

What is claimed is:

1. A polymerization process control method, comprising:
 - performing a polymerization reaction in a polymerization reactor to produce polyethylene, wherein the polymerization reaction is catalyzed by an electron donor-free Ziegler-Natta catalyst and an alkyl aluminum co-catalyst with ethylene and optionally one or more comonomers to produce the polyethylene;
 - removing a portion of the polyethylene from the polymerization reactor;
 - measuring a melt flow ratio (I_{21}/I_2) of the polyethylene removed from the polymerization reactor to determine the amount of long chain branching (LCB) using a predetermined relationship between the melt flow ratio (I_{21}/I_2) and the LCB; and
 - controlling an amount of long chain branching (LCB) of the polyethylene from the polymerization reactor by adjusting a weight concentration of the alkyl aluminum co-catalyst present in the polymerization reactor.
2. The polymerization process control method of claim 1, wherein adjusting the weight concentration of the alkyl aluminum co-catalyst present in the polymerization reactor is done by changing a mole ratio of the alkyl aluminum co-catalyst to active metal in the electron donor-free Ziegler-Natta catalyst.
3. The polymerization process control method of claim 1, further including varying a weight concentration of the alkyl aluminum co-catalyst in the polymerization reactor while performing the polymerization reaction, thereby changing the melt flow ratio (I_{21}/I_2) of the polyethylene from the polymerization reactor to make a predetermined change in at least the LCB or to bring the LCB in the polyethylene into compliance with a predetermined product specification set.
4. The polymerization process control method of claim 3, including:
 - generating melt flow ratio (I_{21}/I_2) data and LCB data from polyethylene produced while varying the weight concentration of the alkyl aluminum co-catalyst in the polymerization reactor; and

developing the predetermined relationship between the melt flow ratio (I_{21}/I_2) and the LCB from the melt flow ratio (I_{21}/I_2) data and LCB data.

5. The polymerization process control method of claim 1, wherein controlling the amount of LCB includes decreasing the weight concentration of the alkyl aluminum co-catalyst present in the polymerization reactor to increase the LCB of the polyethylene produced in the polymerization reactor.

6. The polymerization process control method of claim 1, wherein the polyethylene has LCB greater than about 0.01 per 1,000 carbon atoms and less than about 0.07 per 1,000 carbon atoms and wherein the polyethylene has a melt flow ratio (I_{21}/I_2) ranging from about 35 to about 55 or a density of from 0.91 g/cm³ to about 0.965 g/cm³.

7. The polymerization process control method of claim 1, wherein the electron donor-free Ziegler-Natta catalyst is formed by a process that comprises:

combining one or more supports with one or more magnesium-containing compounds under reaction conditions to form a first reacted product;

combining one or more chloro substituted silanes with the first reacted product under reaction conditions to form a second reacted product; and

combining one or more titanium halides with the second reacted product under reaction conditions to form the electron donor-free Ziegler-Natta catalyst,

wherein the one or more supports comprises silica, alumina, or a combination thereof

wherein the one or more magnesium-containing compounds has the formula: R^1-Mg-R^2 , wherein R^1 and R^2 are independently selected from the group consisting of hydrocarbyl groups and halogen atoms.

8. The polymerization process control method of claim 1, wherein the alkyl aluminum co-catalyst is triethylaluminum (TEAL), triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, trimethylaluminum or any combination thereof.

9. The polymerization process control method of claim 1, wherein the polymerization reactor is selected from the group consisting of a solution reactor, a slurry loop reactor, a supercritical loop reactor, a stirred-bed gas-phase reactor, or a fluidized-bed, gas-phase reactor.

10. A polymerization process control method, comprising:
- performing a polymerization reaction in a polymerization reactor to produce polyethylene, wherein the polymerization reaction is catalyzed by an electron donor-free Ziegler-Natta catalyst and an alkyl aluminum co-catalyst with ethylene and optionally one or more comonomers to produce the polyethylene;
 - measuring an electron donor-free Ziegler-Natta catalyst productivity of the polyethylene from the polymerization reactor;
 - determining an amount of long chain branching (LCB) of the polyethylene from the polymerization reactor using the measured electron donor-free Ziegler-Natta catalyst productivity and a predetermined relationship between the electron donor-free Ziegler-Natta catalyst productivity and the LCB; and
 - controlling an amount of LCB of the polyethylene from the polymerization reactor by adjusting a weight concentration of the alkyl aluminum co-catalyst present in the polymerization reactor.
11. The polymerization process control method of claim 10, wherein adjusting the weight concentration of the alkyl aluminum co-catalyst present in the polymerization reactor is done by changing a mole ratio of the alkyl aluminum co-catalyst to active metal in the electron donor-free Ziegler-Natta catalyst.
12. The polymerization process control method of claim 10, further including varying a weight concentration of the alkyl aluminum co-catalyst in the polymerization reactor while performing the polymerization reaction, thereby implementing a predetermined change in at least the LCB so as to bring the LCB in the polyethylene into compliance with a predetermined product specification set.
13. The polymerization process control method of claim 12, including:
- generating electron donor-free Ziegler-Natta catalyst productivity data and LCB data from polyethylene produced while varying the weight concentration of the alkyl aluminum co-catalyst in the polymerization reactor; and

