in turn delays or prevents fouling of reactor components and/or minimizes spoiling of the properties of the polyolefin product being made thereby. Despite delaying on-set, all other things being equal, many embodiments of the attenuated hybrid catalyst exhibit a catalytic activity/polymerization productivity, expressed as number of grams dried polyolefin product made per gram of catalyst added to reactor-hour (gPE/gcat-hr), that is not significantly less than, and in some embodiments may be more than, that of the faster-light-off non-metallocene catalyst. This result is unpredictable from the art.

[0014] A method of making an attenuated-light-off hybrid catalyst ("attenuated hybrid catalyst"), the method comprising combining a faster-light-off catalyst with an effective amount of a kinetics modifier compound of formula (A^1), (B^1), or (C^1): R^5-C≡C-R^6 (A^1), $(R^5)_2C=C=C(R^6)_2$ (B^1), or $(R^5)(R^7)C=C(R^6)(R^7)$ (C^1) as defined herein under effective reaction conditions to give an attenuated hybrid catalyst that exhibits an attenuated light-off kinetics profile (relative to that of the faster-light-off catalyst); wherein the faster-light-off catalyst has been made by activating a hybrid precatalyst (i.e., an unactivated "coordination entity" or "ligand-metal complex") of structural formula (I): $(Cp)(L)_k(X)_x$ (I) as defined herein.

[0014a] In one aspect, there is provided a method of making an attenuated hybrid catalyst, the method comprising combining a faster-light-off catalyst with an effective amount of a kinetics modifier compound ("KMC") of formula (A^1) or (B^1): R^5-C≡C-R^6 (A^1) or $(R^5)_2C=C=C(R^6)_2$ (B^1) under effective reaction conditions to give an attenuated-light-off hybrid catalyst that exhibits an attenuated light-off kinetics profile (relative to that of the faster-light-off catalyst); wherein the faster-light-off catalyst has been made by activating a hybrid precatalyst of structural formula (I): $(Cp)(L)_k(X)_x$ (I); wherein in formula (A^1) or (B^1) each of R^5 and R^6 independently is H or R^7; and each R^7 independently is a (C_1-C_{20})hydrocarbyl, -C(=O)-O-(unsubstituted C_1-C_{20})hydrocarbyl), a (C_1-C_{19})heterohydrocarbyl, or a tri((C_1-C_{20})hydrocarbyl)silyl, or two R^7 are taken together to form a (C_3-C_6)alkylene; with the proviso that each R^7 lacks a carbon-carbon double bond; wherein each (C_1-C_{20})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 (C_1-C_5)alkyl, -C≡CH, -OH, (C_1-C_5)alkoxy, -C(=O)-(unsubstituted (C_1-C_5)alkyl), -NH_2, -N(H)(unsubstituted (C_1-C_5)alkyl), -N(unsubstituted (C_1-C_5)alkyl)$_2$, -COOH, -C(=O)-NH_2, -C(=O)-N(H)(unsubstituted (C_1-C_5)alkyl), -C(=O)-N(unsubstituted (C_1-C_5)alkyl)$_2$, -S-(unsubstituted (C_1-C_5)alkyl), -S(=O)$_2$-(unsubstituted (C_1-C_5)alkyl), -S(=O)$_2$-NH_2, -S(=O)$_2$-N(H)(unsubstituted (C_1-C_5)alkyl), -S(=O)$_2$-N(unsubstituted (C_1-C_5)alkyl)$_2$, -C(=)S-

(unsubstituted (C_1-C_5)alkyl) and -COO(unsubstituted (C_1-C_5)alkyl); and wherein in formula (I): metal M is Ti, Hf, or Zr; subscript k is 0 or 1; subscript x is 1, 2, or 3; the Cp group is an unsubstituted cyclopentadienyl group; a hydrocarbyl-substituted cyclopentadienyl group; or an organoheterylene-substituted cyclopentadienyl group; group L is a monodentate organoheteryl group; each X is a monodentate group independently selected from a halogen atom, ((C_1-C_{20})alkyl)$_{3-g}$-(phenyl)$_g$Si- wherein subscript g is 0, 1, 2, or 3; CH_3, a (C_2-C_{20})alkyl-CH_2, a (C_6-C_{12})aryl-((C_0-C_{10})alkylene)-CH_2, a (C_1-C_6)alkyl-substituted (C_6-C_{12})aryl, a (C_1-C_6)alkoxy-substituted (C_6-C_{12})aryl, a (C_1-C_6)alkoxy-substituted benzyl, and a (C_1-C_6)alkyl-substituted benzyl.

[0015] In another aspect, there is provided an attenuated hybrid catalyst made by the method as defined herein.

[0015a] In another aspect, there is provided a method of feeding a hybrid 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 hybrid catalyst outside of the reactor and according to the method as defined herein, and feeding the attenuated hybrid 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.

