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(54) PROCATALYST COMPOSITION WITH ADAMANTANE AND METHOD

PROKATALYSATORZUSAMMENSETZUNG MIT ADAMANTAN UND VERFAHREN

COMPOSITION DE PROCATALYSEUR CONTENANT DE L'ADAMANTANE ET PROCÉDÉ

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Description**BACKGROUND**

5 [0001] The present disclosure relates to procatalyst compositions containing an adamantane-based compound and the incorporation of the same in catalyst compositions and the process of making olefin-based polymer using said catalyst compositions and the resultant olefin-based polymers produced therefrom.

10 [0002] Worldwide demand for olefin-based polymers continues to grow as applications for these polymers become more diverse and more sophisticated. Olefin-based polymers with broad molecular weight distribution (MWD), for example, find increasing applications in thermoforming; pipe-, foam-, blow-molding; and films. Known are Ziegler-Natta catalyst compositions for the production of olefin-based polymers, particularly propylene-based polymers, with broad MWD. Ziegler-Natta catalyst compositions typically include a procatalyst composed of a transition metal halide (i.e., titanium, chromium, vanadium) supported on a magnesium compound, the procatalyst complexed with a cocatalyst such as an organoaluminum compound. Production of olefin-based polymers with broad MWD produced by way of Ziegler-Natta catalysts, however, is typically limited to a single reactor process requiring rigorous process control and/or a series reactor process requiring multiple reactors.

15 [0003] Given the perennial emergence of new applications for olefin-based polymers, the art recognizes the need for olefin-based polymers with improved and varied properties. Desirable would a Ziegler-Natta catalyst composition that produces olefin-based polymer, and propylene-based polymer in particular, with broad molecular weight distribution (MWD) with less process constraints and less equipment.

SUMMARY

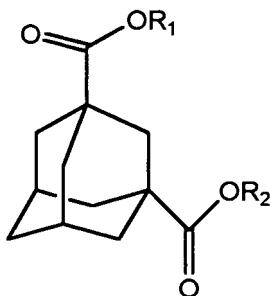
25 [0004] Procatalyst compositions containing an adamantane dicarboxylate as an internal electron donor and the application of the same in catalyst compositions and polymerization processes are described. The adamantane dicarboxylate catalyst compositions of the present disclosure produce propylene-based olefins with high isotacticity and broad molecular weight distribution.

30 [0005] A process for producing a procatalyst composition is described. The process includes reacting an adamantane dicarboxylate a procatalyst precursor, and a halogenating agent. The reaction occurs in a reaction mixture. The process includes forming a procatalyst composition by way of halogenation. The procatalyst composition includes an internal electron donor composed of an adamantanedicarboxylate.

35 [0006] A procatalyst composition is described. The procatalyst composition includes a combination of a magnesium moiety, a titanium moiety and an internal electron donor. The internal electron donor includes an adamantanedicarboxylate. The magnesium moiety and/or the titanium moiety may be a respective halide.

[0007] In an embodiment, the adamantanedicarboxylate has the structure (III):

(III)



50 wherein R₁-R₂ are the same or different. Each of R₁ and R₂ is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, and combinations thereof.

[0008] Another procatalyst composition is also described. In an embodiment, a procatalyst composition is provided which includes a combination of a magnesium moiety, a titanium moiety and a mixed internal electron donor. The mixed internal electron donor includes an adamantanedicarboxylate and an electron donor component.

55 [0009] In an embodiment, the electron donor component is selected from a benzoate, a phthalate, a diether, a silyl diol ester, a diol ester, a succinate, and combinations thereof.

[0010] The present invention relates to a catalyst composition comprising a combination of a magnesium moiety, a titanium moiety, and an internal electron donor comprising an adamantanedicarboxylate; and a cocatalyst. The catalyst

composition thus includes a procatalyst composition as described above and a cocatalyst. The procatalyst composition includes an adamantanedicarboxylate. In another embodiment, the catalyst composition of the invention can include a mixed internal electron donor. The mixed internal electron donor includes an adamantanedicarboxylate and an electron donor component as disclosed above.

5 [0011] In an embodiment, the catalyst composition includes an external electron donor, a mixed external electron donor and/or an activity limiting agent.

[0012] The present disclosure provides a process for producing an olefin-based polymer. In an embodiment, a process is provided which includes contacting, under polymerization conditions, an olefin with a catalyst composition. The catalyst composition includes an adamantanedicarboxylate. The process further includes forming an olefin-based polymer.

10 [0013] In an embodiment, the olefin is propylene. The process includes forming a propylene-based polymer having a polydispersity index from 5.0 to 15.0.

[0014] In an embodiment, the olefin is propylene. The process includes forming a propylene-based polymer having a melt flow rate from 0.01 g/10 min to 800 g/10 min.

15 [0015] The present disclosure provides another process for producing an olefin-based polymer. In an embodiment, a process for producing an olefin-based polymer is provided which includes contacting propylene with a catalyst composition comprising an adamantanedicarboxylate to form a propylene-based polymer. The contact between the propylene and the catalyst composition occurs in a first polymerization reaction under polymerization conditions. The process further includes contacting ethylene and optionally at least one other olefin in the presence of the propylene-based polymer. The contact between the ethylene, the olefin(s), and the propylene-based polymer occurs in a second polymerization reactor under polymerization conditions and forms a propylene impact copolymer.

20 [0016] An advantage of the present disclosure is the provision of an improved procatalyst composition.

[0017] An advantage of the present disclosure is the provision of an improved catalyst composition for the polymerization of olefin-based polymers.

25 [0018] An advantage of the present disclosure is a catalyst composition that produces a propylene-based polymer with broad molecular weight distribution.

[0019] An advantage of the present disclosure is a catalyst composition that produces a propylene-based polymer with broad molecular weight distribution in a single reactor.

[0020] An advantage of the present disclosure is a catalyst composition that produces a propylene-based polymer with broad molecular weight distribution in a single reactor without changing hydrogen concentration.

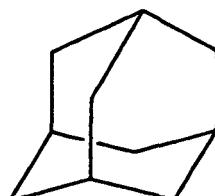
30 [0021] An advantage of the present disclosure is a catalyst composition that contains an adamantanedicarboxylate and produces a propylene-based olefin with high isotacticity and a broad molecular weight distribution.

DETAILED DESCRIPTION

35 [0022] In an embodiment, a process for producing a procatalyst composition is provided. The process includes reacting an adamantane-based compound, a procatalyst precursor, and a halogenating agent. The reaction occurs in a reaction mixture. The reaction results in the formation of a procatalyst composition. The procatalyst composition includes a magnesium moiety, a titanium moiety, and an internal electron donor. The internal electron donor includes an adamantanedicarboxylate.

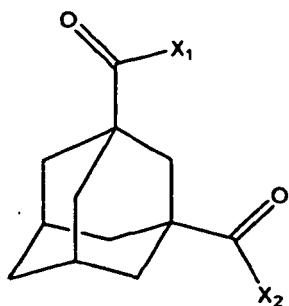
40 [0023] As used herein, an "adamantane-based compound" is a compound including the structure (I) below.

(I)



[0024] Adamantane is a polycyclic alkane with ten carbon atoms and four fused cyclohexane rings. In an embodiment, the adamantane-based compound is functionalized with two carbonyl groups and has the structure (II) below.

(II)

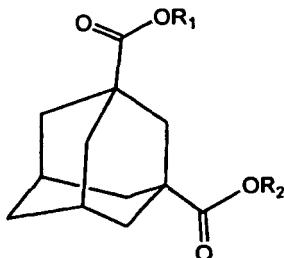


15 X_1 and X_2 may be the same or different. Each of X_1 and X_2 is selected from a halogen (F, Cl, Br, I) and an alkoxy group having 1-20 carbon atoms.

[0025] In an embodiment, the adamantine-based compound is a 1,3-adamantanedicarbonyl dihalide of structure (II). Each of X_1 and X_2 are the same or different, each of X_1 and X_2 including a halogen selected from F, Cl, Br, and I, and optionally a substituted or an unsubstituted hydrocarbyl group having 1-20 carbon atoms.

20 **[0026]** In an embodiment, the adamantine-based compound is a 1,3-adamantanedicarboxylate. The 1,3-adamantanedicarboxylate has the structure (III) below:

(III)



35 wherein R_1 - R_2 are the same or different, each of R_1 and R_2 is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, and combinations thereof.

[0027] As used herein, the term "hydrocarbyl" and "hydrocarbon" refer to substituents containing only hydrogen and carbon atoms, including branched or unbranched, saturated or unsaturated, cyclic, polycyclic, fused, or acyclic species, and combinations thereof. Nonlimiting examples of hydrocarbyl groups include alkyl-, cycloalkyl-, alkenyl-, alkadienyl-, cycloalkenyl-, cycloalkadienyl-, aryl-, aralkyl, alkylaryl, and alkynyl- groups.

40 **[0028]** As used herein, the terms "substituted hydrocarbyl" and "substituted hydrocarbon" refer to a hydrocarbyl group that is substituted with one or more nonhydrocarbyl substituent groups. A nonlimiting example of a nonhydrocarbyl substituent group is a heteroatom. As used herein, a "heteroatom" refers to an atom other than carbon or hydrogen. The heteroatom can be a non-carbon atom from Groups IV, V, VI, and VII of the Periodic Table. Nonlimiting examples of heteroatoms include: halogens (F, Cl, Br, I), N, O, P, B, S, and Si. A substituted hydrocarbyl group also includes a halohydrocarbyl group and a silicon-containing hydrocarbyl group. As used herein, the term "halohydrocarbyl" group refers to a hydrocarbyl group that is substituted with one or more halogen atoms.

[0029] In a further embodiment, at least one of the R_1 and R_2 is a primary alkyl group. As used herein, a "primary alkyl group" is an alkyl group with the α -carbon atom connected to no more than one other carbon atom. Nonlimiting examples of primary alkyl groups include a methyl group, an ethyl group, and an isobutyl group.

50 **[0030]** The procatalyst precursor can include (i) magnesium, (ii) a transition metal compound of an element from Periodic Table groups IV to VIII, (iii) a halide, an oxyhalide, and/or an alkoxide of (i) and/or (ii), and (iv) combinations of (i), (ii), and (iii). Nonlimiting examples of suitable procatalyst precursors include halides, oxyhalides, and alkoxides of magnesium, manganese, titanium, vanadium, chromium, molybdenum, zirconium, hafnium, and combinations thereof.

55 **[0031]** Various methods of making procatalyst precursors are known in the art. These methods are described, *inter alia*, in US-A-6,825,146; 5,034,361; 5,082,907; 5,151,399; 5,229,342; 5,106,806; 5,146,028; 5,066,737; 5,077,357; 4,442,276; 4,540,679; 4,547,476; 4,460,701; 4816,433; 4,829,037; 4,927,797; 4,990,479; 5,066,738; 5,028,671; 5,153,158; 5,247,031; 5,247,032, and elsewhere. In an embodiment, the preparation of the procatalyst precursor involves halogenation of mixed magnesium and titanium alkoxides, and may involve the use of one or more compounds, referred

to as "clipping agents", that aid in forming specific, low molecular weight, compositions of the desired morphology. Nonlimiting examples of suitable clipping agents include trialkylborates, especially triethylborate, phenolic compounds, especially cresol, and silanes.

