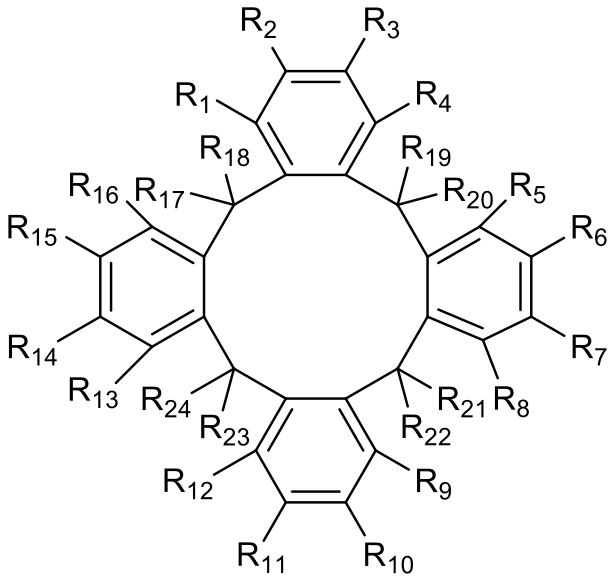
Claims

1. A catalyst system for olefin polymerization, comprising a main catalyst and a cocatalyst, wherein the cocatalyst comprises a twelve-membered ring compound represented by formula (M),



Formula (M)

wherein in the formula (M), R_1-R_{16} are the same or different, each independently selected from a group consisting of hydrogen, hydroxyl, halogen, cyano, nitro, amino, amine, aldehyde, carboxyl, ketone, alkoxy and hydrocarbyl, and when two adjacent groups on a benzene ring are each selected from a group consisting of alkoxy and hydrocarbyl, the two adjacent groups may optionally form a ring with each other, the ring selected from a group consisting of a saturated or unsaturated monocyclic ring, a saturated or unsaturated polycyclic ring and a combination thereof; and wherein R_{17} to R_{24} are the same or different, each independently selected from a group consisting of hydrogen and C_1-C_{10} hydrocarbyl, and the amine, aldehyde, carboxyl, ketone, alkoxy and hydrocarbyl may be optionally substituted by one or more substituents,

wherein the main catalyst comprises (i) a solid catalyst component containing magnesium, titanium, halogen and an internal electron donor compound; (ii) an organic aluminum compound; and optionally (iii) an external electron donor compound.

2. The catalyst system according to claim 1, characterized in that a molar ratio of the external electron donor compound to the titanium element in the solid catalyst

component is (0-500):1, preferably (0.01-200):1, and more preferably (0.1-100):1.

3. The catalyst system according to claim 1 or 2 characterized in that,

in the formula (M), R_1-R_{16} are the same or different, each independently selected from a group consisting of hydrogen, hydroxyl, halogen, cyano, nitro, amino, mono-C_1-C_{10} alkyl amine, bis-C_1-C_{10} alkyl amine, C_1-C_{10} aldehyde, C_1-C_{10} carboxyl, $R_aC(O)$-, R_aO-, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl , C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} aralkyl, 4-12-membered heterocycloalkyl and C_5-C_{20} heteroaryl, and when two adjacent groups on a benzene ring are each selected from a group consisting of $R_aC(O)$-, R_aO-, C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} aralkyl, 4-12-membered heterocycloalkyl and C_5-C_{20} heteroaryl, the two adjacent groups may optionally form a ring with each other, the ring selected from a group consisting of a saturated or unsaturated monocyclic ring, a saturated or unsaturated polycyclic ring and a combination thereof,

wherein R_a is selected from a group consisting of C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_2-C_{20} alkynyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} aralkyl, 4-12-membered heterocycloalkyl and C_5-C_{20} heteroaryl; and

R_{17} to R_{24} are the same or different, each independently selected from a group consisting of hydrogen, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_8 cycloalkyl, C_6-C_{10} aryl, C_7-C_{20} aralkyl, 4-12-membered heterocycloalkyl and C_5-C_{20} heteroaryl, and

any one of the alkyl, alkenyl, alkynyl, cycloalkyl, aryl, aralkyl, heterocycloalkyl and heteroaryl may be optionally substituted by one or more substituents.

