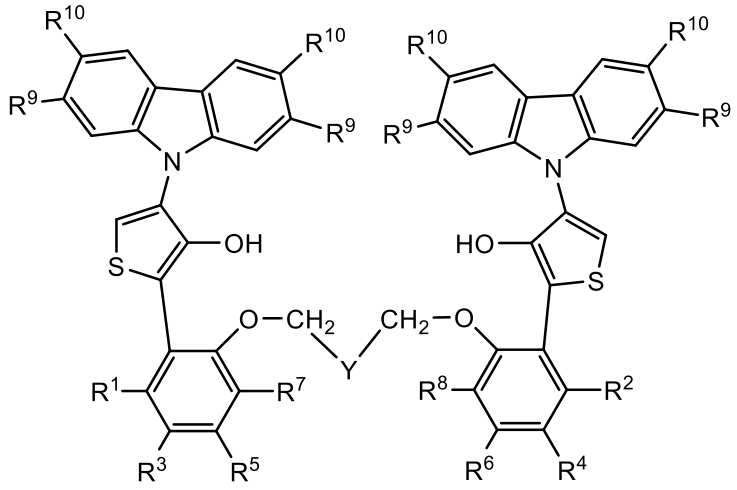
CLAIMS

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



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

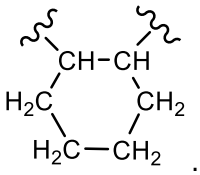
R^1 and R^2 independently are H or a halogen;

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 $Si((C_1\text{-}C_{10})alkyl)_3$;

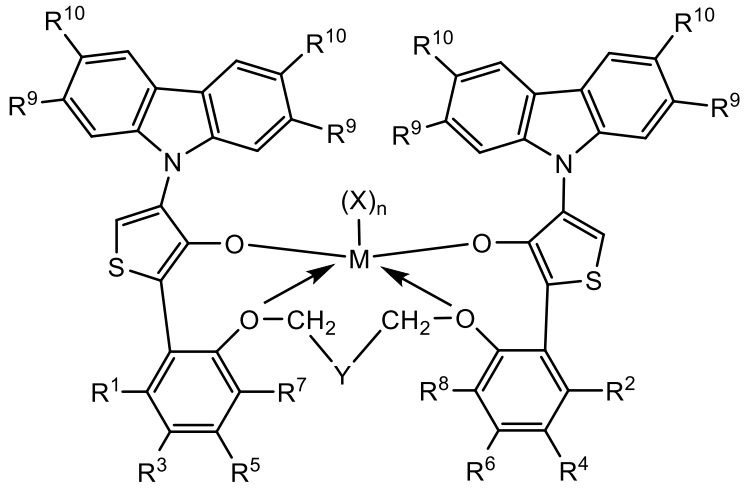
R^5 and R^6 independently are H or a halogen;

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

Y is a vicinal diradical selected from $-CH_2CH_2-$ or *cis*- or *trans*-  .

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;

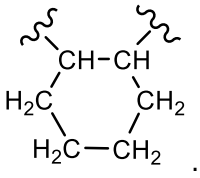
R^1 and R^2 independently are H or a halogen;

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

Y is a vicinal diradical selected from -CH_2CH_2- or *cis*- or *trans*-  .

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 invention 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

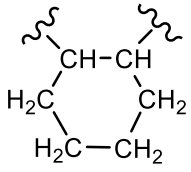
R^3 and R^4 are different, or R^3 and R^4 are identical, or R^3 and R^4 are a halogen, a $(C_1\text{-}C_{20})$hydrocarbyl, a $(C_1\text{-}C_{10})$alkoxy, or a $Si((C_1\text{-}C_{10})alkyl)_3$, or R^3 and R^4 are a $(C_1\text{-}C_{10})$alkyl or a $(C_1\text{-}C_{10})$alkoxy; or

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;

Y is $-CH_2CH_2-$; or

Y is *cis*- or *trans*-  ; or

a combination of the foregoing definitions of R^1 to R^{10} and Y.

6. The invention of claim 2 wherein:

M is Hf or Zr; or

subscript n is 2; or

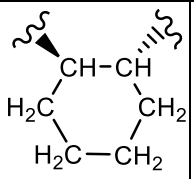
each X is benzyl or each X is Cl; or

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

7. The substituted 2-hydroxythiophene compound of formula (I) of claim 1 selected from the group consisting of compounds 1 to 19 in TABLE 1:

TABLE 1:

Cmpd No.	Y	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}
1	$-CH_2CH_2-$	H	t-Octyl	H	H	H	t-Bu

2	$-CH_2CH_2-$	H	F	H	H	H	t-Bu
3	$-CH_2CH_2-$	H	H	H	H	H	t-Bu
4	$-CH_2CH_2-$	H	CH_3O	H	H	H	t-Bu
5	$-CH_2CH_2-$	H	H	H	H	H	3,5-DtBPh
6	$-CH_2CH_2-$	H	t-Octyl	H	H	H	3,5-DtBPh
7	$-CH_2CH_2-$	H	t-Octyl	H	H	H	3,5-DMePh
8	$-CH_2CH_2-$	H	t-Octyl	H	H	H	4-tBuPh
9	$-CH_2CH_2-$	H	Et_3C	H	H	H	3,5-DMePh
10	$-CH_2CH_2-$	H	Et_3C	H	H	H	3,5-DtBPh
11	$-CH_2CH_2-$	H	Et_3C	H	H	H	4-Et_3CPh
12	$-CH_2CH_2-$	H	OctylO	H	H	H	3,5-DtBPh
13	$-CH_2CH_2-$	H	tHexylO	H	H	H	3,5-DtBPh
14	$-CH_2CH_2-$	H	4-Et_3CPh	H	H	H	3,5-DtBPh
15	$-CH_2CH_2-$	H	Et_3C-	H	H	3,5-DtBPh	H
16		H	H	H	H	H	t-Bu
17	$-CH_2CH_2-$	H	F	F	H	H	t-Bu
18	$-CH_2CH_2-$	F	F	F	H	H	t-Bu
19	$-CH_2CH_2-$	H	F	F	F	H	t-Bu