[0032] In an embodiment, the procatalyst precursor is a magnesium moiety compound (MagMo), a mixed magnesium titanium compound (MagTi), or a benzoate-containing magnesium chloride compound (BenMag). In an embodiment, the procatalyst precursor is a magnesium moiety ("MagMo") precursor. The "MagMo precursor" contains magnesium as the sole metal component. The MagMo precursor includes a magnesium moiety. Nonlimiting examples of suitable magnesium moieties include anhydrous magnesium chloride and/or its alcohol adduct, magnesium alkoxide or aryloxide, mixed magnesium alkoxy halide, and/or carbonated magnesium dialkoxide or aryloxide. In one embodiment, the MagMo precursor is a magnesium di (C_{1-4})alkoxide. In a further embodiment, the MagMo precursor is diethoxymagnesium.

[0033] In an embodiment, the procatalyst precursor is a mixed magnesium/titanium compound ("MagTi"). The "MagTi precursor" has the formula $Mg_dTi(OR^e)_fX_g$ wherein R^e is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms or COR' wherein R' is an aliphatic or aromatic hydrocarbon radical having 1 to 14 carbon atoms; each OR^e group is the same or different; X is independently chlorine, bromine or iodine, preferably chlorine; d is 0.5 to 56, or 5 to 24; f is 2 to 116 or 5 to 15; and g is 0.5 to 116, or 1 to 3. The precursors are prepared by controlled precipitation through removal of an alcohol from the reaction mixture used in their preparation. In an embodiment, a reaction medium comprises a mixture of an aromatic liquid, especially a chlorinated aromatic compound, most especially chlorobenzene, with an alkanol, especially ethanol. Suitable halogenating agents include titanium tetrabromide, titanium tetrachloride or titanium trichloride, especially titanium tetrachloride. Removal of the alkanol from the solution used in the halogenation, results in precipitation of the solid precursor, having especially desirable morphology and surface area. Moreover, the resulting precursors are particularly uniform in particle size.

[0034] In an embodiment, the procatalyst precursor is a benzoate-containing magnesium chloride material ("BenMag"). As used herein, a "benzoate-containing magnesium chloride" ("BenMag") can be a procatalyst (*i.e.*, a halogenated procatalyst precursor) containing a benzoate internal electron donor. The BenMag material may also include a titanium moiety, such as a titanium halide. The benzoate internal donor is labile and can be replaced by other electron donors during procatalyst and/or catalyst synthesis. Nonlimiting examples of suitable benzoate groups include ethyl benzoate, methyl benzoate, ethyl p-methoxybenzoate, methyl p-ethoxybenzoate, ethyl p-ethoxybenzoate, ethyl p-chlorobenzoate. In one embodiment, the benzoate group is ethyl benzoate. Nonlimiting examples of suitable BenMag procatalyst precursors include catalysts of the trade names SHAC™ 103 and SHAC™ 310 available from The Dow Chemical Company, Midland, Michigan. In an embodiment, the BenMag procatalyst precursor may be a product of halogenation of any procatalyst precursor (*i.e.*, a MagMo precursor or a MagTi precursor) in the presence of a benzoate compound.

[0035] The present process includes reacting the adamantane-based compound, a procatalyst precursor, and a halogenating agent in the reaction mixture. The reaction forms a procatalyst composition. In other words, the process produces a reaction product of the procatalyst precursor the halogenating agent and the adamantane-based compound. The procatalyst composition includes a magnesium moiety, a titanium moiety and an internal electron donor. The internal electron donor is an adamantanedicarboxylate.

[0036] The reaction forms a procatalyst composition which includes an internal electron donor. As used herein, an "internal electron donor" is a compound added or otherwise formed during formation of the procatalyst composition that donates at least one pair of electrons to one or more metals present in the resultant procatalyst composition. Not bounded by any particular theory, it is believed that the internal electron donor assists in regulating the formation of active sites and thus enhances catalyst stereoselectivity. In an embodiment, the adamantane-based compound is the internal electron donor.

[0037] In an embodiment, the adamantane-based compound is a 1,3-adamantanedicarbonyl dihalide of structure (II). Upon reaction with the procatalyst precursor and the halogenation agent, the 1,3-adamantanebicarbonyl dihalide is converted into an alkyl ester (*i.e.*, an adamantanedicarboxylate) by reacting with an alkoxy group in the procatalyst precursor.

[0038] In an embodiment, the adamantane-based compound is a 1,3-adamantanedicarboxylate. Reaction of the 1,3-adamantanedicarboxylate with the procatalyst precursor and the halogenation agent forms a procatalyst composition with a magnesium moiety, a titanium moiety and an internal electron donor which includes the 1,3-adamantanedicarboxylate.

[0039] In an embodiment, the procatalyst precursor is converted to a solid procatalyst by way of halogenation and titanation. Halogenation and titanation include contacting the procatalyst precursor with a halogenating agent and a titanating agent in the presence of the internal electron donor. A "halogenating agent," as used herein, is a compound that converts catalyst precursor into a halide form. A "titanating agent," as used herein, is a compound that provides the catalytically active titanium species. Halogenation and titanation convert the magnesium moiety present in the procatalyst precursor into a magnesium halide support upon which the titanium moiety (such as a titanium halide) is deposited. Not wishing to be bound by any particular theory, it is believed that during halogenation and titanation the internal electron donor (1) regulates the position of titanium on the magnesium-based support, (2) facilitates conversion of the magnesium

and titanium moieties into respective halides and (3) regulates the crystallite size of the magnesium halide support during conversion. Thus, provision of the internal electron donor yields a procatalyst composition with enhanced stereoselectivity.

[0040] In an embodiment, the halogenating agent is a titanium halide having the formula $Ti(OR^e)_fX_h$ wherein R^e and X are defined as above, f is an integer from 0 to 3; h is an integer from 1 to 4; and $f + h$ is 4. In this way, the titanium halide is simultaneously the halogenating agent and the titanating agent. In an embodiment, the titanium halide is $TiCl_4$. In a further embodiment, the halogenation and the titanation are conducted in the presence of a chlorinated or a non-chlorinated aromatic liquid, such as dichlorobenzene, o-chlorotoluene, chlorobenzene, benzene, toluene, or xylene. In yet another embodiment, the halogenation and the titanation are conducted by use of a mixture of halogenating agent and chlorinated aromatic liquid comprising from 40 to 60 volume percent halogenating agent, such as $TiCl_4$.

[0041] In an embodiment, the reaction mixture is heated during halogenation. The procatalyst precursor and halogenating agent are contacted initially at a temperature from 0°C to 60°C, or from 20°C to 30°C, and heating is commenced at a rate of 0.1 to 10.0°C/minute, or at a rate of 1.0 to 5.0°C/minute. The adamantane-based compound may be added later, after an initial contact period between the halogenating agent and procatalyst precursor. Temperatures for the halogenation are from 60°C to 150°C (or any value or subrange therebetween), or from 90°C to 120°C. Halogenation may be continued in the substantial absence of the internal electron donor for a period from 5 to 60 minutes, or from 10 to 50 minutes.

[0042] The manner in which the procatalyst precursor, the halogenating agent and the adamantane-based compound are contacted may be varied. In an embodiment, the procatalyst precursor is first contacted with a mixture containing the halogenating agent and a chlorinated aromatic compound. The resulting mixture is stirred and may be heated if desired. Next, the adamantane-based compound is added to the same reaction mixture without isolating or recovering of the precursor. The foregoing process may be conducted in a single reactor with addition of the various ingredients controlled by automated process control.

[0043] In an embodiment, the procatalyst precursor is contacted with the adamantane-based compound before reacting with halogenating agents.

[0044] Contact times of the procatalyst precursor with the adamantane-based compound are at least 10 minutes, or at least 15 minutes, or at least 20 minutes, or at least 1 hour at a temperature from at least 25°C, or at least 50°C, or at least 60°C up to a temperature of 150°C, or up to 120 °C, or up to 115°C, or up to 110°C.

[0045] The halogenation procedure may be repeated one, two, three, or more times as desired. In an embodiment, the resulting solid material is recovered from the reaction mixture and contacted one or more times in the absence (or in the presence) of the same (or different) internal electron donor components with a mixture of the halogenating agent in the chlorinated aromatic compound for at least 10 minutes, or at least 15 minutes, or at least 20 minutes, and up to 1 hour, or up to 45 minutes, or up to 30 minutes, at a temperature from at least 25°C, or at least 50°C, or at least 60°C, to a temperature up to 150°C, or up to 120°C, or up to 115°C.

[0046] After the foregoing halogenation procedure, the resulting solid procatalyst composition is separated from the reaction medium employed in the final process, by filtering for example, to produce a moist filter cake. The moist filter cake may then be rinsed or washed with a liquid diluent to remove unreacted $TiCl_4$ and may be dried to remove residual liquid, if desired. Typically the resultant solid procatalyst composition is washed one or more times with a "wash liquid," which is a liquid hydrocarbon such as an aliphatic hydrocarbon such as isopentane, isoctane, isohexane, hexane, pentane, or octane. The solid procatalyst composition then can be separated and dried or slurried in a hydrocarbon, especially a relatively heavy hydrocarbon such as mineral oil for further storage or use.

[0047] In an embodiment, the resulting solid procatalyst composition has a titanium content of from 1.0 percent by weight to 6.0 percent by weight, based on the total solids weight, or from 1.5 percent by weight to 5.5 percent by weight, or from 2.0 percent by weight to 5.0 percent by weight. The weight ratio of titanium to magnesium in the solid procatalyst composition is suitably between 1:3 and 1:160, or between 1:4 and 1:50, or between 1:6 and 1:30. In an embodiment, the internal electron donor may be present in the procatalyst composition in a molar ratio of internal electron donor to magnesium of from 0.005:1 to 1:1, or from 0.01:1 to 0.4:1. Weight percent is based on the total weight of the procatalyst composition.

[0048] In an embodiment, the procatalyst composition may be further treated by one or more of the following procedures prior to or after isolation of the solid procatalyst composition. The solid procatalyst composition may be contacted (halogenated) with a further quantity of titanium halide compound, if desired; it may be exchanged under metathesis conditions with an acid chloride, such as phthaloyl dichloride or benzoyl chloride; and it may be rinsed or washed, heat treated; or aged. The foregoing additional procedures may be combined in any order or employed separately, or not at all.

[0049] Not wishing to be bound by any particular theory, it is believed that (1) further halogenation by contacting the previously formed procatalyst composition with a titanium halide compound, especially a solution thereof in a halohydrocarbon diluent, and/or (2) further washing the previously formed procatalyst composition with a halohydrocarbon at an elevated temperature (100°C - 150°C), results in desirable modification of the procatalyst composition, possibly by removal of certain inactive metal compounds that are soluble in the foregoing diluent. Accordingly, in an embodiment, the procatalyst is contacted with a halogenating agent, such as a mixture of a titanium halide and a halohydrocarbon

diluent, such as $TiCl_4$ and chlorobenzene, one or more times prior to isolation or recovery. In another embodiment, the procatalyst is washed at a temperature between 100°C to 150°C with chlorobenzene or o-chlorotoluene one or more times prior to isolation or recovery.

[0050] The present process for producing a procatalyst composition may comprise two or more embodiments disclosed herein.

