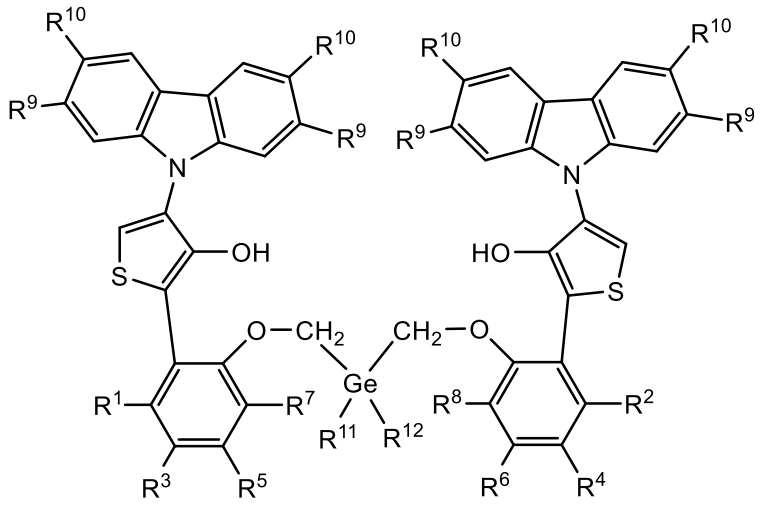
CLAIMS

1. A substituted 2-hydroxythiophene compound of formula (I):



(I), or a Group 1 or Group 2 metal salt thereof, wherein:

R^1 and R^2 independently are H or a halogen;

R^3 and R^4 independently are H, a halogen, a $(C_1\text{-}C_{20})$hydrocarbyl, a $(C_1\text{-}C_{10})$alkoxy, or a $Si((C_1\text{-}C_{10})alkyl)_3$;

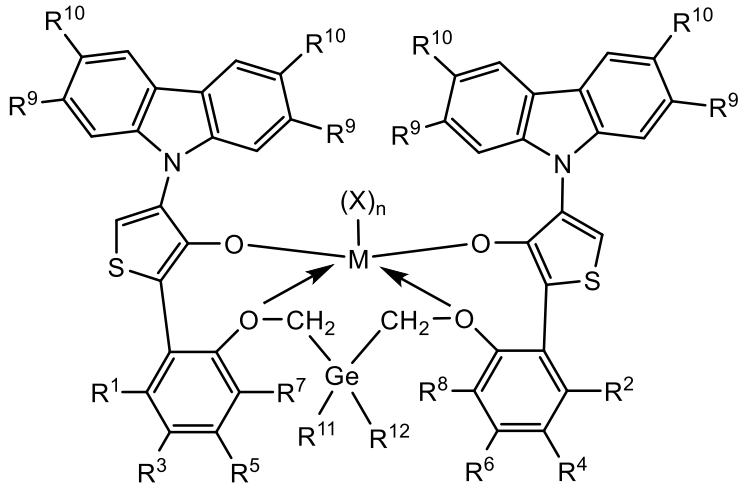
R^5 and R^6 independently are H or a halogen;

R^7 and R^8 independently are H or a halogen;

each R^9 is H and each R^{10} is a $(C_1\text{-}C_{20})$hydrocarbyl; or each R^{10} is H and each R^9 is a $(C_1\text{-}C_{20})$hydrocarbyl; and

R^{11} and R^{12} independently are a $(C_1\text{-}C_{10})$alkyl.

2. A precatalyst of formula (II):



(II);

wherein:

M is Ti, Hf, or Zr;

subscript n is 1 or 2; and

each X independently is selected from a monodentate ligand independently chosen from a hydrogen atom, a (C_1−C_{50})hydrocarbyl, a (C_1−C_{50})heterohydrocarbyl, a (C_1−C_{50})organoheteryl, a halogen atom, a dialkylamino, or a dialkyl carbamate;

R^1 and R^2 independently are H or a halogen;

R^3 and R^4 independently are H, a halogen, a (C_1-C_{20})hydrocarbyl, a (C_1-C_{10})alkoxy, or a Si((C_1-C_{10})alkyl)$_3$;

R^5 and R^6 independently are H or a halogen;

R^7 and R^8 independently are H or a halogen;

each R^9 is H and each R^{10} is a (C_1-C_{20})hydrocarbyl; or each R^{10} is H and each R^9 is a (C_1-C_{20})hydrocarbyl; and

R^{11} and R^{12} independently are a (C_1-C_{10})alkyl.

