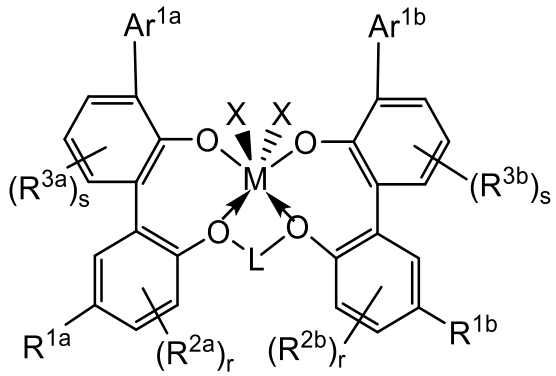
that undesirably vary in flow index and/or density according to particle size.

**[0009]** These problems did not surface with metallocene catalysts, which are catalysts that contain two cyclopentadienyl groups (independently unsubstituted or substituted). Metallocene catalysts are relatively slow to light-off in the above situations.

**[0010]** Our technical solution to the problems arising from the "faster-light-off" post-metallocene catalyst employs an effective amount of a kinetics modifier compound to alter the molecular structure of the post-metallocene catalyst in such a way that the resulting structurally-modified post-metallocene catalyst has a new molecular structure and remains active, but exhibits a characteristic attenuated light-off monomer uptake profile ("attenuated-light-off post-metallocene catalyst", or more simply "attenuated post-metallocene catalyst") when fed separately from olefin monomer feed(s) into a gas-phase polymerization reactor. For example, the attenuated monomer uptake profile may comprise the length of time to peak reaction temperature ($Temp_{peak}$) for the attenuated post-metallocene catalyst is longer and/or the value of $Temp_{peak}$ is lower relative to that of the faster-light-off catalyst from which it was made. The 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.

**[0010a]** In one aspect, there is provided 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 ($A^1$), 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 monomer uptake profile; wherein the faster-light-off catalyst has been made by activating a post-metallocene precatalyst of structural formula (I):




(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): L is a $CH_2CH_2$, $CH_2CH_2CH_2$, $CH_2CH_2CH_2CH_2$, $CH_2C(R^L)_2CH_2$, $CH_2CH(R^L)CH(R^L)CH_2$, $CH_2Ge(R^L)_2CH_2$, or $CH_2Si(R^L)_2CH_2$, wherein each $R^L$ independently is an unsubstituted ($C_1$-$C_{20}$)alkyl; M is Ti, Zr, or Hf; each of $R^{1a}$ and $R^{1b}$ independently is a halogen atom, ($C_1$-$C_{20}$)alkyl, or $Si(CH_3)_2(CH_2)_qCH_3$, wherein subscript q is an integer from 0 to 20; each subscript r independently is an integer from 0 to 3; each of $R^{2a}$ and $R^{2b}$ independently is H, F, Cl, or unsubstituted ($C_1$-$C_{20}$)alkyl; each subscript s independently is an integer from 0 to 3; each of $R^{3a}$ and $R^{3b}$ independently is a halogen, an unsubstituted ($C_1$-$C_{20}$)alkyl, or ($C_1$-$C_{20}$)alkoxy; each $Ar^{1a}$ and $Ar^{1b}$ 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; and each X

independently is a monodentate group independently selected from a halogen atom, $((C_1\text{-}C_{20})alkyl)_{3-g}\text{-}(phenyl)_gSi$- wherein subscript g is 0, 1, 2, or 3; $CH_3$, a $(C_2\text{-}C_{20})$alkyl-$CH_2$, a $(C_6\text{-}C_{12})$aryl-$((C_0\text{-}C_{10})$alkylene)-$CH_2$, 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.

**[0010b]** In another aspect, there is provided an attenuated post-metallocene catalyst made by the method as defined herein.

**[0010c]** 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.

**[0010d]** 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.

**[0010e]** 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.

## DETAILED DESCRIPTION

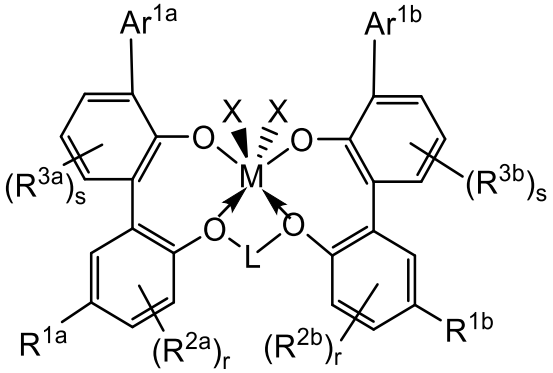
**[0011]** The entire contents of the SUMMARY section are incorporated here by reference. Additional embodiments follow; some are numbered for easy reference.