[0051] In an embodiment, a procatalyst composition is provided which includes a combination of a magnesium moiety, a titanium moiety and an internal electron donor. The internal electron donor includes an adamantanedicarboxylate. The procatalyst composition is produced by way of the foregoing halogenation procedure which converts the procatalyst precursor and the adamantane-based compound into the combination of the magnesium and titanium moieties, into which the internal electron donor is incorporated. The procatalyst precursor from which the procatalyst composition is formed can be the magnesium moiety precursor, the mixed magnesium/titanium precursor, or the benzoate-containing magnesium chloride precursor.

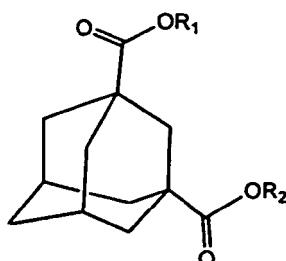
[0052] In an embodiment, the magnesium moiety is a magnesium halide. In another embodiment, the magnesium halide is magnesium chloride.

[0053] In an embodiment, the titanium moiety is a titanium halide such as a titanium chloride. In another embodiment the titanium moiety is titanium tetrachloride.

[0054] In another embodiment, the procatalyst composition includes a magnesium chloride support upon which a titanium chloride is deposited and into which the internal electron donor is incorporated.

[0055] In an embodiment, the internal electron donor of the procatalyst composition includes a 1,3-adamantanedicarboxylate of structure (III):

(III)



wherein R_1 - R_2 are the same or different. Each of R_1 and R_2 is selected from a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, and combinations thereof.

[0056] In an embodiment, at least one of R_1 and R_2 is a primary alkyl group. In another embodiment, each of R_1 and R_2 is a primary alkyl group.

[0057] In an embodiment, R_1 and R_2 are the same or different and each is selected from a C_1 - C_6 alkyl group. Nonlimiting examples of suitable C_1 - C_6 alkyl groups include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, a n-butyl group, an isobutyl group, a sec-butyl group, a pentyl group, a n-hexyl group, and combinations thereof.

[0058] In an embodiment, each of R_1 and R_2 is the same C_1 - C_6 alkyl group. Nonlimiting examples of suitable C_1 - C_6 alkyl groups are the same as the C_1 - C_6 alkyl groups disclosed above. In particular, each of R_1 and R_2 simultaneously can be: a methyl group, an ethyl group, an n-propyl group, an isopropyl group, a n-butyl group, an isobutyl group, a sec-butyl group, a pentyl group, or a hexyl group.

[0059] In an embodiment, R_1 and/or R_2 is a cyclic structure. The cyclic structure may or may not be aromatic. In an embodiment, the cyclic structure is a C_5 membered ring or a C_6 membered ring. In a further embodiment, the cyclic structure is a phenyl group.

[0060] In an embodiment, structure (III) includes R_1 that is a methyl group and R_2 is a methyl group.

[0061] In an embodiment, structure (III) includes R_1 that is an ethyl group and R_2 is an ethyl group.

[0062] In an embodiment, structure (III) includes R_1 that is an n-propyl group and R_2 is an n-propyl group.

[0063] In an embodiment, structure (III) includes R_1 that is an iso-propyl group and R_2 is an iso-propyl group.

[0064] In an embodiment, structure (III) includes R_1 that is an iso-butyl group and R_2 is an iso-butyl group.

[0065] In an embodiment, structure (III) includes R_1 that is a hexyl group and R_2 is a hexyl group.

[0066] In an embodiment, structure (III) includes R_1 that is a cyclohexyl group and R_2 is a cyclohexyl group.

[0067] In an embodiment, structure (III) includes R_1 that is a phenyl group and R_2 is a phenyl group.

[0068] Ethoxide content in the procatalyst composition indicates the completeness of conversion of precursor metal ethoxide into a metal halide. The present internal electron donor assists in converting ethoxide into halide during halogenation. In an embodiment, the procatalyst composition includes from 0.01 wt % to 1.0 wt %, or from 0.05 wt % to 0.5

wt % ethoxide. Weight percent is based on the total weight of the procatalyst composition.

[0069] In an embodiment, the procatalyst composition includes from 0.1 wt % to 20.0 wt %, or from 1.0 wt % to 15.0 wt % adamantanedicarboxylate. Weight percent is based on the total weight of the procatalyst composition.

[0070] In an embodiment, the procatalyst composition includes from 1.0 wt % to 6.0 wt %, or from 1.5 wt % to 5.5 wt % titanium. Weight percent is based on the total weight of the procatalyst composition.

[0071] In an embodiment, the magnesium to internal electron donor molar ratio is from 200:1 to 1:1, or from 100:1 to 2:1, or from 30:1 to 2.5:1, or from 20:1 to 3:1.

[0072] In an embodiment, another procatalyst composition is provided. The procatalyst composition includes a combination of a magnesium moiety, a titanium moiety and a mixed internal electron donor. As used herein, a "mixed internal electron donor" is (i) an adamantanedicarboxylate, (ii) an electron donor component that donates a pair of electrons to one or more metals present in the resultant procatalyst composition, and (iii) optionally other components. In an embodiment, the electron donor component is a benzoate, a phthalate, a diether, a silyl diol ester, a diol ester, a succinate, and combinations thereof. The procatalyst composition with the mixed internal electron donor can be produced by way of the procatalyst production procedure as previously disclosed.

[0073] The benzoate may be any benzoate as disclosed previously. The diether, the diol ester and/or the succinate may be any respective diether/diol ester/succinate as disclosed with respect to the activity limiting agent discussed below. The silyl diol ester may be any silyl diol ester as disclosed in U.S. Patent Application Serial No. 61/117820 filed on November 25, 2008 (Attorney Docket No. 67098).

[0074] The present procatalyst composition may comprise two or more embodiments disclosed herein.

[0075] In an embodiment, a catalyst composition is provided. As used herein, "a catalyst composition" is a composition that forms an olefin-based polymer when contacted with an olefin under polymerization conditions. The catalyst composition includes a procatalyst composition and a cocatalyst. The procatalyst composition can be any of the foregoing procatalyst compositions containing an adamantanedicarboxylate. The catalyst composition may optionally include an external electron donor and/or an activity limiting agent.

[0076] In an embodiment, the internal electron donor of the catalyst composition is an adamantanedicarboxylate. The adamantanedicarboxylate can be any adamantanedicarboxylate as disclosed herein. In a further embodiment, the adamantanedicarboxylate is a 1,3-adamantanedicarboxylate of structure (III).

[0077] In an embodiment, the internal electron donor of the catalyst composition is a mixed internal electron donor as disclosed above.

[0078] The catalyst composition includes a cocatalyst. As used herein, a "cocatalyst" is a substance capable of converting the procatalyst to an active polymerization catalyst. The cocatalyst may include hydrides, alkyls, or aryls of aluminum, lithium, zinc, tin, cadmium, beryllium, magnesium, and combinations thereof. In an embodiment, the cocatalyst is a hydrocarbyl aluminum cocatalyst represented by the formula R_3Al wherein each R is an alkyl, cycloalkyl, aryl, or hydride radical; at least one R is a hydrocarbyl radical; two or three R radicals can be joined in a cyclic radical forming a heterocyclic structure; each R can be the same or different; and each R, which is a hydrocarbyl radical, has 1 to 20 carbon atoms, or 1 to 10 carbon atoms. In a further embodiment, each alkyl radical can be straight or branched chain and such hydrocarbyl radical can be a mixed radical, *i.e.*, the radical can contain alkyl, aryl, and/or cycloalkyl groups. Nonlimiting examples of suitable radicals are: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, neopentyl, n-hexyl, 2-methylpentyl, n-heptyl, n-octyl, isoctyl, 2-ethylhexyl, 5,5-dimethylhexyl, n-nonyl, n-decyl, isodecyl, n-undecyl, n-dodecyl.

[0079] Nonlimiting examples of suitable hydrocarbyl aluminum compounds are as follows: triisobutylaluminum, tri-n-hexylaluminum, diisobutylaluminum hydride, di-n-hexylaluminum hydride, isobutylaluminum dihydride, n-hexylaluminum dihydride, diisobutylhexylaluminum, isobutylidihexylaluminum, trimethylaluminum, triethylaluminum, tri-n-propylaluminum, triisopropylaluminum, tri-n-butylaluminum, tri-n-octylaluminum, tri-n-decylaluminum, tri-n-dodecylaluminum. In an embodiment, the cocatalyst is selected from triethylaluminum, triisobutylaluminum, tri-n-hexylaluminum, diisobutylaluminum hydride, and di-n-hexylaluminum hydride.

[0080] In an embodiment, the cocatalyst is a hydrocarbyl aluminum compound represented by the formula R_nAlX_{3-n} wherein n = 1 or 2, R is an alkyl, and X is a halide or alkoxide. Nonlimiting examples of suitable compounds are as follows: methylaluminoxane, isobutylaluminoxane, diethylaluminum ethoxide, diisobutylaluminum chloride, tetraethylidialuminoxane, tetraisobutylidialuminoxane, diethylaluminum chloride, ethylaluminum dichloride, methylaluminum dichloride, and dimethylaluminum chloride.

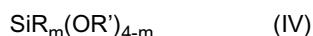
[0081] In an embodiment, the cocatalyst is triethylaluminum. The molar ratio of aluminum to titanium is from 5:1 to 500:1, or from 10:1 to 200:1, or from 15:1 to 150:1, or from 20:1 to 100:1. In another embodiment, the molar ratio of aluminum to titanium is about 45:1.

[0082] In an embodiment, the present catalyst composition includes an external electron donor. As used herein, an "external electron donor" (or "EED") is a compound added independent of procatalyst formation and includes at least one functional group that is capable of donating a pair of electrons to a metal atom. A "mixed external electron donor" (or "MEED") is a mixture of two or more external electron donors. Bounded by no particular theory, it is believed that

provision of one or more external electron donors in the catalyst composition affects the following properties of the formant polymer: level of tacticity (*i.e.*, xylene soluble material), molecular weight (*i.e.*, melt flow), molecular weight distribution (MWD), melting point, and/or oligomer level.

[0083] In an embodiment, the external electron donor may be selected from one or more of the following: a silicon compound, an amine, an ether, a carboxylate, a ketone, an amide, a carbamate, a phosphine, a phosphate, a phosphite, a sulfonate, a sulfone, and/or a sulfoxide. Nonlimiting examples of suitable compounds for the EED include silicon compounds, such as alkoxy silanes; ethers and polyethers, such as alkyl-, cycloalkyl-, aryl-, mixed alkylaryl-, mixed alkyl/cycloalkyl-, and/or mixed cycloalkyl/aryl-ethers and/or polyethers; esters and polyesters, especially alkyl, cycloalkyl- and/or aryl-esters of monocarboxylic or dicarboxylic acids, such as aromatic monocarboxylic- or dicarboxylic- acids; alkyl- or cycloalkyl-ether or thioether derivatives of such esters or polyesters, such as alkyl ether derivatives of alkyl esters or diesters of aromatic monocarboxylic or dicarboxylic acids; and Group 15 or 16 heteroatom-substituted derivatives of all of the foregoing; and amine compounds, such as cyclic, aliphatic or aromatic amines, more especially pyrrol or pyridine compounds; all of the foregoing EED's containing from 2 to 60 carbons total and from 1 to 20 carbons in any alkyl or alkylene group, 3 to 20 carbons in any cycloalkyl or cycloalkylene group, and 6 to 20 carbons in any aryl or arylene group.