3. A supported catalyst system comprising the precatalyst of formula (II) of claim 2, a support material, and an activator.

4. A method of making the supported catalyst system of claim 3 comprising step (a) or comprising steps (b) and (c):

(a) spray drying a mixture of an inert hydrocarbon solvent, the precatalyst of formula (II), the support material, and the activator to make the supported catalyst system; or

(b) spray drying a mixture of an inert hydrocarbon solvent, the support material and the activator to make a spray-dried supported activator, and

(c) mixing the precatalyst of formula (II) with the spray-dried supported activator and an inert hydrocarbon solvent to make the supported catalyst system.

5. The substituted 2-hydroxythiophene compound of formula (I) of claim 1 wherein:

R^1 and R^2 are different, or R^1 and R^2 are identical; or R^1 and R^2 are H; or R^1 and R^2 are F; or

R^3 and R^4 are different, or R^3 and R^4 are identical, or R^3 and R^4 are a halogen, a (C_1-C_{20})hydrocarbyl, a (C_1-C_{10})alkoxy, or a Si((C_1-C_{10})alkyl)$_3$, or R^3 and R^4 are a (C_1-C_{20})alkyl, a (C_1-C_{10})alkoxy, or a fluoro; or

R^5 and R^6 are different, or R^5 and R^6 are identical, or R^5 and R^6 are H, or R^5 and R^6 are F; or

R^7 and R^8 are different, or R^7 and R^8 are identical, or R^7 and R^8 are H, or R^7 and R^8 are F; or

each R^9 is H and each R^{10} is tertiary-butyl, 4-tert-butylphenyl, 4-triethylmethylphenyl, 3,5-dimethylphenyl, or 3,5-di-tert-butylphenyl; or each R^{10} is H and each R^9 is 3,5-di-tert-butylphenyl; or

each R^{11} and R^{12} is identical; or each R^{11} and R^{12} is a $(C_1\text{-}C_{10})$alkyl or a $(C_1\text{-}C_5)$alkyl; or each R^{11} and R^{12} is isopropyl; or

a combination of the foregoing definitions of R^1 to R^{12}.

6. The precatalyst of formula (II) of claim 2 wherein:

M is Hf or Zr; or

subscript n is 2; or

each X is benzyl or each X is Cl; or

M is Hf or Zr, subscript n is 2, and each X is benzyl; or

M is Hf or Zr, subscript n is 2, and X is chloro.

7. The substituted 2-hydroxythiophene compound of formula (I) of claim 1 selected from the group consisting of compounds 1 to 3 in TABLE 1:

TABLE 1:

Cmpd No.	R^1 / R^2 each is	R^3 / R^4 each is	R^5 / R^6 each is	R^7 / R^8 each is	R^9	R^{10}	R^{11} / R^{12} each is
1	H	t-Octyl	H	H	H	t-Bu	i-Pr
2	H	OctylO	H	H	H	t-Bu	i-Pr
3	H	H	H	H	H	3,5-dtBP	i-Pr
4	H	F	H	H	H	t-Bu	i-Pr

wherein “Cmpd No.” is compound number, t-Bu is tertiary-butyl; t-Octyl is $(CH_3)_3CCH_2C(CH_3)_2$-; OctylO is $CH_3(CH_2)_7O$-; F is fluoro; 3,5-dtBP is 3,5-di-tert-butylphenyl; and i-Pr is isopropyl.