developing the predetermined relationship between the electron donor-free Ziegler-Natta catalyst productivity and the LCB from the electron donor-free Ziegler-Natta catalyst productivity data and LCB data.

14. The polymerization process control method of claim 10, where deviations in catalyst productivity function as a leading indicator of impending changes in a polymer MFR and/or LCB, the method further including responding to the deviations in catalyst productivity by adjusting the weight concentration of the alkyl aluminum co-catalyst in the polymerization reactor and/or changing a mole ratio of the alkyl aluminum co-catalyst to active metal in the electron donor-free Ziegler-Natta catalyst whereby the electron donor-free Ziegler-Natta catalyst productivity of the polyethylene from the polymerization reactor is controlled.

15. The polymerization process control method of claim 10, where deviations in catalyst productivity result in changes in the production rate from the polymerization reactor and function as a leading indicator of impending changes in a polymer MFR and/or LCB, the method further including responding to the deviations in catalyst productivity by adjusting a feed rate of the electron donor-free Ziegler-Natta catalyst whereby a constant polyethylene production rate from the polymerization reactor is maintained while adjusting the weight concentration of the alkyl aluminum co-catalyst in the polymerization reactor and/or changing a mole ratio of the alkyl aluminum co-catalyst to active metal in the electron donor-free Ziegler-Natta catalyst to control the polymer MFR and/or an amount of LCB.

16. The polymerization process control method of claim 10, further comprising decreasing the weight concentration of the alkyl aluminum in the polymerization reactor thereby increasing productivity of the electron donor-free Ziegler-Natta catalyst relative to the productivity before the change in weight concentration.

17. The polymerization process control method of claim 10, wherein decreasing the weight concentration of the alkyl aluminum co-catalyst present in the polymerization reactor increases the LCB of the polyethylene produced in the polymerization reactor.

18. The polymerization process control method of claim 10, wherein the polyethylene has LCB greater than about 0.01 per 1,000 carbon atoms and less than about 0.07 per 1,000 carbon atoms and wherein the polyethylene has a melt flow ratio (I_{21}/I_2) ranging from about 35 to about 55 or a density of from 0.91 g/cm³ to about 0.965 g/cm³.
19. The polymerization process control method of claim 10, wherein the electron donor-free Ziegler-Natta catalyst is formed by a process that comprises:
- combining one or more supports with one or more magnesium-containing compounds under reaction conditions to form a first reacted product;
 - combining one or more chloro substituted silanes with the first reacted product under reaction conditions to form a second reacted product; and
 - combining one or more titanium halides with the second reacted product under reaction conditions to form the electron donor-free Ziegler-Natta catalyst,
- wherein the one or more supports comprises silica, alumina, or a combination thereof
 - wherein the one or more magnesium-containing compounds has the formula: R^1-Mg-R^2 , wherein R^1 and R^2 are independently selected from the group consisting of hydrocarbyl groups and halogen atoms.
20. The polymerization process control method of claim 10, wherein the alkyl aluminum co-catalyst is triethylaluminum (TEAl) or comprises triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, trimethylaluminum, or any combination thereof.
21. The polymerization process control method of claim 10, wherein the polymerization reactor is selected from the group consisting of a solution reactor, a slurry loop reactor, a supercritical loop reactor, a stirred-bed gas-phase reactor, or a fluidized-bed, gas-phase reactor.
22. A polymerization method, comprising:
- performing a polymerization reaction in a polymerization reactor to produce polyethylene, wherein the polymerization reaction is catalyzed by an electron donor-free Ziegler-Natta catalyst and an alkyl aluminum co-catalyst with ethylene and optionally one or more comonomers to produce the polyethylene;
 - removing a portion of the polyethylene from the polymerization reactor;

measuring a melt flow ratio (I_{21}/I_2) of the polyethylene removed from the polymerization reactor; and

determining an amount of long chain branching (LCB) of the polyethylene from the polymerization reactor using the measured melt flow ratio and a predetermined relationship between the melt flow ratio (I_{21}/I_2) and the LCB.