[0084] In an embodiment, the EED may be a silicon compound having the general formula (IV):



wherein R independently each occurrence is hydrogen or a hydrocarbyl or an amino group, optionally substituted with one or more substituents containing one or more Group 14, 15, 16, or 17 heteroatoms. R contains up to 20 atoms not counting hydrogen and halogen. R¹ is a C₁₋₂₀ alkyl group, and m is 0, 1, or 2. In an embodiment, R is C₆₋₁₂ aryl, alkyl or aralkyl, C₃₋₁₂ cycloallyl, C₃₋₁₂ branched alkyl, or C₃₋₁₂ cyclic amino group, R' is C₁₋₄ alkyl, and m is 1 or 2.

[0085] In an embodiment, the EED includes a silicon compound selected from one or more of the following: a dimethoxysilane; a dimethoxysilane having at least one secondary alkyl and/or a secondary amino group directly bonded to the silicon atom; a dimethoxysilane containing two linear alkyl groups; a dimethoxysilane containing two alkenyl groups or hydrogen, wherein one or more hydrogen atoms may be substituted by a halogen; a dimethoxysilane containing two alkenyl groups, a diether, and/or a dialkoxybenzene; a trimethoxysilane; a diethoxysilane; a triethoxysilane; a tetraethoxysilane; and any combination thereof.

[0086] Nonlimiting examples of suitable silicon compounds for the EED include dicyclopentyldimethoxysilane, di-tert-butylidimethoxysilane, methylcyclohexyldimethoxysilane, ethylcyclohexyldimethoxysilane, diphenyldimethoxysilane, diisopropyldimethoxysilane, diisobutylidethoxysilane, isobutylisopropyldimethoxysilane, di-n-butylidimethoxysilane, cyclopentyltrimethoxysilane, isopropyltrimethoxysilane, n-propyltrimethoxysilane, n-propyltriethoxysilane, ethyltriethoxysilane, diethylaminotriethoxysilane, isopropylisobutylidimethoxysilane, diisobutylidimethoxysilane, t-butylisopropyldimethoxysilane, cyclopentylpyrrolidinodimethoxysilane, bis(pyrrolidino)dimethoxysilane, bis(perhydroisoquinolino)dimethoxysilane, dimethylidimethoxysilane, vinylmethylidimethoxysilane, n-octylmethylidimethoxysilane, n-octadecylmethylidimethoxysilane, methylidimethoxysilane, 3-chloropropylmethylidimethoxysilane, 2-chloroethylmethylidimethoxysilane, allyldimethoxysilane, (3,3,3-trifluoropropyl)methylidimethoxysilane, n-propylmethylidimethoxysilane, chlororriethylmethylidimethoxysilane, di-n-octyldimethoxysilane, vinyl(chloromethyl)dimethoxysilane, methylcyclohexyldiethoxysilane, vinylmethylidethoxysilane, 1-(triethoxysilyl)-2-(diethoxymethylsilyl)ethane, n-octylmethylidethoxysilane, octaethoxy-1,3,5-trisilapentane, n-octadecylmethylidethoxysilane, methacryloxypropylmethylidethoxysilane, 2-hydroxy-4-(3-methyldiethoxysilylpropoxy)diphenylketone, (3-glycidoxypropyl)methylidethoxysilane, dodecylmethylidethoxysilane, dimethylidethoxysilane, diethylidethoxysilane, 1,1-diethoxy-1-silacyclopent-3-ene, chloromethylmethylidethoxysilane, bis(methylidethoxysilylpropyl)amine, 3-aminopropylmethylidethoxysilane, (methacryloxyethyl)methylidethoxysilane, 1,2-bis(methylidethoxysilyl)ethane, vinyltrimethoxysilane, vinyltriethoxysilane, benzyltriethoxysilane, butenyltriethoxysilane, (triethoxysilyl)cyclohexane, O-(vinyloxybutyl)-N-triethoxysilylpropylcarbamate, 10-undecenyltrimethoxysilane, n-(3-trimethoxysilylpropyl)pyrrole, N-[5-(trimethoxysilyl)-2-aza-1-oxopentyl]caprolactam, (3,3,3-trifluoropropyl)trimethoxysilane, triethoxysilylundecanal ethylene glycol acetal, (S)-N-triethoxysilylpropyl-O-menthocabamate, triethoxysilylpropyl-ethylcarbamate, N-(3-triethoxysilylpropyl)-4,5-dihydroimidazole, (3-triethoxysilylpropyl)-t-butylcarbamate, styrelethyltriethoxysilane, 2-(4-pyridylethyl)triethoxysilane, (S)-N-1-phenylethyl-N'-triethoxysilylpropylurea, (R)-N-1-phenylethyl-N'-triethoxysilylpropylurea, N-phenylaminopropyltrimethoxysilane, N-phenylaminomethyltriethoxysilane, phenethyltrimethoxysilane, pentyltriethoxysilane, n-octyltrimethoxysilane, n-octyltriethoxysilane, 7-octenyltrimethoxysilane, S-(octanoyl)mercaptopropyltriethoxysilane, n-octadecyltrimethoxysilane, n-octadecyltriethoxysilane, methyltrimethoxysilane, methyltriethoxysilane, N-methylaminopropyltrimethoxysilane, 3-methoxypropyltrimethoxysilane, methacryloxypropyltriethoxysilane, methacryloxypropyltriethoxysilane, methacryloxyethyltrimethoxysilane, methacryloxyethyltrimethoxysilane, and O-(methacryloxyethyl)-N-(triethoxysilylpropyl)carbamate, tetramethoxysilane, tetraethoxysilane, methylcyclohexyldiethoxysilane, di-isobutylidethoxysilane, tetraethoxysilane, benzyltriethoxysilane, but-3-enyltriethoxysilane, 1-(triethoxysilyl)-2-pentene, (triethoxysilyl)cyclohexane, and any combination of the foregoing.

[0087] In an embodiment, the EED may be a diether, a dimer of a diether, a dialkoxybenzene, a dimer of a dialkoxybenzene, a dialkoxybenzene linked by a linear hydrocarbon group, and any combination thereof. It is noted that the diethers for the ALA set forth below apply equally as nonlimiting examples for the EED diether.

[0088] In an embodiment, the external electron donor can be a mixture of at least 2 silicon compounds (i.e., a MEED).

5 In a further embodiment, the mixture can be dicyclopentyldimethoxysilane and methylcyclohexyldimethoxysilane, dicyclopentyldimethoxysilane and tetraethoxysilane, or dicyclopentyldimethoxysilane and n-propyltriethoxysilane.

[0089] In an embodiment, the EED includes dicyclopentyldimethoxysilane.

[0090] In an embodiment, the external electron donor is selected from one or more of the following: a benzoate, a succinate, and/or a diol ester.

10 [0091] In an embodiment, the external electron donor includes 2,2,6,6-tetramethylpiperidine.

[0092] It is understood that the EED may comprise any of the foregoing EED compounds. It is further understood that the EED may be a MEED which may comprise two or more of any of the foregoing EED compounds.

15 [0093] In an embodiment, the catalyst composition includes an activity limiting agent (ALA). As used herein, an "activity limiting agent" ("ALA") is a material that reduces catalyst activity at elevated temperature (i.e., temperature greater than 85°C). An ALA inhibits or otherwise prevents polymerization reactor upset and ensures continuity of the polymerization process. Typically, the activity of Ziegler-Natta catalysts increases as the reactor temperature rises. Ziegler-Natta catalysts also typically maintain high activity near the melting point temperature of the polymer produced. The heat generated by the exothermic polymerization reaction may cause polymer particles to form agglomerates and may ultimately lead to disruption of continuity for the polymer production process. The ALA reduces catalyst activity at elevated temperature, thereby preventing reactor upset, reducing (or preventing) particle agglomeration, and ensuring continuity of the polymerization process.

20 [0094] The ALA may or may not be a component of the EED and/or the MEED. The activity limiting agent may be a carboxylic acid ester, a diether, a poly(alkene glycol), a diol ester, and combinations thereof. The carboxylic acid ester can be an aliphatic or aromatic, mono- or poly-carboxylic acid ester. Nonlimiting examples of suitable monocarboxylic acid esters include ethyl and methyl benzoate, ethyl p-methoxybenzoate, methyl p-ethoxybenzoate, ethyl acrylate, methyl methacrylate, ethyl acetate, ethyl p-chlorobenzoate, hexyl p-aminobenzoate, isopropyl naphthenate, n-amyl toluate, ethyl cyclohexanoate and propyl pivalate.

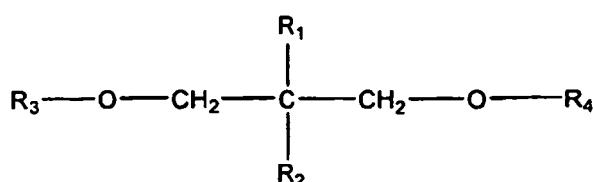
25 [0095] Nonlimiting examples of suitable polycarboxylic acid esters include dimethyl phthalate, diethyl phthalate, di-n-propyl phthalate, diisopropyl phthalate, di-n-butyl phthalate, diisobutyl phthalate, di-tert-butyl phthalate, diisoamyl phthalate, di-tert-amyl phthalate, dineopentyl phthalate, di-2-ethylhexyl phthalate, di-2-ethyldecyl phthalate, diethyl terephthalate, dioctyl terephthalate, and bis[4-(vinyloxy)butyl]terephthalate.

30 [0096] The aliphatic carboxylic acid ester may be a C₄-C₃₀ aliphatic acid ester, may be a mono- or a poly- (two or more) ester, may be straight chain or branched, may be saturated or unsaturated, and any combination thereof. The C₄-C₃₀ aliphatic acid ester may also be substituted with one or more Group 14, 15 or 16 heteroatom containing substituents. Nonlimiting examples of suitable C₄-C₃₀ aliphatic acid esters include C₁₋₂₀ alkyl esters of aliphatic C₄₋₃₀ monocarboxylic acids, C₁₋₂₀ alkyl esters of aliphatic C₈₋₂₀ monocarboxylic acids, C₁₋₄ allyl mono- and diesters of aliphatic C₄₋₂₀ monocarboxylic acids and dicarboxylic acids, C₁₋₄ alkyl esters of aliphatic C₈₋₂₀ monocarboxylic acids and dicarboxylic acids, and C₄₋₂₀ mono- or polycarboxylate derivatives of C₂₋₁₀₀ (poly)glycols or C₂₋₁₀₀ (poly)glycol ethers. In a further embodiment, the C₄-C₃₀ aliphatic acid ester may be a myristate, a sebacate, (poly)(alkylene glycol) mono- or diacetates, (poly)(alkylene glycol) mono- or di-myristates, (poly)(alkylene glycol) mono- or di-lauroates, (poly)(alkylene glycol) mono- or di-oleates, glyceryl tri(acetate), glyceryl tri-ester of C₂₋₄₀ aliphatic carboxylic acids, and mixtures thereof. In a further embodiment, the C₄-C₃₀ aliphatic ester is isopropyl myristate or di-n-butyl sebacate.