**[0012]** 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 ($C^1$): $R^5\text{-}C{\equiv}C\text{-}R^6$ ($A^1$), $(R^5)_2C{=}C{=}C(R^6)_2$ ($B^1$), 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 monomer uptake profile (relative to that of the faster-light-off

catalyst); wherein the faster-light-off catalyst has been made by activating a post-metallocene

CLAIMS

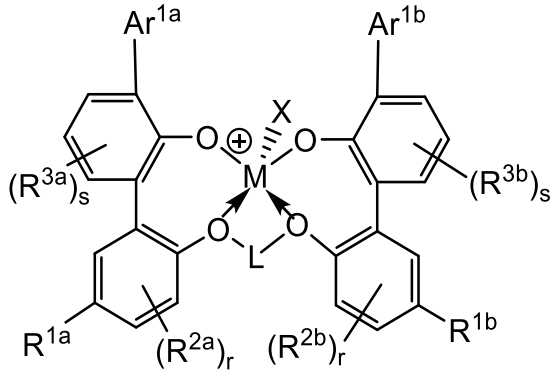
1. A method of making an attenuated post-metallocene catalyst ("attenuated-light-off post-metallocene catalyst"), the method comprising combining a faster-light-off catalyst with an effective amount of a kinetics modifier compound ("KMC") of formula ($A^1$), or ($B^1$): $R^5$-C≡C-$R^6$ ($A^1$), or $(R^5)_2C=C=C(R^6)_2$ ($B^1$) under effective reaction conditions to give an attenuated-light-off post-metallocene catalyst that exhibits an attenuated light-off monomer uptake profile; wherein the faster-light-off catalyst has been made by activating a post-metallocene precatalyst of structural formula (I):



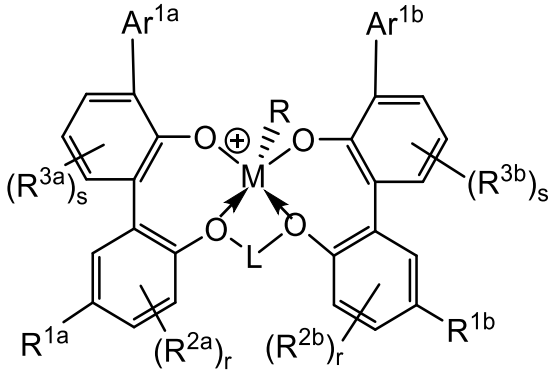

(I); wherein in formula ($A^1$), or ($B^1$) each of $R^5$ and $R^6$ independently is H or $R^7$; and each $R^7$ independently is a ($C_1$-$C_{20}$)hydrocarbyl, -C(=O)-O-(unsubstituted $C_1$-$C_{20}$)hydrocarbyl), a ($C_1$-$C_{19}$)heterohydrocarbyl, or a tri(($C_1$-$C_{20}$)hydrocarbyl)silyl, or two $R^7$ 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): L is a $CH_2CH_2$, $CH_2CH_2CH_2$, $CH_2CH_2CH_2CH_2$, $CH_2C(R^L)_2CH_2$, $CH_2CH(R^L)CH(R^L)CH_2$, $CH_2Ge(R^L)_2CH_2$, or $CH_2Si(R^L)_2CH_2$, wherein each $R^L$ independently is an unsubstituted ($C_1$-$C_{20}$)alkyl; M is Ti, Zr, or Hf; each of $R^{1a}$ and $R^{1b}$ independently is a halogen atom, ($C_1$-$C_{20}$)alkyl, or $Si(CH_3)_2(CH_2)_qCH_3$, wherein subscript q is an integer from 0 to 20; each subscript r independently is an integer from 0 to 3; each of

$R^{2a}$ and $R^{2b}$ independently is H, F, Cl, or unsubstituted ($C_1$-$C_{20}$)alkyl; each subscript s independently is an integer from 0 to 3; each of $R^{3a}$ and $R^{3b}$ independently is a halogen, an unsubstituted ($C_1$-$C_{20}$)alkyl, or ($C_1$-$C_{20}$)alkoxy; each $Ar^{1a}$ and $Ar^{1b}$ 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; and each X independently 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):

