

CLAIMS

1. A method of making an attenuated post-metallocene catalyst, the method comprising combining a faster-light-off catalyst with an effective amount of a kinetics modifier compound of formula (A¹), (B¹), or (C¹): R⁵-C≡C-R⁶ (A¹), (R⁵)₂C=C=C(R⁶)₂ (B¹), or (R⁵)(R⁷)C=C(R⁶)(R⁷) (C¹) under effective reaction conditions to give an attenuated-light-off post-metallocene catalyst that exhibits an attenuated light-off kinetics profile; wherein the faster-light-off catalyst has been made by activating a post-metallocene precatalyst of structural formula (I): (D)_dM(T)_t(Q)_q(X)_x (I); wherein in formula (A¹), (B¹), or (C¹) each of R⁵ and R⁶ independently is H or R⁷; and each R⁷ independently is a (C₁-C₂₀)hydrocarbyl, -C(=O)-O-(unsubstituted C₁-C₁₂)hydrocarbyl, a (C₁-C₁₇)heterohydrocarbyl, or a tri((C₁-C₂₀)hydrocarbyl)silyl, or two R⁷ are taken together to form a (C₃-C₆)alkylene; with the proviso that each R⁷ lacks a carbon-carbon double bond; wherein each (C₁-C₂₀)hydrocarbyl independently is unsubstituted or substituted with from 1 to 4 substituent groups R^S; wherein each substituent group R^S is independently selected from halogen, unsubstituted (C₁-C₅)alkyl, -C≡CH, -OH, -NH₂, -N(H)(unsubstituted (C₁-C₅)alkyl), -N(unsubstituted (C₁-C₅)alkyl)₂, -COOH, and -COO(unsubstituted (C₁-C₅)alkyl); and wherein in formula (I): metal M is Ti, Hf, or Zr; subscript d is 0, 1, or 2; subscript t is 0 or 1; subscript q is 0 or 1; subscript x is 1, 2, or 3; each ligand D independently is the didentate organoheteryl or the didentate organoheterylene; ligand T is the tridentate organoheterylene; and ligand Q is the tetradentate organoheterylene; each X is a monodentate group independently selected from a halogen atom, ((C₁-C₂₀)alkyl)_{3-g}-(phenyl)_gSi- wherein subscript g is 0, 1, 2, or 3; CH₃, a (C₂-C₂₀)alkyl-CH₂, a (C₆-C₁₂)aryl-((C₀-C₁₀)alkylene)-CH₂, a (C₁-C₆)alkyl-substituted (C₆-C₁₂)aryl, a (C₁-C₆)alkoxy-substituted (C₆-C₁₂)aryl, a (C₁-C₆)alkoxy-substituted benzyl, and a (C₁-C₆)alkyl-substituted benzyl; or one X is a 4-(C₁-C₂₀)alkyl-substituted 1,3-butadiene molecule and each of the remaining X, if any, independently is the monodentate group X.
2. The method of claim 1 wherein the faster-light-off catalyst is of formula (II): (D)_d[M⁺](T)_t(Q)_q(X)_{x-1} A⁻ (II); and wherein the attenuated post-metallocene catalyst is of formula (III): (D)_d[M⁺](T)_t(Q)_q(X)_{x-2}(R) A⁻ (III); wherein subscripts d, t, q, and x; metal M; and ligands D, T, Q, and X are as defined for formula (I); wherein A⁻ is an anion; and wherein R is a ligand of formula (A), (B), or (C): -C(R⁵)=C(X)R⁶ (A), -C(R⁵)₂-C(X)=C(R⁶)₂ (B), or -C(R⁵)(R⁷)-C(X)(R⁶)(R⁷) (C), respectively; and wherein R⁵ to R⁷ are as defined previously

for formula (A¹), (B¹), or (C¹) respectively.

3. The method of claim 1 or 2 wherein the post-metallocene precatalyst is of formula (Ia): (D)_dM(X)_x (Ia), wherein metal M is Ti, Hf, or Zr; subscript d is 1 or 2; subscript x is 2 or 3; each ligand D independently is the didentate organoheteryl or the didentate organoheterylene; each X is as defined for formula (I).

4. The method of claim 1 or 2 wherein the post-metallocene precatalyst of formula (I) is of formula (Ib): MT(X)₂ (Ib), wherein metal M is Ti, Hf, or Zr; ligand T is the tridentate organoheterylene; each X is as defined for formula (I).

5. The method of claim 1 or 2 wherein the post-metallocene precatalyst of formula (I) is of formula (Ic): MQ(X)₂ (Ic), wherein metal M is Ti, Hf, or Zr; ligand Q is the tetradentate organoheterylene; each X is as defined for formula (I).

