

CLAIMS

1. A method of polymerizing an olefin using a modified catalyst system that comprises a product of a reaction of a modified Ziegler-Natta procatalyst with an activator in (C) a saturated or aromatic hydrocarbon liquid, the method comprising contacting at least one polymerizable olefin in a reactor with the modified catalyst system under effective conditions to give a polyolefin product; wherein the modified Ziegler-Natta procatalyst is prepared prior to the contacting step by mixing an initial Ziegler-Natta procatalyst and a molecular (pro)catalyst together in (C) a saturated or aromatic hydrocarbon liquid under modifying conditions comprising a modifying temperature less than 100° C. and a modifying time of at least 1 minute, and optionally an activator, to give the modified Ziegler-Natta procatalyst.
2. The method of claim 1 (i) wherein the initial Ziegler-Natta procatalyst is (B) a magnesium halide-supported titanium procatalyst; wherein the (B) magnesium halide-supported titanium procatalyst has been prepared by contacting (D) a solid particulate consisting essentially of magnesium halide with (E) titanium tetrachloride in the (C) saturated or aromatic hydrocarbon liquid so as to give the (B) magnesium halide-supported titanium procatalyst; (ii) wherein the molecular (pro)catalyst consists essentially of a molecular ligand-metal complex (pro)catalyst; or (iii) both (i) and (ii).
3. The method of claim 1 or 2 wherein the modifying conditions comprise: (i) a modifying temperature from 0° C. to 50° C.; (ii) a modifying time from 3 hours to 3 months; (iii) an inert gas atmosphere (e.g., molecular nitrogen, helium, argon, or a mixture of any two or more thereof); (iv) both (i) and (ii); (v) both (i) and (iii); (vi) both (ii) and (iii); or (vii) each of (i), (ii), and (iii).
4. The method of aspect 1 or 2 wherein the modified catalyst system further comprises (G) an organoborate or (H) an organoboron.
5. The method of any one of claims 1 to 4 wherein: (i) the at least one polymerizable olefin is ethylene and the polyolefin product comprises a polyethylene; (ii) the at least one polymerizable olefin is at least one (C₃-C₄₀)alpha-olefin and the polyolefin product comprises a poly((C₃-C₄₀)alpha-olefin); or (iii) the at least one polymerizable olefin comprises a combination of ethylene and at least one (C₃-C₄₀)alpha-olefin and the polyolefin product comprises a poly(ethylene-co-(C₃-C₄₀)alpha-olefin) copolymer.

6. The method of any one of claims 1 to 5 wherein: (i) the initial magnesium halide-supported titanium procatalyst is free of Al (molar ratio of Al/Mg = 0); (ii) the initial magnesium halide-supported titanium procatalyst has a molar ratio of Al/Mg from > 0 to < 0.05 ; (iii) the magnesium halide of the initial magnesium halide-supported titanium procatalyst is magnesium chloride; (iv) the magnesium halide of the initial magnesium halide-supported titanium procatalyst is magnesium bromide; (v) both (i) and (iii); (vi) both (i) and (iv); (vii) both (ii) and (iii); (viii) both (ii) and (iv).

7. The method of any one of claims 1 to 6 wherein: (i) the (D) solid particulate consisting essentially of magnesium halide has a Brunauer, Emmett, Teller (BET) surface area of ≥ 200 square meters per gram (m^2/g) as measured by Brunauer, Emmett, Teller (BET) Surface Area Method; or (ii) the (D) solid particulate consisting essentially of magnesium halide has been prepared by contacting a solution of (F) a dialkylmagnesium compound dissolved in the (C) saturated or aromatic hydrocarbon liquid with 1.95 to 2.05 mole equivalents of hydrogen halide to give a suspension of the (D) solid particulate consisting essentially of magnesium halide in the (C) saturated or aromatic hydrocarbon liquid; or (iii) both (i) and (ii).

8. The method of any one of claims 1 to 7 wherein the activator used with the modified Ziegler-Natta procatalyst comprises (A) a hydrocarbylaluminoxane.

9. The method of any one of claims 1 to 8 wherein the molecular ligand-metal (pro)catalyst comprises: (i) a cyclopentadienyl ligand-metal complex (pro)catalyst; (ii) a cyclopentadienyl-free ligand-metal complex (pro)catalyst; or (iii) both (i) and (ii).

10. The method of any one of claims 1 to 9 wherein the contacting comprises: (i) adding the modified catalyst system into the reactor, which contains the at least one polymerizable olefin; (ii) adding the at least one polymerizable olefin into the reactor, which contains the modified catalyst system; or (iii) adding a first feed of the modified catalyst system into the reactor and a second feed of the at least one polymerizable olefin into the reactor.

11. A solution phase polymerization process of polymerizing an olefin using a modified catalyst system that is a product of a reaction of a modified Ziegler-Natta procatalyst with an activator, the process comprising contacting at least one polymerizable olefin in the reactor

with the modified catalyst system under effective conditions to give a polyolefin product; wherein the modified Ziegler-Natta procatalyst is prepared prior to the contacting step by mixing an initial Ziegler-Natta procatalyst and a molecular ligand-metal complex (pro)catalyst together under modifying conditions comprising a modifying temperature less than 100° C. and a modifying time of at least 1 minute, and optionally an activator, to give the modified Ziegler-Natta procatalyst.

12. A polyolefin product made by the polymerization method of any one of claims 1 to 11.

13. A modified Ziegler-Natta procatalyst as described in any preceding claim.

14. The modified Ziegler-Natta procatalyst of claim 13 (i) further comprising a (A) hydrocarbylaluminoxane; (ii) further comprising an organoborate or an organoboron; (iii) further comprising a trialkylaluminum; (iv) being free of a trialkylaluminum; (v) both (i) and (ii); (vi) both (i) and (iii); (vii) both (i) and (iv); or (viii) each of (i), (ii), and (iv).

15. A modified catalyst system comprising a product of a reaction of the modified Ziegler-Natta procatalyst of claim 13 or 14 with an activator.