieved using a dual reactor configuration and a single or dual catalyst process. In a dual reactor process a single catalyst can be used to make a high molecular weight, lower density component (having higher wt% comonomer) and a low molecular weight high density (lower wt% comonomer) component in separate reactors via independent process controls in the two reactors. The result is a bimodal resin that has a net reverse SCBD across the bimodal distribution. In the case of a dual catalyst single reactor process, one catalyst makes a high molecular weight low density component, while the other makes a low molecular weight high density component, resulting in a bimodal product having reverse SCBD.

[0008] This disclosure includes processes for producing an ethylene-based copolymer having a reverse comonomer distribution. In examples, the process includes polymerizing ethylene and one or more (C_3−C_{12})α-olefin comonomers in the presence of 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 (C_3−C_{12})α-olefin comonomers to the ethylene, wherein: the catalyst system comprises an activated metal−ligand complex having a structure according to formula (Ia); and the ethylene-based copolymer has a unimodal molecular weight distribution as determined by gel permeation chromatography (GPC, e.g., conventional GPC) and a molecular weight comonomer distribution index of greater than 0 as determined by Rapid FT-IR spectroscopy on dissolved polymer of a GPC measurement.

[0009] In one or more examples, the catalyst system includes an activated metal−ligand complex disposed on one or more support materials. The activated metal−ligand complex has a structure according to formula (Ia):

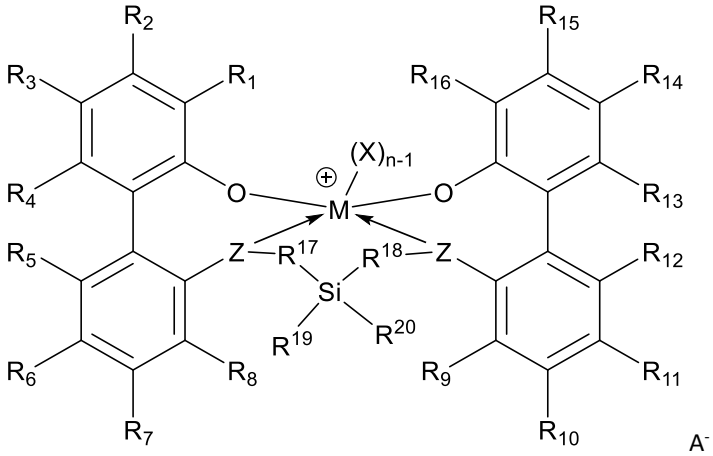
[0015] In formula (I), R^{17} and R^{18} are independently chosen from $–(CR^C_2)_m–$, wherein subscript m is from 1 to 10, and R^C of $–(CR^C_2)_m$ is −H, $(C_1–C_{10})$alkyl.

[0016] In formula (I), R^{19} and R^{20} are independently chosen from linear or branched $(C_1–C_{20})$alkyl.

[0017] In formulas (I), (II), (III), and (IV), each R^C, R^P, and R^N are independently chosen from −H, $(C_1–C_{50})$hydrocarbyl, and $(C_1–C_{50})$heterohydrocarbyl.

[0017a] In one aspect, the present disclosure includes a process for producing an ethylene-based copolymer having a reverse comonomer distribution, the process comprising polymerizing ethylene and one or more $(C_3–C_{12})$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 $(C_3–C_{12})$α-olefin comonomers to the ethylene, wherein:

the catalyst system comprises one or more support materials and an activated metal−ligand complex having a structure according to formula (Ia):



(Ia)

wherein:

A^- is an anion;

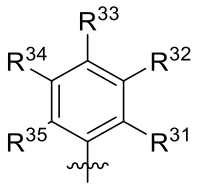
M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

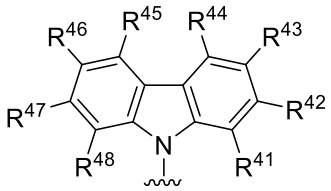
each X is a monodentate ligand independently chosen from unsaturated $(C_2–C_{50})$hydrocarbon, unsaturated $(C_2$-$C_{50})$heterohydrocarbon, $(C_1$-$C_{50})$hydrocarbyl, $(C_1–C_{50})$heterohydrocarbyl, $(C_6–C_{50})$aryl, $(C_4–C_{50})$heteroaryl, halogen, $–N(R^N)_2$, and $–N(R^N)COR^C$;

each Z is–O−;