4. The catalyst system according to any one of claims 1 to 3, characterized in that, in the formula (M), the one or more substituents are selected from a group consisting of alkyl, alkoxyl, hydroxyl, halogen, cyano, nitro, amino, alkyl substituted amino, aldehyde, carboxyl and a heteroatom-containing group; preferably, the one or more substituents are selected from a group consisting of C_1-C_{10} alkyl, C_1-C_{10} alkoxyl, hydroxyl, halogen, cyano, nitro, amino, mono-C_1-C_{10} alkyl amine, bis-C_1-C_{10} alkyl amine, C_1-C_{10} aldehyde, C_1-C_{10} carboxyl and a heteroatom-containing group; and more preferably, the one or more substituents are selected from a group consisting of C_1-C_6 alkyl, C_1-C_6 alkoxyl, hydroxyl, fluorine, chlorine, bromine, iodine, cyano, nitro, amino, mono-C_1-C_6 alkyl amine, bis-C_1-C_6 alkyl amine, C_1-C_6 aldehyde and C_1-C_6

carboxyl.

5. The catalyst system according to any one of claims 1 to 4, characterized in that, in the formula (M), R_1 to R_{16} are the same or different, and are each independently selected from a group consisting of hydrogen, hydroxyl, halogen, cyano, nitro, amino, mono-C_1-C_6 alkyl amine, bis-C_1-C_6 alkyl amine, C_1-C_6 aldehyde, C_1-C_6 carboxyl, $R_aC(O)$-, R_aO-, C_1-C_6 alkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, C_3-C_6 cycloalkyl, C_6-C_{10} aryl, C_7-C_{10} aralkyl, 4-6-membered heterocycloalkyl and C_5-C_{10} heteroaryl, wherein R_a is selected from a group consisting of C_1-C_6 alkyl, C_2-C_6 alkenyl, C_2-C_6 alkynyl, C_3-C_6 cycloalkyl, C_6-C_{10} aryl, C_7-C_{10} aralkyl, 4-6-membered heterocycloalkyl and C_5-C_{10} heteroaryl;

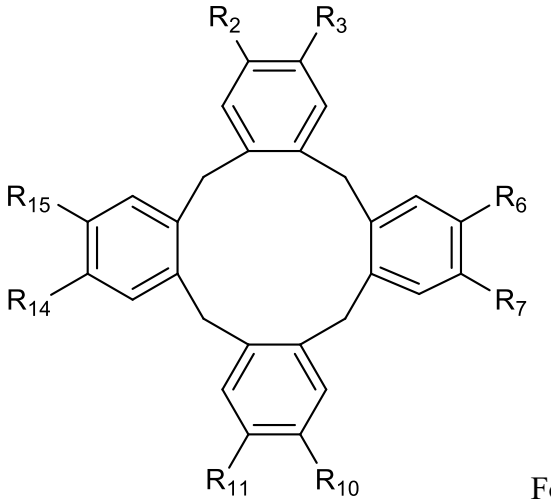
preferably, R_1 to R_{16} are selected from a group consisting of hydrogen, hydroxyl, amino, halogen, C_1-C_6 aldehyde, C_1-C_6 alkoxyl and halogen substituted C_1-C_6 alkoxyl; and

preferably, R_1 to R_{16} are not hydrogen at the same time.

6. The catalyst system according to any one of claims 1 to 5, characterized in that, in the formula (M), R_1, R_4, R_5, R_8, R_9, R_{12}, R_{13} and R_{16} are each independently selected from a group consisting of hydrogen and C_1-C_6 alkyl; R_2, R_3, R_6, R_7, R_{10}, R_{11}, R_{14} and R_{15} are each independently selected from a group consisting of hydroxyl, amino, halogen, C_1-C_6 aldehyde, C_1-C_6 alkoxyl and halogen substituted C_1-C_6 alkoxyl.