40 [0097] In an embodiment, the activity limiting agent includes a diether. The diether can be a 1,3-diether compound represented by the following structure (V):

45

(V)

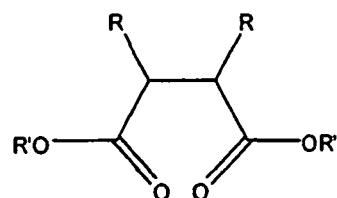


55 wherein R₁ to R₄ are independently of one another an alkyl, aryl or aralkyl group having up to 20 carbon atoms, which may optionally contain a group 14, 15, 16, or 17 heteroatom, and R₁ and R₂ may be a hydrogen atom. The diether may be linear or branched, and may include one or more of the following groups: alkyl, cycloaliphatic, aryl, alkylaryl or arylalkyl radicals with 1-18 carbon atoms, and hydrogen. R₁ and R₂ may be linked to form a cyclic structure, such as cyclo-

tadiene or fluorene.

[0098] In an embodiment, the activity limiting agent includes a succinate composition having the following structure (VI):

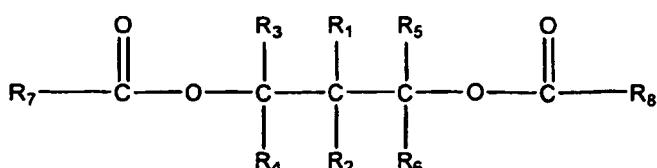
5 (VI)



wherein R and R' may be the same or different, R and/or R' including one or more of the following groups: hydrogen, linear or branched alkyl, alkenyl, cycloalkyl, aryl, arylalkyl or alkylaryl group, optionally containing heteroatoms. One or more ring structures can be formed via one or both 2- and 3-position carbon atom.

[0099] In an embodiment, the activity limiting agent includes a diol ester as represented by the following structure (VII):

20 (VII)



R₁ and R₂, may be the same or different, and each may be selected from hydrogen, methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, t-butyl, allyl, phenyl, or halophenyl group. R₃, R₄, R₅, R₆, R₇, and R₈, may be the same or different, and each may be selected from halogen, substituted, or unsubstituted hydrocarbyl having 1 to 20 carbon atoms. R₅, R₆, R₇, and R₈ may also be hydrogen. R₁-R₆ groups may optionally contain one or more heteroatoms replacing carbon, hydrogen or both, the hetero-atom selected from nitrogen, oxygen, sulfur, silicon, phosphorus and a halogen. R₇ and R₈, may be the same or different, and may be an aliphatic hydrocarbyl group or an aromatic hydrocarbyl group.

[0100] In an embodiment, the external electron donor and/or activity limiting agent can be added into the reactor separately. In another embodiment, the external electron donor and the activity limiting agent can be mixed together in advance and then added to the catalyst composition and/or into the reactor as a mixture. In the mixture, more than one external electron donor or more than one activity limiting agent can be used. In an embodiment, the mixture is dicyclopentyldimethoxysilane and isopropyl myristate, dicyclopentyldimethoxysilane and poly(ethylene glycol) laurate, dicyclopentyldimethoxysilane and isopropyl myristate and poly(ethylene glycol) dioleate, methylcyclohexyldimethoxysilane and isopropyl myristate, n-propyltrimethoxysilane and isopropyl myristate, dimethyldimethoxysilane and methylcyclohexyldimethoxysilane and isopropyl myristate, dicyclopentyldimethoxysilane and n-propyltriethoxysilane and isopropyl myristate, and dicyclopentyldimethoxysilane and tetraethoxysilane and isopropyl myristate, and combinations thereof.

[0101] In an embodiment, the catalyst composition includes any of the foregoing external electron donors in combination with any of the foregoing activity limiting agents.

[0102] The present catalyst composition may comprise two or more embodiments disclosed herein.

[0103] In an embodiment, a process for producing an olefin-based polymer is provided. The process includes contacting an olefin with a catalyst composition under polymerization conditions. The catalyst composition includes an adamantanedicarboxylate. The adamantanedicarboxylate can be any adamantanedicarboxylate as disclosed herein such as a 1,3-adamantanedicarboxylate of structure (III). The process further includes forming an olefin-based polymer.

[0104] In an embodiment, the catalyst composition includes a procatalyst composition and a cocatalyst. The procatalyst composition may be any procatalyst composition as disclosed herein. The procatalyst composition may include an adamantanedicarboxylate as the internal electron donor or a mixed internal electron donor as disclosed herein. The cocatalyst may be any cocatalyst as disclosed herein. The catalyst composition may optionally include an external electron donor and/or an activity limiting agent as previously disclosed.

[0105] In an embodiment, the olefin-based polymer can be a propylene-based olefin, an ethylene-based olefin, and combinations thereof. In an embodiment, the olefin-based polymer is a propylene-based polymer.

[0106] One or more olefin monomers can be introduced into a polymerization reactor to react with the catalyst and to form a polymer, or a fluidized bed of polymer particles. Nonlimiting examples of suitable olefin monomers include ethylene, propylene, C₄₋₂₀ α-olefins, such as 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-decene,

1-dodecene and the like; C₄₋₂₀ diolefins, such as 1,3-butadiene, 1,3-pentadiene, norbornadiene, 5-ethylidene-2-norbornene (ENB) and dicyclopentadiene; C₈₋₄₀ vinyl aromatic compounds including styrene, o-, m-, and p-methylstyrene, divinylbenzene, vinylbiphenyl, vinylnaphthalene; and halogen-substituted C₈₋₄₀ vinyl aromatic compounds such as chlorostyrene and fluorostyrene.

5 [0107] As used herein, "polymerization conditions" are temperature and pressure parameters within a polymerization reactor suitable for promoting polymerization between the catalyst composition and an olefin to form the desired polymer. The polymerization process may be a gas phase, a slurry, or a bulk polymerization process, operating in one, or more than one, polymerization reactor. Accordingly, the polymerization reactor may be a gas phase polymerization reactor, a liquid-phase polymerization reactor, or a combination thereof.

10 [0108] It is understood that provision of hydrogen in the polymerization reactor is a component of the polymerization conditions. During polymerization, hydrogen is a chain transfer agent and affects the molecular weight (and correspondingly the melt flow rate) of the resultant polymer.

15 [0109] In an embodiment, polymerization occurs by way of gas phase polymerization. As used herein, "gas phase polymerization" is the passage of an ascending fluidizing medium, the fluidizing medium containing one or more monomers, in the presence of a catalyst through a fluidized bed of polymer particles maintained in a fluidized state by the fluidizing medium. "Fluidization," "fluidized," or "fluidizing" is a gas-solid contacting process in which a bed of finely divided polymer particles is lifted and agitated by a rising stream of gas. Fluidization occurs in a bed of particulates when an upward flow of fluid through the interstices of the bed of particles attains a pressure differential and frictional resistance increment exceeding particulate weight. Thus, a "fluidized bed" is a plurality of polymer particles suspended in a fluidized state by a stream of a fluidizing medium. A "fluidizing medium" is one or more olefin gases, optionally a carrier gas (such as H₂ or N₂) and optionally a liquid (such as a hydrocarbon) which ascends through the gas-phase reactor.

20 [0110] A typical gas-phase polymerization reactor (or gas phase reactor) includes a vessel (*i.e.*, the reactor), the fluidized bed, a distribution plate, inlet and outlet piping, a compressor, a cycle gas cooler or heat exchanger, and a product discharge system. The vessel includes a reaction zone and a velocity reduction zone, each of which is located above the distribution plate. The bed is located in the reaction zone. In an embodiment, the fluidizing medium includes propylene gas and at least one other gas such as an olefin and/or a carrier gas such as hydrogen or nitrogen.

25 [0111] In an embodiment, the contacting occurs by way of feeding the catalyst composition into a polymerization reactor and introducing the olefin into the polymerization reactor. In an embodiment, the cocatalyst can be mixed with the procatalyst composition (pre-mix) prior to the introduction of the procatalyst composition into the polymerization reactor. In another embodiment, cocatalyst is added to the polymerization reactor independently of the procatalyst composition. The independent introduction of the cocatalyst into the polymerization reactor can occur simultaneously, or substantially simultaneously, with the procatalyst composition feed.

30 [0112] In an embodiment, the polymerization process may include a pre-polymerization step. Pre-polymerization includes contacting a small amount of the olefin with the procatalyst composition after the procatalyst composition has been contacted with the co-catalyst and the selectivity determining agent and/or the activity limiting agent. 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, and optionally one or more of the external electron donor components. Pre-polymerization results in the procatalyst composition being combined with the cocatalyst and the selectivity determining agent and/or the activity limiting agent, the combination being dispersed in a matrix of the formant polymer. Optionally, additional quantities of the selectivity determining agent and/or the activity limiting agent may be added.

35 [0113] In an embodiment, the polymerization process may include a pre-activation step. Pre-activation includes contacting the procatalyst composition with the co-catalyst and the selectivity determining agent and/or the activity limiting agent. The resulting preactivated catalyst stream is subsequently introduced into the polymerization reaction zone and contacted with the olefin monomer to be polymerized, and optionally one or more of the external electron donor components. Pre-activation results in the procatalyst composition being combined with the cocatalyst and the selectivity determining agent and/or the activity limiting agent. Optionally, additional quantities of the selectivity determining agent and/or the activity limiting agent may be added.

40 [0114] In an embodiment, the process includes mixing the external electron donor (and optionally the activity limiting agent) with the procatalyst composition. The external electron donor can be complexed with the cocatalyst and mixed with the procatalyst composition (pre-mix) prior to contact between the catalyst composition and the olefin. In another embodiment, the external electron donor and/or the activity limiting agent can be added independently to the polymerization reactor. In an embodiment, the external electron donor is dicyclopentylmethoxysilane or n-propyltrimethoxysilane.

45 [0115] In another embodiment, the catalyst composition includes dicyclopentylmethoxysilane and/or n-propyltrimethoxysilane and an activity limiting agent such as isopropyl myristate.

50 [0116] In an embodiment, the olefin is propylene. The process includes forming a propylene-based polymer having a melt flow rate (MFR) from 0.01 g/10 min to 800 g/10 min, or from 0.1 g/10 min to 200 g/10 min, or from 0.5 g/10 min to 150 g/10 min. In a further embodiment, the propylene-based polymer is a polypropylene homopolymer.

[0117] In an embodiment, the olefin is propylene. The process includes forming a propylene-based polymer having a xylene solubles content from 0.5% to 10%, or from 1% to 8%, or from 1% to 4%. In a further embodiment, the propylene-based polymer is a polypropylene homopolymer.

5 [0118] In an embodiment, the olefin is propylene. The process includes forming a propylene-based polymer having a polydispersity index (PDI) from 5.0 to 15.0, or from 6.0 to 15, or from 6.5 to 10, or from 7.0 to 9.0. In a further embodiment, the propylene-based polymer is a propylene homopolymer.

10 [0119] The present disclosure provides another process for producing an olefin-based polymer. In an embodiment, a process for producing an olefin-based polymer is provided which includes contacting propylene with a catalyst composition comprising an adamantanedicarboxylate to form a propylene-based polymer. The contact between the propylene and the catalyst composition occurs in a first polymerization reaction under polymerization conditions. The process further includes contacting ethylene and optionally at least one other olefin in the presence of the propylene-based polymer. The contact between the ethylene, the olefin(s), and the propylene-based polymer occurs in a second polymerization reactor under polymerization conditions and forms a propylene impact copolymer.