R^1 and R^{16} are independently chosen from radicals having formula (II), or radicals having formula (III):



(II)



(III)

wherein $R^{31–35}$ and $R^{41–48}$ are independently chosen from –H, (C_1−C_{50})hydrocarbyl, (C_1−C_{50})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)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R^N)−, (R^C)$_2$NC(O)−, or halogen;

R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, and R^{15} are independently chosen from −H, (C_1−C_{50})hydrocarbyl, (C_1−C_{50})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)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R)−, (R^C)$_2$NC(O)−, and halogen;

R^{17} and R^{18} are independently chosen from –(CR^C_2)$_m$ –, wherein subscript m is from 1 to 10;

R^{19} and R^{20} are independently chosen from linear or branched (C_1−C_{20})alkyl; and

each R^C, R^P, and R^N are independently chosen from −H, (C_1−C_{50})hydrocarbyl, and (C_1−C_{50})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 on dissolved copolymer during the gel permeation chromatography (GPC) measurement.

[0018] The present disclosure also includes methods for producing a catalyst system. The method includes contacting one or more support materials, one or more activators, and a metal-ligand complex in an inert hydrocarbon solvent to produce the catalyst system.

[0019] The present disclosure also includes a process for producing polyethylene. The process includes contacting ethylene and, optionally, one or more (C_3−C_{12})α-olefin comonomers with a catalyst system in a gas-phase polymerization reactor. The catalyst system comprises a metal-ligand complex disposed on one or more support materials.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] FIG. 1 is a graphical depiction of the reverse comonomer distributions and molecular weight distributions of inventive Examples 1 and 4.

[0021] FIG. 2 is a graphical depiction of the reverse comonomer distributions and molecular weight distributions of inventive Example 12.

[0022] FIG. 3 is a graphical depiction of the reverse comonomer distributions and molecular weight distributions of inventive Example 13.

[0023] FIG. 4 is a graphical depiction of the reverse comonomer distributions and molecular weight distributions of inventive Examples 15 and 16.

DETAILED DESCRIPTION

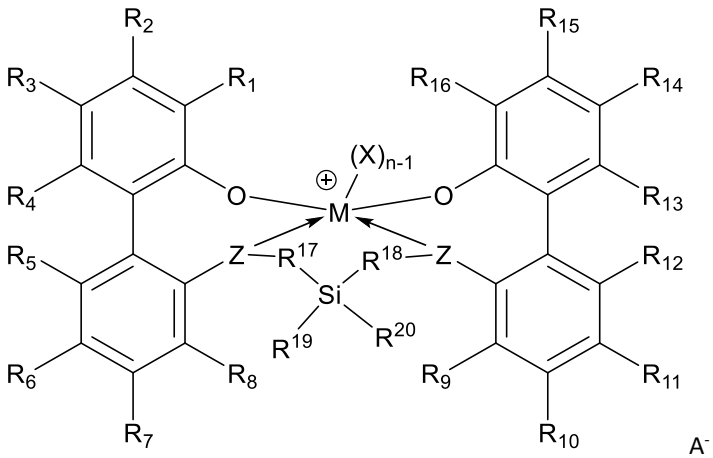
[0024] Specific embodiments of procatalysts, catalyst systems, methods of producing catalyst systems, and processes for producing polyethylene will now be described. However, it should be understood that the systems, methods, and processes of the present disclosure may be embodied in different forms, and should not be construed as limited to the specific embodiments set forth in the present disclosure. Rather, embodiments are provided so that the present disclosure will be thorough and complete, and will fully convey the scope of the disclosed subject matter to those skilled in the art.