7. The catalyst system according to any one of claims 1 to 6, characterized in that, in the formula (M), R_{17} to R_{24} are each independently selected from a group consisting of hydrogen and C_1-C_{10} alkyl, preferably selected from a group consisting of hydrogen and C_1-C_6 alkyl, and more preferably selected from a group consisting of hydrogen and C_1-C_4 alkyl.

8. The catalyst system according to any one of claims 1 to 7, characterized in that, the twelve-membered ring compound represented by the formula (M) is represented by formula (N),



Formula (N)

and preferably, the twelve-membered ring compound represented by the formula (M) is selected from one or more of the following compounds:

Compound A: in the formula (N), $R_2=R_3=R_6=R_7=R_{10}=R_{11}=R_{14}=R_{15}=OCH_3$;

Compound B: in the formula (N), $R_2=R_3=R_6=R_7=R_{10}=R_{11}= R_{14}=R_{15}=OCH_2CH_3$;

Compound C: in the formula (N), $R_2=R_3=R_6=R_7=R_{10}=R_{11}=R_{14}=R_{15}=OCH_2CH_2CH_3$;

Compound D: in the formula (N), $R_2=R_3=R_6=R_7=R_{10}=R_{11}=R_{14}=R_{15}=OCH(CH_3)_2$;

Compound E: in the formula (N), $R_2=R_3=R_6=R_7=R_{10}=R_{11}=R_{14}=R_{15}=OCH_2CH_2CH_2CH_3$;

Compound F: in the formula (N), $R_2=R_6=R_{10}=R_{14}=OCH_3$ and $R_3=R_7=R_{11}=R_{15}=OCH_2CH_3$;

Compound G: in the formula (N), $R_2=R_6=R_{10}=R_{14}=OCH_3$ and $R_3=R_7=R_{11}=R_{15}=OCH_2CH_2CH_3$;

Compound H: in the formula (N), $R_2=R_6=R_{10}=R_{14}=OCH_3$ and $R_3=R_7=R_{11}=R_{15}=OCH_2CH_2CH_2CH_3$;

Compound I: in the formula (N), $R_2=R_3=R_6=R_7=R_{10}=R_{11}=R_{14}=R_{15}=OH$;

Compound J: in the formula (N), $R_2=R_6=R_{10}=R_{14}=OCH_3$ and $R_3=R_7=R_{11}=R_{15}=OH$;

Compound K: in the formula (N), $R_2=R_6=R_{10}=R_{14}=OCH_3$ and $R_3=R_7=R_{11}=R_{15}=NH_2$;

Compound L: in the formula (N), $R_2=R_6=R_{10}=R_{14}=OCH_3$ and $R_3=R_7=R_{11}=R_{15}=Cl$;

Compound M: in the formula (N), $R_2=R_6=R_{10}=R_{14}=OCH_3$ and

R_3=R_7=R_{11}=R_{15}=Br;

Compound N: in the formula (N), R_2=R_6=R_{10}=R_{14}=OCH_3 and R_3=R_7=R_{11}=R_{15}=I;

Compound O: in the formula (N), R_2=R_6=R_{10}=R_{14}=OCH_3 and R_3=R_7=R_{11}=R_{15}=CHO;

Compound P: in the formula (N), R_2=R_6=R_{10}=R_{14}=OCH_3 and R_3=R_7=R_{11}=R_{15}=$OCH_2CH_2CH_2Br$;

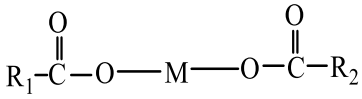
Compound Q: in the formula (N), R_2=R_3=R_6=R_7=R_{10}=R_{11}=R_{14}=R_{15}=OCH_2CH_2Cl; and

Compound R: in the formula (N), R_2=R_6=R_{10}=R_{14}=OH and R_3=R_7=R_{11}=R_{15}=OCH_2CH_3.

