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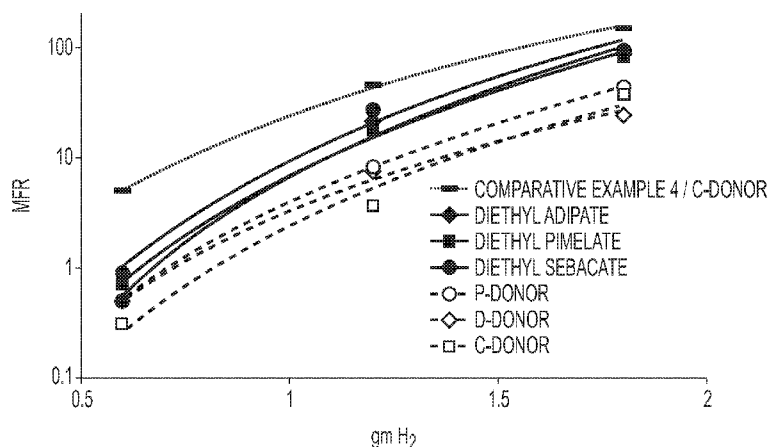


FIG. 1

(57) Abstract: This invention relates to a non-phthalate catalyst system for olefin polymerization. The non-phthalate catalyst system comprises (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, a Group 2 metal, and one or more halogens; and one or more internal electron donor compounds; and (b) one or more external electron donor compounds.

NON-PHTHALATE CATALYST SYSTEM AND ITS USE IN THE POLYMERIZATION OF OLEFINS

[0001] This application claims the benefit of priority to U.S. Provisional Patent Application Serial No. 62/273,584, filed December 31, 2015, and U.S. Provisional Patent Application Serial No. 62/278,256, filed January 13, 2016; which are hereby incorporated by reference in their entirety.

FIELD OF THE INVENTION

[0002] This invention relates to a non-phthalate catalyst system with a novel external electron donor for olefin polymerization.

BACKGROUND OF THE INVENTION

[0003] Phthalate-based catalysts have been widely used in the commercial production of polypropylene worldwide. Extensive research and development have shown that the use of certain alkoxysilanes as external donors leads to optimum performance of phthalate-based catalysts (Kissin, *Alkene Polymerizations with Transition Metal Catalysts*, Studies in Surface Science and Catalysis 173: 224-243 (Elsevier, Amsterdam, 2007); Pasquini, *Polypropylene Handbook* (2nd Ed., Hanser Publishers, Munich, 2005); Moore, *The Rebirth of Polypropylene: Supported Catalysts* (Hanser Publishers, Munich, 1998)). The use of these silane donors allows for the production of a wide range of polypropylene products, due to the varied effect of these donors on the hydrogen response (characterized by melt flow rate (MFR)), isotacticity (characterized by % xylene solubles (%XS) or the isotactic pentad contents (mmmm) of the xylene-insoluble fraction (XI)), and molecular weight distribution (MWD).

[0004] Yet the use of these phthalate-based catalysts has caused regulatory and human health and safety concerns. Non-phthalate catalysts have been evaluated as replacements for the phthalate-based systems. However, the current non-phthalate catalysts generally do not match the performance of the phthalate systems.

[0005] Non-phthalate catalysts have certain limitations compared to the phthalate systems, for instance, very high initial activity, fast decay of polymerization activity, insufficient catalyst activity or low gas phase activity in sequential polymerization process for impact copolymer production. Additionally, non-phthalate catalysts often exhibit one or more of the following characteristics: low hydrogen response (characterized by low MFR)

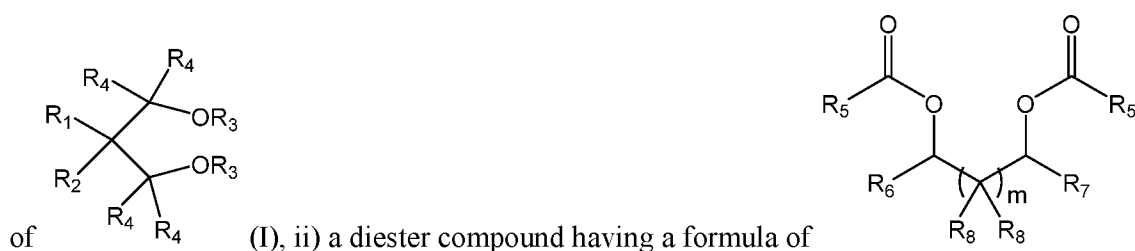
and low isotacticity. These limitations of the non-phthalate catalysts often render the properties of the polymers made with non-phthalate systems poorer than those of the polymers made with the phthalate-based catalysts.

[0006] There thus remains a need in the art to improve the technology of these non-phthalate catalyst systems to overcome the above-described limitations in the non-phthalate catalyst systems. This invention answers that need.

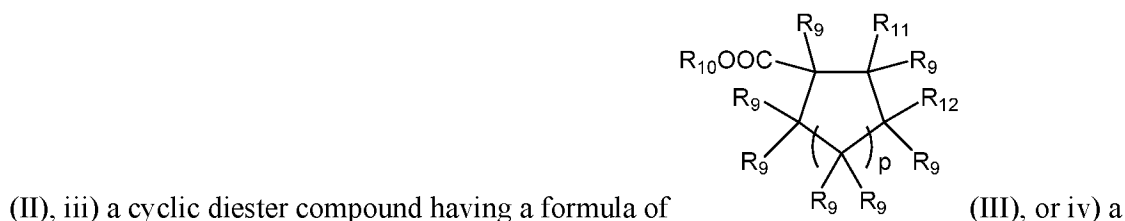
SUMMARY OF THE INVENTION

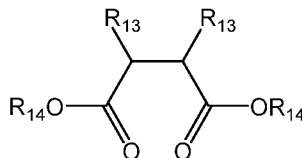
[0007] One aspect of the invention relates to a non-phthalate catalyst system for olefin polymerization. The non-phthalate catalyst system comprises (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, a Group 2 metal, and one or more halogens; and one or more internal electron donor compounds; and (b) one or more external electron donor compounds.

[0008] The internal electron donor compound is i) a diether compound having a formula



(I), ii) a diester compound having a formula of

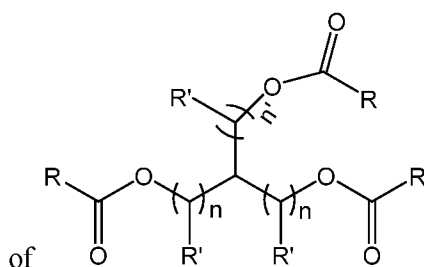


succinate compound having a formula of  (IV). In these formulas,

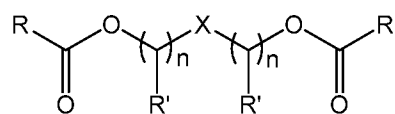
each of R₁ and R₂ is independently H or an alkyl, cycloalkyl, aryl, or aralkyl group, each having from 1 to 18 carbon atoms; or, R₁ and R₂ together form one or more saturated or unsaturated mono- or poly- cyclic structures. Each R₃ is independently an alkyl, aryl, or aralkyl group having from 1 to 18 carbon atoms. Each R₄ is H or R₃. Each R₅ is independently a C₁ to C₁₈ hydrocarbonyl group which can optionally form one or more

saturated or unsaturated mono- or poly- cyclic structures. Each of R_6 and R_7 is independently H or a C_1 to C_{18} hydrocarbyl group; or, R_6 and R_7 together form one or more saturated or unsaturated mono- or poly- cyclic structures. Each R_8 is independently absent, H, or a C_1 to C_{18} hydrocarbyl group. Each R_9 is independently H, halogen, or a C_1 to C_{18} hydrocarbyl group. Each R_{10} is independently a C_1 to C_{20} hydrocarbyl group. Each of R_{11} and R_{12} is independently R_9 or $-\text{COOR}_{10}$, provided that at least one of R_{11} and R_{12} is $-\text{COOR}_{10}$. Each of R_{13} and R_{14} is independently a C_1 to C_{18} hydrocarbyl group. The integer m is 0 or 1. The integer p ranges from 1 to 6. Each of $R_1, R_2, R_3, R_4, R_5, R_6, R_7, R_8, R_9, R_{13}$, and R_{14} can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group.

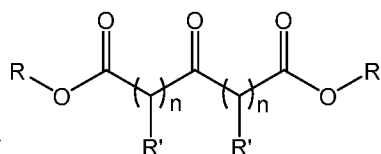
[0009] The external electron donor compound is i) a triester compound having a formula



of (V), ii) a diester compound having a formula of



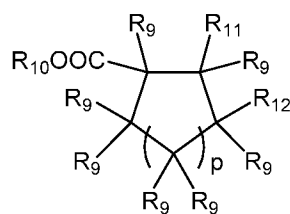
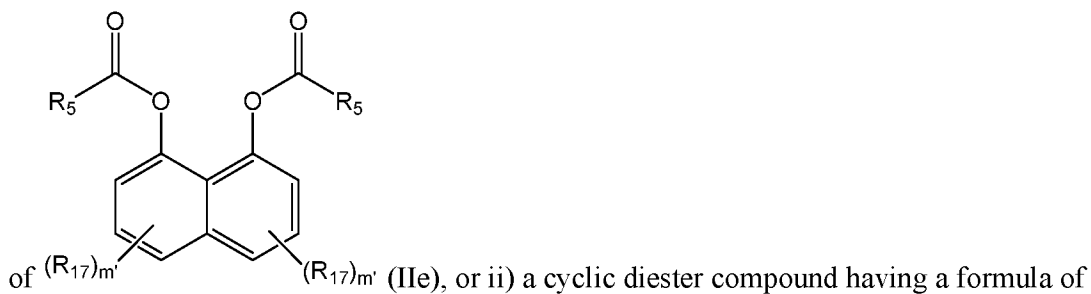
(VI), or iii) an oxo-substituted diester compound having a



formula of (VII). In these formulas, X is CH_2 or O. Each R is independently a C_1 - C_{10} hydrocarbyl group. Each R' is independently H or R. Each n is independently an integer from 1 to 4. The integer n' ranges from 0 to 4.

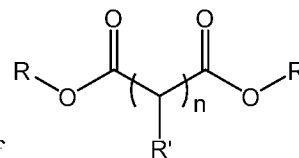
[0010] Another aspect of the invention relates to a non-phthalate catalyst system for olefin polymerization. The non-phthalate catalyst system comprises (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, a Group 2 metal, and one or more halogens; and one or more internal electron donor compounds; and (b) one or more external electron donor compounds.

[0011] The internal electron donor compound is i) a diester compound having a formula



(III). In these formulas, each R_5 is independently a C_1 to C_{18}

hydrocarbyl group which can optionally form one or more saturated or unsaturated mono- or poly- cyclic structures. Each R_{17} is independently H, halogen, or C_1 to C_{18} hydrocarbyl group which can optionally form one or more saturated or unsaturated cyclic structures with the phenyl group it is attached to. Each R_9 is independently H, halogen, or C_1 to C_{18} hydrocarbyl group. Each R_{10} is independently C_1 to C_{20} hydrocarbyl group. Each of R_{11} and R_{12} is independently R_9 or $-\text{COOR}_{10}$, provided that at least one of R_{11} and R_{12} is $-\text{COOR}_{10}$. Each m' is independently an integer from 0 to 5. The integer p ranges from 1 to 6. Each of R_5 , R_9 , and R_{17} can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group.



[0012] The external electron donor compound has a formula of

(VIII), wherein the external electron donor compound does not contain an alkoxy silane compound. In formula VIII, each R is independently a C_1 to C_{10} hydrocarbyl group, and can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group. R' is H or R. The integer n ranges from 1 to 10.

[0013] Another aspect of the invention relates to a process for preparing a polyolefin.

The process comprises polymerizing one or more olefins, in the presence of the non-phthalate

catalyst system under reaction conditions sufficient to form the polyolefin. The non-phthalate catalyst system may be any non-phthalate catalyst system described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] **Figure 1** is a graph showing the hydrogen responses of polymers prepared with Example No. 2 procatalyst (non-phthalate) in combination with a conventional alkoxysilane external donor and non-silane aliphatic diester external donors (1-gallon reactor, 75 °C, ratio of donor / Ti compound = 10), as compared to a phthalate procatalyst in combination with a conventional alkoxysilane external donor.

[0015] **Figure 2** is a graph showing the ethylene incorporation into an impact copolymer using Example No. 3 procatalyst (non-phthalate) in combination with a conventional alkoxysilane external donor and non-silane ester external donors, as compared to a phthalate procatalyst (Comparative Example 1) in combination with the conventional alkoxysilane external donor (2-gallon reactor, ratio of donor / Ti compound = 10).

[0016] **Figure 3** is a graph showing the %XS in an impact copolymer using Example No. 3 procatalyst (non-phthalate) in combination with a conventional alkoxysilane external donor and non-silane ester external donors, as compared to a phthalate procatalyst (Comparative Example 1) in combination with the conventional alkoxysilane external donor (2-gallon reactor, ratio of donor / Ti compound = 10).

[0017] **Figure 4** is a graph showing the hydrogen responses of Example No. 1 procatalyst (non-phthalate) in combination with conventional alkoxysilane external donors and non-silane aliphatic diester external donors (1-gallon reactor, 75 °C, ratio of donor / Ti compound = 10).

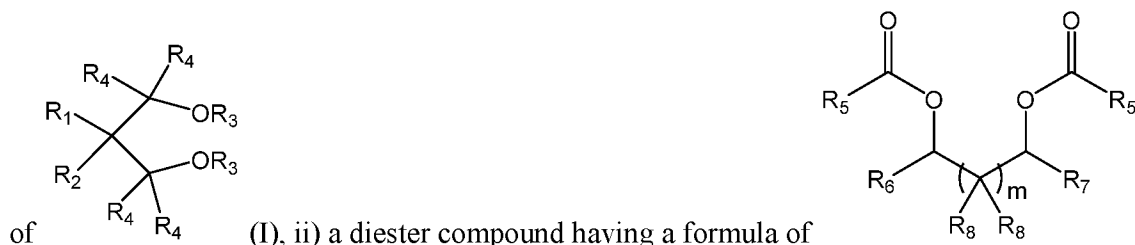
DETAILED DESCRIPTION OF THE INVENTION

[0018] This invention relates to a non-phthalate catalyst system capable to produce polyolefins with good catalyst activity, high isotacticity, and increased hydrogen response. Previously, non-phthalate catalyst systems have typically focused on using conventional alkoxysilane external donors. However, the non-phthalate catalysts often respond poorly to the changes in the type of conventional alkoxysilane external donors used, and the conventional alkoxysilane external donors generally have little modifying effect on the performance of the non-phthalate catalysts and the resulting polymer properties. In this

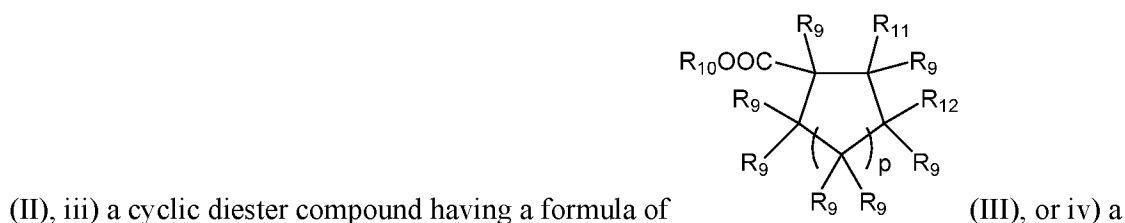
invention, the inventors have discovered a series of novel catalyst/ non-silane external donor systems that are chemically different from catalyst/alkoxysilane external donor systems. These non-silane external donors can modify the non-phthalate catalysts more significantly than the well-known alkoxysilane external donors and, thus, significantly improving the performance of the resulting polymer.

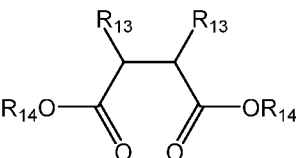
[0019] One aspect of the invention relates to a non-phthalate catalyst system for olefin polymerization. The non-phthalate catalyst system comprises (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, a Group 2 metal, and one or more halogens; and one or more internal electron donor compounds; and (b) one or more external electron donor compounds.

[0020] The internal electron donor compound is i) a diether compound having a formula



(I), ii) a diester compound having a formula of

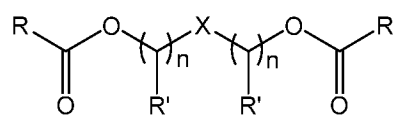
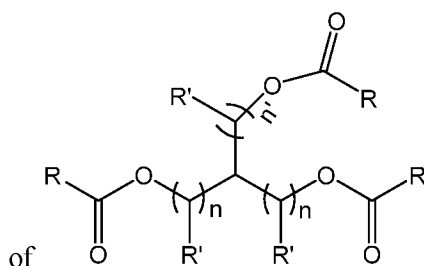


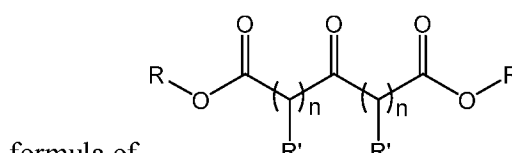
succinate compound having a formula of  (IV). In these formulas,

each of R₁ and R₂ is independently H or an alkyl, cycloalkyl, aryl, or aralkyl group, each having from 1 to 18 carbon atoms; or, R₁ and R₂ together form one or more saturated or unsaturated mono- or poly- cyclic structures. Each R₃ is independently an alkyl, aryl, or aralkyl group having from 1 to 18 carbon atoms. Each R₄ is H or R₃. Each R₅ is independently a C₁ to C₁₈ hydrocarbyl group which can optionally form one or more saturated or unsaturated mono- or poly- cyclic structures. Each of R₆ and R₇ is independently H or a C₁ to C₁₈ hydrocarbyl group; or, R₆ and R₇ together form one or more saturated or unsaturated mono- or poly- cyclic structures. Each R₈ is independently absent, H, or a C₁ to

C₁₈ hydrocarbyl group. Each R₉ is independently H, halogen, or a C₁ to C₁₈ hydrocarbyl group. Each R₁₀ is independently a C₁ to C₂₀ hydrocarbyl group. Each of R₁₁ and R₁₂ is independently R₉ or –COOR₁₀, provided that at least one of R₁₁ and R₁₂ is –COOR₁₀. Each of R₁₃ and R₁₄ is independently a C₁ to C₁₈ hydrocarbyl group. The integer m is 0 or 1. The integer p ranges from 1 to 6. Each of R₁, R₂, R₃, R₄, R₅, R₆, R₇, R₈, R₉, R₁₃, and R₁₄ can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group.

[0021] The external electron donor compound is i) a triester compound having a formula



formula of  (VII). In these formulas, X is CH₂ or O. Each R is independently a C₁-C₁₀ hydrocarbyl group. Each R' is independently H or R. Each n is independently an integer from 1 to 4. The integer n' ranges from 0 to 4.

Solid Ziegler-Natta catalyst composition

[0022] Catalyst systems for the stereospecific polymerization of olefins are well known in the art. The most common type of catalyst system is the Ziegler-Natta family, which comprises a solid catalyst composition containing a Ziegler-Natta procatalyst composition, an internal electron donor, and an external electron donor.

[0023] Any Ziegler-Natta procatalyst known in the art may be used in the non-phthalate catalyst system. For instance, the Ziegler-Natta procatalyst composition typically contains a transition metal compound and a Group 2 metal compound. The transition metal compound may be a solid complex derived from a transition metal compound, for example, titanium-,

zirconium-, chromium- or vanadium-hydrocarbyloxides, hydrocarbyls, halides, or mixtures thereof. In a typical Ziegler-Natta procatalyst composition, the transition metal is titanium, the Group 2 metal is magnesium, and the halogen is chloride.

[0024] The transition metal compound may have the general formulas of TrX_x or $\text{Tr(OQ)}_g\text{X}_{4-g}$. Tr is the transition metal, for instance, Tr may be a Group 4, 5, or 6 metal. In one embodiment, Tr is a Group 4 metal, such as titanium. In another embodiment, Tr is Group 5 metal, such as vanadium. Each Q independently represents a hydrocarbon group, such as a C_1 - C_{10} alkyl group. X represents a halogen atom, such as chloride, bromide, or iodide; x is an integer from 3 to 4; and g is an integer from 0 to 4. Exemplary transition metal compounds include titanium trihalides such as TiCl_3 , TiBr_3 , and TiI_3 ; titanium tetrahalides such as TiCl_4 , TiBr_4 , and TiI_4 ; alkoxytitanium trihalides such as $\text{Ti(OCH}_3\text{)Cl}_3$, $\text{Ti(OC}_2\text{H}_5\text{)Cl}_3$, $\text{Ti(OC}_4\text{H}_9\text{)Cl}_3$, $\text{Ti(OC}_2\text{H}_5\text{)Br}_3$, and $\text{Ti(OC}_4\text{H}_9\text{)Br}_3$; dialkoxytitanium dihalides such as $\text{Ti(OCH}_3\text{)}_2\text{Cl}_2$, $\text{Ti(OC}_2\text{H}_5\text{)}_2\text{Cl}_2$, $\text{Ti(OC}_4\text{H}_9\text{)}_2\text{Cl}_2$ and $\text{Ti(OC}_2\text{H}_5\text{)}_2\text{Br}_2$; trialkoxytitanium monohalides such as $\text{Ti(OCH}_3\text{)}_3\text{Cl}$, $\text{Ti(OC}_2\text{H}_5\text{)}_3\text{Cl}$, $\text{Ti(OC}_4\text{H}_9\text{)}_3\text{Cl}$, and $\text{Ti(OC}_2\text{H}_5\text{)}_3\text{Br}$; and tetraalkoxytitaniums such as $\text{Ti(OCH}_3\text{)}_4$, $\text{Ti(OC}_2\text{H}_5\text{)}_4$ and $\text{Ti(OC}_4\text{H}_9\text{)}_4$. Mixtures of two or more such transition metal compounds may be used as well. The transition metal compound may be used individually or in solutions of hydrocarbon compounds or halogenated hydrocarbons.