[0025] Common abbreviations used in the present disclosure are listed below:

CLAIMS

1. A process for producing an ethylene-based copolymer having a reverse comonomer distribution, the process comprising polymerizing ethylene and one or more (C_3–C_{12})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 (C_3–C_{12})α-olefin comonomers to the ethylene, wherein:

the catalyst system comprises one or more support materials and an activated metal–ligand complex having a structure according to formula (Ia):



(Ia)

wherein:

A^- is an anion;

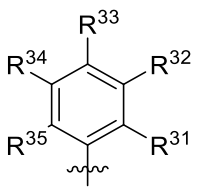
M is titanium, zirconium, or hafnium;

n is 1, 2, or 3;

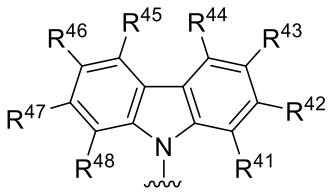
each X is a monodentate ligand independently chosen from unsaturated (C_2–C_{50})hydrocarbon, unsaturated (C_2-C_{50})heterohydrocarbon, (C_1-C_{50})hydrocarbyl, (C_1–C_{50})heterohydrocarbyl, (C_6–C_{50})aryl, (C_4–C_{50})heteroaryl, halogen, –$N(R^N)_2$, and –$N(R^N)COR^C$;

each Z is–O–;

R^1 and R^{16} are independently chosen from radicals having formula (II), or radicals having formula (III):



(II)



(III)

wherein $R^{31–35}$ and $R^{41–48}$ are independently chosen from –H, (C_1−C_{50})hydrocarbyl, (C_1−C_{50})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)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R^N)−, (R^C)$_2$NC(O)−, or halogen;

R^2, R^3, R^4, R^5, R^6, R^7, R^8, R^9, R^{10}, R^{11}, R^{12}, R^{13}, R^{14}, and R^{15} are independently chosen from −H, (C_1−C_{50})hydrocarbyl, (C_1−C_{50})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)$_2$C=N−, R^CC(O)O−, R^COC(O)−, R^CC(O)N(R)−, (R^C)$_2$NC(O)−, and halogen;

R^{17} and R^{18} are independently chosen from –(CR^C_2)$_m$ −, wherein subscript m is from 1 to 10;

R^{19} and R^{20} are independently chosen from linear or branched (C_1−C_{20})alkyl; and

each R^C, R^P, and R^N are independently chosen from −H, (C_1−C_{50})hydrocarbyl, and (C_1−C_{50})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 on dissolved copolymer during the gel permeation chromatography (GPC) measurement.

2. The process of claim 1, wherein R^1 and R^{16} are the same.

3. The process of either one of claim 1 or claim 2, wherein at least one of R^1 and R^{16} is a radical having formula (II) and at least one of R^{32} and R^{34} is *tert*-butyl.

4. The process of either one of claim 1 or claim 2, wherein at least one of R^1 and R^{16} is a radical having formula (III).

5. The process of claim 4, wherein at least one of R^{42}, R^{43}, R^{46}, and R^{47} is *tert*-butyl.

6. The process of claim 5, wherein $R^{41\text{-}48}$ 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 comprises spray-dried particles.

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 weight percent comonomer content of the ethylene-based copolymer is greater than or equal to 10,000; or wherein a ratio of a weight average molecular weight of the ethylene-based copolymer to weight percent comonomer content of the ethylene-based copolymer is greater than or equal to 20,000; or wherein a ratio of a weight average molecular weight of the ethylene-based copolymer to weight percent comonomer content of the ethylene-based copolymer is greater than or equal to 30,000.

11. The process of any one of the preceding claims, wherein the catalyst system further comprises one or more activators.

12. The process of claim 11, wherein the one or more activators comprises methylalumoxane (MAO).

13. The process of any one of the preceding claims, 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.

14. The process of any one of the preceding claims, 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.

15. The process of any one of the preceding claims, wherein the molecular weight of the ethylene-based copolymer is greater than 200,000 g/mol; or wherein the ethylene-based copolymer comprises a molecular weight of greater than 500,000 g/mol.

16. The process of any one of the preceding claims, 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 of a GPC measurement.