[0016] A method of feeding a hybrid catalyst to a gas-phase polymerization reactor containing an olefin monomer and a moving bed of polyolefin polymer, the method comprising making the attenuated hybrid catalyst according to the above method, and feeding the attenuated hybrid catalyst in neat form (e.g., dry powder) or as a solution or slurry thereof in an inert hydrocarbon liquid through a feed line free of olefin monomer into the gas-phase polymerization reactor.

[0017] A multimodal (e.g., bimodal or trimodal) catalyst system comprising the attenuated hybrid catalyst and one or more a different olefin polymerization catalyst(s).

[0017a] In another aspect, there is provided a multimodal catalyst system comprising the attenuated hybrid catalyst as defined herein and at least one second catalyst selected from the group consisting of an unattenuated a hybrid catalyst described herein, a different attenuated hybrid catalyst, a post-metallocene catalyst, and a metallocene catalyst.

[0018] A method of feeding a multimodal (e.g., bimodal or trimodal) catalyst system to a gas-phase polymerization reactor containing an olefin monomer and a moving bed of polyolefin polymer, the method comprising making the attenuated hybrid catalyst according to the above method, contacting a solution of the attenuated hybrid catalyst and an activated metallocene catalyst in an inert hydrocarbon solvent with a support material (e.g., fumed silica) so as to make a slurry of a multimodal (e.g., bimodal or trimodal) catalyst system consisting essentially of the attenuated hybrid catalyst and the activated metallocene catalyst co-supported on the

same support material and suspended in the inert hydrocarbon solvent; optionally removing the inert hydrocarbon solvent from the slurry to make the multimodal catalyst system in neat (dry powder) form; and feeding the slurry of the multimodal catalyst system or the neat form of the multimodal catalyst system through a feed line free of olefin monomer into the gas-phase polymerization reactor.

[0019] A method of making a polyolefin polymer, the method comprising contacting at least one 1-alkene monomer with the attenuated hybrid catalyst or the multimodal (e.g., bimodal or trimodal) catalyst system under gas-phase polymerization conditions in a gas-phase polymerization reactor containing a moving bed of polyolefin resin, thereby making the polyolefin polymer.

[0019a] In another aspect, there is provided a method of making a polyolefin polymer, the method comprising contacting at least one 1-alkene monomer with the attenuated hybrid catalyst made by the method as defined herein, or the multimodal catalyst system as defined herein, 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.

[0020] A polyolefin polymer made by the method of making same.

[0021] A manufactured article made from the polyolefin polymer.

DETAILED DESCRIPTION

[0022] The entire contents of the SUMMARY section are incorporated here by reference. Additional embodiments follow; some are numbered for easy reference.

[0023] Aspect 1. A method of making an attenuated hybrid catalyst ("attenuated-light-off hybrid catalyst"), the method comprising combining a faster-light-off catalyst with an effective amount of a kinetics modifier compound ("KMC") of formula (A^1), (B^1), or (C^1): R^5-C≡C-R^6 (A^1), $(R^5)_2C=C=C(R^6)_2$ (B^1), or $(R^5)(R^7)C=C(R^6)(R^7)$ (C^1) under effective reaction conditions to give an attenuated-light-off hybrid catalyst that exhibits an attenuated light-off kinetics profile (relative to that of the faster-light-off catalyst); wherein the faster-light-off catalyst has been made by activating a hybrid precatalyst of structural formula (I): $(Cp)(L)_k(X)_x$ (I); wherein in formula (A^1), (B^1), or (C^1) each of R^5 and R^6 independently is H or R^7; and each R^7 independently is a (C_1-C_{20})hydrocarbyl, -C(=O)-O-(unsubstituted C_1-C_{20})hydrocarbyl), a (C_1-C_{19})heterohydrocarbyl, or a tri((C_1-C_{20})hydrocarbyl)silyl, or two R^7 are taken together to form a (C_3-C_6)alkylene; with the proviso that each R^7 lacks a carbon-carbon double bond; wherein each (C_1-C_{20})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 (e.g., F), unsubstituted (C_1-C_5)alkyl (e.g., CH_3), -C≡CH, -OH, (C_1-C_5)alkoxy, -C(=O)-(unsubstituted (C_1-C_5)alkyl), -NH_2, -N(H)(unsubstituted (C_1-C_5)alkyl), -N(unsubstituted (C_1-C_5)alkyl)$_2$, -COOH, -C(=O)-NH_2, -C(=O)-N(H)(unsubstituted (C_1-C_5)alkyl), -C(=O)-N(unsubstituted (C_1-C_5)alkyl)$_2$, -S-(unsubstituted (C_1-C_5)alkyl), -S(=O)$_2$-(unsubstituted (C_1-C_5)alkyl), -S(=O)$_2$-NH_2, -S(=O)$_2$-N(H)(unsubstituted (C_1-