8. The precatalyst of formula (II) of claim 2 selected from the group consisting of precatalyst numbers 1 to 9 in TABLE 2:

TABLE 2:

Precatalyst No.	Made from Formula (I) Compound No.	M	X each is	n
1	1	Zr	Benzyl	2
2	1	Hf	Benzyl	2
3	2	Zr	Benzyl	2
4	2	Hf	Benzyl	2
5	3	Zr	Benzyl	2
6	3	Hf	Benzyl	2
7	1	Zr	Cl	2
8	4	Zr	Benzyl	2
9	4	Hf	Benzyl	2

9. The supported catalyst system of claim 3 selected from the group consisting of spray-dried supported catalyst system numbers SCS 1 to 7 and the undried supported catalyst system number SCS 8 to 10 in TABLE 3:

TABLE 3:

SCS No.	Made from Formula (II) Precatalyst No.	Support Material	Activator	Catalyst Drying Method
SCS 1	1	HPFS1	MAO	Spray
SCS 2	2	HPFS1	MAO	Spray
SCS 3	3	HPFS1	MAO	Spray
SCS 4	4	HPFS1	MAO	Spray
SCS 5	5	HPFS1	MAO	Spray
SCS 6	6	HPFS1	MAO	Spray
SCS 7	7	HPFS1	MAO	Spray
SCS 8	1	SMAO		None (undried)
SCS 9	8	SMAO		None (undried)
SCS 10	9	SMAO		None (undried)

wherein “HPFS1” is a hydrophobic fumed silica made from untreated fumed silica and a hydrophobing agent that is dichlorodimethylsilane; and “MAO” is methylaluminoxane; and wherein “SMAO” is spray dried methylaluminoxane/HPFS1, wherein HPFS1 is made from untreated fumed silica and a hydrophobing agent that is dichlorodimethylsilane.

10. The supported catalyst system of claim 3 is that which has been shown to make by gas phase polymerization an ethylene/1-hexene copolymer having a weight-average

molecular weight greater than 500,000 grams per mole and/or a z-average molecular weight greater than 2,000,000 grams per mole.

11. A method of making a polyolefin in a gas phase polymerization process, the method comprising contacting one or more olefin monomers with the supported catalyst system of claim 3 in a gas phase polymerization reactor under gas phase polymerization conditions to make a polyolefin polymer.

12. The method of claim 11 having any one of limitations (i) to (v):

(i) wherein the one or more olefin monomers comprises ethylene or a combination of ethylene and propylene or a combination of ethylene and a (C_4-C_{20})alpha-olefin and wherein the polyolefin polymer is an ethylene homopolymer or an ethylene/propylene copolymer or an ethylene/(C_4-C_{20})alpha-olefin copolymer;

(ii) wherein the one or more olefin monomers comprises ethylene or a combination of ethylene and a (C_4-C_{20})alpha-olefin and the polyolefin polymer is an ethylene homopolymer or an ethylene/(C_4-C_{20})alpha-olefin copolymer; wherein the ethylene homopolymer or an ethylene/(C_4-C_{20})alpha-olefin copolymer has a weight-average molecular weight 500,000 grams per mole or greater, or a z-average molecular weight of 2,000,000 grams per mole or greater, or both; or

(iii) wherein the one or more olefin monomers comprises a combination of ethylene and a (C_4-C_{20})alpha-olefin and wherein the polyolefin polymer is an ethylene/(C_4-C_{20})alpha-olefin copolymer having a polydispersity index (PDI) of a ratio of weight-average molecular weight to number-average molecular weight (Mw/Mn) of greater than or equal to 4.0, or a broad molecular weight distribution of a ratio of z-average molecular weight to weight-average molecular weight (Mz/Mw) greater than or equal to 3.5, or both;

(iv) any one of limitations (i) to (iii) wherein the (C_4-C_{20})alpha-olefin is 1-hexene;

(v) a combination of limitations (ii) and (iii) or a combination of limitations (ii), (iii), and (iv).

13. A method of making a polyolefin in a slurry phase polymerization process, the method comprising contacting one or more olefin monomers with the supported catalyst system of claim 3 in a slurry phase polymerization reactor under slurry phase polymerization conditions to make a polyolefin polymer.

14. The method of claim 13 wherein the one or more olefin monomers comprises ethylene or a combination of ethylene and propylene or a combination of ethylene and a (C_4-C_{20})alpha-olefin and the polyolefin polymer comprises an ethylene homopolymer or an ethylene/propylene copolymer or an ethylene/(C_4-C_{20})alpha-olefin copolymer.