[0025] Suitable Group 2 metal compounds include magnesium halides, such as magnesium chloride and magnesium bromide; alkoxy magnesiums, such as ethoxymagnesium, isopropoxymagnesium, butoxymagnesium, and 2-ethylhexoxymagnesium; dialkoxy magnesiums, such as diethoxymagnesium; alkoxy magnesium halides, such as methoxymagnesium chloride, ethoxymagnesium chloride, isopropoxy magnesium chloride, butoxy magnesium chloride, and octoxy magnesium chloride; magnesium oxyhalides; dialkylmagnesiums; aryloxymagnesiums, such as phenoxymagnesium and methylphenoxy magnesium chloride; and carboxylates of magnesium, such as magnesium laurate and magnesium stearate. These magnesium compounds may be in the liquid or solid state. Typically, the Group 2 metal compound is magnesium dichloride.

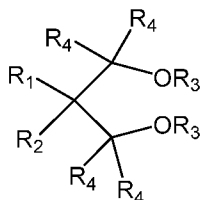
Internal donor

[0026] The Ziegler-Natta procatalyst composition includes an internal electron donor. The internal electron donor provides tacticity control and catalyst crystallite sizing. Suitable internal electron donors include diethers, diesters, cyclic diesters, and succinates, and combinations thereof.

[0027] As used herein, a “hydrocarbyl” is a linear or branched aliphatic radical, such as alkyl, alkenyl, and alkynyl; alicyclic radical, such as cycloalkyl, cycloalkenyl; aromatic radical, such as monocyclic or polycyclic aromatic radical; as well as combinations thereof, such as alkaryl and aralkyl.

i) Diether Compound

[0028] The internal electron donor can be a diether compound, such as a 1,3-diether

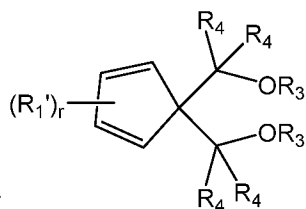


having a formula of (I). Each of R_1 and R_2 is independently H or an alkyl, cycloalkyl, aryl, or aralkyl group, each having from 1 to 18 carbon atoms; or, R_1 and R_2 together form one or more saturated or unsaturated mono- or poly- cyclic structures. Each R_3 is independently an alkyl, aryl, or aralkyl group having from 1 to 18 carbon atoms. Each R_4 is H or R_3 . The alkyl, cycloalkyl, and aryl for each R group can be further substituted with one or more of alkyl, cycloalkyl, aryl, or halogen groups. Each of R_1 , R_2 , R_3 , and R_4 can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group. Typically, R_1 and R_2 are each independently H, C_1 - C_6 alkyl, C_2 - C_{10} mono- or di- cycloalkyl, phenyl, benzyl, or naphthyl; R_3 is a C_1 - C_6 alkyl such as methyl; and R_4 is hydrogen.

[0029] In some embodiments, when one of R_1 and R_2 is hydrogen, the other can be ethyl, butyl, 2-ethylhexyl, cyclohexylethyl, diphenylmethyl, p-chlorophenyl, 1-naphthyl, or 1-decahydronaphthyl. In some embodiments, when one of R_1 and R_2 is methyl, ethyl, or propyl; the other can be ethyl, propyl, butyl, pentyl, 2-ethylhexyl, cyclopentyl, cyclohexyl, methylcyclohexyl, phenyl, or benzyl. In some embodiments, both R_1 and R_2 can be ethyl, propyl, isopropyl, butyl, pentyl, phenyl, benzyl, cyclohexyl, or cyclopentyl. Exemplary

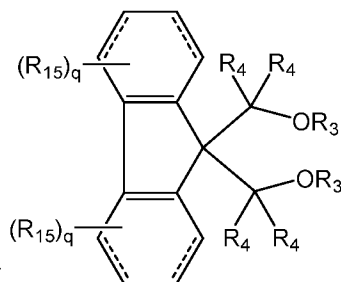
diether compounds include, but are not limited to, 2-(2-ethylhexyl)-1,3-dimethoxypropane, 2-isopropyl-1,3-dimethoxypropane, 2-butyl-1,3-dimethoxypropane, 2-sec-butyl-1,3-dimethoxypropane, 2-cyclohexyl-1,3-dimethoxypropane, 2-phenyl-1,3-dimethoxypropane, 2-tert-butyl-1,3-dimethoxypropane, 2-cumyl-1,3-dimethoxypropane, 2-(2-phenylethyl)-1,3-dimethoxypropane, 2-(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-(p-chlorophenyl)-1,3-dimethoxypropane, 2-(diphenylmethyl)-1,3-dimethoxypropane, 2-(1-naphthyl)-1,3-dimethoxypropane, 2-(p-fluorophenyl)-1,3-dimethoxypropane, 2-(1-decahydronaphthyl)-1,3-dimethoxypropane, 2-(p-tert-butylphenyl)-1,3-dimethoxypropane, 2,2-dicyclohexyl-1,3-dimethoxypropane, 2,2-diethyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-dimethoxypropane, 2,2-dibutyl-1,3-dimethoxypropane, 2,2-diethyl-1,3-diethoxypropane, 2,2-dicyclopentyl-1,3-dimethoxypropane, 2,2-dipropyl-1,3-diethoxypropane, 2,2-dibutyl-1,3-diethoxypropane, 2-methyl-2-ethyl-1,3-dimethoxypropane, 2-methyl-2-propyl-1,3-dimethoxypropane, 2-methyl-2-benzyl-1,3-dimethoxypropane, 2-methyl-2-phenyl-1,3-dimethoxypropane, 2-methyl-2-cyclohexyl-1,3-dimethoxypropane, 2-methyl-2-methylcyclohexyl-1,3-dimethoxypropane, 2,2-bis(p-chlorophenyl)-1,3-dimethoxypropane, 2,2-bis(2-phenylethyl)-1,3-dimethoxypropane, 2,2-bis(2-cyclohexylethyl)-1,3-dimethoxypropane, 2-methyl-2-isobutyl-1,3-dimethoxypropane, 2-methyl-2-(2-ethylhexyl)-1,3-dimethoxypropane, 2,2-bis(2-ethylhexyl)-1,3-dimethoxypropane, 2,2-bis(p-methylphenyl)-1,3-dimethoxypropane, 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2,2-diphenyl-1,3-dimethoxypropane, 2,2-dibenzyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2,2-bis(cyclohexylmethyl)-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-diethoxypropane, 2,2-diisobutyl-1,3-dibutoxypropane, 2-isobutyl-2-isopropyl-1,3-dimethoxypropane, 2,2-di-sec-butyl-1,3-dimethoxypropane, 2,2-di-tert-butyl-1,3-dimethoxypropane, 2,2-dineopentyl-1,3-dimethoxypropane, 2-iso-propyl-2-isopentyl-1,3-dimethoxypropane, 2-phenyl-2-benzyl-1,3-dimethoxypropane, 2-cyclohexyl-2-cyclohexylmethyl-1,3-dimethoxypropane. Mixtures of two or more such diether compounds may be used as well.

[0030] In some embodiments, R_1 and R_2 together form one or more unsaturated mono- or poly- cyclic structures, such as cyclopentadiene. The resulting diether compound has a



formula of (Ia). R_3 and R_4 are defined as above. Each R_1' is independently H, halogen, or an alkyl, cycloalkyl, aryl, or aralkyl group, each having from 1 to 18 carbon atoms; or, two or more of R_1' , together with the pentadiene ring, form fused di- or tri- cyclic structures. The alkyl, cycloalkyl, and aryl for each R_1' group can be further substituted with one or more of alkyl, cycloalkyl, aryl, or halogen groups. Each R_1' and its substituent group can optionally contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms. The integer r ranges from 0 to 4. Typically, R_3 is a C_1 - C_6 alkyl such as methyl; and R_4 is hydrogen. Typically, each R_1' is H, halogen such as fluoro or chloro; C_1 - C_6 alkyl; C_2 - C_6 cycloalkyl; phenyl; or two of the R_1' groups form an indene with the pentadiene ring. Exemplary pentadiene- or indiene- containing compounds are 1,1-bis(methoxymethyl)-cyclopentadiene; 1,1-bis(methoxymethyl)-2,3,4,5-tetramethylcyclopentadiene; 1, 1-bis(methoxymethyl)-2,3,4,5-tetraphenylcyclopentadiene; 1,1-bis(methoxymethyl)-2,3,4,5-tetrafluorocyclopentadiene; 1,1-bis(methoxymethyl)-3,4-dicyclopentylcyclopentadiene; 1,1-bis(methoxymethyl)indene; 1,1-bis(methoxymethyl)-2,3-dimethylindene; 1,1-bis(methoxymethyl)-4,5,6,7-tetrahydroindene; 1,1-bis(methoxymethyl)-2,3,6,7-tetrafluoroindene; 1,1-bis(methoxymethyl)-4,7-dimethylindene; 1,1-bis(methoxymethyl)-3,6-dimethylindene; 1,1-bis(methoxymethyl)-4-phenylindene; 1,1-bis(methoxymethyl)-4-phenyl-2-methylindene; 1,1-bis(methoxymethyl)-4-cyclohexylindene; 1,1-bis(methoxymethyl)-7-(3,3,3-trifluoropropyl)indene; 1,1-bis(methoxymethyl)-7-trimethylsilylindene; 1,1-bis(methoxymethyl)-7-trifluoromethylindene; 1,1-bis(methoxymethyl)-4,7-dimethyl-4,5,6,7-tetrahydroindene; 1,1-bis(methoxymethyl)-7-methylindene; 1,1-bis(methoxymethyl)-7-cyclopentylindene; 1,1-bis(methoxymethyl)-7-isopropylindene; 1,1-bis(methoxymethyl)-7-cyclohexylindene; 1,1-bis(methoxymethyl)-7-tert-butylindene; 1,1-bis(methoxymethyl)-7-tert-butyl-2-methylindene; 1,1-bis(methoxymethyl)-7-phenylindene; 1,1-bis(methoxymethyl)-2-phenylindene; 1,1-bis(methoxymethyl)-1H-benz[e]indene; and 1,1-bis(methoxymethyl)-1H-2-methylbenz[e]indene. Mixtures of two or more such diether compounds may be used as well.

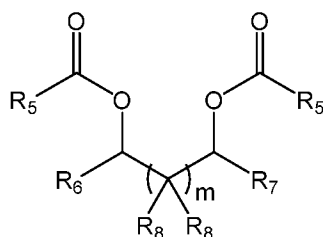
[0031] Alternatively, two or more of R_1' groups, together with the pentadiene ring, form fused di- or tri- cyclic structures, such as fluorene. The resulting diether compound has a



formula of (Ib). R_3 and R_4 are defined as above. Each R_{15} is independently H, halogen, or an alkyl, cycloalkyl, aryl, alkylaryl, or aralkyl group, each having from 1 to 18 carbon atoms; or one or more R_{15} groups, together with the benzene ring, form fused rings. The integer q ranges from 0 to 4. The symbol “====” in the formula refers to a saturated bond or unsaturated bond. Typically, R_{15} is H; halogen such as fluoro or chloro; C_1 - C_6 alkyl; C_2 - C_6 cycloalkyl; or two or more R_{15} form benzofluorene with the benzene ring(s). Exemplary fluorene-containing diether compounds are 9,9-bis(methoxymethyl)fluorene; 9,9-bis(methoxymethyl)-2,3,6,7-tetramethylfluorene; 9,9-bis(methoxymethyl)-2,3,4,5,6,7-hexafluorofluorene; 9,9-bis(methoxymethyl)-2,3-benzofluorene; 9,9-bis(methoxymethyl)-2,3,6,7-dibenzofluorene; 9,9-bis(methoxymethyl)-2,7-diisopropylfluorene; 9,9-bis(methoxymethyl)-1,8-dichlorofluorene; 9,9-bis(methoxymethyl)-2,7-dicyclopentylfluorene; 9,9-bis(methoxymethyl)-1,8-difluorofluorene; 9,9-bis(methoxymethyl)-1,2,3,4-tetrahydrofluorene; 9,9-bis(methoxymethyl)-1,2,3,4,5,6,7,8-octahydrofluorene; and 9,9-bis(methoxymethyl)-4-tert-butylfluorene. A typical fluorene-containing diether compound is 9,9-bis(methoxymethyl)fluorene. Mixtures of two or more such diether compounds may be used as well.

ii) Diester Compound

[0032] The internal electron donor can be a diester compound having a formula of

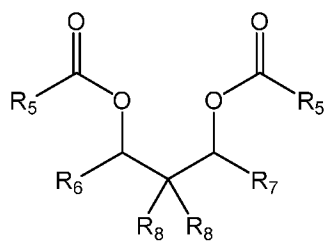


(II). Each R_5 is independently a C_1 to C_{18} hydrocarbyl group

which can optionally form one or more saturated or unsaturated mono- or poly- cyclic structures. Each of R_6 and R_7 is independently H or a C_1 to C_{18} hydrocarbyl group; or, R_6 and R_7 together form one or more saturated or unsaturated mono- or poly- cyclic structures. Each R_8 is independently absent, H, or a C_1 to C_{18} hydrocarbyl group. The integer m is 0 or 1. Each of R_5 , R_6 , R_7 , and R_8 can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group.

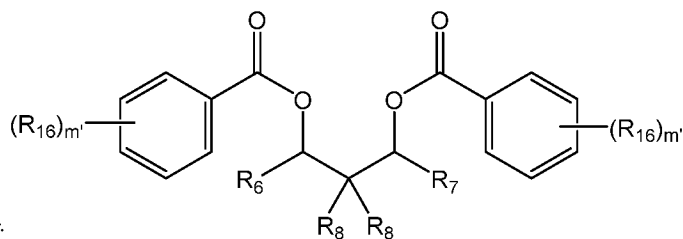
[0033] R_5 can be a C_1 to C_{18} alkyl such as C_1 to C_{10} alkyl; C_2 to C_{18} alkenyl such as C_2 to C_8 alkenyl; C_3 to C_{18} cycloalkyl such as C_5 to C_6 cycloalkyl; C_3 to C_{18} cycloalkenyl such as C_5 to C_6 cycloalkenyl; aryl such as phenyl; heteroaryl, e.g., 5- or 6- membered ring heteroaryl, containing one or more heteroatoms N, O, or S, such as furanyl; each of these groups can be further substituted by one or more halogen atoms such as chloro or fluoro, C_1 - C_{10} alkyl, or C_1 - C_{10} alkoxy. Each of R_6 and R_7 can be independently C_1 - C_{15} alkyl (e.g., C_1 - C_{10} alkyl or C_1 - C_6 alkyl), C_6 - C_{14} aryl (e.g., phenyl), C_3 - C_{15} cycloalkyl (e.g., C_5 - C_6 cycloalkyl), C_7 - C_{15} arylalkyl (e.g., C_7 - C_{12} aralkyl), or C_7 - C_{15} alkylaryl (e.g., C_7 - C_{12} alkylaryl). Each R_8 can be independently absent, hydrogen, C_1 - C_{15} alkyl (e.g., C_1 - C_{10} alkyl or C_1 - C_6 alkyl), C_2 to C_{18} alkenyl (e.g., C_2 to C_8 alkenyl), C_6 - C_{14} aryl (e.g., phenyl, naphthyl, or halophenyl), C_3 - C_{15} cycloalkyl (e.g., C_5 - C_6 cycloalkyl), C_7 - C_{15} arylalkyl (e.g., C_7 - C_{12} aralkyl), or C_7 - C_{15} alkylaryl (e.g., C_7 - C_{12} alkylaryl).

[0034] In some embodiments, m is 1. The diester compound has a formula of:



(IIa). R_5 , R_6 , R_7 , and R_8 are defined as above. In certain

embodiments, each R_5 is independently an aryl. For instance, the diester compound can have



a formula of:

(IIb). Each R_{16} is

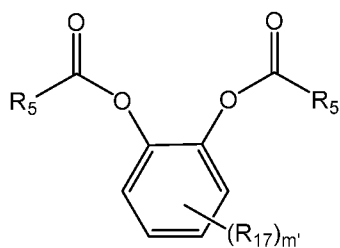
independently H, halogen, or a C_1 to C_{18} hydrocarbyl group which can optionally form one or

more saturated or unsaturated cyclic structures with the phenyl group it attaches to. Each R_{16} can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group. For instance, each R_{16} can be independently H, halogen, a C_1 - C_{15} alkyl (e.g., C_1 - C_{10} alkyl or C_1 - C_6 alkyl), C_1 - C_{15} alkoxy (e.g., C_1 - C_{10} alkoxy or C_1 - C_6 alkoxy), C_6 - C_{14} aryl (e.g., phenyl), C_3 - C_{15} cycloalkyl, C_7 - C_{15} arylalkyl (e.g., C_7 - C_{12} aralkyl), or C_7 - C_{15} alkylaryl (e.g., C_7 - C_{12} alkylaryl). Exemplary R_{16} groups are H, halogen such as chloro or fluoro, a C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, C_7 - C_{12} aralkyl, or C_7 - C_{12} alkylaryl. Each m' is independently an integer from 0 to 5, for instance, from 0 to 3. Exemplary R_6 and R_7 groups are C_1 - C_6 alkyl, phenyl, C_5 - C_6 cycloalkyl, C_7 - C_{12} arylalkyl, or C_7 - C_{12} alkylaryl. Exemplary R_8 groups are hydrogen; C_1 - C_6 alkyl; C_2 to C_8 alkenyl; phenyl, naphthyl, or halophenyl; C_5 - C_6 cycloalkyl; C_7 - C_{12} arylalkyl; or C_7 - C_{12} alkylaryl.

[0035] Exemplary diester compounds for formula IIb are 2,4-pentanediol dibenzoate, 3-methyl-2,4-pentanediol dibenzoate, 3-ethyl-2,4-pentanediol dibenzoate, 3-n-propyl-2,4-pentanediol dibenzoate, 3-i-propyl-2,4-pentanediol dibenzoate, 3-n-butyl-2,4-pentanediol dibenzoate, 3-i-butyl-2,4-pentanediol dibenzoate, 3-t-butyl-2,4-pentanediol dibenzoate, 3-n-pentyl-2,4-pentanediol dibenzoate, 3-i-pentyl-2,4-pentanediol dibenzoate, 3-cyclopentyl-2,4-pentanediol dibenzoate, 3-cyclohexyl-2,4-pentanediol dibenzoate, 3-phenyl-2,4-pentanediol dibenzoate, 3-(2-naphthyl)-2,4-pentanediol dibenzoate, 3-allyl-2,4-pentanediol dibenzoate, 3,3-dimethyl-2,4-pentanediol dibenzoate, 3-ethyl-3-methyl-2,4-pentanediol dibenzoate, 3-methyl-3-i-propyl-2,4-pentanediol dibenzoate, 3,3-diisopropyl-2,4-pentanediol dibenzoate, 3-i-pentyl-2-i-propyl-2,4-pentanediol dibenzoate, 3,5-heptanediol dibenzoate, 4,6-nonanediol dibenzoate, 2,6-dimethyl-3,5-heptanediol dibenzoate, 5,7-undecanediol dibenzoate, 2,8-dimethyl-4,6-nonanediol dibenzoate, 2,2,6,6-tetramethyl-3,5-heptanediol dibenzoate, 6,8-tridecanediol dibenzoate, 2,10-dimethyl-5,7-undecanediol dibenzoate, 1,3-dicyclopentyl-1,3-propanediol dibenzoate, 1,3-dicyclohexyl-1,3-propanediol dibenzoate, 1,3-diphenyl-1,3-propanediol dibenzoate, 1,3-bis(2-naphthyl)-1,3-propanediol dibenzoate, 2,4-hexanediol dibenzoate, 2,4-heptanediol dibenzoate, 2-methyl-3,5-hexanediol dibenzoate, 2,4-octanediol dibenzoate, 2-methyl-4,6-heptanediol dibenzoate, 2,2-dimethyl-3,5-hexanediol dibenzoate, 2-methyl-5,7-octanediol dibenzoate, 2,4-nonanediol dibenzoate, 1-cyclopentyl-1,3-butanediol dibenzoate, 1-cyclohexyl-1,3-butanediol dibenzoate, 1-phenyl-1,3-butanediol dibenzoate, 1-(2-naphthyl)-1,3-butanediol dibenzoate, 2,4-pentanediol-bis(4-methylbenzoate), 2,4-

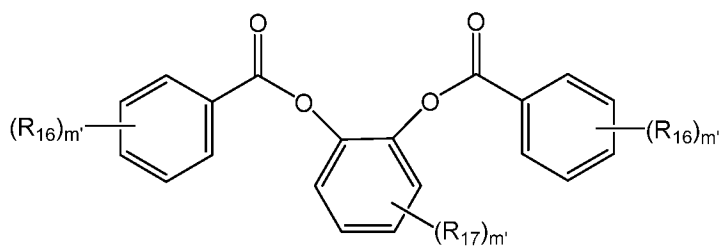
pentanediol-bis(3-methylbenzoate), 2,4-pentanediol-bis(4-ethylbenzoate), 2,4-pentanediol-bis(4-n-propylbenzoate), 2,4-pentanediol-bis(4-n-butylbenzoate), 2,4-pentanediol-bis(4-i-propylbenzoate), 2,4-pentanediol-bis(4-i-butylbenzoate), 2,4-pentanediol-bis(4-t-butylbenzoate), 2,4-pentanediol-bis(4-phenylbenzoate), 2,4-pentanediol-bis(3,4-dimethylbenzoate), 2,4-pentanediol-bis(2,4,6-trimethylbenzoate), 2,4-pentanediol-bis(2,6-dimethylbenzoate), 2,4-pentanediol-di-(2-naphthoate), 3-methyl-2,4-pentanediol-bis(4-n-propylbenzoate), 3-i-pentyl-2,4-pentanediol-bis(4-n-propylbenzoate), 1,1,1,5,5,5-hexafluoro-2,4-pentanediol-bis(4-ethylbenzoate), 1,1,1-trifluoro-2,4-pentanediol-bis(4-ethylbenzoate), 1,3-bis(4-chlorophenyl)-1,3-propanediol-bis(4-ethylbenzoate), 1-(2,3,4,5,6-pentafluorophenyl)-1,3-butanediol-bis(4-ethylbenzoate), 1,1-difluoro-4-phenyl-2,4-butanediol-bis(4-n-propylbenzoate), 1,1,1-trifluoro-5,5-dimethyl-2,4-hexandiol-bis(4-n-propylbenzoate), 1,1,1-trifluoro-4-(2-furyl)-2,4-butanediol-bis(4-n-propylbenzoate), 1,1,1-trifluoro-4-phenyl-2,4-butanediol-bis(4-n-propylbenzoate), 1,1,1-trifluoro-4-(2-thienyl)-2,4-butanediol-bis(4-n-propylbenzoate), 1,1,1-trifluoro-4-(4-chloro-phenyl)-2,4-butanediol-bis(4-n-propylbenzoate), 1,1,1-trifluoro-4-(2-naphthyl)-2,4-butanediol-bis(4-n-propylbenzoate), and 3-chloro-2,4-pentanediol-bis(4-n-propylbenzoate).

