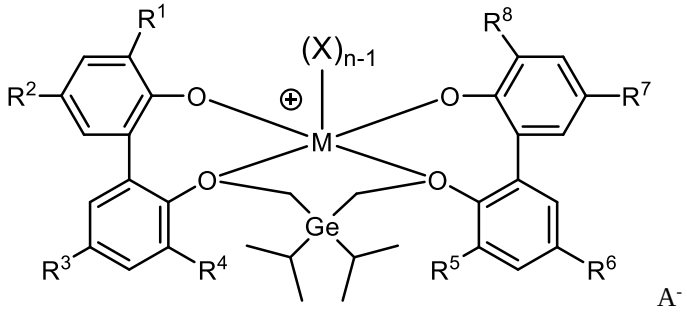
## CLAIMS

1. A process for producing polyethylene, the process comprising contacting ethylene and, optionally, one or more ($C_3$−$C_{12}$)α-olefin comonomers with a catalyst system in a gas-phase polymerization reactor at a reactor temperature of 70 °C to less than or equal to 150 °C with an ethylene partial pressure greater than or equal to 150 psi, and a molar feed ratio of less than or equal to 0.030 of one or more ($C_3$-$C_{12}$)α-olefin comonomers to ethylene using the catalyst system comprising a metal−ligand complex disposed on one or more support materials, wherein the metal−ligand complex has a structure according to formula (Ia):




(Ia)

wherein:

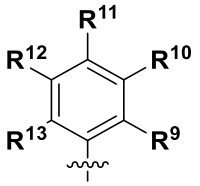
$A^-$ is an anion;

M is titanium, zirconium, or hafnium;

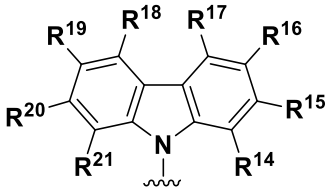
n is 1, 2, or 3;

each X is a monodentate ligand independently selected from a group consisting of ($C_1$−$C_{50}$)hydrocarbyl, ($C_1$−$C_{50}$)heterohydrocarbyl, ($C_6$−$C_{50}$)aryl, ($C_2$−$C_{50}$)heteroaryl, and halogen;

$R^1$ and $R^8$ are independently selected from a group consisting of radicals having formula (II), and radicals having formula (III):




(II)




(III)

wherein $R^{9–13}$, and $R^{14–21}$ are independently chosen from –H, ($C_1$−$C_{50}$)hydrocarbyl, ($C_1$−$C_{50}$)heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, or halogen;

$R^2$, $R^3$, $R^4$, $R^5$, $R^6$, and $R^7$ are independently chosen from −H, ($C_1$−$C_{50}$)hydrocarbyl, ($C_1$−$C_{50}$)heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, and halogen; and

an amount of ethylene consumed during the first 5 minutes upon injection of the catalyst system into the gas-phase polymerization reactor is less than 25% of the total ethylene consumed for the time of the entirety of the average residence time, $t_R$, upon initial addition of the catalyst system, wherein the time at which 25% of the total ethylene uptake ($t_{25\%}$) is calculated by the equation according to formula (IV):

$$\frac{\sum_{t=0}^{t_{25\%}} C2(t)}{\sum_{t=0}^{t_R} C2(t)} = 0.25, and\ t_{25\%} > 5\ \text{min} \qquad \text{(IV)}.$$

2. The process of claim 1, wherein the process further comprises an uptake ratio ($U_t$) at a specific time, $t$, during the entirety of the average residence time, $t_R$, can be calculated according to formula (V):

$$\cup_t = \frac{\sum_{t=0}^{t} C2(t)}{\sum_{t=0}^{t_R} C2(t)} \qquad \text{(V)}$$

and $U_t$ of the catalyst system is less than or equal to 0.02 (2 percent) at the time point of 0.5 minutes (30 seconds) after the catalyst system is fed into the reactor as given by the formulae (X) and (XI):

$$Uptake\ at\ 30\ sec\ (0.5\ min), U_{0.5} = \frac{\sum_{t=0}^{0.5} C2(t)}{\sum_{t=0}^{t_R} C2(t)} \leq 0.02 \qquad \text{(X)}$$

$$Uptake\ at\ 30\ sec\ (0.5\ min), U_{0.5} = \int_0^{0.5} \mathrm{C2(t)dt} \leq 0.02 \qquad \text{(XI)}$$