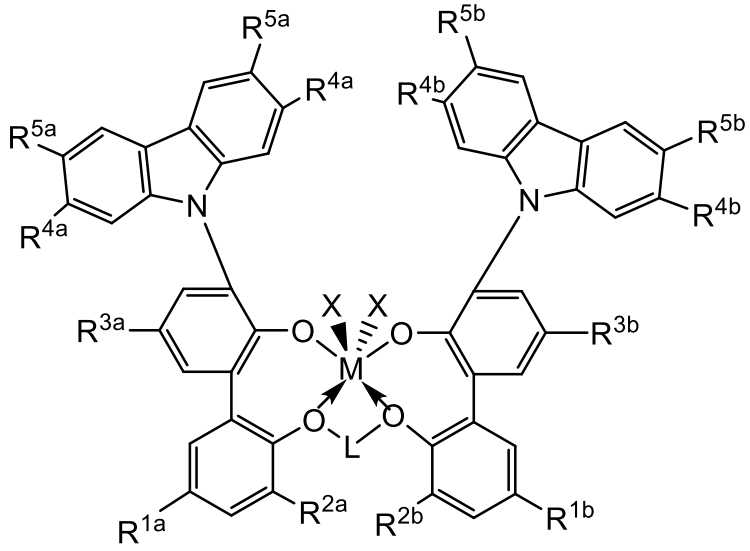



$A^-$ (II); and wherein the attenuated post-metallocene catalyst is of formula (III):




$A^-$ (III); wherein subscripts r and s; groups $R^{1a}$ to $R^{3a}$, $R^{1b}$ to $R^{3b}$, $Ar^{1a}$, $Ar^{1b}$, L, and X; and metal M 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 of formula (I) is a post-metallocene precatalyst of formula (Ia):



(Ia); wherein L is a $CH_2CH_2$, $CH_2CH_2CH_2$, $CH_2CH_2CH_2CH_2$, $CH_2C(R^L)_2CH_2$, $CH_2CH(R^L)CH(R^L)CH_2$, $CH_2Ge(R^L)_2CH_2$, or $CH_2Si(R^L)_2CH_2$, wherein each $R^L$ independently is an unsubstituted $(C_1\text{-}C_{20})$alkyl; M is Zr or Hf; each of $R^{1a}$ and $R^{1b}$ independently is F, $(C_1\text{-}C_{20})$alkyl, or $Si(CH_3)_2(CH_2)_qCH_3$, wherein subscript q is an integer from 0 to 9; each of $R^{2a}$ and $R^{2b}$ independently is H or $CH_3$; each of $R^{3a}$ and $R^{3b}$ independently is an unsubstituted 1,1-dimethyl-($C_2$ to $C_8$)alkyl; each of $R^{4a}$, $R^{4b}$, $R^{5a}$, $R^{5b}$ independently is H, unsubstituted $(C_1\text{-}C_{20})$alkyl, $((C_1\text{-}C_{20})\text{alkyl})_{3-g}\text{-(phenyl)}_gSi$- wherein subscript g is 0, 1, 2, or 3, or an unsubstituted 1,1-dimethyl-($C_2$ to $C_6$)alkyl; and each X independently is as defined for formula (I).

4. The method of claim 1 or 3, wherein the precatalyst of formula (I) or (Ia), respectively, is defined by any one of limitations (i) to (vi): (i) each of $R^{1a}$ and $R^{1b}$ is the same; (ii) each of $R^{2a}$ and $R^{2b}$ is the same; (iii) each of $R^{3a}$ and $R^{3b}$ is the same; (iv) each of $R^{4a}$ and $R^{4b}$ is the same; (v) each of $R^{5a}$ and $R^{5b}$ is the same; and (vi) a combination of any two or more of limitations (i) to (v).

5. The method of claim 1, 3 or 4 wherein the precatalyst of formula (I) or (Ia), respectively, is defined by any one of limitations (i) to (vi): (i) L is $CH_2CH_2CH_2$, $CH_2CH_2CH_2CH_2$, or $CH_2Si(CH(CH_3)_2)_2CH_2$; (ii) M is Zr; (iii) M is Hf; (iv) each X is independently a $(C_7\text{-}C_{20})$aralkyl; (v) one X is a $(C_7\text{-}C_{20})$aralkyl and the other X is F, Cl, or methyl; and (vi) a combination of any two or more of limitations (i) to (v).

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-($CH_2$)$_m$$CH_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 ($B^1$): ($R^5$)$_2$C=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 further comprising, before the combining step, a step of making the faster-light-off catalyst by activating the precatalyst of formula (I) with the activator under effective activating conditions, thereby making the faster-light-off catalyst. In some embodiments the activator is an alkylaluminoxane, an organoborane compound, or an organoborate salt.

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. An attenuated post-metallocene catalyst made by the method of any one of claims 1 to 9.

11. 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 9, 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.

12. A multimodal catalyst system comprising the attenuated post-metallocene catalyst of claim 10 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.

13. 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 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.