[0036] In some embodiments, m is 0, and R_6 and R_7 can form one or more saturated or unsaturated mono- or poly- cyclic structures. For instance, R_6 and R_7 can form an aryl group having the formula of:



(IIc). R_5 is defined as above. In certain embodiments, both R_5

groups are an aryl. For instance, the diester compound can have a formula of:



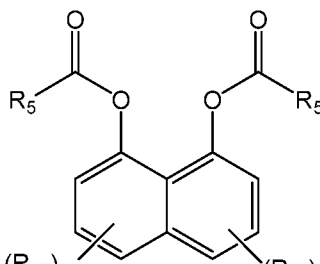
(IId). Each of R_{16} and R_{17} is

independently H, halogen, or a C_1 to C_{18} hydrocarbyl group which can optionally form one or

more saturated or unsaturated cyclic structures with the phenyl group it attaches to. Each of R_{16} and R_{17} can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group. For instance, each of R_{16} and R_{17} can be independently H, halogen (e.g., chloro or fluoro), or a C_1 - C_{15} alkyl (e.g., C_1 - C_{10} alkyl or C_1 - C_6 alkyl), C_1 - C_{15} alkoxy (e.g., C_1 - C_{10} alkoxy or C_1 - C_6 alkoxy), C_6 - C_{14} aryl (e.g., phenyl), C_3 - C_{15} cycloalkyl, C_7 - C_{15} arylalkyl (e.g., C_7 - C_{12} aralkyl), or C_7 - C_{15} alkylaryl (e.g., C_7 - C_{12} alkylaryl). Exemplary R_{16} and R_{17} groups are H, halogen such as chloro or fluoro, a C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, C_7 - C_{12} aralkyl, or C_7 - C_{12} alkylaryl. Each m' is independently an integer from 0 to 5, for instance, from 0 to 3.

Exemplary compounds for formula IIc include those containing one or two R_{17} groups and one R_{16} on each benzoate moiety. For instance, exemplary compounds for formula IIc can contain two R_{17} groups, one at para- position and one at ortho- position to the $-O-C(O)-$ group; and can contain one R_{16} on each benzoate moiety, each at para- position to the $-C(O)-O-$ group. A typical compound for formula IIc is 5-(tert-butyl)-3-methyl-1,2-phenylene dibenzoate.

[0037] In some embodiments, m is 1, R_8 is absent, and R_6 and R_7 can form a fused ring structure. For instance, R_6 and R_7 can form a naphthalene group, forming a 1,8-naphthalene

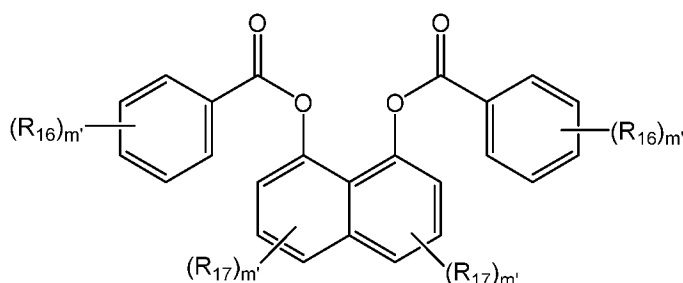


diester compound having the formula of: $(R_{17})_{m'}$ (IIe). R_5 is defined as above. Each R_{17} is independently H, halogen, or a C_1 to C_{18} hydrocarbyl group which can optionally form one or more saturated or unsaturated cyclic structures with the phenyl group it attaches to. Each R_{17} can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group. For instance, each R_{17} can be independently H, halogen (e.g., chloro or fluoro), or a C_1 - C_{15} alkyl (e.g., C_1 - C_{10} alkyl or C_1 - C_6 alkyl), C_1 - C_{15} alkoxy (e.g., C_1 - C_{10} alkoxy or C_1 - C_6 alkoxy), C_6 - C_{14} aryl (e.g., phenyl), C_3 - C_{15} cycloalkyl, C_7 - C_{15} arylalkyl (e.g., C_7 - C_{12} aralkyl), or C_7 - C_{15} alkylaryl (e.g., C_7 - C_{12} alkylaryl). Exemplary R_{17} groups are H, halogen

such as chloro or fluoro, a C₁-C₆ alkyl, C₁-C₆ alkoxy, phenyl, C₇-C₁₂ aralkyl, or C₇-C₁₂ alkylaryl. Each m' is independently an integer from 0 to 5, for instance, from 0 to 3.

[0038] In formula IIe, exemplary R₅ groups are C₁-C₁₀ alkyl; C₂-C₁₀ alkenyl; C₅-C₆ cycloalkyl; C₅-C₆ cycloalkenyl; aryl such as phenyl; or heteroaryl, e.g., 5- or 6- membered ring heteroaryl, containing one or more heteroatoms N, O, or S, such as furanyl; each of these groups can be further substituted by one or more halogen atoms such as chloro or fluoro, C₁-C₁₀ alkyl, or C₁-C₁₀ alkoxy. R₅ may be the same or different.

[0039] In certain embodiments, both R₅ groups are an aryl. For instance, the 1,8-naphthalene diester compound can have a formula of:

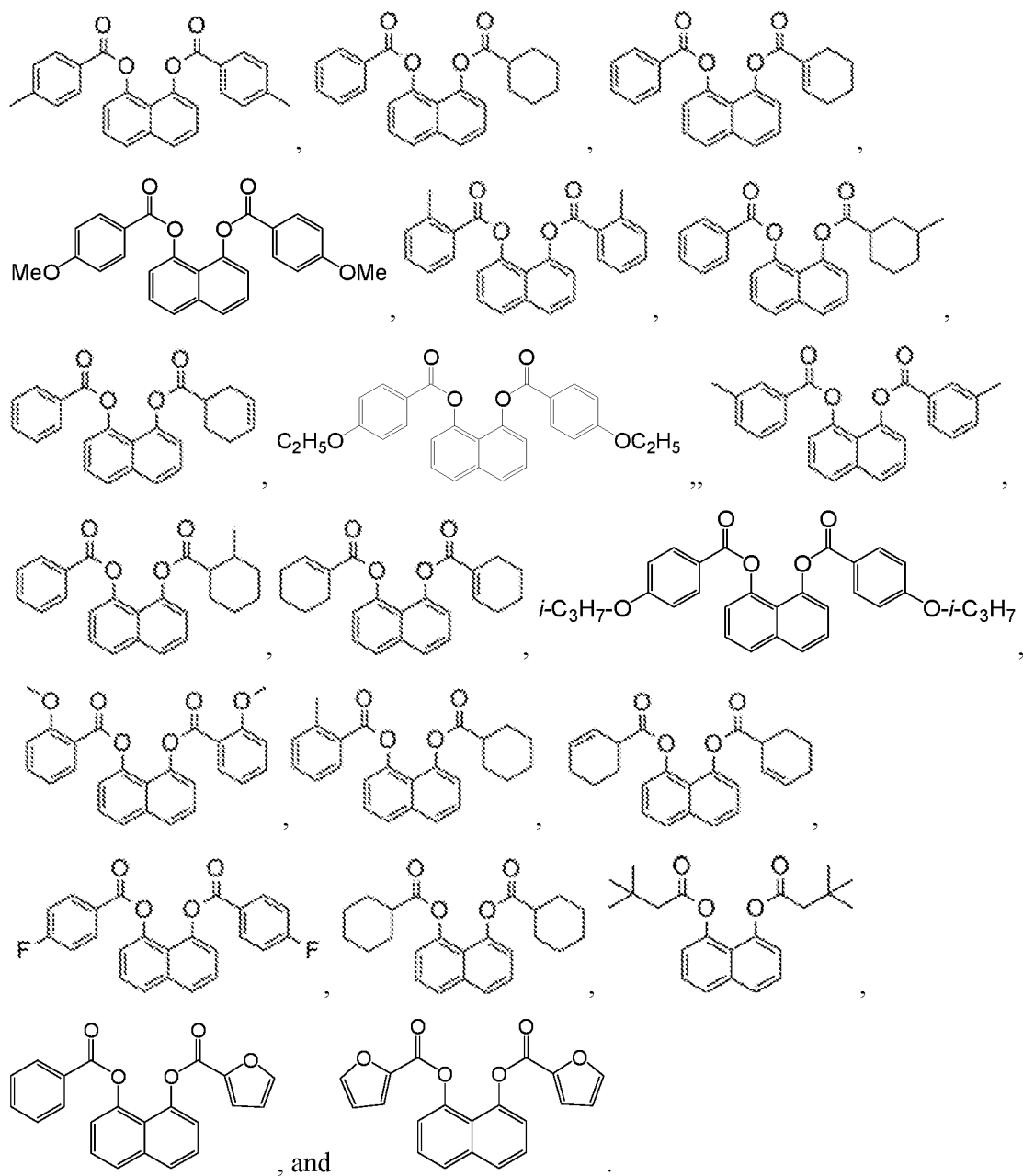


(IIf). The definition of R₁₆ is the

same as the definition of R₁₇, which is defined above. The integer m' is defined as above.

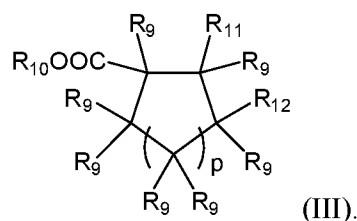
Exemplary 1,8-naphthalene diester compounds for formula IIf are 1,8-naphthyl dibenzoate; 1,8-naphthyl di-4-methylbenzoate; 1,8-naphthyl di-3-methylbenzoate; 1,8-naphthyl di-2-methylbenzoate; 1,8-naphthyl di-4-ethylbenzoate; 1,8-naphthyl di-4-n-propylbenzoate; 1,8-naphthyl di-4-isopropylbenzoate; 1,8-naphthyl di-4-n-butylbenzoate; 1,8-naphthyl di-4-isobutylbenzoate; 1,8-naphthyl di-4-t-butylbenzoate; 1,8-naphthyl di-4-phenylbenzoate; 1,8-naphthyl di-4-fluorobenzoate; 1,8-naphthyl di-3-fluorobenzoate; 1,8-naphthyl di-2-fluorobenzoate; 1,8-naphthyl di-4-chlorobenzoate; 1,8-naphthyl di-3-chlorobenzoate; 1,8-naphthyl di-2-chlorobenzoate; 1,8-naphthyl di-4-bromobenzoate; 1,8-naphthyl di-3-bromobenzoate; 1,8-naphthyl di-2-bromobenzoate; 1,8-naphthyl di-4-cyclohexylbenzoate; 1,8-naphthyl di-2,3-dimethylbenzoate; 1,8-naphthyl di-2,4-dimethylbenzoate; 1,8-naphthyl di-2,5-dimethylbenzoate; 1,8-naphthyl di-2,6-dimethylbenzoate; 1,8-naphthyl di-3,4-dimethylbenzoate; 1,8-naphthyl di-3,5-dimethylbenzoate; 1,8-naphthyl di-2,3-dichlorobenzoate; 1,8-naphthyl di-2,4-dichlorobenzoate; 1,8-naphthyl di-2,5-dichlorobenzoate; 1,8-naphthyl di-2,6-dichlorobenzoate; 1,8-naphthyl di-3,4-dichlorobenzoate; 1,8-naphthyl di-3,5-dichlorobenzoate; and 1,8-naphthyl di-3,5-di-t-butylbenzoate. A typical diester compound for formula IIf is 1,8-naphthyl dibenzoate.

[0040] Additional exemplary 1,8-naphthalene diester compounds for formula IIe are

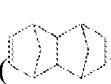


iii) Cyclic Diester Compound

[0041] The internal electron donor can be a cyclic diester compound having a formula of



[0042] Each R_9 is independently H, halogen, or a C_1 to C_{18} hydrocarbyl group. R_9 can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group. For instance, R_9 can be C_1 to C_{18} alkyl such as C_1 to C_8 alkyl; C_2 to C_{18} alkenyl such as C_2 to C_8 alkenyl; C_3 to C_{18} cycloalkyl such as C_5 to C_6 cycloalkyl; aryl such as phenyl; C_1 to C_{18} alkoxy such as C_1 to C_8 alkoxy; siloxy; aldehyde; or acetyl. Exemplary R_9 groups are methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, n-pentyl, cyclopentyl, n-hexyl, cyclohexyl, octyl, vinyl, or phenyl. Typically, R_9 is methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, or sec-butyl. Two or more R_9 groups may also be bonded to each other to form a saturated or unsaturated mono- or poly- cyclic structure backbone, e.g., a fused ring and/or bridged polycyclic backbone. Exemplary fused ring and/or bridged polycyclic backbone are

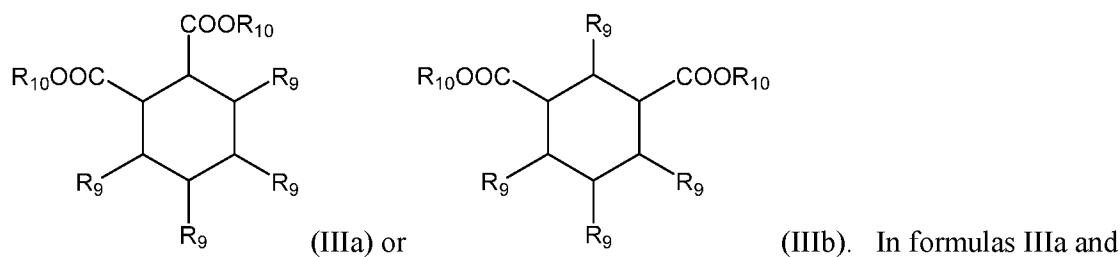
norbornane () and tetracyclododecene (.

[0043] Each R_{10} is independently a C_1 to C_{20} hydrocarbyl group. For example, R_{10} can be a C_1 to C_{20} alkyl, C_1 to C_{10} alkyl, C_2 to C_8 alkyl, or C_4 to C_8 alkyl. Exemplary R_{10} groups are ethyl, n-propyl, isopropyl, n-butyl, isobutyl, hexyl, heptyl, octyl, 2-ethylhexyl, decyl, dodecyl, tetradecyl, hexadecyl, octadecyl, or eicosyl. Typically, R_{10} is n-butyl or isobutyl.

[0044] Each R_{11} and R_{12} is independently R_9 or $-\text{COOR}_{10}$, provided that at least one of R_{11} and R_{12} is $-\text{COOR}_{10}$.

[0045] The integer p ranges from 1 to 6. For instance p can be 1, 2, 3. Typically, p is 2.

[0046] In some embodiments, the cyclic diester compound has a formula of



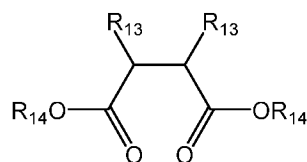
In formulas IIIa and IIIb, each R_{10} is independently a C_1 to C_{10} alkyl, and each R_9 is independently H or a C_1 to C_8 alkyl, C_3 to C_6 cycloalkyl, C_2 to C_6 alkenyl, or phenyl. Exemplary cyclic diester compounds for formulas IIIa and IIIb are diisobutyl cyclohexane-1,2-dicarboxylate, diethyl 3-methylcyclohexane-1,2-dicarboxylate, di-n-propyl 3-methylcyclohexane-1,2-dicarboxylate, diisopropyl 3-methylcyclohexane-1,2-dicarboxylate, di-n-butyl 3-methylcyclohexane-1,2-dicarboxylate, diisobutyl 3-methylcyclohexane-1,2-dicarboxylate, dihexyl 3-methylcyclohexane-1,2-dicarboxylate, diheptyl 3-methylcyclohexane-1,2-dicarboxylate, dioctyl 3-methylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3-methylcyclohexane-1,2-dicarboxylate, didecyl 3-methylcyclohexane-1,2-dicarboxylate, diethyl 4-methylcyclohexane-1,3-dicarboxylate, diisobutyl 4-methylcyclohexane-1,3-dicarboxylate, diethyl 4-methylcyclohexane-1,2-dicarboxylate, di-n-propyl 4-methylcyclohexane-1,2-dicarboxylate, diisopropyl 4-methylcyclohexane-1,2-dicarboxylate, di-n-butyl 4-methylcyclohexane-1,2-dicarboxylate, diisobutyl 4-methylcyclohexane-1,2-dicarboxylate, dihexyl 4-methylcyclohexane-1,2-dicarboxylate, diheptyl 4-methylcyclohexane-1,2-dicarboxylate, dioctyl 4-methylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 4-methylcyclohexane-1,2-dicarboxylate, didecyl 4-methylcyclohexane-1,2-dicarboxylate, diethyl 5-methylcyclohexane-1,3-dicarboxylate, diisobutyl 5-methylcyclohexane-1,3-dicarboxylate, diethyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, di-n-propyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, diisopropyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, di-n-butyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, diisobutyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, dihexyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, diheptyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, dioctyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, didecyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, diethyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, di-n-propyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, diisopropyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, di-n-butyl 3,6-dimethylcyclohexane-1,2-

dicarboxylate, diisobutyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, dihexyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, diheptyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, dioctyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, didecyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, diethyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, di-n-propyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, diisopropyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, di-n-butyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, diisobutyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, dihexyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, dioctyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, didecyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, diethyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-n-propyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diisopropyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-n-butyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diisobutyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, dihexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diheptyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, dioctyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, didecyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diethyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-n-propyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diisopropyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-n-butyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diisobutyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, dihexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diheptyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, dioctyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, didecyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diethyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, di-n-propyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, diisopropyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, di-n-butyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, diisobutyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, dihexyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, diheptyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, dioctyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, dodecyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, diethyl 3-hexylcyclohexane-1,2-dicarboxylate, diisobutyl 3-hexylcyclohexane-1,2-dicarboxylate, diethyl 3,6-dihexylcyclohexane-1,2-dicarboxylate, and diisobutyl 3-hexyl-6-pentylcyclohexane-1,2-

dicarboxylate. Typically, the cyclic diester compound is diisobutyl cyclohexane-1,2-dicarboxylate or diisobutyl 3,6-dimethylcyclohexane-1,2-dicarboxylate. Mixtures of two or more such cyclic diester compounds may be used as well.

iv) Succinate Compound

[0047] The internal electron donor can be a succinate compound having a formula of



(IV). Each of R_{13} and R_{14} is independently a C_1 to C_{18} hydrocarbyl

group. For instance, each of R_{13} and R_{14} can be C_1 to C_{18} alkyl, C_2 to C_{18} alkenyl, C_3 to C_{18} cycloalkyl, or aryl. The alkyl, alkenyl, cycloalkyl, and aryl for each R group can be further substituted with one or more of alkyl, cycloalkyl, aryl, or halogen groups. Each of R_{13} and R_{14} can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group. Typically, R_{13} is C_1 to C_6 alkyl, C_5 - C_6 cycloalkyl, phenyl, fluorenyl; each of these groups can be optionally substituted with one or more of C_1 to C_6 alkyl, C_5 - C_6 cycloalkyl, phenyl, or halogen atoms such as fluoro or chloro. Typically, R_{14} is C_1 to C_6 alkyl.