3. The process of claim 2, wherein the $U_t$ of the catalyst system is less than or equal to 0.05 (5 percent) at the time point of 1.5 minutes (90 seconds) after the catalyst system is fed into the reactor, given by the expression:

$$U_{1.5} = \frac{\sum_{t=0}^{1.5} C2(t)}{\sum_{t=0}^{t_R} C2(t)} \leq 0.05 \qquad \text{(XIII)}$$

4. The process of claim 2 or claim 3, wherein the $U_t$ of the catalyst system is less than or equal to 0.15 (15 percent) at the time point of 3.0 minutes (180 seconds) after the catalyst system is fed into the reactor, given by the expression:

$$U_{3.0} = \frac{\sum_{t=0}^{3.0} C2(t)}{\sum_{t=0}^{t_R} C2(t)} \leq 0.15 \qquad \text{(XIV)}$$

5. The process of any one of claims 1 to 4, wherein the $U_t$ of the catalyst system is less than or equal to 0.10 (10 percent) at the time point of 3.0 minutes (180 seconds) after the catalyst system is fed into the reactor, given by the expression:

$$U_{3.0} = \frac{\sum_{t=0}^{3.0} C2(t)}{\sum_{t=0}^{t_R} C2(t)} \leq 0.10 \qquad \text{(XIV)}$$

6. The process of any one of claims 1 to 5, wherein the amount of ethylene consumed during the first 18 minutes upon injection of the catalyst system into the gas-phase polymerization reactor is less than 50% of the total ethylene consumed for the time of the entirety of the average residence time, $t_R$, upon initial addition of the catalyst system, wherein the time at which 50% of the total ethylene uptake ($t_{25\%}$) is calculated by the equation according to formula (IV):

$$\frac{\sum_{t=0}^{t_{50\%}} C2(t)}{\sum_{t=0}^{t_R} C2(t)} = 0.50, and\ t_{25\%} > 20\ \text{min} \qquad \text{(XV)}.$$

7. The process of any one of claims 1 to 6, wherein the percent exotherm ($\%_{exo}$) is less than 10%, or wherein the percent exotherm ($\%_{Exo}$) is less than 5%.

8. The process of any one of claims 1 to 7, wherein $R^1$ and $R^8$ are the same; or

wherein at least one of $R^1$ and $R^8$ is a radical having formula (II) and at least one of $R^{10}$ and $R^{12}$ is *tert*-butyl; or

wherein one of $R^1$ and $R^8$ is a radical having formula (III); or

wherein at least one of $R^{15}$, $R^{16}$, $R^{19}$, and $R^{20}$ is *tert*-butyl; or

wherein $R^{14\text{-}21}$ are –H.

9. The process of any one of the preceding claims, wherein one or more support materials comprise fumed silica.

10. The process of any one of the preceding claims, wherein the anion is an aluminate.

11. A method of preparing the catalyst system of claim 1, wherein the method comprises:

disposing the one or more activators on the one or more support materials to produce a supported activator; and

contacting the supported activator with a solution or slurry of the neutral metal-ligand complex in the inert hydrocarbon solvent.