15 [0120] In an embodiment, the first reactor and the second reactor operate in series whereby the effluent of the first reactor (*i.e.*, the propylene-based polymer) is charged to the second reactor. Additional olefin monomer is added to the second polymerization reactor to continue polymerization. Additional catalyst composition (and/or any combination of individual catalyst components-*i.e.*, procatalyst, cocatalyst, EED, ALA) may be added to the second polymerization reactor. The additional catalyst composition/components added to the second reactor may be the same or different than the catalyst composition/components introduced in the first reactor.

20 [0121] In an embodiment, the propylene-based polymer produced in the first reactor is a propylene homopolymer. The propylene homopolymer is charged to the second reactor where ethylene and propylene are contacted with each other in the presence of the propylene homopolymer. This forms a propylene impact copolymer having a propylene homopolymer continuous (or matrix) phase and a discontinuous phase (or rubber phase) selected from a propylene-based copolymer (*i.e.*, a propylene/ethylene copolymer) or an ethylene-based copolymer (*i.e.*, an ethylene/propylene copolymer). The discontinuous phase is dispersed in the continuous phase.

[0122] The propylene impact copolymer may have an Fc value from 1 wt % to 50 wt %, or from 10 wt % to 40 wt %, or from 20 wt % to 30 wt %. As used herein, "fraction copolymer" ("Fc") is the weight percent of the discontinuous phase present in the heterophasic copolymer. The Fc value is based on the total weight of the propylene impact copolymer.

30 [0123] The propylene impact copolymer may have an Ec value from 1 wt % to 100 wt %, or from 20 wt % to 90 wt %, or from 30 wt % to 80 wt %, or from 40 wt % to 60 wt %. As used herein, "ethylene content" ("Ec") is the weight percent of ethylene present in the discontinuous phase of the propylene impact copolymer. The Ec value is based on the total weight of the discontinuous (or rubber) phase.

35 [0124] Not wishing to be bound by any particular theory, it is believed that the present catalyst compositions with adamantanedicarboxylate internal electron donor yield olefin-based polymers with a broad molecular weight distribution and high stereoselectivity.

[0125] The present processes for production olefin-based polymer may comprise two or more embodiments disclosed herein.

DEFINITIONS

40 [0126] All references to the Periodic Table of the Elements herein shall refer to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2003. Also, any references to a Group or Groups shall be to the Groups or Groups reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. Unless stated to the contrary, implicit from the context, or customary in the art, all parts and percents are based on weight.

45 [0127] The term "comprising," and derivatives thereof, is not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound whether polymeric or otherwise, unless stated to the contrary. In contrast, the term, "consisting essentially of" excludes from the scope of any succeeding recitation any other component, step or procedure, excepting those that are not essential to operability. The term "consisting of" excludes any component, step or procedure not specifically delineated or listed. The term "or", unless stated otherwise, refers to the listed members individually as well as in any combination.

55 [0128] Any numerical range recited herein, includes all values from the lower value to the upper value, in increments of one unit, provided that there is a separation of at least 2 units between any lower value and any higher value. As an example, if it is stated that the amount of a component, or a value of a compositional or a physical property, such as, for example, amount of a blend component, softening temperature, melt index, etc., is between 1 and 100, it is intended that all individual values, such as, 1, 2, 3, etc., and all subranges, such as, 1 to 20, 55 to 70, 197 to 100, etc., are expressly enumerated in this specification. For values which are less than one, one unit is considered to be 0.0001, 0.001, 0.01 or 0.1, as appropriate. These are only examples of what is specifically intended, and all possible combinations of numerical

values between the lowest value and the highest value enumerated, are to be considered to be expressly stated in this application. In other words, any numerical range recited herein includes any value or subrange within the stated range. Numerical ranges have been recited, as discussed herein, reference melt index, melt flow rate, and other properties.

[0129] The terms "blend" or "polymer blend," as used herein, is a blend of two or more polymers. Such a blend may or may not be miscible (not phase separated at molecular level). Such a blend may or may not be phase separated. Such a blend may or may not contain one or more domain configurations, as determined from transmission electron spectroscopy, light scattering, x-ray scattering, and other methods known in the art.

[0130] The term "composition," as used herein, includes a mixture of materials which comprise the composition, as well as reaction products and decomposition products formed from the materials of the composition.

[0131] The term "polymer" is a macromolecular compound prepared by polymerizing monomers of the same or different type. "Polymer" includes homopolymers, copolymers, terpolymers, interpolymers, and so on. The term "interpolymer" means a polymer prepared by the polymerization of at least two types of monomers or comonomers. It includes, but is not limited to, copolymers (which usually refers to polymers prepared from two different types of monomers or comonomers, terpolymers (which usually refers to polymers prepared from three different types of monomers or comonomers), tetrapolymers (which usually refers to polymers prepared from four different types of monomers or comonomers), and the like.

[0132] The term "interpolymer," as used herein, refers to polymers prepared by the polymerization of at least two different types of monomers. The generic term interpolymer thus includes copolymers, usually employed to refer to polymers prepared from two different monomers, and polymers prepared from more than two different types of monomers.

[0133] The term "olefin-based polymer" is a polymer containing, in polymerized form, a majority weight percent of an olefin, for example ethylene or propylene, based on the total weight of the polymer. Nonlimiting examples of olefin-based polymers include ethylene-based polymers and propylene-based polymers.

[0134] The term, "ethylene-based polymer," as used herein, refers to a polymer that comprises a majority weight percent polymerized ethylene monomer (based on the total weight of polymerizable monomers), and optionally may comprise at least one polymerized comonomer.

[0135] The term, "ethylene/α-olefin interpolymer," as used herein, refers to an interpolymer that comprises a majority weight percent polymerized ethylene monomer (based on the total amount of polymerizable monomers), and at least one polymerized α-olefin.

[0136] The term, "propylene-based polymer," as used herein, refers to a polymer that comprises a majority weight percent polymerized propylene monomer (based on the total amount of polymerizable monomers), and optionally may comprise at least one polymerized comonomer.

[0137] The term "alkyl," as used herein, refers to a branched or unbranched, saturated or unsaturated acyclic hydrocarbon radical. Nonlimiting examples of suitable alkyl radicals include, for example, methyl, ethyl, n-propyl, i-propyl, 2-propenyl (or allyl), vinyl, n-butyl, t-butyl, i-butyl (or 2-methylpropyl), etc. The alkyls have 1 to 20 carbon atoms.

[0138] The term "substituted alkyl," as used herein, refers to an alkyl as just described in which one or more hydrogen atom bound to any carbon of the alkyl is replaced by another group such as a halogen, aryl, substituted aryl, cycloalkyl, substituted cycloalkyl, heterocycloalkyl, substituted heterocycloalkyl, halogen, haloalkyl, hydroxy, amino, phosphido, alkoxy, amino, thio, nitro, and combinations thereof. Suitable substituted alkyls include, for example, benzyl and trifluoromethyl.

[0139] The term "aryl," as used herein, refers to an aromatic substituent which may be a single aromatic ring or multiple aromatic rings which are fused together, linked covalently, or linked to a common group such as a methylene or ethylene moiety. The aromatic ring(s) may include phenyl, naphthyl, anthracenyl, and biphenyl, among others. The aryls have 1 and 20 carbon atoms.

45 TEST METHODS

[0140] Melt flow rate is measured in accordance with ASTM D 1238-01 test method at 230°C with a 2.16 kg weight for propylene-based polymers.

[0141] Xylene Solubles (XS) is the weight percent of resin that stays in the solution after the resin is dissolved in hot xylene and the solution is allowed to cool to 230°C. XS is measured using a ¹H NMR method as described in U.S. Patent No. 5,539,309.

[0142] Polydispersity Index (PDI) is measured by an AR-G2 rheometer which is a stress control dynamic spectrometer manufactured by TA Instruments using a method according to Zeichner GR, Patel PD (1981) "A comprehensive Study of Polypropylene Melt Rheology" Proc. of the 2nd World Congress of Chemical Eng., Montreal, Canada. An ETC oven is used to control the temperature at 180°C ± 0.1°C. Nitrogen is used to purge the inside the oven to keep the sample from degradation by oxygen and moisture. A pair of 25mm in diameter cone and plate sample holder is used. Samples are compress molded into 50mm x 100mm x 2mm plaque. Samples are then cut into 19mm square and loaded on the center of the bottom plate. The geometries of upper cone is (1) Cone angle: 5:42:20 (deg:min:sec); (2) Diameter: 25

mm; (3) Truncation gap: 149 μm (micron). The geometry of the bottom plate is 25mm cylmder.

Testing procedure:

5 [0143]

- (1) The cone & plate sample holder are heated in the ETC oven at 180°C for 2 hours. Then the gap is zeroed under blanket of nitrogen gas.
- (2) Cone is raised to 2.5mm and sample loaded unto the top of the bottom plate.
- 10 (3) Start timing for 2 minutes.
- (4) The upper cone is immediately lowered to slightly rest on top of the sample by observing the normal force.
- (5) After two minutes the sample is squeezed down to 165 μm (micron) gap by lower the upper cone.
- (6) The normal force is observed. When the normal force is down to <0.05 Newton the excess sample is removed from the edge of the cone and plate sample holder by a spatula.
- 15 (7) The upper cone is lowered again to the truncation gap which is 14 μm (micron).
- (8) An Oscillatory Frequency Sweep test is performed under these conditions:
 - (i) Test delayed at 180°C for 5 minutes.
 - (ii) Frequencies: 628.3r/s to 0.1 r/s.
 - 20 (iii) Data acquisition rate: 5 point/decade.
 - (iv) Strain: 10%
- (9) When the test is completed the crossover modulus (G_c) is detected by the Rheology Advantage Data Analysis program furnished by TA Instruments.
- 25 (10) $\text{PDI} = 100,000 \div G_c$ (in Pa units).

30 [0144] Final melting point (T_{MF}) is the temperature to melt the most perfect crystal in the sample and is regarded as a measure for isotacticity and inherent polymer crystallizability. The test is conducted using a TA Q100 Differential Scanning Calorimeter. A sample is heated from 0°C to 240°C at a rate of 80°C/min, cooled at the same rate to 0°C, then heated again at the same rate up to 150°C, held at 150°C for 5 minutes and the heated from 150°C to 180°C at 1.25 °C/min. The T_{MF} is determined from this last cycle by calculating the onset of the baseline at the end of the heating curve.

Testing procedure:

35 [0145]

- (1) Calibrate instrument with high purity indium as standard.
- (2) Purge the instrument head/cell with a constant 50 ml/min flow rate of nitrogen constantly.
- 40 (3) Sample preparation:

Compression mold 1.5 g of powder sample using a 30-G302H-18-CX Wabash Compression Molder 30,481.5 kg (30 ton): (a) heat mixture at 230 °C for 2 minutes at contact; (b) compress the sample at the same temperature with 20,321 kg (20 ton) pressure for 1 minute; (c) cool the sample to 72 °C (45°F) and hold for 2 minutes with 20,321 kg (20 ton) pressure; (d) cut the plaque into 4 of about the same size, stack them together, and repeat steps (a) - (c) in order to homogenize sample.
- 45 (4) Weigh a piece of sample (preferably between 5 to 8 mg) from the sample plaque and seal it in a standard aluminum sample pan. Place the sealed pan containing the sample on the sample side of the instrument head/cell and place an empty sealed pan in the reference side. If using the auto sampler, weigh out several different sample specimens and set up the machine for a sequence.
- 50 (5) Measurements:
 - (i) Data storage: off
 - (ii) Ramp 80.00 °C/min to 240.00 °C
 - 55 (iii) Isothermal for 1.00 min
 - (iv) Ramp 80.00 °C/min to 0.00 °C
 - (v) Isothermal for 1.00 min
 - (vi) Ramp 80.00 °C/min to 150.00 °C

(vii) Isothermal for 5.00 min
 (viii) Data storage: on
 (ix) Ramp 1.25 °C/min to 180.00 °C
 (x) End of method

5

(6) Calculation: T_{MF} is determined by the interception of two lines. Draw one line from the base-line of high temperature. Draw another line from through the deflection of the curve close to the end of the curve at high temperature side.