[0048] Exemplary succinate compounds are diethyl 2-sec-butyl-3-methylsuccinate, diethyl 2-(3,3,3-trifluoropropyl)-3-methylsuccinate, diethyl 2,3-bis(2-ethylbutyl) succinate, diethyl 2,3-diethyl-2-isopropylsuccinate, diethyl 2,3-diisopropyl-2-methylsuccinate, diethyl 2,3-dicyclohexyl-2-methylsuccinate, diethyl 2,3-dibenzylsuccinate, diethyl 2,3-diisopropylsuccinate, diethyl 2,3-bis (cyclohexylmethyl)succinate, diethyl 2,3-di-t-butylsuccinate, diethyl 2,3-diisobutylsuccinate, diethyl 2,3-dineopentylsuccinate, diethyl 2,3-diisopentylsuccinate, diethyl 2,3-(1-trifluoromethyl-ethyl)succinate, diethyl 2-(9-fluorenyl)succinate, diethyl 2-isopropyl-3-isobutylsuccinate, diethyl 2-t-butyl-3-isopropylsuccinate, diethyl 2-isopropyl-1,3-cyclohexylsuccinates diethyl 2-isopentyl-3-cyclohexylsuccinate, diethyl 2-cyclohexyl-3-cyclopentylsuccinate, diethyl 2,2,3,3-tetramethylsuccinate, diethyl 2,2,3,3-tetraethylsuccinate, diethyl 2,2,3,3-tetra-n-propylsuccinate, diethyl 2,3-diethyl-2,3-diisopropylsuccinate, diisobutyl 2,3-bis(trimethylsilyl)succinate, diisobutyl 2-sec-butyl-3-methylsuccinate, diisobutyl 2-(3,3,3-trifluoropropyl)-3-methylsuccinate, diisobutyl 2,3-bis(2-ethylbutyl)succinate, diisobutyl 2,3-

diethyl-2-isopropylsuccinate, diisobutyl 2,3-diisopropyl-2-methylsuccinate, diisobutyl 2,3-dicyclohexyl-2-methylsuccinate, diisobutyl 2,3-dibenzylsuccinate, diisobutyl 2,3-diisopropylsuccinate, diisobutyl 2,3-bis(cyclohexylmethyl)succinate, diisobutyl 2,3-di-t-butylsuccinate, diisobutyl 2,3-diisobutylsuccinate, diisobutyl 2,3-dineopentylsuccinate, diisobutyl 2,3-diisopentylsuccinate, diisobutyl 2,3-bis(3,3,3-trifluoropropyl)succinate, diisobutyl 2,3-di-n-propylsuccinate, diisobutyl 2-(9-fluorenyl)succinate, diisobutyl 2-isopropyl-3-isobutylsuccinate, diisobutyl 2-t-butyl-3-isopropylsuccinate, diisobutyl 2-isopropyl-3-cyclohexylsuccinate, diisobutyl 2-isopentyl-3-cyclohexylsuccinate, diisobutyl 2-n-propyl-3-(cyclohexylmethyl)succinate, diisobutyl 2-cyclohexyl-3-cyclopentylsuccinate, diisobutyl 2,2,3,3-tetramethylsuccinate, diisobutyl 2,2,3,3-tetraethylsuccinate, diisobutyl 2,2,3,3-tetra-n-propylsuccinate, diisobutyl 2,3-diethyl-2,3-diisopropylsuccinate, dineopentyl 2,3-bis(trimethylsilyl)succinate, dineopentyl 2,2-di-sec-butyl-3-methylsuccinate, dineopentyl 2-(3,3,3-trifluoropropyl)-3-methylsuccinate, dineopentyl 2,3 bis-(2-ethylbutyl)succinate, dineopentyl 2,3-diethyl-2-isopropylsuccinate, dineopentyl 2,3-diisopropyl-2-methylsuccinate, dineopentyl 2,3-dicyclohexyl-2-methylsuccinate, dineopentyl 2,3-dibenzylsuccinate, dineopentyl 2,3-diisopropylsuccinate, dineopentyl 2,3-bis-(cyclohexylmethyl)succinate, dineopentyl 2,3-di-t-butylsuccinate, dineopentyl 2,3-diisobutylsuccinate, dineopentyl 2,3-dineopentylsuccinate, dineopentyl 2,3-diisopentylsuccinate, dineopentyl 2,3-bis(3,3,3-trifluoropropyl)succinate, dineopentyl 2,3-n-propylsuccinate, dineopentyl 2-(9-fluorenyl)succinate, dineopentyl 2-isopropyl-3-isobutylsuccinate, dineopentyl 2-t-butyl-3-isopropylsuccinate, dineopentyl 2-isopropyl-3-cyclohexylsuccinate, dineopentyl 2-isopentyl-3-cyclohexylsuccinate, dineopentyl 2-n-propyl-3-(cyclohexylmethyl)succinate, dineopentyl 2-cyclohexyl-3-cyclopentylsuccinate, dineopentyl 2,2,3,3-tetramethylsuccinate, dineopentyl 2,2,3,3-tetra-ethylsuccinate, dineopentyl 2,2,3,3-tetra-n-propylsuccinate, dineopentyl 2,3-diethyl-2,3-diisopropylsuccinate, diethyl 1,2-cyclohexanedicarboxylate, and diethyl norbornene-2,3-dicarboxylate. Typically, the succinate compound is diethyl 2,3-diisopropylsuccinate. Mixtures of two or more such succinate compounds may be used as well.

Preparation of Solid Ziegler-Nata Catalyst Composition

[0049] The solid Ziegler-Nata procatalyst composition can be carried out by various methods known to one skilled in the art. For instance, the titanium compound, the

magnesium dichloride in an anhydrous state, and the electron donor compounds can be milled together under conditions in which activation of the magnesium dichloride occurs. The product can be treated one or more times with an excess of TiCl_4 at a temperature about 80 to 135 °C, followed by washings with hydrocarbon solvents until chloride ions disappear. Alternatively, magnesium dichloride is preactivated by methods known to one skilled in the art, and then treated with an excess of TiCl_4 at a temperature of about 80 to 135 °C in the presence of the electron donor compounds. The treatment with TiCl_4 can be repeated and the solid can be washed with a hydrocarbon solvent such as hexane to eliminate any non-reacted TiCl_4 .

[0050] In another example, the titanium compound, the magnesium chloride in an anhydrous state, the electron donor compounds can be milled together under conditions in which activation of the magnesium chloride occurs. The product can be treated with halogenated hydrocarbons such as 1,2-dichloroethane, chlorobenzene, dichloromethane, etc., for about 1 and 4 hours and at temperature of from 40 °C to the boiling point of the halogenated hydrocarbon. The product is then washed with inert hydrocarbon solvents such as hexane.

[0051] In another example, the solid catalyst component can be prepared by reacting a titanium compound of formula TiX_x or $\text{Ti}(\text{OQ})_g\text{X}_{4-g}$ with a magnesium chloride deriving from an adduct of formula $(\text{MgCl}_2)_p\text{ROH}$, in which p is a number between 0.1 and 6, for instance, between 2 to 3.5; and R is a $\text{C}_1\text{-C}_{18}$ hydrocarbyl. The adduct can be suitably prepared in spherical form by mixing alcohol and magnesium chloride in the presence of an inert hydrocarbon immiscible with the adduct, operating under stirring conditions at the melting temperature of the adduct (100-130 °C). The emulsion can then be quenched, causing the solidification of the adduct in form of spherical particles. Examples of spherical adducts prepared according to this procedure are described in U.S. Patent Nos. 4,399,054 and 4,469,648, which are incorporated herein by reference in their entirety. The obtained adduct can be directly reacted with the titanium compound. Alternatively, the obtained adduct can be first subjected to thermally controlled dealcoholation (at 80-130 °C) to obtain an adduct in which the number of moles of alcohol is generally lower than 3, for instance, between 0.1 and 2.5. The reaction of the adduct with the titanium compound can be carried out by suspending the adduct (dealcoholated or not) in cold TiCl_4 (generally at 0 °C), and heating the mixture to about 80-130 °C (the temperature can be kept at this range for about 0.5-2 hours). The

treatment with TiCl_4 can be carried out one or more times. The electron donor compounds can be added during the treatment with TiCl_4 , and can be added together in the same treatment with TiCl_4 or separately in two or more treatments.

[0052] The preparations of the solid catalyst components in spherical forms are described, for example, in WO98/44001 and U.S. Patent Application Publication No. 2013/0197173, which are incorporated herein by reference in their entirety.

[0053] The solid Ziegler-Natta procatalyst composition can contain from about 0.5 to about 6.0 wt% titanium; from about 10 to about 25 wt% magnesium; from about 40 to about 70 wt% halogen; from about 1 to about 50 wt% internal electron donor compound; and optionally inert diluent from about 0 to about 15 wt%. For instance, the Ziegler-Natta procatalyst composition contains from about 2 to about 20 wt% of one or more of the internal electron donor compounds, or from about 5 to about 15wt % of one or more of the internal electron donor compounds.

[0054] The amounts of the components used in preparing the solid Ziegler-Natta procatalyst composition may vary depending upon the method of preparation. For instance, from about 0.01 to about 5 moles of the total internal electron donor compounds and from about 0.01 to about 500 moles of the titanium compound are used per mole of the magnesium compound used to make the solid procatalyst composition. Typically, from about 0.05 to about 2 moles of the total internal electron donor compounds and from about 0.05 to about 300 moles of the titanium compound are used per mole of the magnesium compound used to make the solid procatalyst composition.

[0055] The Ziegler-Natta procatalyst composition may also include an inert support material. The support material may be an inert solid which does not adversely alter the catalytic performance of the transition metal compound. Exemplary inert support materials include metal oxides, such as alumina, and metalloid oxides, such as silica.

Cocatalyst

[0056] The non-phthalate catalyst system may further comprise an organometallic cocatalyst. The metal element in the organometallic cocatalyst is a Group 13 metal, for instance, aluminum. Suitable organoaluminum compounds include those having at least one aluminum-carbon bond in the molecule, such as alkylaluminum, alkylaluminum hydride, alkylaluminum halide, and alkylaluminum alkoxide containing from 1-10 or 1-6 carbon

atoms in each alkyl or alkoxide group. Exemplary organoaluminum compounds are trialkyl aluminums, such as triethyl aluminum and tributyl aluminum; trialkenyl aluminums such as triisoprenyl aluminum; dialkyl aluminum alkoxides such as diethyl aluminum ethoxide and dibutyl aluminum butoxide; alkyl aluminum sesquialkoxides such as ethyl aluminum sesquiethoxide and butyl aluminum sesquibutoxide; dialkyl aluminum halides such as diethyl aluminum chloride, dibutyl aluminum chloride and diethyl aluminum bromide; alkyl aluminum sesquihalides such as ethyl aluminum sesquichloride, butyl aluminum sesquichloride, and ethyl aluminum sesquibromide; partially halogenated alkyl aluminums, e.g., alkyl aluminum dihalides such as ethyl aluminum dichloride, propyl aluminum dichloride, and butyl aluminum dibromide; dialkyl aluminum hydrides such as diethyl aluminum hydride and dibutyl aluminum hydride; other partially hydrogenated alkyl aluminum, e.g., alkyl aluminum dihydrides such as ethyl aluminum dihydride and propyl aluminum dihydride; and partially alkoxyated and halogenated alkyl aluminums, such as ethyl aluminum ethoxychloride, butyl aluminum butoxychloride, and ethyl aluminum ethoxybromide.

[0057] The organometallic cocatalyst used in the non-phthalate catalyst system is in an amount that the molar ratio of the metal in the organometallic cocatalyst to transition metal in the Ziegler-Natta procatalyst composition is from about 5 to about 1000, for instance, from about 10 to about 700, from about 25 to about 400, or from about 100 to about 300.

External donor

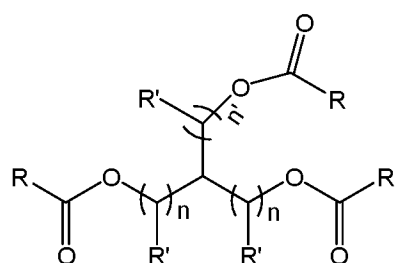
[0058] The non-phthalate catalyst system also includes one or more non-silane external electron donor compounds. The external electron donor is a compound added independent of the Ziegler-Natta procatalyst formation, and contains at least one functional group that is capable of donating a pair of electrons to a metal atom. The external electron donor compound serves as one component of the non-phthalate Ziegler-Natta catalyst system for olefin polymerization, often contributing to the ability to obtain a polymer having a controllable molecular weight distribution and controllable crystallinity. In fact, when an external donor compound is absent, the isotactic index of the resulting polymer is not sufficiently high even if the internal donor is used. Also, for the non-phthalate catalyst system, the conventional alkoxysilane external donors often times do not have significant modifying effect on the performance of the non-phthalate catalyst system. The non-silane

external donors below are chemically different from alkoxy silanes and provide improvements in the performance of the non-phthalate catalyst system.

[0059] The external donor compound is used in the non-phthalate catalyst system in an amount that the molar ratio of the total external donor compounds to the transition metal in the Ziegler-Natta procatalyst composition (e.g., titanium compound) ranges from about 0.5 to about 90, for instance, from about 1 to about 70, or from about 1 to about 30.

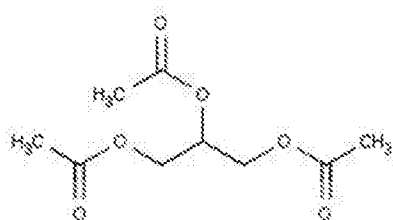
i) Triester Compound

[0060] The external electron donor can be a triester compound having a formula of



(V). Each R is independently a C₁-C₁₀ hydrocarbonyl group.

For instance, each R is a C₁ to C₁₀ alkyl, such as methyl, ethyl, or isobutyl; optionally substituted with methyl, isobutyl, or 2-ethylhexyl. Each R' is independently H or R. Each n is independently an integer from 1 to 4, for instance, from 1 to 2, or 1. The integer n' ranges from 0 to 4, for instance, from 0 to 2 or 0. A typical triester compound is glyceryl triacetate (

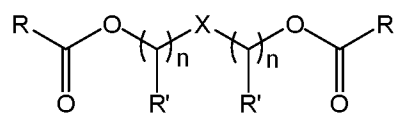


, also referred to as triacetin), in which R is methyl, R' is H,

n is 1, and n' is 0.

ii) Diester Compound

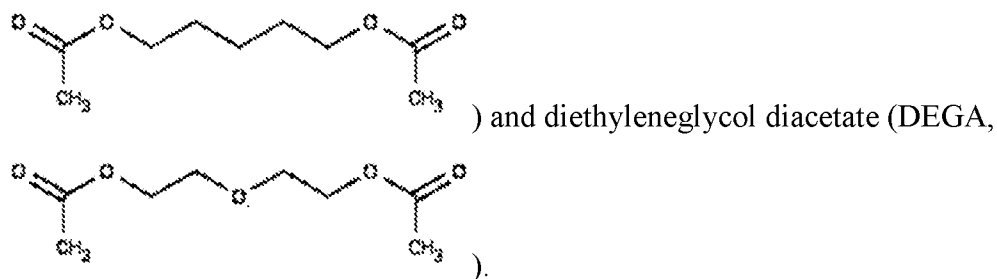
[0061] The external electron donor can be a diester compound having a formula of



(VI). X is CH₂ or O. Each R is independently a C₁-C₁₀

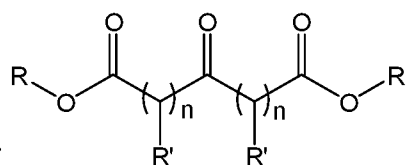
hydrocarbonyl group. For instance, each R is a C₁ to C₁₀ alkyl, such as methyl, ethyl, or isobutyl; optionally substituted with methyl, isobutyl, or 2-ethylhexyl. Each R' is

independently H or R. Each n is independently an integer from 1 to 4, for instance, from 1 to 2. Typical diester compounds include those having R as methyl, R' as H, and n as 2. For instance, two typical diester compounds are 1,5-pentanediol diacetate (PDOA,

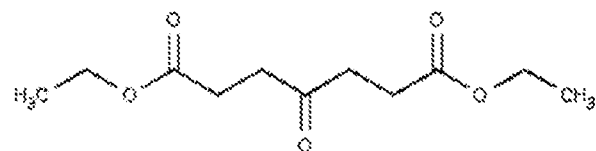


iii) *Oxo-substituted Diester Compound*

[0062] The external electron donor can be an oxo-substituted triester compound having a



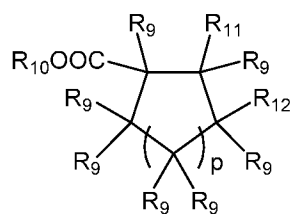
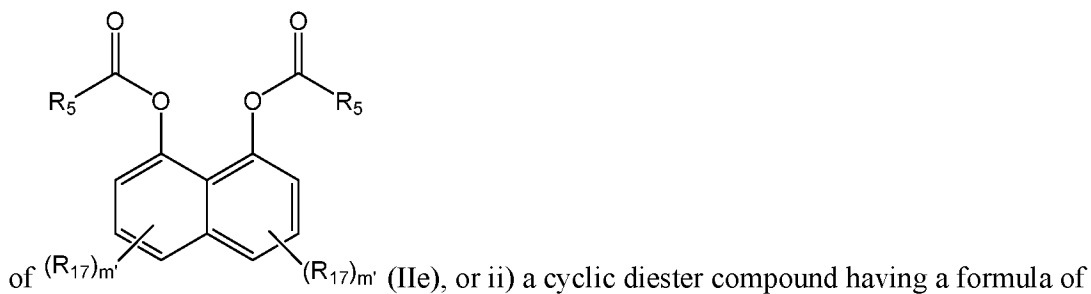
formula of (VII). Each R is independently a C_1 - C_{10} hydrocarbyl group. For instance, each R is a C_1 to C_{10} alkyl, such as methyl, ethyl, or isobutyl; optionally substituted with methyl, isobutyl, or 2-ethylhexyl. Each R' is independently H or R. Each n is independently an integer from 1 to 4, for instance, from 1 to 2. A typical oxo-substituted triester compound is diethyl-4-oxopimelate (DEOP,



), in which each R is methyl, each R' is H, and each n is 2.

[0063] A second aspect of the invention relates to a non-phthalate catalyst system for olefin polymerization. The non-phthalate catalyst system comprises (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, a Group 2 metal, and one or more halogens; and one or more internal electron donor compounds; and (b) one or more external electron donor compounds.

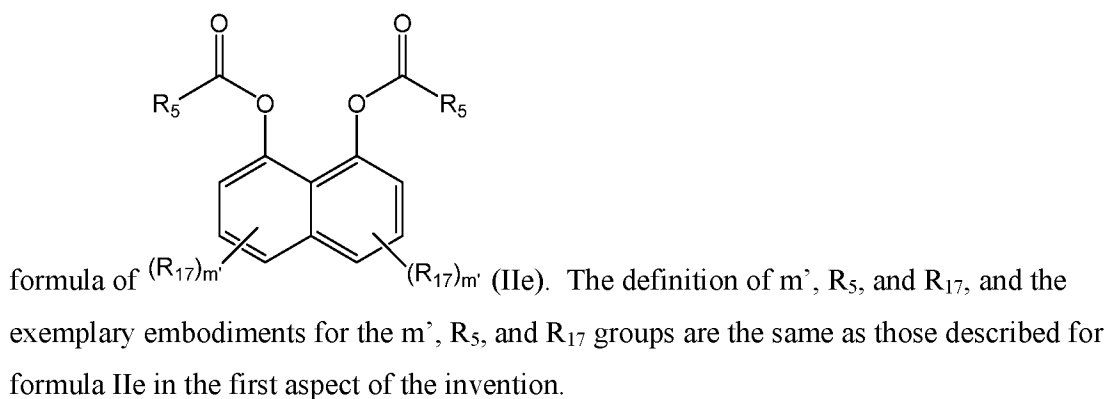
[0064] The internal electron donor compound is i) a diester compound having a formula



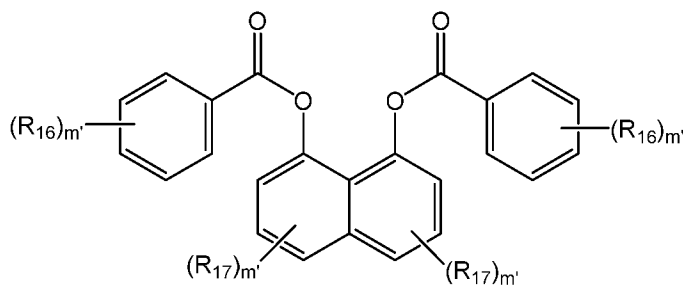
(III). In these formulas, each R_5 is independently a C_1 to C_{18}

hydrocarbyl group which can optionally form one or more saturated or unsaturated mono- or poly- cyclic structures. Each R_{17} is independently H, halogen, or C_1 to C_{18} hydrocarbyl group which can optionally form one or more saturated or unsaturated cyclic structures with the phenyl group it is attached to. Each R_9 is independently H, halogen, or C_1 to C_{18} hydrocarbyl group. Each R_{10} is independently C_1 to C_{20} hydrocarbyl group. Each of R_{11} and R_{12} is independently R_9 or $-\text{COOR}_{10}$, provided that at least one of R_{11} and R_{12} is $-\text{COOR}_{10}$. Each m' is independently an integer from 0 to 5. The integer p ranges from 1 to 6. Each of R_5 , R_9 , and R_{17} can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group.

[0065] In certain embodiments, the internal donor is a diester compound having a



[0066] A typical diester compound has a formula of:

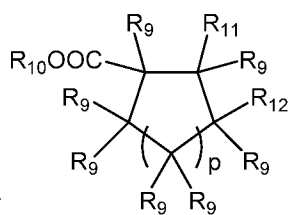


(IIf). The definition of m' , R_{16} , and

R_{17} and the exemplary embodiments for the m' , R_{16} , and R_{17} groups are the same as those described for formula IIf in the first aspect of the invention. The exemplary 1,8-naphthalene diester compounds are the same as those exemplary 1,8-naphthalene diester compounds described for formula IIf in the first aspect of the invention.

[0067] Additional exemplary 1,8-naphthalene diester compounds described for formula IIf in the first aspect of the invention also can be used in this aspect of the invention as the internal electron donor.

