Claims

1. A method of chemically converting a unimodal ligand-metal precatalyst into a bimodal ligand-metal catalyst, the method comprising combining in any order constituents consisting essentially of a first unimodal ligand-metal precatalyst, an effective amount of an activator, and an effective amount of a modality-increasing organic compound under conditions effective for the activator and the modality-increasing organic compound chemically converting the first unimodal ligand-metal precatalyst into a bimodal ligand-metal catalyst, thereby making the bimodal ligand-metal catalyst; wherein the modality-increasing organic compound is 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); wherein 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_8)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).

2. The method of claim 1 wherein the modality-increasing organic 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;

(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; or

(C^1) (R^5)(R^7)C=C(R^6)(R^7) (C^1) and the modality-increasing compound of formula (C^1) is an internal alkene

3. The method of claim 1 wherein the modality-increasing organic compound is selected from the group consisting of: cyclohexylallene; phenylacetylene; and 3,4-difluorophenylacetylene.

4. The method of any one of claims 1 to 5 wherein in the combining step either (i) the first unimodal ligand-metal precatalyst and bimodal ligand-metal catalyst are unsupported (i.e., free of a support material); or (ii) the first unimodal ligand-metal precatalyst is unsupported and the method further comprises, after the combining step, adding a support material to the bimodal ligand-metal catalyst so as to give a bimodal catalyst system, which comprises the support material and the bimodal ligand-metal catalyst.

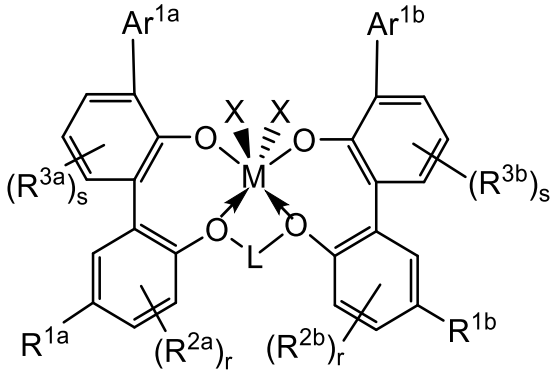
5. The method of claim 1 comprising combining in any order constituents consisting essentially of the modality-increasing organic compound, the activator, and a bimodal precatalyst system that consists essentially of the first unimodal ligand-metal precatalyst, a second unimodal ligand-metal precatalyst that has a ligand that is different in composition than the ligand(s) of the first unimodal ligand-metal precatalyst, and a support material; wherein the method makes a trimodal catalyst system that consists essentially of the bimodal ligand-metal catalyst, a second unimodal ligand-metal catalyst (e.g., a metallocene-type catalyst) made from the second unimodal ligand-metal precatalyst and the activator, and the support material.

6. The method of any one of claims 1, 4, or 5 further comprising, during or after the combining step, contacting the bimodal ligand-metal catalyst (claim 1), the bimodal catalyst system (claim 4), or the trimodal catalyst system (claim 5) with ethylene and an alpha-olefin in a polymerization reactor under steady-state polymerizing conditions so as to make a poly(ethylene-*co*-alpha-olefin) copolymer having a bimodal molecular weight distribution (“bimodal copolymer”; claim 1 or 4) or having a trimodal molecular weight distribution (“trimodal copolymer”; claim 5), as determined by gel permeation chromatography (GPC).

7. The method of any one of claims 1, 4, or 5comprising a step of transitioning a polymerization process being run in a polymerization reactor from a process of making a unimodal poly(ethylene-*co*-alpha-olefin) copolymer to a process of making a bimodal or trimodal poly(ethylene-*co*-alpha-olefin) copolymer, the method further comprising, before the combining step, contacting a first unimodal ligand-metal catalyst, made from the first unimodal ligand-metal precatalyst and activator in absence of the modality-increasing organic compound, with ethylene and an alpha-olefin in a polymerization reactor under steady-state polymerizing conditions so as to make a poly(ethylene-*co*-alpha-olefin) copolymer having a unimodal molecular weight

distribution ("unimodal copolymer"), as determined by GPC; and after the combining step contacting the bimodal ligand-metal catalyst (claim 1), the bimodal catalyst system (claim 4), or the trimodal catalyst system (claim 5) with the ethylene and alpha-olefin in the polymerization reactor under steady-state polymerizing conditions so as to make a poly(ethylene-*co*-alpha-olefin) copolymer having a bimodal or trimodal molecular weight distribution, as determined by GPC.