C_5)alkyl), -S(=O)$_2$-N(unsubstituted (C_1-C_5)alkyl)$_2$, -C(=)S-(unsubstituted (C_1-C_5)alkyl) and -COO(unsubstituted (C_1-C_5)alkyl); and wherein in formula (I): metal M is Ti, Hf, or Zr; subscript k is 0 or 1; subscript x is 1, 2, or 3; the Cp group is an unsubstituted cyclopentadienyl group; a hydrocarbyl-substituted cyclopentadienyl group; or an organoheterylene-substituted cyclopentadienyl group; group L is a monodentate organoheteryl group; each X is a

CLAIMS

1. A method of making an attenuated hybrid catalyst, the method comprising combining a faster-light-off catalyst with an effective amount of a kinetics modifier compound ("KMC") of formula (A^1) or (B^1): R^5-C≡C-R^6 (A^1) or $(R^5)_2C=C=C(R^6)_2$ (B^1) under effective reaction conditions to give an attenuated-light-off hybrid catalyst that exhibits an attenuated light-off kinetics profile (relative to that of the faster-light-off catalyst); wherein the faster-light-off catalyst has been made by activating a hybrid precatalyst of structural formula (I): $(Cp)(L)_k(X)_x$ (I); wherein in formula (A^1) or (B^1) each of R^5 and R^6 independently is H or R^7; and each R^7 independently is a (C_1-C_{20})hydrocarbyl, -C(=O)-O-(unsubstituted C_1-C_{20})hydrocarbyl), a (C_1-C_{19})heterohydrocarbyl, or a tri((C_1-C_{20})hydrocarbyl)silyl, or two R^7 are taken together to form a (C_3-C_6)alkylene; with the proviso that each R^7 lacks a carbon-carbon double bond; wherein each (C_1-C_{20})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 (C_1-C_5)alkyl, -C≡CH, -OH, (C_1-C_5)alkoxy, -C(=O)-(unsubstituted (C_1-C_5)alkyl), -NH_2, -N(H)(unsubstituted (C_1-C_5)alkyl), -N(unsubstituted (C_1-C_5)alkyl)$_2$, -COOH, -C(=O)-NH_2, -C(=O)-N(H)(unsubstituted (C_1-C_5)alkyl), -C(=O)-N(unsubstituted (C_1-C_5)alkyl)$_2$, -S-(unsubstituted (C_1-C_5)alkyl), -S(=O)$_2$-(unsubstituted (C_1-C_5)alkyl), -S(=O)$_2$-NH_2, -S(=O)$_2$-N(H)(unsubstituted (C_1-C_5)alkyl), -S(=O)$_2$-N(unsubstituted (C_1-C_5)alkyl)$_2$, -C(=)S-(unsubstituted (C_1-C_5)alkyl) and -COO(unsubstituted (C_1-C_5)alkyl); and wherein in formula (I): metal M is Ti, Hf, or Zr; subscript k is 0 or 1; subscript x is 1, 2, or 3; the Cp group is an unsubstituted cyclopentadienyl group; a hydrocarbyl-substituted cyclopentadienyl group; or an organoheterylene-substituted cyclopentadienyl group; group L is a monodentate organoheteryl group; each X is a monodentate group independently selected from a halogen atom, ((C_1-C_{20})alkyl)$_{3-g}$-(phenyl)$_g$Si- wherein subscript g is 0, 1, 2, or 3; CH_3, a (C_2-C_{20})alkyl-CH_2, a (C_6-C_{12})aryl-((C_0-C_{10})alkylene)-CH_2, a (C_1-C_6)alkyl-substituted (C_6-C_{12})aryl, a (C_1-C_6)alkoxy-substituted (C_6-C_{12})aryl, a (C_1-C_6)alkoxy-substituted benzyl, and a (C_1-C_6)alkyl-substituted benzyl.

2. The method of claim 1 wherein the faster-light-off catalyst is of formula (II): $(Cp)(L)_k(X)_{x-1}$ A^- (II), wherein subscript k; metal M; and ligand L, and leaving group X are as defined for formula (I), wherein subscript x is 2 or 3; and wherein the attenuated hybrid catalyst is of formula (III): $(Cp)(L)_k(X)_{x-2}(R)$ A^- (III); wherein subscript k; metal M; and ligand L are as defined for formula (I) , wherein subscript x is 2 or 3; each X is the monodentate group as

defined for formula (I); wherein A^- is an anion (used to formally balance the positive charge of metal M); and wherein R is a ligand of formula (A) or (B): $-C(R^5)=C(X)R^6$ (A) or $-C(R^5)_2-C(X)=C(R^6)_2$ (B), respectively; and wherein R^5 to R^7 are as defined previously for formula (A^1) or (B^1) respectively.