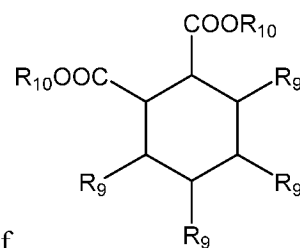
[0068] In certain embodiments, the internal donor is a cyclic diester compound having a



formula of

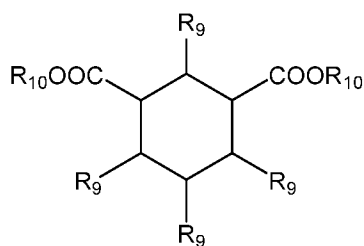
(III). The definitions of p , R_9 , R_{10} , R_{11} , and R_{12} and the

exemplary embodiments for the p , R_9 , R_{10} , R_{11} , and R_{12} groups are the same as those described for formula III in the first aspect of the invention.



(IIIa)

[0069] A typical cyclic diester compound has a formula of

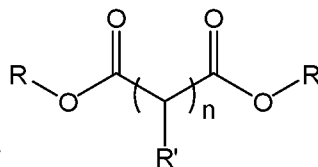


or

(IIIb). The definitions of R_9 and R_{10} , and the exemplary

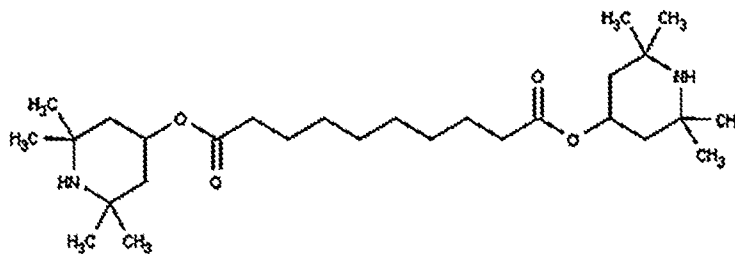
embodiments for the R₉ and R₁₀ groups are the same as those described for formula IIIa and IIIb in the first aspect of the invention. The exemplary cyclic diester compounds are the same as those exemplary cyclic diester compounds described for formulas IIIa and IIIb in the first aspect of the invention.

[0070] The non-phthalate catalyst system also includes one or more external electron



donor compounds having a formula of (VIII). The external electron donor compound does not contain an alkoxysilane compound. In formula VIII, each R is independently a C₁ to C₁₀ hydrocarbyl group, and can contain one or more heteroatoms, selected from the group consisting of halogens, P, N, O, S, and Si, that replace one or more carbon atoms in the hydrocarbyl group. R' is H or R. For instance, each R is a C₁ to C₁₀ alkyl, such as methyl, ethyl, propyl, butyl, or hexyl; C₃-C₈ cycloalkyl, such as C₅-C₆ cycloalkyl; or C₃-C₈ heterocycloalkyl, such as C₅-C₆ heterocycloalkyl containing one or more heteroatoms N, O, or S (e.g., piperidinyl); each of these groups can be optionally substituted with one or more C₁ to C₁₀ alkyl, such as methyl, ethyl, isobutyl, or 2-ethylhexyl. The integer n ranges from 1 to 10, for instance, from 1 to 8.

[0071] Exemplary external electron donor compounds for formula VIII include those containing R as methyl, ethyl, propyl, butyl, hexyl, or piperidinyl; optionally substituted with one or more C₁-C₆ alkyl; R' as H; and n as 1 to 8. Typical external electron donor compounds for formula VIII are diethyl malonate, diethyl succinate, diethyl glutarate, diethyl adipate, diisopropyl adipate, dibutyl adipate, diisobutyl adipate, bis (2-ethylhexyl) adipate, diethyl pimelate, diethyl azelate, diethyl sebacate, and bis(2,2,6,6-tetramethyl-4-piperidyl)



sebacate (e.g., Tinuvin[®] 770,).

[0072] In this aspect of the invention, the transition metal compound and Group 2 metal compounds in the Ziegler-Natta procatalyst, and the preparation of solid Ziegler-Natta procatalyst composition are the same as those described in the first aspect of the invention.

The organometallic cocatalyst in the non-phthalate catalyst system is the same as those described in the first aspect of the invention.

Process of polymerization

[0073] Another aspect of the invention relates to a process for preparing a polyolefin. The process comprises polymerizing one or more olefins, in the presence of the non-phthalate catalyst system under reaction conditions known by one skilled in the art sufficient to form the polyolefin. The non-phthalate catalyst system may be any non-phthalate catalyst system described herein according to the embodiments in the first and second aspects of the invention.

[0074] The reaction conditions are temperature and pressure ranges within a polymerization reactor suitable for promoting polymerization and/or copolymerization between one or more olefins and the non-phthalate catalyst system to form the desired polymer. The polymerization process may be performed in any manner including gas phase, slurry, or a bulk polymerization process, with the polymerization occurring in one or more reactor(s).

[0075] The olefins may be linear or branched olefins having 2 to 20 carbon atoms, 2 to 16 carbon atoms, or 2 to 12 carbon atoms. Typically, the olefin used to prepare the polyolefin is an α -olefin. Exemplary linear or branched α -olefins includes, but are not limited to, ethylene, propylene, 1-butene, 2-butene, 1-pentene, 3-methyl-1-butene, 4-methyl-1-pentene, 3-methyl-1-pentene, 1-hexene, 3,5,5-trimethyl-1-hexene, 4,6-dimethyl-1-heptene, 1-octene, 1-decene, 1-undecene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicocene. For instance, the olefin used to prepare a polyolefin is propylene. These olefins may contain one or more heteroatoms such as an oxygen, nitrogen, or silicon. The olefin may be used individually or in mixture, either the gaseous state or the liquid state.

[0076] The polymerization process may include a pre-activation step. Pre-activation includes contacting the Ziegler-Natta procatalyst composition with the cocatalyst and the external electron donor compound. The resulting preactivated catalyst stream is subsequently introduced into the polymerization reaction zone and contacted with the olefin monomer to be polymerized. Optionally, one or more of the external electron donor components may be added at this time. Pre-activation results in the combination of the procatalyst composition with the cocatalyst and the external electron donor compounds.

[0077] Alternatively, the polymerization process may include a pre-polymerization step. Pre-polymerization includes contacting a small amount of the olefin with the Ziegler-Natta procatalyst composition after the procatalyst composition has been contacted with the cocatalyst and the external donor compound. Then, the resulting preactivated catalyst stream is introduced into the polymerization reaction zone and contacted with the remainder of the olefin monomer to be polymerized. Optionally, one or more of the external electron donor components may be added at this time. Pre-polymerization results in the procatalyst composition being combined with the cocatalyst and the external electron donor compounds, with the combination being dispersed in a matrix of the polymer during polymerization, to facilitate the polymerization.

[0078] Typically, a catalyst is considered to be pre-polymerized when the amount of the polymer produced is from about 0.1 to about 1000 gram per gram of the solid catalyst system. The pre-polymerization step can be carried out at temperatures from about 0 °C to about 80 °C, for instance, from 5 °C to 50 °C, in liquid or gas phase. The pre-polymerization step can be performed in-line as a part of a continuous polymerization process or separately in a batch process.

[0079] Any kind of polymerization process suitable for preparing a polyolefin can be used with the non-phthalate catalyst system. The polymerization can be carried out, for example, in bulk phase using a liquid monomer (e.g., propylene) as a reaction medium, in slurry using an inert liquid (e.g., hydrocarbon) as a diluent, in solution using either monomers or inert hydrocarbons as solvent for the nascent polymer, or in gas phase, operating in one or more fluidized or mechanically agitated bed reactors.

[0080] The polymerization process can be a gas phase polymerization process, operating in one or more reactors. A suitable gas phase polymerization process includes the use of condensing mode as well as super condensing mode wherein gaseous components (including addition of inert low boiling compounds) are injected into the reactor in liquid form. When multiple reactors are employed, it is desirable that they operate in series, e.g., the effluent from the first reactor is charged to the second reactor, with an additional monomer (for homopolymerization) or different monomer (for copolymerization) added to continue the polymerization. Additional amount of the same or different non-phthalate catalyst system or catalyst components (e.g., the procatalyst composition, cocatalyst, or external donor compound) may be added.

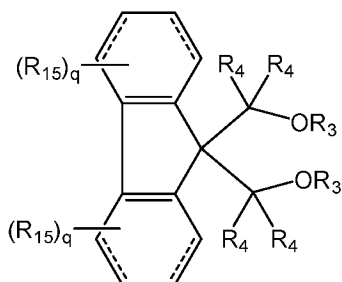
[0081] As an example, the polymerization process includes preparing an ethylene-propylene copolymer by contacting propylene and ethylene with the non-phthalate catalyst system. For instance, the polymerization process can be conducted in two reactors in which two olefins, such as propylene and ethylene, are contacted to prepare a copolymer. Polypropylene is prepared in the first reactor by a bulk phase (e.g., solution) homopolymerization, and a copolymer of ethylene and propylene is prepared in the second reactor in the presence of the polypropylene from the first reactor by a gas phase copolymerization. Alternatively, the polymerization process can be conducted in one reactors but in two sequential steps, with a bulk phase homopolymerization of polypropylene in the first step, and a gas phase copolymerization of ethylene and propylene in the presence of the polypropylene in the second step. This process is exemplified in Example 2. Regardless of the polymerization technique employed, it is understood that the procatalyst composition, the cocatalyst, and the external electron donor thereof may be contacted in the absence of other polymerization components, especially monomer, prior to addition to the reactor.

[0082] The temperature of the polymerization process can range from about 20 to about 130 °C, from about 60 to about 100 °C, or from about 70 °C to about 85 °C. For instance, when the polymerization is carried out in gas phase, the temperature of the polymerization process can range from about 75 to about 85 °C, for instance at about 80 °C; when the polymerization is carried out in bulk phase, the temperature of the polymerization process can range from about 70 to about 80 °C, for instance at about 75 °C. When the polymerization is carried out in gas phase, the operating pressure generally ranges from about 0.5 to about 10 MPa, from about 0.9 to about 5 MPa, or from about 4 to about 5 MPa. In the bulk polymerization, the operating pressure generally ranges from about 0.5 to about 6 MPa, from about 0.9 to about 4 MPa, or from about 3.5 to about 4 MPa.

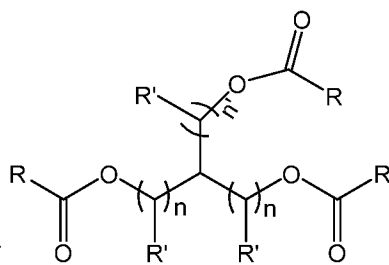
[0083] The resulting polymer prepared according to the above process, using the non-phthalate catalyst system described in this invention, has an improved isotacticity. Moreover, the resulting polymer prepared according to the process of the invention has an improved hydrogen response characterized by melt flow rate. Surprisingly, the polymer prepared by the non-phthalate catalyst system described in this invention, with the non-silane external donors, can have improved hydrogen response and isotacticity at the same time. This is surprising behavior because, in a typical Ziegler-Natta catalyst system, the external donors

that increase hydrogen response (i.e., characterized by MFR) typically decrease isotacticity (i.e., characterized by increased % XS).

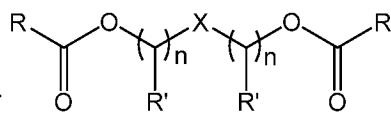
[0084] In some embodiments, the non-phthalate catalyst system used contains the internal electron donor compound that is a diether compound having a formula of



(Ib); and the external electron donor compound that is a triester



compound having a formula of (V) or a diester compound

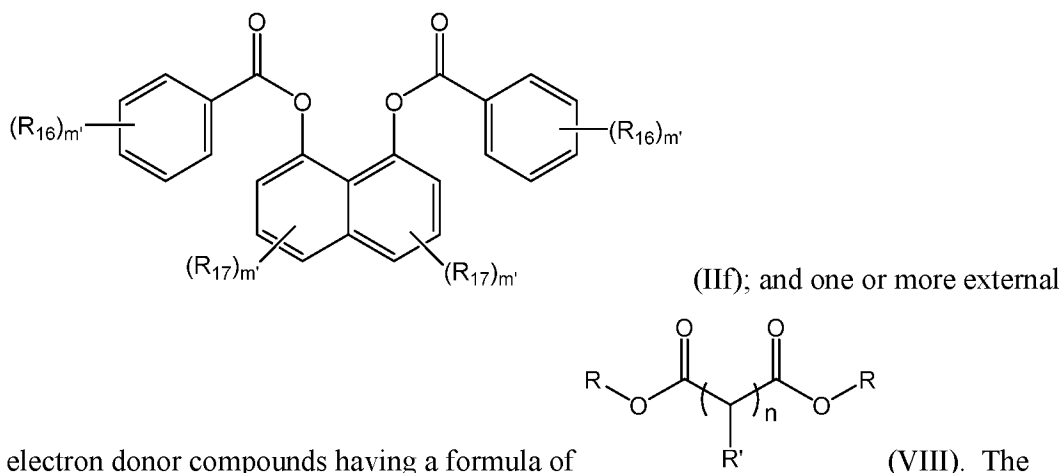


having a formula of (VI). The definitions of R_3 , R_4 , R_{15} , R , R' , q , and n are the same as those described for formula Ib, V, and VI in the first aspect of the invention. The exemplary internal donor compounds and external donor compounds are the same as those exemplary compounds described for formulas Ib, V, and VI in the first aspect of the invention.

[0085] For instance, in a typical non-phthalate catalyst system, the internal electron donor compound is 9,9-bis(methoxymethyl)fluorene, and the external electron donor compound is triacetin, 1,5-pentanediol diacetate, diethyl-4-oxopimelate, or diethyleneglycol diacetate. For instance, one non-phthalate catalyst system uses 9,9-bis(methoxymethyl)fluorene as the internal electron donor compound and triacetin as the external electron donor compound; another non-phthalate catalyst system uses 9,9-bis(methoxymethyl)fluorene as the internal electron donor compound and diethyl-4-oxopimelate as the external electron donor compound. In these embodiments, the polymer prepared according to the process of the invention has an improved isotacticity. Moreover, the resulting polymer prepared according to the process of the invention has an improved hydrogen response characterized by melt

flow rate. Surprisingly, the polymer prepared by the non-phthalate catalyst system described in this invention, with the non-silane external donors, can have improved hydrogen response and isotacticity at the same time. This is surprising behavior because, in a typical Ziegler-Natta catalyst system, the external donors that increase hydrogen response (i.e., characterized by MFR) mostly decrease isotacticity (i.e., characterized by increased % XS).

[0086] In some embodiments, the non-phthalate catalyst system used contains the internal electron donor compound that is a diester compound having a formula of



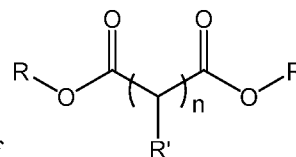
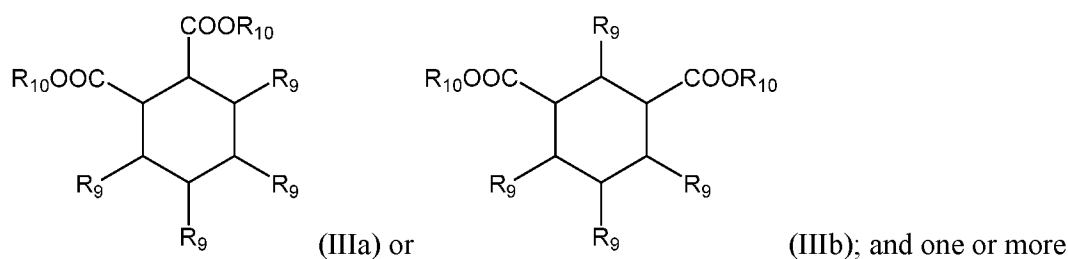
electron donor compounds having a formula of

definitions of R_{16} , R_{17} , R , R' , m' , and n are the same as those described for formula II and VIII in the first and second aspect of the invention. The exemplary internal donor compounds and external donor compounds are the same as those exemplary compounds described for formulas II and VIII in the first and second aspect of the invention.

[0087] For instance, in a typical non-phthalate catalyst system, the internal electron donor compound is 1,8-naphthyl dibenzoate, and the external electron donor compound is diethyl adipate, diethyl pimelate, diethyl sebacate, triacetin, Tinuvin 770[®] (bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate), 1,5-pentanediol diacetate, diethyl-4-oxopimelate, or diethyleneglycol diacetate. For instance, one non-phthalate catalyst system uses 1,8-naphthyl dibenzoate as the internal electron donor compound and triacetin as the external electron donor compound; another non-phthalate catalyst system uses 1,8-naphthyl dibenzoate as the internal electron donor compound and diethyl-4-oxopimelate as the external electron donor compound. In these embodiments, the polymer prepared according to the process of the invention has an improved isotacticity. Moreover, the resulting polymer prepared according to the process of the invention has an improved hydrogen response characterized by melt flow rate.

Surprisingly, the polymer prepared by the non-phthalate catalyst system described in this invention, with the non-silane external donors, can have improved hydrogen response and isotacticity at the same time. This is surprising behavior because, in a typical Ziegler-Natta catalyst system, the external donors that increase hydrogen response (i.e., characterized by MFR) mostly decrease isotacticity (i.e., characterized by increased % XS).

[0088] In some embodiments, the non-phthalate catalyst system used contains the internal electron donor compound that is a cyclic diester compound having a formula of



external electron donor compounds having a formula of (VIII). The definitions of R_9 , R_{10} , R , R' , and n are the same as those described for formula IIIa, IIIb, and VIII in the first and second aspect of the invention. The exemplary internal donor compounds and external donor compounds are the same as those exemplary compounds described for formulas IIIa, IIIb, and VIII in the first and second aspect of the invention.

[0089] For instance, in a typical non-phthalate catalyst system, the internal electron donor compound is selected from the group consisting of diisobutyl cyclohexane-1,2-dicarboxylate, diethyl 3-methylcyclohexane-1,2-dicarboxylate, di-n-propyl 3-methylcyclohexane-1,2-dicarboxylate, diisopropyl 3-methylcyclohexane-1,2-dicarboxylate, di-n-butyl 3-methylcyclohexane-1,2-dicarboxylate, diisobutyl 3-methylcyclohexane-1,2-dicarboxylate, dihexyl 3-methylcyclohexane-1,2-dicarboxylate, diheptyl 3-methylcyclohexane-1,2-dicarboxylate, dioctyl 3-methylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3-methylcyclohexane-1,2-dicarboxylate, didecyl 3-methylcyclohexane-1,2-dicarboxylate, diethyl 4-methylcyclohexane-1,3-dicarboxylate, diisobutyl 4-methylcyclohexane-1,3-dicarboxylate, diethyl 4-methylcyclohexane-1,2-dicarboxylate, di-n-propyl 4-methylcyclohexane-1,2-dicarboxylate, diisopropyl 4-methylcyclohexane-1,2-dicarboxylate, di-n-butyl 4-methylcyclohexane-1,2-dicarboxylate, diisobutyl 4-methylcyclohexane-1,2-

dicarboxylate, dihexyl 4-methylcyclohexane-1,2-dicarboxylate, diheptyl 4-methylcyclohexane-1,2-dicarboxylate, dioctyl 4-methylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 4-methylcyclohexane-1,2-dicarboxylate, didecyl 4-methylcyclohexane-1,2-dicarboxylate, diethyl 5-methylcyclohexane-1,3-dicarboxylate, diisobutyl 5-methylcyclohexane-1,3-dicarboxylate, diethyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, di-n-propyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, diisopropyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, di-n-butyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, diisobutyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, dihexyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, diheptyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, dioctyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, didecyl 3,4-dimethylcyclohexane-1,2-dicarboxylate, diethyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, di-n-propyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, diisopropyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, di-n-butyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, diisobutyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, dihexyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, diheptyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, dioctyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, didecyl 3,6-dimethylcyclohexane-1,2-dicarboxylate, diethyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, di-n-propyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, diisopropyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, di-n-butyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, diisobutyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, dihexyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, dioctyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, didecyl 3,6-diphenylcyclohexane-1,2-dicarboxylate, diethyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-n-propyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diisopropyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-n-butyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diisobutyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, dihexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diheptyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, dioctyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, didecyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diethyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-n-propyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diisopropyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-n-butyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diisobutyl 3-

methyl-6-ethylcyclohexane-1,2-dicarboxylate, dihexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diheptyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, dioctyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, didecyl 3-methyl-6-ethylcyclohexane-1,2-dicarboxylate, diethyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, di-n-propyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, diisopropyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, di-n-butyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, diisobutyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, dihexyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, diheptyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, dioctyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, di-2-ethylhexyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, dodecyl 3-methyl-6-n-propylcyclohexane-1,2-dicarboxylate, diethyl 3-hexylcyclohexane-1,2-dicarboxylate, diisobutyl 3-hexylcyclohexane-1,2-dicarboxylate, diethyl 3,6-dihexylcyclohexane-1,2-dicarboxylate, and diisobutyl 3-hexyl-6-pentylcyclohexane-1,2-dicarboxylate; and the external electron donor compound is diethyl adipate, diethyl pimelate, diethyl sebacate, triacetin, 1,5-pentanediol diacetate, diethyl-4-oxopimelate, or diethyleneglycol diacetate. For instance, the non-phthalate catalyst system uses one of the above-listed compounds as the internal electron donor compound, and triacetin or diethyl-4-oxopimelate as the external electron donor compound. In these embodiments, the polymer prepared according to the process of the invention has an improved isotacticity, an improved hydrogen response characterized by melt flow rate, and in some cases an increased gas phase activity and/or broadened molecular weight distribution. Surprisingly, the polymer prepared by the non-phthalate catalyst system described in this invention, with the non-silane external donors, can have improved hydrogen response and isotacticity at the same time. This is surprising behavior because, in a typical Ziegler-Natta catalyst system, the external donors that increase hydrogen response (i.e., characterized by MFR) mostly decrease isotacticity (i.e., characterized by increased % XS).