10 [0146] By way of example and not by limitation, examples of the present disclosure will now be provided.

EXAMPLES

1. Synthesis of Internal Electron Donor

15 [0147] Diisobutyl phthalate (DIBP) and dimethyl adamantanedicarboxylate (DMADC) are purchased from Aldrich and used without further purification.

20 [0148] Diethyl 1,3-adamantanedicarboxylate, diisobutyl 1,3-adamantanedicarboxylate, and di-n-butyl, 1,3-adamantanedicarboxylate are prepared by way of the following procedure. A 250 mL round bottom flask is charged with 1,3-adamantanedicarboxylic acid (10.0 g, 44.0 mmol), and anhydrous acetonitrile (50 ml). To this stirred solution is added a solution of alkyl iodide (88.0 mmol) in acetonitrile (20 ml) and a solution of 1,8-diazabicyclo[5.4.0]undec-7-ene (13.6 g, 88.0 mmol) in acetonitrile (20 ml) simultaneously. The mixture is stirred overnight. After the solvent is evaporated with a rotorvap, the residue is dissolved in ether (100 ml). The ether solution is washed with water, and dried with $MgSO_4$. After filtration, the filtrate is concentrated, and the residue is distilled *in vacuo* to yield the product as a colorless oil.

25 [0149] 1H NMR data is obtained on a Brüker 500 MHz NMR spectrometer using $CDCl_3$ as solvent (in ppm).

A. **2007-148 (Diethyl 1,3-adamantanedicarboxylate):** Yield 10.9 g (88.0 %). 1H NMR: δ 4.13 (q, 4H, J = 6.8 Hz), 2.14-2.19 (m, 2H), 2.03 (s, 2H), 1.82-1.92 (m, 8H), 1.68-1.71 (m, 2H), 1.21 (t, 6H, J = 6.8 Hz).

B. **2008-LC-032 (Diisobutyl 1,3-adamantanedicarboxylate):** Yield 5.3 g (35.8%). 1H NMR: δ 3.85 (d, 4H, J = 6.3 Hz), 2.13-2.19 (m, 2H), 2.05 (d, 2H, J = 8.9 Hz), 1.84-1.98 (m, 10H), 1.68-1.70 (m, 2H), 0.93 (d, 12H, J = 6.3 Hz).

30 C. **2008-LC-033 (Di-n-butyl 1,3-adamantanedicarboxylate):** Yield 9.7 g (65.5%). 1H NMR: δ 4.06 (t, 4H, J = 6.6 Hz), 2.12-2.16 (m, 2H), 2.02 (s, 2H), 1.82-1.90 (m, 8H), 1.68 (m, 2H), 1.57-1.63 (m, 4H), 1.35-1.41 (m, 4H), 0.93 (t, 6H, J = 7.4 Hz).

35 [0150] 2. Diisopropyl 1,3-adamantanedicarboxylate is prepared by way of the following procedure. A 50 mL round bottom flask equipped with magnetic stir bar is charged with 1,3-adamantanedicarboxylic acid (2.76 g, 12.3 mmol), 2-iodopropane (3.07 mL, 30.8 mmol) and 1,8-diazabicycloundec-7-ene (4.60 mL, 30.8 mmol) in 25 mL acetonitrile. The mixture is heated to reflux overnight and cooled to room temperature. The reaction is diluted with 100 mL of ethyl acetate and washed with saturated $NH_4Cl/1N HCl$, water, saturated sodium bicarbonate, and then brine. The organic layer is dried over sodium sulfate. After filtration, the filtrate is concentrated, and the residue is dried *in vacuo*. The crude product is further purified by distillation in *vacuo* to yield the product as a white liquid.

40 [0151] **2008-LC-176 (Diisopropyl 1,3-adamantanedicarboxylate):** 1H -NMR: 4.98 (sep, 2H), 2.12 (s, 2H), 1.97 (s, 2H), 1.82 ((t, 9H), 1.70 (s, 1H), 1.20 (d, 12H).

45 [0152] 3. Di-n-propyl 1,3-adamantanedicarboxylate is prepared by way of the following procedure. A 50 mL round bottom flask equipped with a magnetic stir bar is charged with 1,3-adamantanedicarboxylic acid (3.36 g, 15.0 mmol), 1-bromopropane (3.28 mL, 36.0 mmol) and 1,8-diazabicycloundec-7-ene (5.38 mL, 36.0 mmol) in 25 mL acetonitrile. The mixture is heated to reflux overnight and cooled to room temperature. The reaction is diluted with 100 mL of ethyl acetate and washed with saturated $NH_4Cl/1N HCl$, water, saturated sodium bicarbonate, and then brine. The organic layer is dried over sodium sulfate. After filtration, the filtrate is concentrated, and the residue is dried *in vacuo*. The crude product is further purified by distillation in *vacuo* to yield the product as a white liquid.

50 [0153] **2008-LC-177 (Di-n-propyl 1,3-adamantanedicarboxylate):** 1H -NMR: 3.99 (t, 4H), 2.12 (s, 2H), 2.10 (s, 2H), 1.83 ((t, 8H), 1.56~1.70 (m, 6H), 0.90 (s, 6H).

55 [0154] 4. Dicyclohexyl 1,3-adamantanedicarboxylate is prepared by way of the following procedure. (A) A 100 mL round bottom flask equipped with a magnetic stir bar is charged with 1,3-adamantanedicarboxylic acid (10.0 g, 44.6 mmol) and thionyl chloride (14.5 mL, 0.20 mole). The mixture is refluxed under nitrogen for 4 hrs and cooled to room temperature. Excess thionyl chloride is removed under vacuum and the solid chloride is used for the next step without further purification. (B) A 50 mL round bottom flask equipped with magnetic stir bar is charged with cyclohexanol (4.0 g, 40.0 mmol), pyridine (3.24 mL, 40.0 mmol) in 50 mL of methylene chloride. The flask is cooled to 0°C in ice-water bath, and 1,3-adamantanedicarboxyl chloride (5.22 g, 20.0 mmol) in 10 mL of methylene chloride is added dropwise. The reaction mixture is

stirred overnight at room temperature. The solvent is removed under vacuum and the residue is dissolved in 60 ml of ether and filtered to remove solid. The filtrate is concentrated and purified with flash column chromatography to give a pure product.

[0155] **2008-LC-178 (Dicyclohexyl 1,3-adamantanedicarboxyate):** $^1\text{H-NMR}$: 4.76 (p, 2H), 2.12 (s, 2H), 1.99 (s, 2H), 1.83 (t, 8H), 1.66~1.76 (m, 10H), 1.27~1.51 (m, 12H).

[0156] 5. Di-n-hexyl 1,3-adamantanedicarboxylate is prepared by way of the following procedure: (A) A 100 mL round bottom flask equipped with a magnetic stir bar is charged with 1,3-adamantanedicarboxylic acid (10.0 g, 44.6 mmol) and thionyl chloride (14.5 mL, 0.20 mole). The mixture is refluxed under nitrogen for 4 hrs and cooled to room temperature. Excess thionyl chloride is removed under vacuum and the solid chloride is used for the next step without further purification. (B) A 50 mL round bottom flask equipped with magnetic stirrer is charged with 1-octanol (5.2 g, 40.0 mmol), pyridine (3.24 mL, 40.0 mmol) in 50 mL of methylene chloride. The flask is cooled to 0°C in ice-water bath, and 1,3-adamantanedicarboxyl chloride (5.22 g, 20.0 mmol) in 10 mL of methylene chloride is added dropwise. The reaction mixture is stirred overnight at room temperature. The solvent is removed under vacuum and the residue is dissolved in 60 ml of ether, and filtered to remove solid. The filtrate is concentrated and purified with flash column chromatography to give pure product.

[0157] **2008-LC-180 (Di-n-hexyl 1,3-adamantanedicarboxylate):** $^1\text{H-NMR}$: 4.05 (t, 4H), 2.15 (s, 2H), 2.02 (s, 2H), 1.86 (t, 8H), 1.68 (s, 2H), 1.60 (m, 4H), 1.28 (m, 20H), 0.88 (t, 6H).

2. Catalyst Preparation

[0158] A procatalyst precursor is charged, according to the weight shown in Table 1, into a flask equipped with mechanical stirring and with bottom filtration. 60 ml of a mixed solvent of TiCl_4 and chlorobenzene (1/1 by volume) is introduced into the flask and then 2.52 mmol of internal electron donor is added. The mixture is heated to 115°C and remains at the same temperature for 60 minutes with stirring at 250 rpm before filtering off the liquid. 60 ml of mixed solvent is added again and the reaction is allowed to continue at the same desired temperature for 60 minutes with stirring followed by filtration. This process is repeated once. 70 ml of iso-octane is used to wash the resultant solid at ambient temperature. After the solvent is removed by filtration, the solid is dried by N_2 flow. For the catalysts made via double IED additions, the second amount of 2.52 mmol of internal electron donor is added after the addition of mixed solvent in the 2nd TiCl_4 -contacting step.

Table 1

Procatalyst Precursor	Weight
MagTi-1	3.0g
SHAC™ 310	2.0g

[0159] MagTi-1 is a mixed Mag/Ti precursor with composition of $\text{Mg}_3\text{Ti}(\text{OEt})_8\text{Cl}_2$ (a MagTi precursor prepared according to example 1 in U.S. Patent No. 6,825,146) with an average particle size of 50 μm (micron). SHAC™ 310 is a benzoate-containing catalyst (a BenMag procatalyst precursor with an average particle size of 27 μm (micron) with ethyl benzoate as the internal electron donor made according to Example 2 in U.S. Patent No. 6,825,146. Catalyst compositions are listed in Tables 2-3.

3. Polymerization

[0160] Polymerization is performed in liquid propylene in a 1-gallon autoclave. After conditioning, the reactors are charged with 1375 g of propylene and a targeted amount of hydrogen and brought to 62°C. The external electron donor component(s) is added to a 0.27-M triethylaluminum solution in isoctane, followed by addition of a 5.0 wt% catalyst slurry in mineral oil (as indicated in data tables below). The mixture is premixed at ambient temperature for 20 minutes before being injected into the reactor to initiate the polymerization. The premixed catalyst components are flushed into the reactor with isoctane using a high pressure catalyst injection pump. After the exotherm, the temperature is controlled to 67°C. Total polymerization time is 1 hour.

[0161] Catalyst composition and catalyst performance data is provided in Tables 2 and 3 below.