9. The catalyst system according to any one of claims 1 to 8, characterized in that the internal electron donor compound is selected from one or more of a diether compound, an alcohol ester compound, an aromatic carboxylic acid ester compound, a succinate compound or a ketone compound.

10. The catalyst system according to claim 9, characterized in that,

the alcohol ester compound is a glycol ester compound represented by formula B,

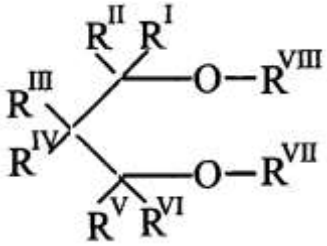


Formula B

wherein, in the formula B, R_1 and R_2 are the same or different, each independently selected from a group consisting of C_1-C_{20} alkyl, C_2-C_{20} alkenyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkaryl, C_7-C_{20} aralkyl and C_{10}-C_{20} fused ring aryl, and preferably each independently selected from a group consisting of C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_3-C_{10} cycloalkyl, C_6-C_{10} aryl, C_7-C_{10} alkaryl, C_7-C_{10} aralkyl and C_{10}-C_{15} fused ring aryl, the alkyl, alkenyl, cycloalkyl, aryl, alkaryl, aralkyl and fused ring aryl optionally substituted by one or more substituents selected from a group consisting of C_1-C_{10} alkyl, C_1-C_{10} alkoxyl, hydroxyl, halogen, cyano, nitro, amino, mono-C_1-C_6 alkyl amine, bis-C_1-C_6 alkyl amine, aldehyde, carboxyl and a heteroatom; and M is a divalent linking group, preferably selected from a group consisting of C_1-C_{20} alkylene, C_3-C_{20} cycloalkylene and C_6-C_{20} arylene, the alkylene,

cycloalkylene and/or arylene substituted by a substituent selected from a group consisting of C_1-C_{20} alkyl, C_1-C_{20} alkoxyl and halogen, the substituent optionally bonded to form one or more rings, and a carbon atom or/and a hydrogen atom in M optionally substituted by a nitrogen, oxygen, sulfur, silicon, phosphorus or halogen atom;

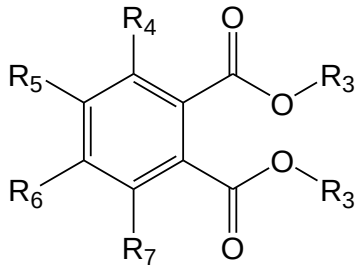
the diether compound is a 1,3-diether compound represented by formula E,



Formula E

wherein, in the formula E, $R^{I,}$ R^{II}, R^{III}, R^{IV}, R^{V} and R^{VI} are the same or different, and are each independently selected from a group consisting of hydrogen, halogen, C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} aralkyl and C_7-C_{20} alkaryl; R^{VII} and R^{VIII} are the same or different, and are each independently selected from a group consisting of C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} aralkyl and C_7-C_{20} alkaryl, wherein any one of the alkyl, cycloalkyl, aryl, aralkyl and alkaryl may be optionally substituted by one or more substituents which are selected from a group consisting of hydroxyl, halogen, cyano, nitro, amino, mono-C_1-C_{10} alkyl amine, bis-C_1-C_{10} alkyl amine, aldehyde, carboxyl and a heteroatom; or, two or more of R^{I}, R^{II}, R^{III}, R^{IV}, R^{V} and R^{VI} are bonded to each other to form a saturated or unsaturated monocyclic or polycyclic ring, such as a fluorene ring;

a structure of the aromatic carboxylic acid ester compound is as shown in formula F:

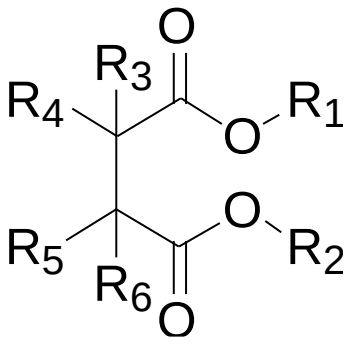


Formula F

wherein, in the formula F, each R_3 is the same or different, which is independently C_1-C_8 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{15} aryl, C_7-C_{15} alkaryl or C_7-C_{15}

aralkyl, and hydrogen on carbon of the C_1-C_8 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{15} aryl, C_7-C_{15} alkaryl or C_7-C_{15} aralkyl may be optionally substituted by a substituent selected from a group consisting of an alkane and a halogen atom, and preferably substituted by one or more substituents selected from a group consisting of C_1-C_6 alkyl, a fluorine atom, a chlorine atom, a bromine atom and an iodine atom; and R_4-R_7 may be the same or different, which are hydrogen, halogen, C_1-C_6 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} alkaryl or C_7-C_{20} aralkyl, and hydrogen on carbon of the C_1-C_8 alkyl, C_5-C_{10} cycloalkyl, C_6-C_{15} aryl, C_7-C_{15} alkaryl or C_7-C_{15} aralkyl may be optionally substituted by a substituent selected from a group consisting of an alkane and a halogen atom, and preferably substituted by one or more substituents selected from a group consisitng of C_1-C_6 alkyl, a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom; and

a structure of the succinate compound is as shown in formula G,

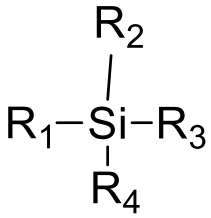


Formula G

wherein, in the formula G, R_1 and R_2 are the same or different, each independently selected from a group consisting of a C_1-C_{20} alkyl group, a C_3-C_{20} cycloalkyl group, a C_6-C_{20} aryl group, a C_7-C_{20} arylalkyl group or a C_7-C_{20} alkylaryl group, and optionally containing a heteroatom; and R_3, R_4, R_5 and R_6 are the same or different, each independently selected from a group consisting of hydrogen, a C_1-C_{20} alkyl group, a cycloalkyl group, an aryl group, an arylalkyl group or an alkylaryl group, and optionally containing a heteroatom, and groups may be connected to form a ring.

11. The catalyst system according to any one of claims 1 to 10, characterized in that, the external electron donor compound is selected from one or more of a silane compound, an ester compound, an ether compound or a ketone compound.

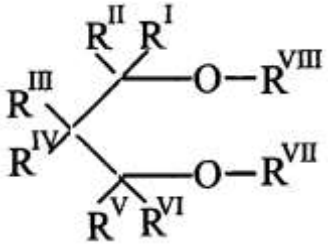
12. The catalyst system according to claim 11, characterized in that, a structure of the silane compound is shown in formula D:



Formula D

wherein in the formula D, R_1 to R_4 are the same or different, each independently selected from a group consisting of hydrogen, C_1-C_{10} alkyl, C_2-C_{10} alkenyl, C_1-C_{10} alkoxyl, C_2-C_{10} enyloxy, C_2-C_{10} alkynyl, C_2-C_{10} ynoxy, C_3-C_{10} cycloalkyl, C_6-C_{15} aryl, C_3-C_{10} cycloalkoxyl, C_6-C_{15} aryloxyl and amino, wherein the alkyl, alkenyl, alkynyl, alkoxyl, enyloxy, ynoxy, cycloalkyl, aryl, cycloalkoxyl, aryloxyl and amino may be optionally subsitituted by one or more substituents selected from a group consisting of halogen, C_1-C_6 alkyl, C_3-C_6 cycloalkyl, C_6-C_{10} aryl and amino; and