[0090] Additional aspects, advantages and features of the invention are set forth in this specification, and in part will become apparent to those skilled in the art on examination of the following, or may be learned by practice of the invention. The inventions disclosed in this application are not limited to any particular set of or combination of aspects, advantages and features. It is contemplated that various combinations of the stated aspects, advantages and features make up the inventions disclosed in this application.

EXAMPLES

[0091] The following examples are for illustrative purposes only and are not intended to limit, in any way, the scope of the present invention.

Materials & Procedures

[0092] Table 1 lists the phthalate catalysts tested as reference systems (or comparative examples).

Table 1. Phthalate catalysts tested as reference systems:

Comparative Catalyst Example	Internal Donor
1	Diisobutylphthalate
2	Diisobutylphthalate
3	Diisobutylphthalate
4	Di-n-butylphthalate

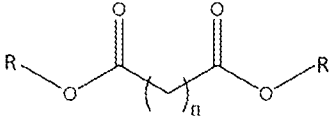
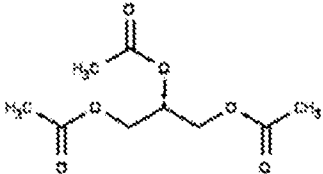
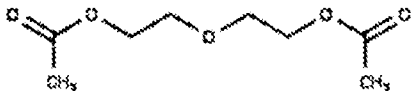
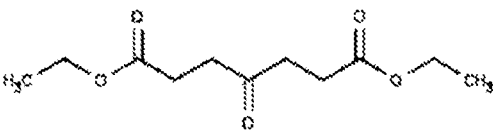
[0093] The alkoxysilanes used as reference systems in the comparative examples were C-donor (cyclohexylmethyl dimethoxysilane), D-donor (dicyclopentyl dimethoxysilane), P-donor (diisopropyl dimethoxysilane), and DIBS (diisobutyl dimethoxysilane).

[0094] Table 2 lists the non-phthalate procatalysts falling within the scope of this invention, listed below as Catalyst Example Nos. 1-5.

Table 2. Non-phthalate catalysts tested

Catalyst Example No.	Internal Donor
1	9,9-bis(methoxymethyl)fluorene [“Diether”]
2	1,8-Naphthyl dibenzoate
3	Cyclohexanedicarboxylate ester
4	Cyclohexanedicarboxylate ester
5	Cyclohexanedicarboxylate ester

[0095] Structures of the non-silane aliphatic ester external donors, tested in combination with Catalyst Example Nos. 1-5, are shown below.

<u>Diesters:</u>  Diethyl malonate (n = 1, R = ethyl) Diethyl glutarate (n = 3, R = ethyl) Diethyl adipate (n = 4, R = ethyl) Diisopropyl adipate (n = 4, R = isopropyl) Dibutyl adipate (n = 4, R = n-butyl or isobutyl) Bis (2-ethylhexyl) adipate (n = 4, R = 2-ethylhexyl) Diethyl pimelate (n = 5, R = ethyl) Diethyl azelate (n = 7, R = ethyl) Diethyl sebacate (n = 8, R = ethyl) Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate (Tinuvin[®] 770) (n = 8, R = 2,2,6,6-tetramethyl-4-piperidyl)	<u>Triester:</u>  Glyceryl Triacetate (Triacetin)
<u>Diacetates:</u>  1,5-Pentandiol Diacetate (PDOA)  Diethyleneglycol diacetate (DEGA)  Diethyl-4-oxopimelate (DEOP)	

[0096] Polymerizations were carried out in either a 1- or 2- gallon autoclave reactor in bulk liquid propylene (2000 grams in 1 gallon, 3000 grams in 2 gallon). Polymerization

temperature and the amount of hydrogen added varied. Prior to the polymerization, triethylaluminum (TEAL), external donor, and procatalysts (including the internal donors) were injected to the reactor sequentially at room temperature and low pressure (< 5 psig). Propylene and hydrogen were then added, and the reactor temperature was increased to the desired set point.

[0097] Impact copolymers were made by sequential bulk homopolymerization and gas phase copolymerization in a 2 gallon reactor. After the homopolymerization stage (at 75 °C), the reactor was depressured and purged with N₂ for 15 minutes before feeding ethylene, propylene, and hydrogen gas into the reactor. The gases were fed continuously to the reactor and constant pressure was maintained using a back pressure regulator thus ensuring a constant gas ratio. The gas phase copolymerization conditions were: 80 °C, 140 psi, and molar ratios of the components in the gas phase are: ethylene / (ethylene + propylene) = 0.43; and H₂/ ethylene = 0.067.

[0098] Molecular weight distribution of the polymers was measured by either GPC (M_w/M_n) or dynamic rheology (Polydispersity Index - PI). Polymer isotacticity was measured by xylene fractionation (%XS) or 500 MHz ¹³C NMR (Bruker). DSC thermal fractionation was carried out by heating a sample to 200 °C at 10 °C/minute, equilibrating for two hours, and then lowering the temperature by 10 °C increments to 120 °C. The sample was allowed to equilibrate for two hours at each successive temperature. At the end of this cycle, the sample was heated up to 200 °C at 10 °C/minute, and the melting endotherm was measured.

Results and Discussion

[0099] The different phthalate and non-phthalate procatalyst systems listed in Table 1 and Table 2, respectively, were analyzed with conventional alkoxysilane external donors and analyzed in Table 3 and Table 4, respectively, below.

[0100] Unlike phthalate-based catalysts, most non-phthalate catalysts are not strongly influenced by the type of alkoxysilane external donor used. This is illustrated in Table 4 for several different non-phthalate systems. Note that the ranges of MFR and %XS are much narrower for the phthalate procatalysts in Table 3 than for the non-phthalate procatalysts in Table 4.

Table 3. The phthalate procatalysts with conventional alkoxysilane external donors

Comparative Catalyst Example No.	External Donor	kg Polypropylene/ g Procatalyst	MFR	%XS
1 ¹	C-donor	35	80	4.0
	P-donor	33	70	3.0
	D-donor	30	25	2.7
1 ²	C-donor	31	120	3.3
	P-donor	34	100	2.9
	D-donor	38	40	2.8
2 ²	C-donor	34	100	3.0
	P-donor	40	80	2.5
	D-donor	44	25	2.0
3 ³	C-donor	38	8	2.6
	P-donor	36	3	2.2
	D-donor	35	2	2.2
	DIBS	34	6	3.5
3 ⁴	C-donor	38	20	2.7
	P-donor	39	10	2.1
	DIBS	39	20	2.7

¹ 2-gallon reactor, 70 °C, 3.5 g H₂, ratio of donor / Ti compound = 10² 2-gallon reactor, 75 °C, 4.75 g H₂, ratio of donor / Ti compound = 10³ 1-gallon reactor, 75 °C, 0.6 g H₂, ratio of donor / Ti compound = 10⁴ 1-gallon reactor, 75 °C, 0.9 g H₂, ratio of donor / Ti compound = 10

Table 4. The non-phthalate procatalysts (see Table 2 for internal donors for each example) with conventional alkoxysilane external donors (1-gallon reactor, 75 °C, ratio of donor / Ti compound = 10)

Catalyst Example	External Donor	kg Polypropylene / g Procatalyst	MFR	%XS
1	C-Donor	40	45	1.4
	P-Donor	40	50	1.5
	D-Donor	39	50	1.4
2	C-Donor	47	4	2.0
	P-Donor	44	9	2.0
	D-Donor	43	8	1.7

3	C-Donor	33	20	2.4
	P-Donor	33	30	2.5
	D-Donor	30	15	2.4
4	C-Donor	29	6	2.4
	P-Donor	30	8	2.2
5	C-Donor	35	28	2.9
	D-Donor	37	24	2.7

[0101] The effects of non-silane aliphatic diester external donors on different phthalate and non-phthalate procatalyst systems listed in Table 2 were analyzed. As shown in results below, each of these non-phthalate procatalysts had a particular deficiency that could not be influenced by alkoxysilanes, but were influenced by the new external donors.

Example No. 2 procatalyst

[0102] Example No. 2 procatalyst is a non-phthalate catalyst containing 1,8-naphthyl dibenzoate as an internal donor (see U.S. Patent No. 8,003,558, which is incorporated herein by reference in its entirety). With typical alkoxysilane external donors (C, D, and P), Example No. 2 procatalyst had a significantly lower hydrogen response compared to a phthalate catalyst (Comparative Example 4) (see Figure 1). Furthermore, Figure 1 also shows that the type of alkoxysilane external donor has very little influence on the hydrogen response of Example No. 2 procatalyst.

[0103] A series of non-silane aliphatic diester molecules were tested as external donors to improve the hydrogen response of Example No. 2 procatalyst. The results are shown in Figure 1, Table 5.2, and Table 5.3. Table 5.1 illustrates the Example No. 2 procatalyst with varied Do/Ti ratios (1-gallon reactor, at 75 °C, 1.8 gm H₂). While the aliphatic diesters somewhat decreased the catalyst activity, the hydrogen response gap between Example No. 2 procatalyst (non-phthalate) and Comparative Example 4 procatalyst (phthalate) was significantly reduced, especially at higher hydrogen levels. In addition, the polymers produced using the non-silane aliphatic diester external donors had a higher isotacticity (i.e., lower % XS) than those produced with the conventional alkoxysilane external donors at the same donor level.

[0104] At least some of the activity appeared to be recovered at a lower ratio of donor / Ti compound. Therefore, lowering the ratio of donor / Ti compound may be desirable to

provide an improved performance comparable to conventional alkoxysilane external donors. Lowering the ratio of donor / Ti compound may also result in lower donor residues in the final product as well as providing an economic advantage over conventional alkoxysilane external donors.

Table 5.1. Example No. 2 procatalyst with varied Do/Ti ratios (1-gallon reactor, at 75 °C, 1.8 gm H₂)

Donor	Do/Ti	kg Polypropylene/ g Procatalyst
P-donor	10	43
	30	46
Diethyl Adipate	2	49
	5	47
	10	33
	30	11

Table 5.2. Comparison of Example No. 2 procatalyst with conventional alkoxysilane external donors and with non-silane aliphatic diester external donors (2-gallon reactor, at 75 °C, Do/Ti= 10, 4.0 gm H₂)

External Donor	kg Polypropylene/ g Procatalyst	MFR	%XS
C-donor	60	27	1.8
Diethylene Glycol Diacetate	18	71	1.6
1,5-Pentanediol Diacetate	27	54	1.4
Triacetin	43	45	2.6
Diethyl Malonate	73	44	3.6
Diethyl 4-Oxopimelate	40	41	1.8
Diethyl Adipate	35	34	1.6
Tinuvin 770	56	25	2.0

Table 5.3. Comparison of Example No. 2 procatalyst with conventional alkoxysilane external donors and with non-silane aliphatic diester external donors (1-gallon reactor, at 75 °C, Do/Ti=10, 1.8 gm H₂)

External Donor	kg Polypropylene/ g Procatalyst	MFR	%XS
C- Donor	46	37	2.2
D- Donor	48	24	2.2
P- Donor	43	43	2.1
Diethyl Sebacate	31	94	1.5
Diethyl Pimelate	34	83	2.2
Diethyl Adipate	33	81	1.5
Diisopropyl Adipate	46	47	2.2
Dibutyl Adipate	42	44	2.1
Diethyl Azelate	41	42	2.0
Diethyl Glutarate	46	41	2.7
Diethyl Malonate	51	25	3.4
Diisobutyl Adipate	50	23	2.6
Bis (2-ethylhexyl) Adipate	56	18	2.9

Example No. 5 procatalyst

[0105] Example No. 5 is a non-phthalate procatalyst based on a cyclohexanedicarboxylate internal donor (see U.S. Patent Nos. 7,649,062 and 7,888,438, which are incorporated herein by reference in their entirety). Table 6 shows that Example No. 5 procatalyst with conventional alkoxysilane external donor provided somewhat lower MFR and higher xylene solubles than Comparative Example 1 procatalyst (phthalate). However, using diethyladipate as the external donor increased both the hydrogen response and isotacticity of Example No. 5 procatalyst. The increase in isotacticity was enough to make this non-phthalate catalyst system comparable to Comparative Example 1 (a phthalate catalyst system).

[0106] Similar to Example No. 2 procatalyst and aliphatic diester external donors, the catalyst activity when using Example No. 5 procatalyst with an aliphatic diester external donor was somewhat decreased compared to the conventional alkoxysilane external donor at the same donor / Ti compound ratio.

Table 6. Comparison of Example No. 5 procatalyst with conventional alkoxysilane external donors and with non-silane aliphatic diester external donors to Comparative Example 1 procatalyst (phthalate) with conventional alkoxysilane external donors (1-gallon reactor, 75 °C, ratio of donor / Ti compound = 10)

Catalyst	External Donor	g H ₂	kg Polypropylene/ g Procatalyst	MFR	%XS
Example No. 5	P-Donor	1.8	54	60	3.3
		1.2	52	19	3.6
		0.6	45	3	4.0
Example No. 5	Diethyl Adipate	1.8	38	290	2.5
		1.2	36	78	2.5
		0.6	32	8	3.2
Comparative Example 1	P-donor	1.8	44	110	3.2
		1.2	40	30	2.6
		0.6	30	3	2.7

Example No. 3 procatalyst

[0107] Example No. 3 is a non-phthalate procatalyst based on a cyclohexanedicarboxylate internal donor which produces very broad MWD products (see U.S. Patent No. 8,729,189, which is incorporated herein by reference in its entirety).

[0108] A comparison of polymerization with Example No. 3 procatalyst in combination with a conventional alkoxysilane external donor and in combination with the non-silane aliphatic diester external donors is shown in Tables 7.1 and 7.2. Although the catalyst activity was decreased, the hydrogen response was in some cases increased by the diester external donors compared to the conventional alkoxysilane external donor, isotacticity was improved and the MWD remained the same or was broadened.

Table 7.1. Comparison of Example No. 3 procatalyst with a conventional alkoxysilane external donor and non-silane aliphatic diester external donors (1-gallon reactor, 75 °C, ratio of donor / Ti compound = 10, 1.8g H₂)

External Donor	kg Polypropylene/ g Procatalyst	MFR	%XS
C- Donor	32	71	2.4
D- Donor	34	58	2.1
P- Donor	33	140	2.6
Triacetin	18	148	2.6
Diethyl 4-Oxopimelate	15	146	2.2
1,5-Pentanediol Diacetate	13	125	1.7
Diethyl Malonate	39	105	4.7
Diethyl Adipate	14	100	2.0
Diethyl Sebacate	16	96	2.0
Diethyl Pimelate	18	90	2.0
Diethylene Glycol Diacetate	6	90	1.4
Tinuvin 770	23	138	2.3

Table 7.2. Comparison of Example No. 3 procatalyst with a conventional alkoxysilane external donor and non-silane aliphatic diester external donors (1-gallon reactor, 75 °C, ratio of donor / Ti compound = 10, 0.6g H₂)

External Donor	PI
P- Donor	5.6
Triacetin	8.4
Diethyl 4-Oxopimelate	7.8
1,5-Pentanediol Diacetate	7.8
Diethyl Adipate	7.6
Diethyl Pimelate	6.5
Diethylene Glycol Diacetate	8.8
Tinuvin 770	7.5

[0109] It was previously observed that Example No. 3 procatalyst has relatively low gas phase activity in the production of impact copolymer compared to the phthalate catalyst of Comparative Example 1. Figure 2 illustrates the gap in gas phase production between

Example No. 3 procatalyst (non-phthalate) and Comparative Example 1 procatalyst (phthalate) when using P-donor as the external donor. This shows that Example No. 3, procatalyst (non-phthalate) in combination with the conventional alkoxysilane external donors, does not have as good of a performance as the phthalate catalyst of Comparative Example 1 in the production of an impact copolymer.

[0110] However, when the non-silane aliphatic ester compounds were used with Example No. 3 procatalyst, much more promising gas phase production was observed (Figures 2 and 3). Diethyladipate external donor gave similar or slightly better ethylene incorporation than the phthalate/alkoxysilane system, and the triester donor (triacetin) improved the ethylene incorporation beyond that of the phthalate catalyst.

Example No. 1 procatalyst

[0111] Example No. 1 is a commercial non-phthalate diether procatalyst (see U.S. Patent No. 5,723,400, which is incorporated herein by reference in its entirety). Diether catalysts typically produce polypropylenes having lower crystallinity and stiffness than the phthalate catalysts, due to a narrower MWD and more regioirregular chain structure (Tables 8 and 10). Diether procatalysts also do not respond very differently to different alkoxysilane donors (see Tables 4 and 8).

[0112] Example No. 1 procatalyst was tested with alternative external donors to improve the attributes of the polymer product compared to the conventional alkoxysilane systems and to create products more similar to phthalate-based catalysts.

Table 8. Comparison of Example No. 1 procatalyst with conventional alkoxysilane external donors and non-silane aliphatic ester donors (1-gallon reactor, 75 °C, ratio of donor / Ti Compound = 10, 1.2 gm H₂)

External Donor	kg Polypropylene / g Procatalyst	MFR	%XS
D-donor	35	270	1.5
C-donor	36	290	1.7
P-donor	37	310	2.1
Diethylene Glycol Diacetate	19	610	1.1
Diethyl 4-Oxopimelate	24	530	0.9
1,5-Pentanediol Diacetate	25	490	0.9

Triacetin	31	470	1.5
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[0113] One particular advantage of the alternative external donors with Example No. 1 procatalyst is the increase in the isotacticity of polymers, while the polydispersity index (PI) appeared to be essentially unchanged (Table 9). Thus, these new donors can modify the polymer structure in a way that differs from conventional alkoxysilane donors.

Table 9. Comparison of Example No. 1 procatalyst with conventional alkoxysilane external donors and non-silane aliphatic ester external donors (1-gallon reactor, 75°C, ratio of donor / Ti Compound = 10, 0.6 gm H₂)

External Donor	kg Polypropylene/ g Procatalyst	MFR	%XS	PI
D-donor	36	3.2	1.3	3.4
C-Donor	37	3.5	1.7	-
P-Donor	47	2.3	1.8	-
Triacetin	27	25	1.1	3.3
Diethylene Glycol Diacetate	14	13	1.1	3.7
Diethyl 4-Oxopimelate	21	9	1.4	3.4
1,5-Pentanediol Diacetate	18	7	1.0	3.7

[0114] The positive effect of the alternative donors on the hydrogen response of Example No. 1 procatalyst is illustrated in Figure 4. As shown in Figure 4, the new external donors in combination with the diether procatalysts produced a higher MFR product, which can lead to the production of a wider range of products than currently possible with conventional alkoxysilane external donors.

[0115] The above results show that aliphatic di- and tri-ester donors appeared to improve both hydrogen response and isotacticity at the same time. This is a desirable and novel behavior compared to the conventional response of the Ziegler-Natta procatalysts to the external donors. Typically, external donors that increase MFR also decrease isotacticity (increase %XS).

[0116] Compared to conventional alkoxysilane external donors, a relatively lower activity is seen at the same donor / Ti compound with the diester external donors. However, at least some of the activity appeared to be recovered at a lower donor / Ti compound. Therefore, lowering the ratio of donor / Ti compound may be desirable to provide an improved

performance comparable to conventional alkoxysilane external donors. Lowering the ratio of donor / Ti compound may also result in lower donor residues in the final product as well as providing an economic advantage over conventional alkoxysilane external donors.

[0117] The results of the new aliphatic ester external donors in combination with the non-phthalate procatalyst are surprising as the phthalate catalysts typically do not respond well to these non-silane aliphatic ester external donors. As shown in Table 10, when these non-silane aliphatic ester external donors in combination with the phthalate procatalyst, the catalyst activity was dramatically reduced and both the MFR and %XS were significantly increased.

Table 10. Comparison of the phthalate procatalyst of Comparative Example 1 with a conventional alkoxysilane external donor and a non-silane aliphatic diester external donor (1-gallon reactor, 75 °C, ratio of donor / Ti Compound = 10)

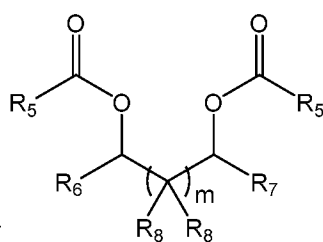
External Donor	g H ₂	kg Polypropylene/ g Procatalyst	MFR	%XS
P-Donor	1.8	44	110	3.2
	1.2	40	30	2.6
	0.6	30	3	2.7
Diethyl Adipate	1.8	6	1000	4.5
	1.2	5	400	5.1
	0.6	4	70	6.8

[0118] Although preferred embodiments have been depicted and described in detail herein, it will be apparent to those skilled in the relevant art that various modifications, additions, substitutions, and the like can be made without departing from the spirit of the invention and these are therefore considered to be within the scope of the invention as defined in the claims which follow.