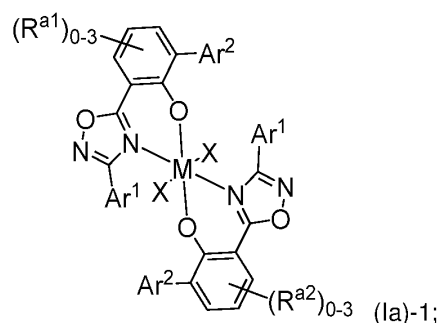
6. The method of any one of claims 1 to 5 wherein the kinetics modifier compound is of formula (A¹): R⁵-C≡C-R⁶ (A¹) that is selected from phenylacetylene; a (substituted-phenyl)acetylene; diphenylacetylene; a substituted diphenylacetylene; a cycloalkylacetylene; an acetylene of formula HC≡CSi(phenyl)_h((C₁-C₂₀)alkyl)_{3-h}, wherein subscript h is an integer from 0 to 3; and an acetylene of formula HC≡C-(CH₂)_mCH₃, wherein subscript m is an integer from 1 to 15.

7. The method of any one of claim 1 to 5 wherein the kinetics modifier compound is of formula (B¹) (R⁵)₂C=C=C(R⁶)₂ (B¹) and is selected from a cycloalkylallene; an alkylallene; a dialkylallene; a trialkylallene; a trialkylsilyllallene; a vinylidenecycloalkane; and an alkyl ester of an allenecarboxylic acid.

8. The method of any one of claims 1 to 5 wherein the kinetics modifier compound is of formula (C¹) (R⁵)(R⁷)C=C(R⁶)(R⁷) (C¹) and the kinetics modifier compound of formula (C¹) is an internal alkene.

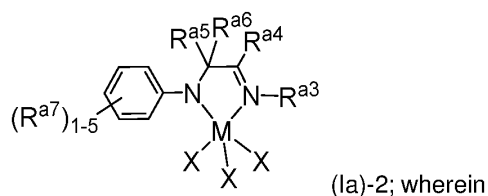
9. The method of any one of claims 1 to 8 wherein the method further comprises making a mixture of the attenuated post-metallocene catalyst, a support material, and an inert hydrocarbon solvent and removing the inert hydrocarbon solvent from the mixture so as to give the attenuated post-metallocene catalyst disposed on the support material.

10. The method of any one of claims 1 to 3 and 6 to 9 wherein the post-metallocene precatalyst of formula (I) is selected from the group consisting of:



a post-metallocene precatalyst of formula (Ia)-1

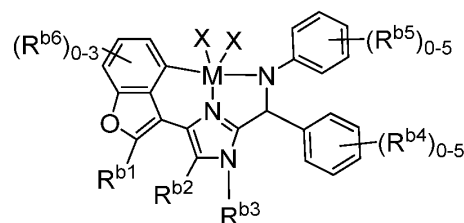
wherein each Ar¹ and Ar² independently is an unsubstituted or substituted aromatic group selected from phenyl, substituted phenyl, biphenyl, substituted biphenyl, anthracene, substituted anthracene, carbazolyl, and substituted carbazolyl, wherein each substituent of the substituted aromatic group independently is alkyl; each group Ra¹ and Ra² independently is H or a (C₁-C₂₀)alkyl; each subscript 0-3 independently is 0, 1, 2, or 3; and M and X are as defined for formula (I); and



a post-metallocene precatalyst of formula (Ia)-2:

M and X are as defined for formula (I); each subscript 1-5 independently is 1, 2, 3, 4, or 5; and each of Ra³ and Ra⁷ independently is (C₁-C₂₀)alkyl or (C₆-C₁₂)aryl and each of Ra⁴ to Ra⁶ independently is (C₁-C₂₀)alkyl or Ra⁴ to Ra⁶ are taken together to form a trivalent group of formula =C(H)-CH₂CH₂CH₂-.

11. The method of any one of claims 1, 2, 4, and 6 to 9 wherein the post-metallocene precatalyst of formula (I) is



a post-metallocene precatalyst of formula (Ib)-1

(Ib)-1; wherein M is Ti, Hf, or Zr; each subscript 0-3 independently is 0, 1, 2, or 3; each of groups R^{b1} to R^{b6} independently is H or a (C₁-C₂₀)alkyl; and X is as defined for formula (I).

12. An attenuated post-metallocene catalyst made by the method of any one of claims 1 to 11.

13. A method of feeding a post-metallocene catalyst to a slurry-phase or gas-phase polymerization reactor containing an olefin monomer and a moving bed of polyolefin polymer, the method comprising making the attenuated post-metallocene catalyst outside of the reactor and according to the method of any one of claims 1 to 11, and feeding the attenuated post-metallocene catalyst in neat form or as a solution or slurry thereof in an inert hydrocarbon liquid through a feed line free of olefin monomer into the slurry-phase or gas-phase polymerization reactor.

14. A multimodal catalyst system comprising the attenuated post-metallocene catalyst of claim 12 and at least one second catalyst selected from the group consisting of an unattenuated a post-metallocene catalyst described herein, a different attenuated post-metallocene catalyst, and a metallocene catalyst.

15. A method of making a polyolefin polymer, the method comprising contacting at least one 1-alkene monomer with the attenuated post-metallocene catalyst made by the method of any one of claims 1 to 11, or the multimodal catalyst system of claim 14, under slurry-phase or gas-phase polymerization conditions in a slurry-phase or gas-phase polymerization reactor containing a moving bed of polyolefin resin, thereby making the polyolefin polymer.