3. The method of claim 1 or 2 wherein the hybrid precatalyst is of formula (Ia): $CpM(X)_x$ (Ia), wherein metal M is Ti, Hf, or Zr; subscript x is 1, 2 or 3; Cp is the organoheterylene-substituted cyclopentadienyl group; and each X is as defined for formula (I).

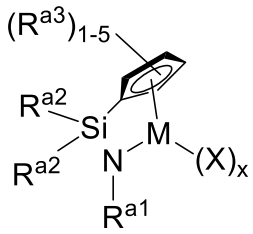
4. The method of claim 1 or 2 wherein the hybrid precatalyst of formula (I) is of formula (Ib): $(Cp)(L)(X)_x$ (Ib); wherein M, L, X, and subscript x are as defined for formula (I); and Cp is the unsubstituted cyclopentadienyl group or hydrocarbyl-substituted cyclopentadienyl group.

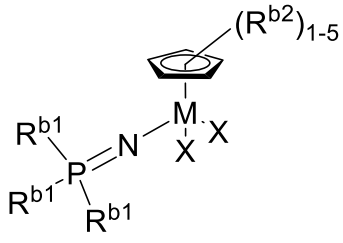
5. The method of any one of claims 1 to 4 wherein the kinetics modifier compound is of formula (A^1): R^5-C≡C-R^6 (A^1) that is selected from phenylacetylene; a (substituted-phenyl)acetylene; diphenylacetylene; a substituted diphenylacetylene; a cycloalkylacetylene; an acetylene of formula $HC≡CSi(phenyl)_h((C_1-C_{20})alkyl)_{3-h}$, wherein subscript h is an integer from 0 to 3; and an acetylene of formula $HC≡C-(CH_2)_mCH_3$, wherein subscript m is an integer from 1 to 15.

6. The method of any one of claim 1 to 4 wherein the kinetics modifier compound is of formula (B^1) $(R^5)_2C=C=C(R^6)_2$ (B^1) and is selected from a cycloalkylallene; an alkylallene; a dialkylallene; a trialkylallene; a trialkylsilylallene; a vinylidenecycloalkane; and an alkyl ester of an allenecarboxylic acid.

7. The method of any one of claims 1 to 6 wherein the method further comprises making a mixture of the attenuated hybrid catalyst, a support material, and an inert hydrocarbon solvent and removing the inert hydrocarbon solvent from the mixture so as to give the attenuated hybrid catalyst disposed on the support material.

8. The method of any one of claims 1 to 3 wherein the hybrid precatalyst of formula (I)

is of formula (Ia)-1  (Ia)-1; wherein each group R^{a1} and R^{a2} independently is a (C_1-C_{20})alkyl; and each group R^{a3} independently is H or a (C_1-C_{20})alkyl; each subscript 1-5 independently is 0, 1, 2, 3, 4, or 5; and M, X, and subscript x are as defined for formula (I).

9. The method of any one of claims 1, 2, and 4 wherein the hybrid precatalyst is of formula (Ib)-1:  (Ib)-1, wherein each group R^{b1} independently is a (C_1-C_{20})alkyl; and each group R^{b2} independently is H or a (C_1-C_{20})alkyl; each subscript 1-5 independently is 0, 1, 2, 3, 4, or 5; and M and X are as defined for formula (I).

10. An attenuated hybrid catalyst made by the method of any one of claims 1 to 9.

11. A method of feeding a hybrid 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 hybrid catalyst outside of the reactor and according to the method of any one of claims 1 to 9, and feeding the attenuated hybrid 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.

12. A multimodal catalyst system comprising the attenuated hybrid catalyst of claim 10 and at least one second catalyst selected from the group consisting of an unattenuated a hybrid catalyst described herein, a different attenuated hybrid catalyst, a post-metallocene catalyst, and a metallocene catalyst.

13. A method of making a polyolefin polymer, the method comprising contacting at least one 1-alkene monomer with the attenuated hybrid catalyst made by the method of any one of claims 1 to 9, or the multimodal catalyst system of claim 12, 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.

14. The method of claim 13, further comprising before the contacting step a step comprising feeding the attenuated hybrid catalyst made by the method of any one of claims 1 to 9 into the slurry-phase or gas-phase polymerization reactor containing the moving bed of polyolefin resin and at least one 1-alkene monomer under slurry-phase or gas-phase polymerization conditions, respectively, so as to allow attenuated light-off of the attenuated hybrid catalyst and subsequent polymerization of the at least one 1-alkene monomer, thereby making the polyolefin polymer.

15. The method of claim 13 or 14, wherein the reactor is a first gas-phase polymerization reactor and is under first gas-phase polymerization conditions.