What is claimed is:

1. A non-phthalate catalyst system for olefin polymerization, comprising:

- (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, a Group 2 metal, and one or more halogens; and
one or more internal electron donor compounds having the structure of a diester



compound having a formula of

(II),

wherein:

each R₅ is independently a C₁ to C₁₈ hydrocarbyl group which can optionally form one or more saturated or unsaturated mono- or poly- cyclic structures;

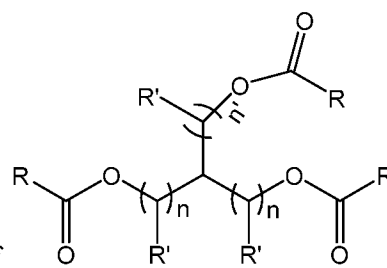
each of R₆ and R₇ is independently H or a C₁ to C₁₈ hydrocarbyl group; or, R₆ and R₇ together form one or more saturated or unsaturated mono- or poly- cyclic structures;

each R₈ is independently absent, H, or a C₁ to C₁₈ hydrocarbyl group;

m is 0 or 1;

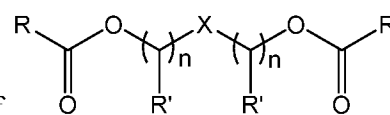
wherein each of R₅, R₆, R₇, and R₈, can contain one or more heteroatoms that replace one or more carbon atoms in the hydrocarbyl group, wherein the one or more heteroatoms are selected from the group consisting of halogens, P, N, O, S, and Si;
and

(b) one or more external electron donor compounds selected from the group consisting of:



i) a triester compound having a formula of

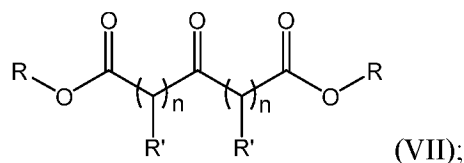
(V),



ii) a diester compound having a formula of

(VI), and

iii) an oxo-substituted diester compound having a formula of



wherein:

X is CH₂ or O,

each R is independently a C₁-C₁₀ hydrocarbyl group,

each R' is independently H or R,

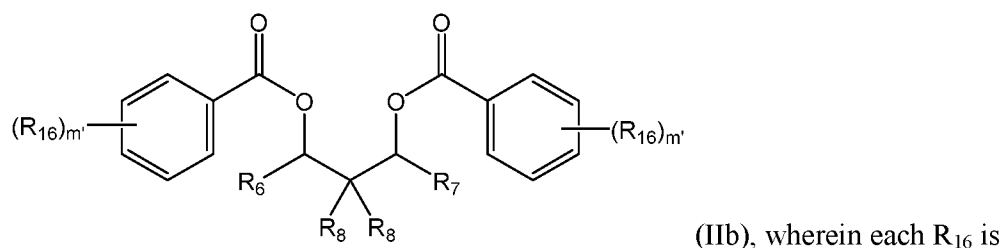
each n is independently an integer from 1 to 4, and

n' is an integer from 0 to 4.

2. The non-phthalate catalyst system of claim 1, wherein the transition metal is titanium, the Group 2 metal is magnesium, and the halogen is chloride.

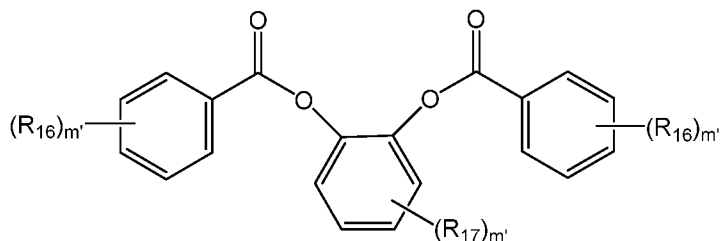
3. The non-phthalate catalyst system of claim 1, wherein the catalyst system further comprises an organoaluminum cocatalyst selected from the group consisting of alkylaluminum, alkylaluminum hydride, alkylaluminum halide, and alkylaluminum alkoxide.

4. The non-phthalate catalyst system of claim 1, wherein the internal electron donor compound is a diester compound having a formula of:



independently H, halogen, or a C₁ to C₁₈ hydrocarbyl group which can optionally form one or more saturated or unsaturated cyclic structures with the phenyl group it attaches to, and can contain one or more heteroatoms that replace one or more carbon atoms in the hydrocarbyl group, wherein the one or more heteroatoms are selected from the group consisting of halogens, P, N, O, S, and Si; and each m' is independently an integer from 0 to 5.

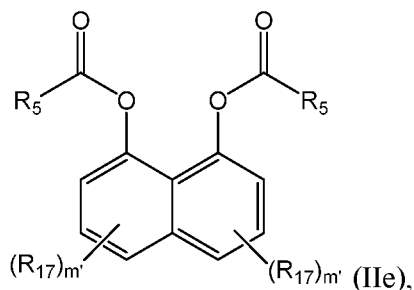
5. The non-phthalate catalyst system of claim 1, wherein the internal electron donor compound is a diester compound having a formula of:



is independently H, halogen, or a C_1 to C_{18} hydrocarbyl group which can optionally form one or more saturated or unsaturated cyclic structures with the phenyl group it attaches to, and can contain one or more heteroatoms that replace one or more carbon atoms in the hydrocarbyl group, wherein the one or more heteroatoms are selected from the group consisting of halogens, P, N, O, S, and Si; and each m' is independently an integer from 0 to 5.

6. The non-phthalate catalyst system of claim 5, wherein each m' is 0-3, and each of R_{16} and R_{17} is independently H, halogen, a C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, C_7 - C_{12} aralkyl, or C_7 - C_{12} alkylaryl.

7. The non-phthalate catalyst system of claim 1, wherein the internal electron donor compound is a diester compound having a formula of:



wherein:

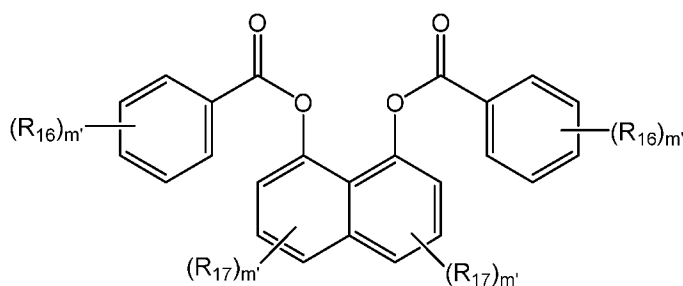
each m' is 0-3;

each R_{17} is independently H, halogen, or a C_1 to C_{18} hydrocarbyl group which can optionally form one or more saturated or unsaturated cyclic structures with the phenyl group it attaches to, and can contain one or more heteroatoms that replace one or more carbon

atoms in the hydrocarbonyl group, wherein the one or more heteroatoms are selected from the group consisting of halogens, P, N, O, S, and Si; and

each R_5 is independently a C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_5 - C_6 cycloalkyl, C_5 - C_6 cycloalkenyl, aryl, or heteroaryl; each of these groups can be further substituted by halogen, C_1 - C_{10} alkyl, or C_1 - C_{10} alkoxy.

8. The non-phthalate catalyst system of claim 7, wherein the internal electron donor compound is a diester compound having a formula of:



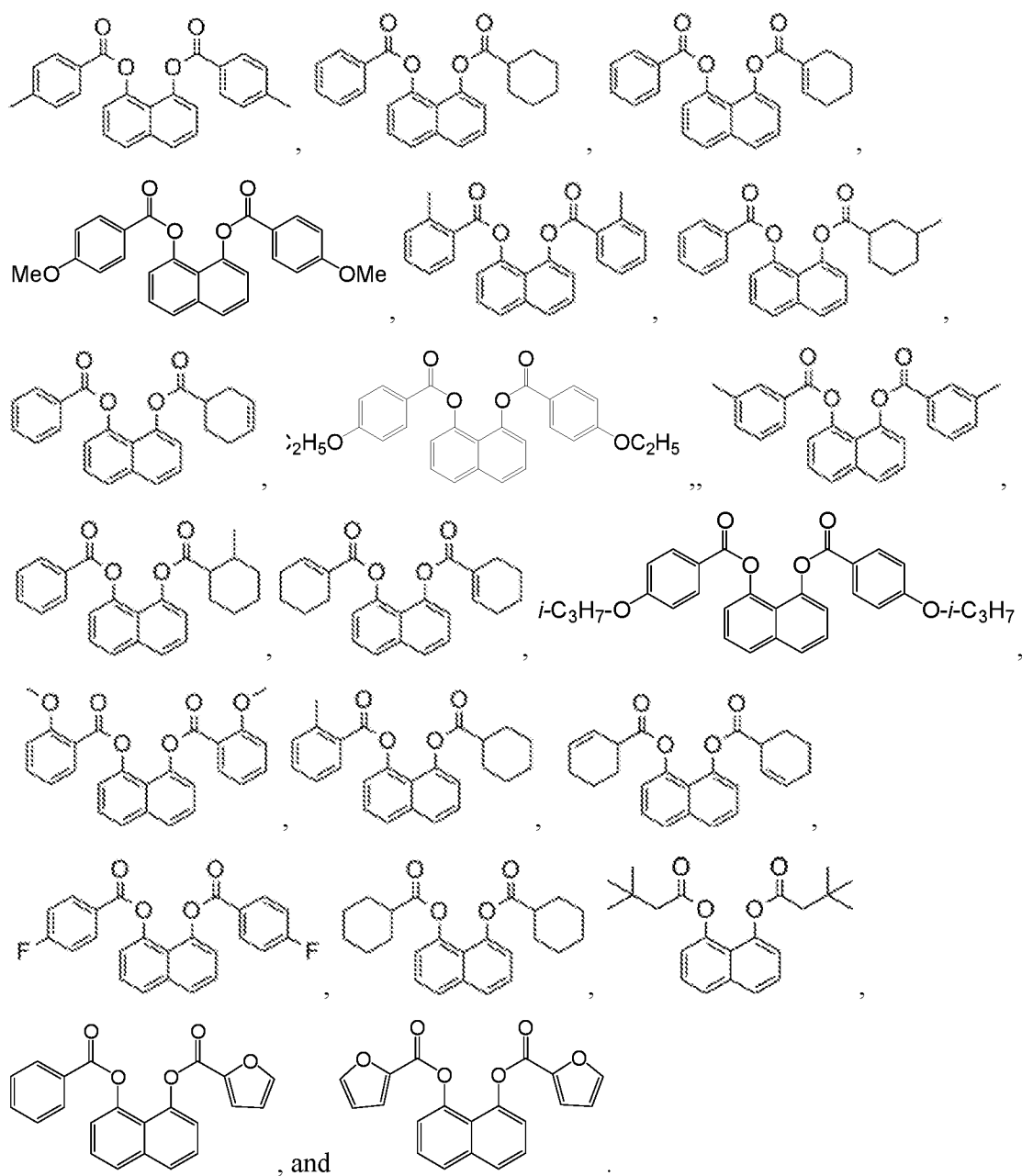
(IIf), wherein each of R_{16} and R_{17} is

independently H, halogen, a C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, C_7 - C_{12} aralkyl, or C_7 - C_{12} alkylaryl.

9. The non-phthalate catalyst system of claim 8, wherein the diester compound is selected from the group consisting of 1,8-naphthyl dibenzoate; 1,8-naphthyl di-4-methylbenzoate; 1,8-naphthyl di-3-methylbenzoate; 1,8-naphthyl di-2-methylbenzoate; 1,8-naphthyl di-4-ethylbenzoate; 1,8-naphthyl di-4-n-propylbenzoate; 1,8-naphthyl di-4-isopropylbenzoate; 1,8-naphthyl di-4-n-butylbenzoate; 1,8-naphthyl di-4-isobutylbenzoate; 1,8-naphthyl di-4-t-butylbenzoate; 1,8-naphthyl di-4-phenylbenzoate; 1,8-naphthyl di-4-fluorobenzoate; 1,8-naphthyl di-3-fluorobenzoate; 1,8-naphthyl di-2-fluorobenzoate; 1,8-naphthyl di-4-chlorobenzoate; 1,8-naphthyl di-3-chlorobenzoate; 1,8-naphthyl di-2-chlorobenzoate; 1,8-naphthyl di-4-bromobenzoate; 1,8-naphthyl di-3-bromobenzoate; 1,8-naphthyl di-2-bromobenzoate; 1,8-naphthyl di-4-cyclohexylbenzoate; 1,8-naphthyl di-2,3-dimethylbenzoate; 1,8-naphthyl di-2,4-dimethylbenzoate; 1,8-naphthyl di-2,5-dimethylbenzoate; 1,8-naphthyl di-2,6-dimethylbenzoate; 1,8-naphthyl di-3,4-dimethylbenzoate; 1,8-naphthyl di-3,5-dimethylbenzoate; 1,8-naphthyl di-2,3-dichlorobenzoate; 1,8-naphthyl di-2,4-dichlorobenzoate; 1,8-naphthyl di-2,5-dichlorobenzoate; 1,8-naphthyl di-2,6-dichlorobenzoate; 1,8-naphthyl di-3,4-

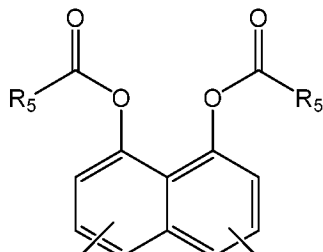
dichlorobenzoate; 1,8-naphthyl di-3,5-dichlorobenzoate; and 1,8-naphthyl di-3,5-di-*t*-butylbenzoate.

10. The non-phthalate catalyst system of claim 7, wherein the diester compound is selected from the group consisting of



11. The non-phthalate catalyst system of claim 1, wherein the external electron donor is a triester compound.
12. The non-phthalate catalyst system of claim 11, wherein each R is a C₁ to C₁₀ alkyl, each R' is H or CH₃, each n is an integer from 1 to 2, and n' is an integer from 0 to 2.
13. The non-phthalate catalyst system of claim 12, wherein each R is methyl, each R' is H, each n is 1, and n' is 0.
14. The non-phthalate catalyst system of claim 1, wherein the external electron donor is a diester compound.
15. The non-phthalate catalyst system of claim 14, wherein each R is a C₁ to C₁₀ alkyl, each R' is H or CH₃, and each n is an integer from 1 to 2.
16. The non-phthalate catalyst system of claim 15, wherein each R is methyl, each R' is H, and each n is 2.
17. The non-phthalate catalyst system of claim 1, wherein the external electron donor is an oxo-substituted diester compound.
18. The non-phthalate catalyst system of claim 17, wherein each R is a C₁ to C₁₀ alkyl, each R' is H or CH₃, and each n is an integer from 1 to 2.
19. The non-phthalate catalyst system of claim 18, wherein each R is methyl, each R' is H, and each n is 2.
20. A non-phthalate catalyst system for olefin polymerization, comprising:
 - (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, a Group 2 metal, and one or more halogens; and

one or more internal electron donor compounds having the structure of a diester



compound having a formula of $(R_{17})_{m'}$ (IIe),

wherein:

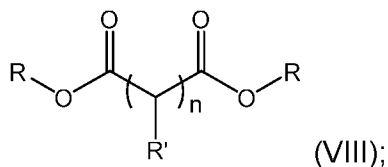
each R_5 is independently a C_1 to C_{18} hydrocarbyl group which can optionally form one or more saturated or unsaturated mono- or poly- cyclic structures;

each R_{17} is independently H, halogen, or a C_1 to C_{18} hydrocarbyl group which can optionally form one or more saturated or unsaturated cyclic structures with the phenyl group it attaches to;

each m' is independently an integer from 0 to 5; and

wherein each of R_5 and R_{17} can contain one or more heteroatoms that replace one or more carbon atoms in the hydrocarbyl group, wherein the one or more heteroatoms are selected from the group consisting of halogens, P, N, O, S, and Si; and

(b) one or more external electron donor compounds having a formula of



wherein:

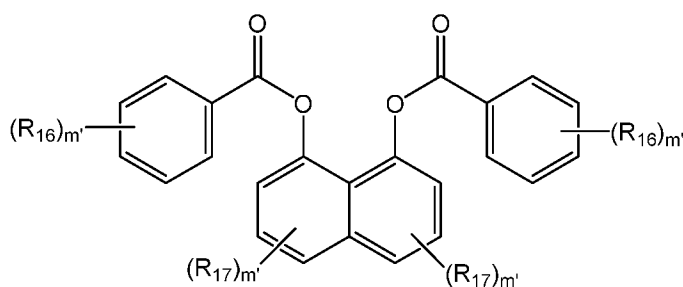
each R is independently a C_1 to C_{10} hydrocarbyl group, and can contain one or more heteroatoms that replace one or more carbon atoms in the hydrocarbyl group, wherein the one or more heteroatoms are selected from the group consisting of halogens, P, N, O, S, and Si;

R' is H or R, and

n is an integer from 1 to 10,

wherein the external electron donor compound does not contain an alkoxysilane compound.

21. The non-phthalate catalyst system of claim 20, wherein the transition metal is titanium, the Group 2 metal is magnesium, and the halogen is chloride.
22. The non-phthalate catalyst system of claim 20, wherein the catalyst system further comprises an organoaluminum cocatalyst selected from the group consisting of alkylaluminum, alkylaluminum hydride, alkylaluminum halide, and alkylaluminum alkoxide.
23. The non-phthalate catalyst system of claim 20, wherein the internal electron donor compound is a diester compound, wherein m' is 0-3, and each R_5 is a C_1 - C_{10} alkyl, C_2 - C_{10} alkenyl, C_5 - C_6 cycloalkyl, C_5 - C_6 cycloalkenyl, aryl, or heteroaryl; each of these groups can be further substituted by halogen, C_1 - C_{10} alkyl, or C_1 - C_{10} alkoxy.
24. The non-phthalate catalyst system of claim 20, wherein the internal electron donor compound is a diester compound having a formula of:



(IIIf), wherein each of R_{16} and R_{17} is

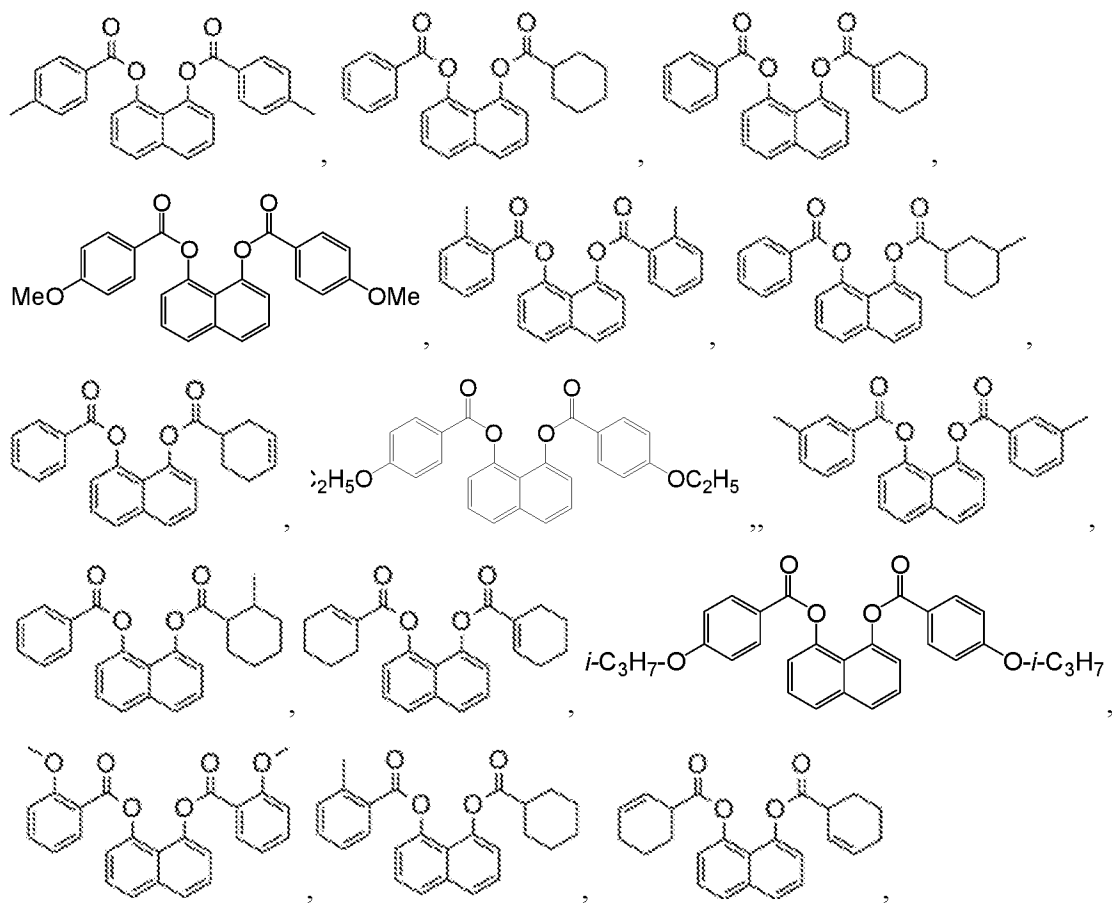
independently H, halogen, a C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, C_7 - C_{12} aralkyl, or C_7 - C_{12} alkylaryl.