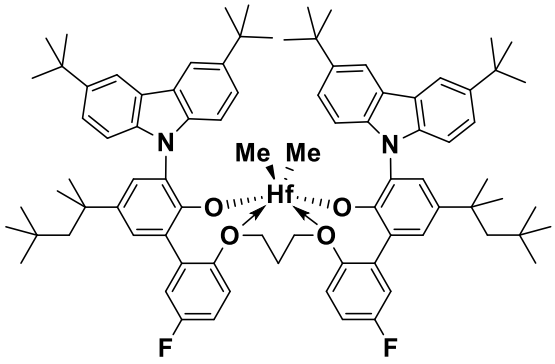
8. The method of claim 1 wherein the first unimodal ligand-metal precatalyst is a biphenylphenoxy-type (BPP-type) ligand-metal precatalyst of formula (I):



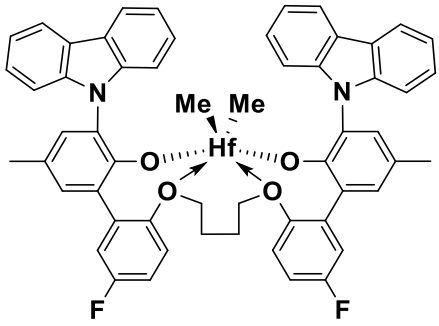
(I); wherein L is a CH_2CH_2, $CH_2CH_2CH_2$, $CH_2CH_2CH_2CH_2$, $CH_2C(R^L)_2CH_2$, $CH_2CH(R^L)CH(R^L)CH_2$, $CH_2Ge(R^L)_2CH_2$, or $CH_2Si(R^L)_2CH_2$, wherein each R^L independently is an unsubstituted $(C_1\text{-}C_{20})$alkyl; M is Zr or Hf; each of R^{1a} and R^{1b} independently is F, $(C_1\text{-}C_{20})$alkyl, or $Si(CH_3)_2(CH_2)_qCH_3$, wherein subscript q is an integer from 0 to 20; each subscript r independently is an integer from 0 to 3; each of R^{2a} and R^{2b} independently is H, F, Cl, $(C_1\text{-}C_5)$alkyl, or R^{2a} and R^{2b} may be bonded together to form a unsubstituted or substituted cycloalkyl group; each subscript s independently is an integer from 0 to 3; each of R^{3a} and R^{3b} independently is an unsubstituted $(C_1\text{-}C_{20})$alkyl or $(C_1\text{-}C_{20})$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 or each X is part of a multidentate (e.g., bidentate) group independently selected from a halogen atom, $((C_1\text{-}C_{20})\text{alkyl})_{3\text{-}g}\text{-}(\text{phenyl})_gSi$- 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$)\text{-}CH_2$ (e.g., benzyl when $(C_6\text{-}C_{12})$aryl is phenyl and $(C_0\text{-}C_{10})$alkylene is (C_0)alkylene), a $(C_1\text{-}C_6)$alkyl-substituted $(C_6\text{-}C_{12})$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.

9. The method of claim 8 wherein the BPP-type ligand-metal precatalyst of structural formula (I) is any one of compounds (1) to (2):



(1) and



(2), wherein each Me is methyl.

10. The method of claim 1 wherein the metal of the first unimodal ligand-metal precatalyst is M, wherein the activator is an organoaluminum compound, and wherein the effective amount of the activator is an Al/M molar ratio of from 0.5 to 10,000, alternatively from 0.95 to 200, alternatively from 1.0 to 150, alternatively from 10 to 100; and/or wherein the effective amount of the modality-increasing organic compound comprises a molar ratio of modality-increasing organic compound-to-first unimodal ligand-metal precatalyst (MIOC/FUC molar ratio) of from 0.5:1.0 to 50.0:1.0, alternatively from 0.9:1.0 to 20.0:1.0, alternatively from 0.9:1.0 to 11:1.0, alternatively from 0.95:1.0 to 6:1.0.