the ether compound is the 1,3-diether compound represented by the formula E,



Formula E

wherein, in the formula E, $R^{I,}$ R^{II}, R^{III}, R^{IV}, R^{V} and R^{VI} are the same or different, and are each independently selected from a group consisting of hydrogen, halogen, C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} aralkyl and C_7-C_{20} alkaryl; R^{VII} and R^{VIII} are the same or different, and are each independently selected from a group consisting of C_1-C_{20} alkyl, C_3-C_{20} cycloalkyl, C_6-C_{20} aryl, C_7-C_{20} aralkyl and C_7-C_{20} alkaryl, wherein any one of the alkyl, cycloalkyl, aryl, aralkyl and alkaryl may be optionally substituted by one or more substituents which are selected from a group consisting of hydroxyl, halogen, cyano, nitro, amino, mono-C_1-C_{10} alkyl amine, bis-C_1-C_{10} alkyl amine, aldehyde, carboxyl and a heteroatom; or, two or more of R^{I}, R^{II}, R^{III}, R^{IV}, R^{V} and R^{VI} are bonded to each other to form a saturated or unsaturated monocyclic or polycyclic ring, such as a fluorene ring.

13. The catalyst system according to any one of claims 1 to 12, characterized in that, a molar ratio of the twelve-membered ring compound represented by the formula (M) to the external electron donor compound is 1:100-100:1, preferably 1:50-50:1, and more preferably 1:20-20:1.

14. The catalyst system according to any one of claims 1 to 13, characterized in that, the organic aluminum compound is an alkyl aluminum compound; prerferably, a general formula of the alkyl aluminum compound is AlR_3, wherein each R is independently selected from a group cponsisting of hydrogen, halogen, C_1-C_{20} alkyl, C_1-C_{20} alkoxyl or halogenated C_1-C_{20} alkyl, and at least one of three Rs is C_1-C_{20} alkyl; more preferably, the general formula of the alkyl aluminum compound is AlR_3, wherein each R is independently selected from a group consisting of hydrogen, halogen, C_1-C_{10} alkyl, C_1-C_{10} alkoxyl or halogenated C_1-C_{10} alkyl, and at least one of the three Rs is C_1-C_{10} alkyl; and

further preferably, the alkyl aluminum compound is one or more of triethyl aluminum, tri-n-propyl aluminum, tri-isopropyl aluminum, tri-n-butyl aluminum, tri-isobutyl aluminum, tri-n-hexyl aluminum, tri-n-octyl aluminum, diethyl aluminum monohydrogen, diisobutyl aluminum monohydrogen, diethyl aluminum chloride, diisobutyl aluminum chloride, ethyl aluminum dichloride, $Al(n\text{-}C_6H_{13})_3$ and $Al(n\text{-}C_8H_{17})_3$.

15. The catalyst system according to any one of claims 1 to 14, characterized in that, a molar ratio of the twelve-membered ring compound represented by the formula (M) to the organic aluminum compound in terms of aluminum is 1:(0.1-500), and preferably 1:(1-200); and

a molar ratio of the solid catalyst component in terms of the titanium element to the organic aluminum compound in terms of aluminum is 1:(5-5000), and preferably 1:(20-2000).

16. A prepolymerized catalyst composition for olefin polymerization, which comprises the catalyst system according to any one of claims 1 to 15 and a prepolymer obtained by the olefin prepolymerization, preferably a prepolymerization multiple of the prepolymer being 0.1-1000 g olefin polymer/g solid catalyst

component.

17. A method for olefin polymerization, comprising: polymerizing an olefin having a general formula of CH_2=CHR in the presence of the catalyst system according to any one of claims 1 to 15 and/or the prepolymerized catalyst composition according to claim 16, wherein R is hydrogen or C_1-C_8 alkyl, and preferably hydrogen or C_1-C_6 alkyl.

18. The method according to claim 17, characterized in that, the olefin is selected from one or more of ethylene, propylene, 1-butene, 4-methyl-1-pentene and 1-hexene; and preferably ethylene, propylene, or a mixture of the ethylene and the propylene.