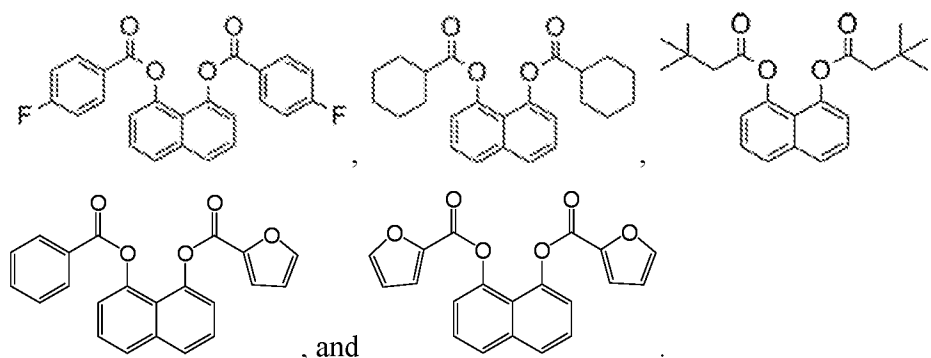
25. The non-phthalate catalyst system of claim 24, wherein the diester compound is selected from the group consisting of 1,8-naphthyl dibenzoate; 1,8-naphthyl di-4-methylbenzoate; 1,8-naphthyl di-3-methylbenzoate; 1,8-naphthyl di-2-methylbenzoate; 1,8-naphthyl di-4-ethylbenzoate; 1,8-naphthyl di-4-n-propylbenzoate; 1,8-naphthyl di-4-isopropylbenzoate; 1,8-naphthyl di-4-n-butylbenzoate; 1,8-naphthyl di-4-isobutylbenzoate; 1,8-naphthyl di-4-t-butylbenzoate; 1,8-naphthyl di-4-phenylbenzoate; 1,8-naphthyl di-4-fluorobenzoate; 1,8-naphthyl di-3-fluorobenzoate; 1,8-naphthyl di-2-fluorobenzoate; 1,8-naphthyl di-4-chlorobenzoate; 1,8-naphthyl di-3-chlorobenzoate; 1,8-naphthyl di-2-chlorobenzoate; 1,8-naphthyl di-4-bromobenzoate; 1,8-naphthyl di-3-bromobenzoate; 1,8-

naphthyl di-2-bromobenzoate; 1,8-naphthyl di-4-cyclohexylbenzoate; 1,8-naphthyl di-2,3-dimethylbenzoate; 1,8-naphthyl di-2,4-dimethylbenzoate; 1,8-naphthyl di-2,5-dimethylbenzoate; 1,8-naphthyl di-2,6-dimethylbenzoate; 1,8-naphthyl di-3,4-dimethylbenzoate; 1,8-naphthyl di-3,5-dimethylbenzoate; 1,8-naphthyl di-2,3-dichlorobenzoate; 1,8-naphthyl di-2,4-dichlorobenzoate; 1,8-naphthyl di-2,5-dichlorobenzoate; 1,8-naphthyl di-2,6-dichlorobenzoate; 1,8-naphthyl di-3,4-dichlorobenzoate; 1,8-naphthyl di-3,5-dichlorobenzoate; and 1,8-naphthyl di-3,5-di-*t*-butylbenzoate.

26. The non-phthalate catalyst system of claim 25, wherein the diester compound is 1,8-naphthyl dibenzoate.

27. The non-phthalate catalyst system of claim 20, wherein the diester compound is selected from the group consisting of





28. The non-phthalate catalyst system of claim 20, wherein, for the external electron donor, each R is a C₁-C₁₀ alkyl, C₃-C₈ cycloalkyl, or C₃-C₈ heterocycloalkyl, optionally substituted with one or more alkyl, each R' is H or CH₃, and n is an integer from 1 to 8.

29. The non-phthalate catalyst system of claim 28, wherein each R is methyl, ethyl, propyl, butyl, or 2-ethyl hexyl, and each R' is H.

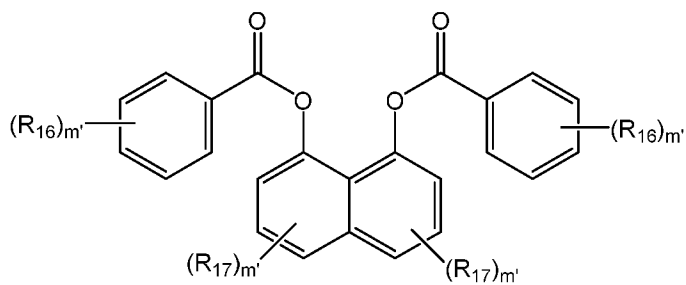
30. The non-phthalate catalyst system of claim 28, wherein each R is piperidinyl, optionally substituted with one or more C₁-C₆ alkyl; and each R' is H.

31. A process for preparing a polyolefin, comprising:
polymerizing one or more olefins, in the presence of the non-phthalate catalyst system according to claim 1, under reaction conditions sufficient to form the polyolefin.

32. A process for preparing polyolefin, comprising:
polymerizing one or more olefins, in the presence of the non-phthalate catalyst system according to claim 20, under reaction conditions sufficient to form the polyolefin.

33. The process of claim 32, wherein in the non-phthalate catalyst system:

the internal electron donor compound is a diester compound having a formula of

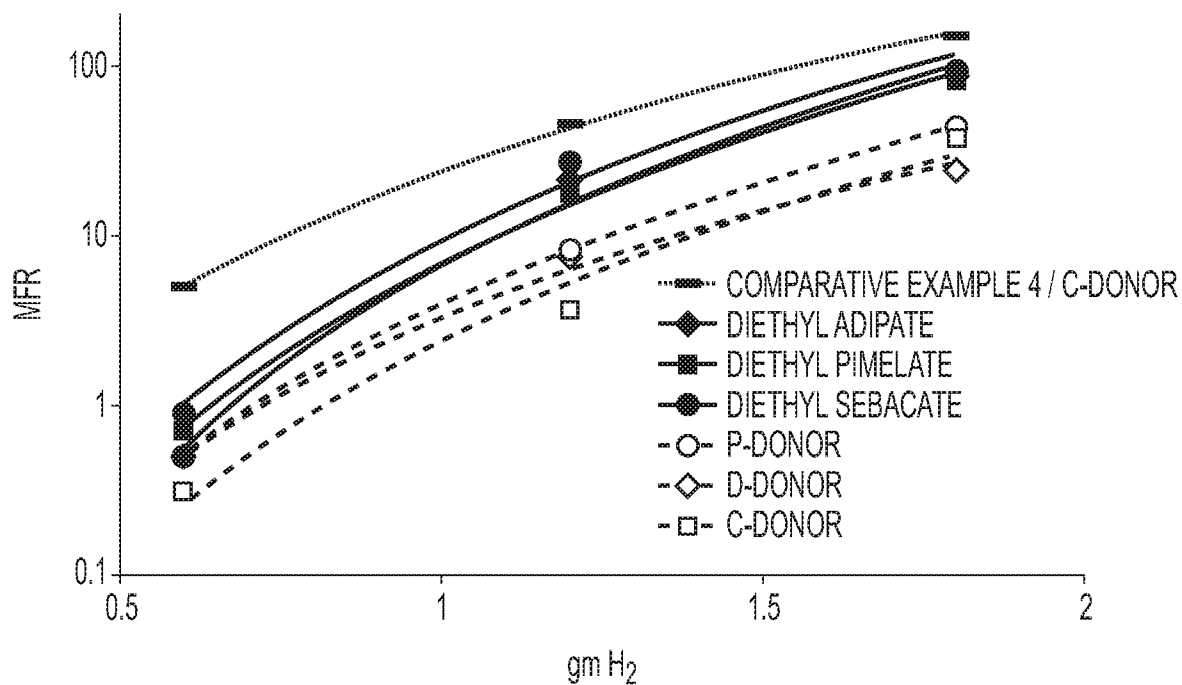
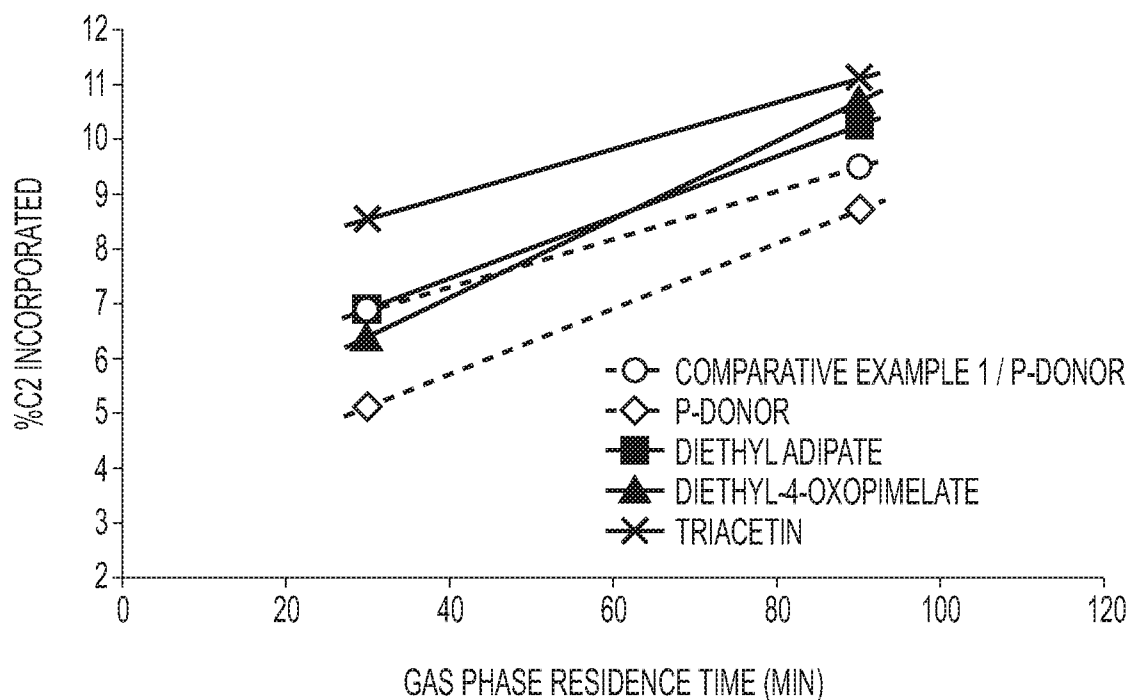


(IIf), wherein each of R_{16} and R_{17} is

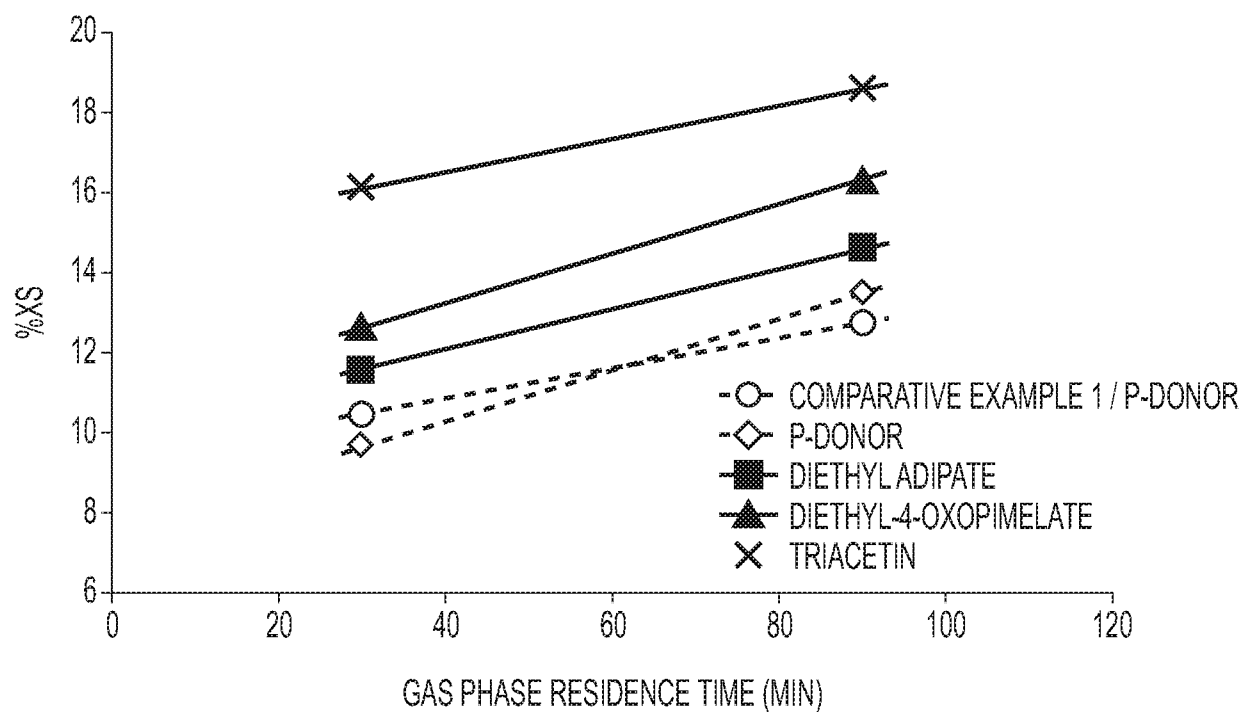
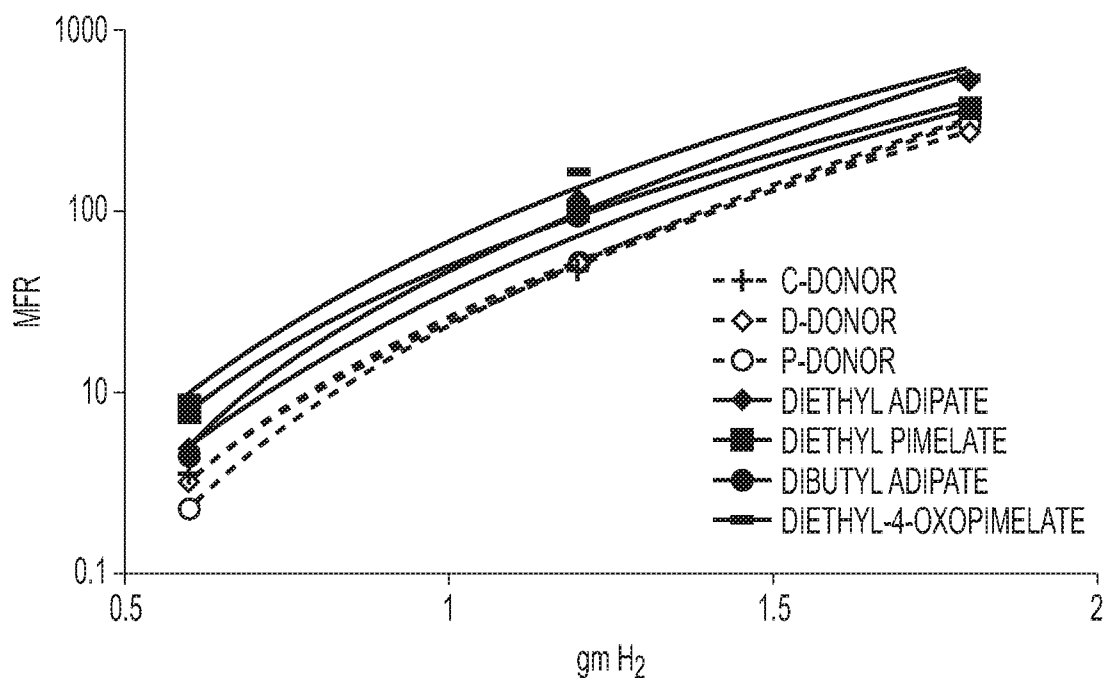
independently H, halogen, a C_1 - C_6 alkyl, C_1 - C_6 alkoxy, phenyl, C_7 - C_{12} aralkyl, or C_7 - C_{12} alkylaryl.

34. The process of claim 33, wherein the internal electron donor compound is 1,8-naphthyl dibenzoate; and the external electron donor compound is diethyl adipate, diethyl pimelate, diethyl sebacate, triacetin, Tinuvin 770[®] ((bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate)), 1,5-pentanediol diacetate, diethyl-4-oxopimelate, or diethyleneglycol diacetate.

1/2

**FIG. 1****FIG. 2**

2/2

**FIG. 3****FIG. 4**

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/069299

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C08F 4/64; B01J 31/38; C08F 2/00; C08F 4/00; C08F 4/654 (2017.01)

CPC - C08L 2314/02; B01J 27/138; B01J 31/02; C08F 4/6494; C08F 4/654 (2017.02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2012/007430 A1 (BOREALIS AG) 19 January 2012 (19.01.2012) entire document	1-3, 11-13, 31
A	CA 2947095 A1 (CHINA PETROLEUM & CHEMICAL CORPORATION) 29 October 2015 (29.10.2015) entire document	1-3, 11-13, 31
A	US 2014/0275456 A1 (FORMOSA PLASTICS CORPORATION, USA) 18 September 2014 (18.09.2014) entire document	1-3, 11-13, 31
A	US 2005/0239636 A1 (GAO et al) 27 October 2005 (27.10.2005) entire document	1-3, 11-13, 31

☐ Further documents are listed in the continuation of Box C.☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

30 March 2017

Date of mailing of the international search report

26 APR 2017

Name and mailing address of the ISA/US

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PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2016/069299

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Extra Sheet

Claims 1-3, 11-13, and 31 have been analyzed subject to the restriction that claims read on a non-phthalate catalyst system for olefin polymerization, comprising: (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, wherein the transition metal is titanium, a Group 2 metal, wherein the Group 2 metal is magnesium, and one halogen, wherein the halogen is chloride; and one internal electron donor compound having the structure of a diester compound having a formula (II), wherein each R5 is C1 hydrocarbyl; each of R6 and R7 is independently H; each R8 is independently absent; m is 0; (b) one external electron donor compound selected from a triester compound having a formula (V), wherein each R is C1 hydrocarbyl group, each R' is H, each n is 1, and n' is 0; and processes thereof.

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-3, 11-13, 31

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Continued from Box No. III Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees need to be paid.

Group I+: claims 1-34 are drawn to non-phthalate catalyst systems and processes for preparing a polyolefin.

The first invention of Group I+ is restricted to a non-phthalate catalyst system for olefin polymerization, comprising: (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, wherein the transition metal is titanium, a Group 2 metal, wherein the Group 2 metal is magnesium, and one halogen, wherein the halogen is chloride; and one internal electron donor compound having the structure of a diester compound having a formula (II), wherein each R5 is C1 hydrocarbyl; each of R6 and R7 is independently H; each R8 is independently absent; m is 0; (b) one external electron donor compound selected from a triester compound having a formula (V), wherein each R is C1 hydrocarbyl group, each R' is H, each n is 1; and n' is 0; and processes thereof. It is believed that claims 1-3, 11-13, and 31 read on this first named invention and thus these claims will be searched without fee to the extent that they read on the above embodiment.

Applicant is invited to elect additional formula(e) for each additional compound to be searched in a specific combination by paying an additional fee for each set of election. Each additional elected formula(e) requires the selection of a single definition for each compound variable. An exemplary election would be to a non-phthalate catalyst system for olefin polymerization, comprising: (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, wherein the transition metal is titanium, a Group 2 metal, wherein the Group 2 metal is magnesium, and one halogen, wherein the halogen is chloride; and one internal electron donor compound having the structure of a diester compound having a formula (II), wherein each R5 is C2 hydrocarbyl; each of R6 and R7 is independently H; each R8 is independently C18 hydrocarbyl group; m is 1; (b) one external electron donor compound selected from a triester compound having a formula (V), wherein each R is C1 hydrocarbyl group, each R' is H, each n is 1; and n' is 0; and processes thereof. Additional formula(e) will be searched upon the payment of additional fees. Applicants must specify the claims that read on any additional elected inventions. Applicants must further indicate, if applicable, the claims which read on the first named invention if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the "+" group(s) will result in only the first claimed invention to be searched/examined.

The inventions listed in Groups I+ do not relate to a single general inventive concept under PCT Rule 13.1, because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The Groups I+ formulae do not share a significant structural element requiring the selection of alternatives for the compound variables R5, R6, R7, R8, m, m', R17 R, R', n, n', and X.

The Groups I+ share the technical features of a non-phthalate catalyst system for olefin polymerization, comprising: (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, a Group 2 metal, and one or more halogens; one or more internal electron donor compounds having the structure of a diester compound having a formula (II) and a diester compound having the core structure of formula (IIe); (b) one or more external electron donor compound selected from the group consisting of: i) a triester compound having a formula (V); ii) a diester compound having a formula (VI); and iii) an oxo-substituted diester compound having a formula (VII); and a process for preparing a polyolefin, comprising: polymerizing one or more olefins, in the presence of the non-phthalate catalyst system, under reaction conditions sufficient to form the polyolefin. However, these shared technical features do not represent a contribution over the prior art.

Specifically, US 2005/0239636 A1 to Gao et al. teach a non-phthalate catalyst system for olefin polymerization (Abstract; Claim 1; Para. [0003]; Para. [0822], Comparative Example No. 2 does not use a phthalate in the catalyst system), comprising: (a) a solid Ziegler-Natta catalyst composition comprising a transition metal, a Group 2 metal, and one or more halogens (Claim 1; Para. [0010]); one or more internal electron donor compounds having the structure of a diester compound having a formula (II) wherein each R5 is independently C1 to C18 hydrocarbyl group which can optionally form one or more unsaturated monocyclic structures; each of R6 and R7 is independently H; each R8 is H; m is 1 (Claim 10, ..., 1,3-propylene-glycol dibenzoate...); (b) one or more external electron donor compound selected from the group consisting of: ii) a diester compound having a formula (VI) wherein: X is CH2, each R is independently a C1-C10 hydrocarbyl group; each R' is H; each n is 2 (Para. [0160], 1,3-pentanediol dipropionate); and a process for preparing a polyolefin (Claim 35; Para. [0019]), comprising: polymerizing one or more olefins (Claim 35; Para. [0019]), in the presence of the non-phthalate catalyst system, under reaction conditions sufficient to form the polyolefin (Claim 35; Para. [0019]).

Additionally, CA 2 947 095 A1 to China Petroleum and Chemical Company teach a non-phthalate catalyst system for olefin polymerization (Pg. 1, Lns. 15-20) a solid catalyst composition comprising a transition metal, a Group 2 metal, and one or more halogens (Claim 1) comprising one or more internal electron donor compounds having the structure of a diester compound having the core structure of formula (II) (Claim 1; Claim 9, 4-butyl-1,8-dibenzoyloxynaphthalene); (b) one or more external electron donor compound (Pg. 25, Lns. 17-28); and a process for preparing a polyolefin (Claim 18), comprising: polymerizing one or more olefins (Claim 18).

The inventions listed in Groups I+ therefore lack unity under Rule 13 because they do not share a same or corresponding special technical feature.