length of the delay is long enough to decrease or prevent agglomerates formation, which 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 post-metallocene 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 post-metallocene catalyst ("attenuated post-metallocene catalyst" or "attenuated P-M 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 post-metallocene 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 post-metallocene precatalyst (i.e., an unactivated "coordination entity" or "ligand-metal complex") of structural formula (I): $(D)_dM(T)_t(Q)_q(X)_x$ (I) as defined herein.

[0014a] In one aspect, there is provided 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 (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 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 (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_{12})hydrocarbyl), a (C_1-C_{17})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, -NH_2, -N(H)(unsubstituted (C_1-C_5)alkyl), -N(unsubstituted (C_1-C_5)alkyl)$_2$, -COOH, and -COO(unsubstituted (C_1-C_5)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, $((C_1\text{-}C_{20})\text{alkyl})_{3-g}\text{-(phenyl)}_g\text{Si-}$ wherein subscript g is 0, 1, 2, or 3; CH_3, a $(C_2\text{-}C_{20})\text{alkyl-}CH_2$, a $(C_6\text{-}C_{12})\text{aryl-}((C_0\text{-}C_{10})\text{alkylene})\text{-}CH_2$, a $(C_1\text{-}C_6)$alkyl-substituted $(C_6\text{-}C_{12})$aryl, a $(C_1\text{-}C_6)$alkoxy-substituted $(C_6\text{-}C_{12})$aryl, a $(C_1\text{-}C_6)$alkoxy-substituted benzyl, and a $(C_1\text{-}C_6)$alkyl-substituted benzyl; or one X is a 4-$(C_1\text{-}C_{20})$alkyl-substituted 1,3-butadiene molecule and each of the remaining X, if any, independently is the monodentate group X.

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

[0016] A method of feeding a post-metallocene catalyst to a gas-phase polymerization reactor containing an olefin monomer and a moving bed of polyolefin polymer, the method comprising making the attenuated post-metallocene catalyst according to the above method, and feeding the attenuated post-metallocene 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.

[0016a] In another aspect, there is provided 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 as defined herein, 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

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

[0017a] In another aspect, there is provided a multimodal catalyst system comprising the attenuated post-metallocene catalyst as defined herein 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

[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 post-metallocene catalyst according to the above method, contacting a solution of the attenuated post-metallocene 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 post-metallocene 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 post-metallocene 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 post-metallocene 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 post-metallocene catalyst ("attenuated-light-off post-metallocene 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 post-metallocene 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 post-metallocene precatalyst of structural formula (I): $(D)_dM(T)_t(Q)_q(X)_x$ (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;

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 (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 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 (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_{12})hydrocarbyl), a (C_1-C_{17})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, -NH_2, -N(H)(unsubstituted (C_1-C_5)alkyl), -N(unsubstituted (C_1-C_5)alkyl)$_2$, -COOH, and -COO(unsubstituted (C_1-C_5)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, ((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; or one X is a 4-(C_1-C_{20})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), 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 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).

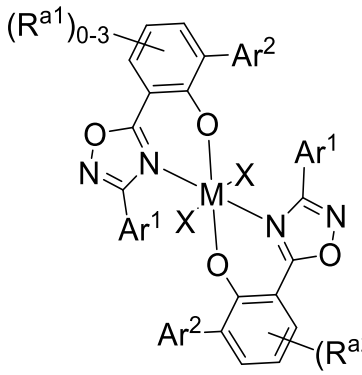
5. The method of claim 1 or 2 wherein the post-metallocene precatalyst of formula (I) is of formula (Ic): $MQ(X)_2$ (Ic), wherein metal M is Ti, Hf, or Zr; ligand Q is the tetradentate organoheterylene; each X is as defined for formula (I).

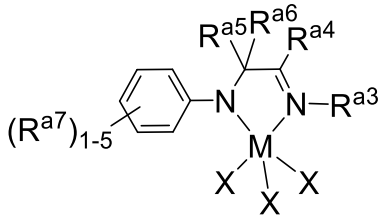
6. The method of any one of claims 1 to 5 wherein the kinetics modifier compound is of formula (A^1): R^5-C≡C-R^6 (A^1) that is selected from phenylacetylene; a (substituted-phenyl)acetylene; diphenylacetylene; a substituted diphenylacetylene; a cycloalkylacetylene; an acetylene of formula HC≡CSi(phenyl)$_h$((C$_1$-C$_{20}$)alkyl)$_{3-h}$, 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.

7. The method of any one of claim 1 to 5 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.

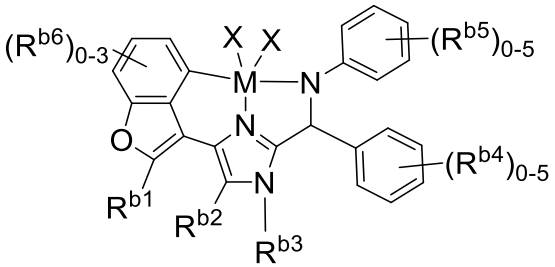
8. The method of any one of claims 1 to 7 wherein the method further comprises making a mixture of the attenuated post-metallocene catalyst, a support material, and an inert hydrocarbon solvent and removing the inert hydrocarbon solvent from the mixture so as to give the attenuated post-metallocene catalyst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

9. The method of any one of claims 1 to 3 and 6 to 8 wherein the post-metallocene precatalyst of formula (I) is selected from the group consisting of:

a post-metallocene precatalyst of formula (Ia)-1  (Ia)-1; wherein each Ar^1 and Ar^2 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 R^{a1} and R^{a2} independently is H or a $(C_1\text{-}C_{20})$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:  (Ia)-2; wherein M and X are as defined for formula (I); each subscript 1-5 independently is 1, 2, 3, 4, or 5; and each of R^{a3} and R^{a7} independently is $(C_1\text{-}C_{20})$alkyl or $(C_6\text{-}C_{12})$aryl and each of R^{a4} to R^{a6} independently is $(C_1\text{-}C_{20})$alkyl or R^{a4} to R^{a6} are taken together to form a trivalent group of formula =C(H)-$CH_2CH_2CH_2$-.

10. The method of any one of claims 1, 2, 4, and 6 to 8 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 $(C_1\text{-}C_{20})$alkyl; and X is as defined for formula (I).

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

12. 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 10, 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.

13. A multimodal catalyst system comprising the attenuated post-metallocene catalyst of claim 11 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.

14. 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 10, or the multimodal catalyst system of claim 13, 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.