wherein “Cmpd No.” is compound number; H is hydrogen atom; t-Octyl means $(CH_3)_3CCH_2C(CH_3)_2$-; t-Bu means tertiary-butyl (1,1-dimethylethyl); F is fluorine atom; MeO is methoxy (CH_3O-); 35DtBPh means 3,5-di-tert-butylphenyl; 35DMePh means 3,5-dimethylphenyl; 4tBuPh means 4-tert-butylphenyl; Et_3C means triethylmethyl; 4-Et_3CPh means 4-(triethylmethyl)phenyl; OctylO means $CH_3(CH_2)_7O$-; and tHexylO means $(CH_3)_3CCH_2CH_2O$-; and 4OxPh means 4-octyloxyphenyl.

8. The precatalyst of formula (II) of claim 2 selected from the group consisting of precatalyst numbers 1 to 37 in TABLE 2:

TABLE 2:

Precatalyst No.	Make 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	4	Zr	Benzyl	2
8	4	Hf	Benzyl	2
9	5	Zr	Benzyl	2
10	5	Hf	Benzyl	2
11	6	Zr	Benzyl	2
12	6	Hf	Benzyl	2
13	7	Zr	Benzyl	2
14	7	Hf	Benzyl	2
15	8	Zr	Benzyl	2
16	8	Hf	Benzyl	2
17	9	Zr	Benzyl	2
18	9	Hf	Benzyl	2
19	10	Zr	Benzyl	2
20	10	Hf	Benzyl	2
21	11	Zr	Benzyl	2
22	11	Hf	Benzyl	2
23	12	Zr	Benzyl	2
24	12	Hf	Benzyl	2
25	13	Zr	Benzyl	2
26	13	Hf	Benzyl	2
27	14	Zr	Benzyl	2
28	14	Hf	Benzyl	2
29	15	Zr	Benzyl	2
30	15	Hf	Benzyl	2
31	16	Zr	Benzyl	2
32	16	Hf	Benzyl	2
33	17	Zr	Benzyl	2
34	17	Hf	Benzyl	2
35	18	Zr	Benzyl	2

36	18	Hf	Benzyl	2
37	19	Zr	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 SCS 19 in TABLE 3a:

TABLE 3a:

Spray dried SCS No.	Make from Formula (II) Precatalyst No.	Support Material	Activator	Drying Method
1	1	HPFS1	MAO	Spray
2	2	HPFS1	MAO	Spray
3	3	HPFS1	MAO	Spray
4	4	HPFS1	MAO	Spray
5	5	HPFS1	MAO	Spray
6	6	HPFS1	MAO	Spray
7	7	HPFS1	MAO	Spray
8	8	HPFS1	MAO	Spray
9	11	HPFS1	MAO	Spray
10	13	HPFS1	MAO	Spray
11	15	HPFS1	MAO	Spray
12	19	HPFS1	MAO	Spray
13	20	HPFS1	MAO	Spray
14	21	HPFS1	MAO	Spray
15	23	HPFS1	MAO	Spray
16	25	HPFS1	MAO	Spray
17	28	HPFS1	MAO	Spray
18	31	HPFS1	MAO	Spray
19	32	HPFS1	MAO	Spray

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

10. The supported catalyst system of claim 3 selected from the group consisting of undried supported catalyst system numbers SCS 20 to SCS 56 in TABLE 3b:

TABLE 3b:

Undried SCS No.	Make from Formula (II) Precatalyst No.	Support Material	Activator	Catalyst Drying Method

20	1	SMAO	None (Undried)
21	2	SMAO	None (Undried)
22	3	SMAO	None (Undried)
23	4	SMAO	None (Undried)
24	5	SMAO	None (Undried)
25	6	SMAO	None (Undried)
26	7	SMAO	None (Undried)
27	8	SMAO	None (Undried)
28	9	SMAO	None (Undried)
29	10	SMAO	None (Undried)
30	11	SMAO	None (Undried)
31	12	SMAO	None (Undried)
32	13	SMAO	None (Undried)
33	14	SMAO	None (Undried)
34	15	SMAO	None (Undried)
35	16	SMAO	None (Undried)
36	17	SMAO	None (Undried)
37	18	SMAO	None (Undried)
38	19	SMAO	None (Undried)
39	20	SMAO	None (Undried)
40	21	SMAO	None (Undried)
41	22	SMAO	None (Undried)
42	23	SMAO	None (Undried)
43	24	SMAO	None (Undried)
44	25	SMAO	None (Undried)
45	26	SMAO	None (Undried)
46	27	SMAO	None (Undried)
47	28	SMAO	None (Undried)
48	29	SMAO	None (Undried)
49	30	SMAO	None (Undried)
50	31	SMAO	None (Undried)
51	32	SMAO	None (Undried)
52	33	SMAO	None (Undried)
53	34	SMAO	None (Undried)
54	35	SMAO	None (Undried)

55	36	SMAO	None (Undried)
56	37	SMAO	None (Undried)

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

11. 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.

12. 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, described above, in a gas phase polymerization reactor under gas phase polymerization conditions to make a polyolefin polymer.

13. The method of claim 12 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).

14. 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,

described above, in a slurry phase polymerization reactor under slurry phase polymerization conditions to make a polyolefin polymer.

15. The method of claim 14 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.