12. The method of claim 1511 wherein the activator comprises methylalumoxane (MAO).

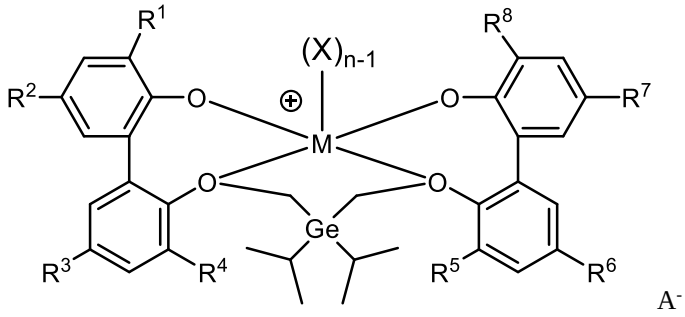
13. The method of any one of claims 1 to 12, wherein the catalyst system is fed to the gas-phase polymerization reactor in neat form, as a solution, or as a slurry.

14. The method of any one of claims 1 to 13, wherein the catalyst system comprises spray-dried particles.

15. The process of any one of claims 1-14, wherein the ethylene partial pressure in the reactor is greater or equal to 150 psi, or wherein the ethylene partial pressure is greater or equal to 170 psi, or wherein the ethylene partial pressure is greater or equal to 200 psi.

16. The process of any one of claims 1-15, wherein the reactor temperature is less than or equal to 120°C; or wherein the reactor temperature is 75°C to 110°C; or wherein the reactor temperature is 80°C to 105°C; or wherein the reactor temperature is 85°C to 100°C.

17. A process for producing polyethylene, the process comprising contacting ethylene and, optionally, one or more ($C_3$–$C_{12}$)α-olefin comonomers with a catalyst system in a gas-phase polymerization reactor at a reactor temperature of 70 °C to less than or equal to 150 °C with an ethylene partial pressure of 50 psi to 150 psi, and a molar feed ratio of less than or equal to 0.030 of one or more ($C_3$-$C_{12}$)α-olefin comonomers to ethylene using the catalyst system comprising a metal–ligand complex disposed on one or more support materials, wherein the metal–ligand complex has a structure according to formula (Ia):

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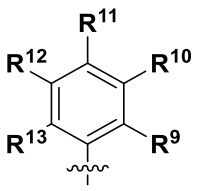


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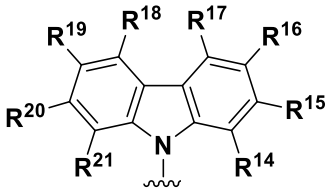


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$R^2$, $R^3$, $R^4$, $R^5$, $R^6$, and $R^7$ are independently chosen from −H, ($C_1$–$C_{50}$)hydrocarbyl, ($C_1$–$C_{50}$)heterohydrocarbyl, $-Si(R^C)_3$, $-Ge(R^C)_3$, $-P(R^P)_2$, $-N(R^N)_2$, $-OR^C$, $-SR^C$, and halogen; and

an amount of ethylene consumed during the first 25 minutes upon injection of the catalyst system into the gas-phase polymerization reactor is less than 50% of the total ethylene consumed for the time of the entirety of the average residence time, $t_R$, upon initial addition of the catalyst system, wherein the time at which 25% of the total ethylene uptake ($t_{25\%}$) is calculated by the equation according to formula (IV):

$$\frac{\sum_{t=0}^{t_{25\%}} C2(t)}{\sum_{t=0}^{t_R} C2(t)} = 0.25, and\ t_{25\%} > 5\ \text{min} \qquad \text{(IV)}.$$

18. The process of claim 17, wherein the ethylene partial pressure is from 80 psi to 115 psi, or from 90 psi to 130 psi, or from 100 to 150 psi.

19. The process of claim 17, wherein the amount of ethylene consumed during the first 30 minutes upon initial injection of the catalyst system into the gas-phase polymerization reactor is less than 50% of the total ethylene consumed for the time of the entirety of the average residence time.

20. The process of claims 17 to 19, wherein the percent exotherm ($\%_{exo}$) is less than 5%, or wherein the percent exotherm ($\%_{Exo}$) is less than 2%.