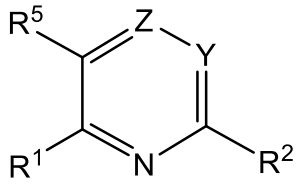
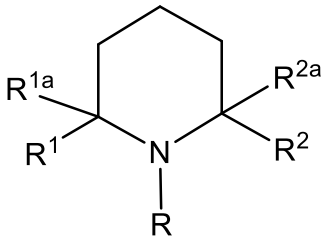
CLAIMS

1. A procatalyst system suitable for making an olefin polymerization catalyst and consisting essentially of a blend of (A) a pre-made solid procatalyst and (B) an azaheterocycle;

wherein the (A) pre-made solid procatalyst consists essentially of a titanium compound, magnesium chloride solids, and optionally a silica;

wherein the magnesium chloride solids consist essentially of $MgCl_2$ and, optionally, at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether; and

wherein the procatalyst system is free of any other electron donor organic compound.

2. The procatalyst system of claim 1 wherein the (B) azaheterocycle is -an aromatic azaheterocycle of formula (I):  (I) or a saturated azaheterocycle of formula (II):  (II); wherein Y is N or C-R^3; wherein Z is N or C-R^4; wherein R is H or an unsubstituted (C_1-C_{10})alkyl; wherein each of R^1, R^2, R^3, R^4, R^5, R^{1a}, and R^{2a} independently is H, a halogen atom, -OH, an unsubstituted (C_1-C_{10})alkyl group, a halo-substituted (C_1-C_{10})alkyl group, or a hydroxyl-substituted (C_1-C_{10})alkyl group, or formula (I) is defined by any one of limitations (i) to (iv): (i) R^1 and R^5 are taken together to be a divalent group that is 1,3-butadien-1,4-diyl, (ii) when Y is C-R^3, R^2 and R^3 are taken together to be a divalent group that is 1,3-butadien-1,4-diyl, (iii) wherein in formula (I) when Z is C-R^4, R^4 and R^5 are taken together to be a divalent group that is 1,3-butadien-1,4-diyl, or (iv) both limitation (i) and (ii). In some embodiments at least one of R^1, R^2, R^3, R^4, R^5, R^{1a}, and R^{2a}, alternatively at least R^1 is a halogen atom, -OH, an unsubstituted (C_1-C_{10})alkyl group, a halo-substituted (C_1-C_{10})alkyl group, or a hydroxyl-substituted (C_1-C_{10})alkyl group; alternatively at least one of R^1, R^2, R^3, R^4, R^5, R^{1a}, and R^{2a}, alternatively at least R^1 is a halogen atom or -OH; alternatively at least one of R^1, R^2, R^3, R^4, R^5, R^{1a}, and R^{2a}, alternatively at least R^1 is an unsubstituted (C_1-C_{10})alkyl group, a halo-substituted (C_1-C_{10})alkyl group, or a hydroxyl-substituted (C_1-C_{10})alkyl group; alternatively at least one of R^1, R^2, R^3, R^4, R^5,

R^{1a}, and R^{2a}, alternatively at least R^1 is an unsubstituted (C_1-C_{10})alkyl group.

3. The procatalyst system of any one of claims 1 to 2 wherein the magnesium chloride solids are free of the at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether.

4. The procatalyst system of any one of claims 1 to 2 wherein the magnesium chloride, solids consist essentially of $MgCl_2$ and the at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol, or a hydroxyl-substituted cyclic (C_3-C_7)ether

5. The procatalyst system of any one of claims 1 to 4 wherein the titanium compound is at least one compound of formula (III): TiX_4 (III), wherein each X independently is Cl, Br, I, or a (C_1-C_6)alkoxy.

6. The procatalyst system of any one of claims 1 to 5 further consisting essentially of a ligand-metal complex of formula (IV): MX_4 (IV), wherein M is Hf or Zr and each X independently is Cl, Br, I, or a (C_1-C_6)alkoxy.

7. A method of synthesizing a procatalyst system, the method comprising drying a mixture consisting essentially of a solution and, optionally, a silica, and being free of (B) an azaheterocycle and any other electron donor organic compound, wherein the solution consists essentially of a titanium compound, magnesium chloride, and, optionally, at least one of a cyclic (C_2-C_6)ether and a (C_1-C_6)alcohol mixed in a hydrocarbon solvent; thereby removing the hydrocarbon solvent from the mixture and crystallizing the magnesium chloride so as to give (A) a pre-made solid procatalyst; and contacting the (A) pre-made solid procatalyst with the (B) azaheterocycle; thereby making the blend of the procatalyst system of any one of claims 1 to 6. ~~The titanium compound, magnesium chloride, and any cyclic (C_2-C_6)ether and/or a (C_1-C_6)alcohol are all mixed in the hydrocarbon solvent.~~

8. A method of making a catalyst system suitable for polymerizing an olefin, the method comprising contacting the procatalyst system of any one of claims 1 to 6, or the procatalyst system made by the method of claim 7, with an activating effective amount of (C) an activator, thereby making the catalyst system; wherein the catalyst system is free of the any other electron donor organic compound and is suitable for polymerizing an olefin.

9. A method of making a catalyst system suitable for polymerizing an olefin, the method comprising contacting (A) a pre-made solid procatalyst, (B) an azaheterocycle, and an activating effective amount of (C) an activator, thereby making the catalyst system; wherein the (A) pre-made solid procatalyst consists essentially of a titanium compound, magnesium chloride solids, and optionally a silica; wherein the magnesium chloride solids consist essentially of $MgCl_2$ and, optionally, at least one of a cyclic (C_2-C_6)ether, a (C_1-C_6)alcohol,

or a hydroxyl-substituted cyclic (C_3-C_7)ether; and wherein the catalyst system is free of the any other electron donor organic compound and is suitable for polymerizing an olefin.

10. A catalyst system made by the method of claim 8 or claim 9.

11. A method of synthesizing a polyolefin polymer, the method comprising contacting at least one olefin monomer with the catalyst system of claim 10 under effective polymerization conditions in a polymerization reactor, thereby making the polyolefin polymer.