Table 2

Composition of Procatalyst Containing 1,3-Adamantanedicarboxylate as Internal Electron Donors							
	Donor Structure	Procatalyst Preparation Condition	Pro-catalyst Number	Ti (%)	OEt (%)	EB (%)	ED (%)
5		DiBP/MagTi	*1	4.58	0.27		14.67
10		DMADC/MagTi	2-A	2.83	0.50		11.19
15		DMADC/SHACT™ 310	2-B	5.15	0.18	1.56	19.90
20		2007-148 x1/MagTi	3-A	2.12	0.32		13.93
25		2007-148 x2/MagTi	3-B	3.66	0.24		25.35
30		2008-LC-177/MagTi	4-A	3.74	0.25		21.05
35		2008-LC-177/SHAC™ 310	4-B	2.76	0.07	0.67	13.85
40		2008-LC-033 x1/MagTi	5	2.90	0.34		24.16
45		2008-LC-032 x1/MagTi	6-A	3.24	0.11		18.41
50		2008-LC-032 x2/MagTi	6-B	4.59	0.28		10.96
55		2008-LC-180/MagTi	7-A	2.65	0.50		30.35
60		2008-LC-180/ SHAC™ 310	7-B	2.34	0.29	ND	33.22

* For comparison

EB = ethyl benzoate

IED = internal electron donor

ND = Not detected

OEt = ethoxide

x1 = single addition of IED

x2 = double addition of IED

Table 3
Performance of Catalysts Containing 1,3-Adamantanedicarboxylate as Internal Electron Donors

Pro-catalyst Number	EED	Pro-catalyst (mg)	EED (mmol)	Al/EED (mol/mol)	H ₂ (sec)	Catalyst Activity (kg/g-hr)	BD (g/cc)	MF (min/10 g)	Xs (%)	PDI	Tmf (°C)
*1	N	15.7	0.25	8.00	1000	24.9	0.36	0.9	3.1	3.72	169.39
	D	15.7	0.25	8.00	1500	25.0	0.39	3.0	4.6	4.73	171.06
2-A	N	14.9	0.25	8.00	1000	3.5	0.37	1.9	5.4	7.99	170.41
	D	14.9	0.25	8.00	1500	4.4	0.39	2.2	5.8	9.31	171.16
2-B	N	16.2	0.25	8.00	1000	8.3	0.37	2.5	7.6		
	D	16.2	0.25	8.00	1500	9.7	0.37	2.1	7.7		
3-A	N	16.6	0.25	6.84	1000	2.5					
	D	16.6	0.25	6.84	1500	4.3		3.2	4.4	6.97	171.38
3-B	N	16.6	0.25	6.84	1000	2.3					
	D	16.6	0.25	6.84	1500	3.9		2.6	4.1	7.66	171.66
4-A	N	13.5	0.25	8.00	1000	5.2	0.27	3.7	4.6	6.31	169.83
	D	13.5	0.25	8.00	1500	6.2	0.24	3.2	4.5	7.91	170.74
4-B	N	16.2	0.25	8.00	1000	13.4	0.37	1.9	6.6	5.95	170.15
	D	16.2	0.25	8.00	1500	18.3	0.37	1.4	6.9	8.08	171.21
5	N	15.2	0.25	8.00	1000	8.4	0.36	2.6	5.9	6.67	170.18
	D	15.2	0.25	8.00	1500	11.0	0.37	1.7	6.5	9.09	171.18
6-A	N	15.6	0.25	8.00	1000	6.5	0.34	2.4	5.5	6.71	170.27
	D	15.6	0.25	8.00	1500	10.0	0.35	1.9	5.9	8.83	171.02
6-B	N	14.7	0.25	8.00	1000	5.4	0.33	1.6	5.9	8.45	170.32
	D	14.7	0.25	8.00	1500	7.1	0.38	1.7	6.5	9.71	171.18
7-A	N	15.7	0.25	8.00	1000	8.6	0.39	11.1	7.4	5.91	169.53
	D	15.7	0.25	8.00	1500	12.3	0.40	10.4	6.1	7.99	170.68

(continued)

Performance of Catalysts Containing 1,3-Adamandanedicarboxylate as Internal Electron Donors

Pro-catalyst Number	EED	Pro-catalyst (mg)	EED (mmol)	AI/EED (mol/mol)	H ₂ (sec)	Catalyst Activity (kg/g-hr)	BD (g/cc)	MF (min/10 g)	XS (%)	PDI	Tmf (°C)
7-B	N	16.2	0.25	8.00	1000	9.7	0.39	2.3	6.9	6.66	169.99
	D	16.2	0.25	8.00	1500	12.2	0.40	1.9	5.5	8.98	170.90

* For comparison
 BD = bulk density
 D = dicyclopentylmethoxysilane
 EED = external electron donor
 N = n-propyltrimethoxysilane

[0162] Surprisingly, the PDI (a measurement of MWD) for the propylene homopolymers produced with the adamantanedicarboxylate-containing catalysts is greater than the PDI of propylene homopolymer produced with conventional catalyst containing DiBP as internal electron donor (Procatalyst 1). The PDI for propylene homopolymer produced with a procatalyst having a primary alkyl adamantadicarboxylate ester is substantially higher. The H₂ response for the present adamantane carboxylate containing catalysts is similar or better than the H₂ response for the catalyst containing procatalyst 1. T_{MF}, an indicator of polymer isotacticity, for the adamantanedicarboxylate-containing catalysts is also comparable to those for SHAC™ 320 at similar XS using the same EED.

[0163] In some embodiments, SHAC™ 310 is also used as a precursor in place of MagTi. This change increases catalyst activity for the esters of the short chain alcohols while moderately elevating XS. The broadening effect on PDI is similar to the double donor addition.

[0164] The binding mode of the adamantanedicarboxylates is different than other bidentate ligands, such as DiBP. In the DiBP molecule, the distance between 2 possible coordinating O atoms is about 0.25 nm (2.5 Å) which is different than the distance between coordinating O atoms in the rigid adamantanedicarboxylate molecule, (about 0.49 nm (4.9 Å)), which is greater than the distance between 2 adjacent Mg atoms on a MgCl₂ crystallite.

[0165] The catalyst compositions of Tables 2 and 3 produce propylene homopolymer with a high PDI when compared to a propylene homopolymer produced with a conventional Ziegler-Natta catalyst composition including DiBP internal donor and similar external donor under similar polymerization conditions.

[0166] Tables 2 and 3 show the increase in PDI resulting from the present catalyst compositions. Catalyst compositions containing adamantanedicarboxylate may produce propylene homopolymer with a PDI greater than 5.0, or greater than 6.0, or greater than 7.0, or greater than 8.0, or greater than 9.0, with low xylene solubles content. On the other hand, conventional catalyst composition with DiBP as the internal electron donor (and similar EED and polymerization conditions) produces a propylene homopolymer with a PDI from about 3.5 to less than 5.0.

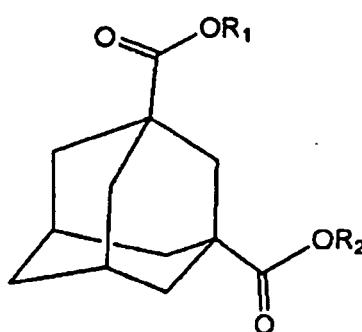
25 Claims

1. A catalyst composition comprising:

30 a combination of a magnesium moiety, a titanium moiety, and an internal electron donor comprising an adamantanedicarboxylate; and a cocatalyst

2. The catalyst composition of claim 1 wherein the adamantanedicarboxylate has the structure (III):

35 (III)



50 wherein R₁-R₂ are the same or different, each of R₁ and R₂ is selected from the group consisting of a substituted hydrocarbyl group having 1 to 20 carbon atoms, an unsubstituted hydrocarbyl group having 1 to 20 carbon atoms, and combinations thereof.

55 3. The catalyst composition of claim 2 wherein at least one of R₁ and R₂ is a primary alkyl group.

4. The catalyst composition of any of claims 2-3 wherein R₁ and R₂ are the same or different and each is selected from the group consisting of a C₁-C₆ alkyl group.

5. The catalyst composition of any of claims 2-4 wherein R₁ and R₂ are the same or different and each is selected from the group consisting of a methyl group, an ethyl group, a n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a pentyl group, a n-hexyl group, and combinations thereof.

5 6. The catalyst composition of claim 1 wherein the internal electron donor comprises an electron donor component selected from the group consisting of a benzoate, a phthalate, a diether, a diol ester, a silyl diol ester, a succinate, and combinations thereof.

10 7. The catalyst composition of claim 1 comprising a member selected from the group consisting of an external electron donor, a mixed external electron donor, an activity limiting agent, and combinations thereof.

15 8. The catalyst composition of claim 7 wherein the external electron donor comprises an alkoxy silane.

9. The catalyst composition of claim 8 comprising an activity limiting agent selected from the group consisting of a carboxylic acid ester, a diether, a poly(alkene glycol), a diol ester, and combinations thereof.

10. A process for producing an olefin-based polymer comprising:

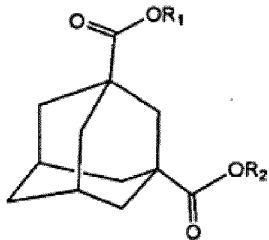
20 contacting, under polymerization conditions, an olefin with a catalyst composition comprising an adamantane-dicarboxylate; and forming an olefin-based polymer.

Patentansprüche

25 1. Katalysatorzusammensetzung, die eine Kombination aus einer Magnesiumkomponente, einer Titankomponente und einem internen Elektronendonator, der ein Adamantandicarboxylat umfasst, und einen Cokatalysator umfasst.

30 2. Katalysatorzusammensetzung nach Anspruch 1, wobei das Adamantandicarboxylat die Struktur (III) aufweist:

(III)



45 in der R₁-R₂ gleich oder verschieden sind, wobei jedes R₁ und R₂ aus der Gruppe bestehend aus einer substituierten Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen, einer unsubstituierten Kohlenwasserstoffgruppe mit 1 bis 20 Kohlenstoffatomen und Kombination davon ausgewählt ist.

50 3. Katalysatorzusammensetzung nach Anspruch 2, wobei mindestens eines von R₁ und R₂ eine primäre Alkylgruppe ist.

4. Katalysatorzusammensetzung nach einem der Ansprüche 2 bis 3, wobei R₁ und R₂ gleich oder verschieden sind und jeweils aus der Gruppe bestehend aus einer C₁-C₆-Alkylgruppe ausgewählt sind.

55 5. Katalysatorzusammensetzung nach einem der Ansprüche 2 bis 4, wobei R₁ und R₂ gleich oder verschieden sind und jeweils aus der Gruppe bestehend aus einer Methylgruppe, einer Ethylgruppe, einer n-Propylgruppe, einer Isopropylgruppe, einer n-Butylgruppe, einer Isobutylgruppe, einer sec-Butylgruppe, einer Pentylgruppe, einer n-Hexylgruppe und Kombinationen davon ausgewählt sind.

6. Katalysatorzusammensetzung nach Anspruch 1, wobei der interne Elektronendonator eine Elektronendonorkompo-

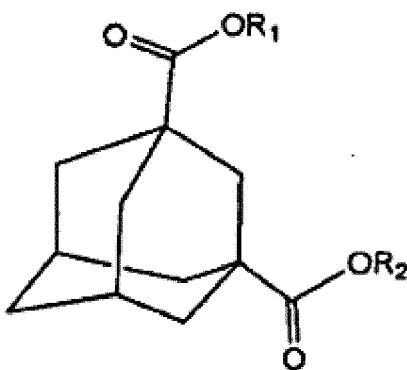
nente umfasst, die aus der Gruppe bestehend aus einem Benzoat, einem Phthalat, einem Diether, einem Diolester, einem Silyldiolester, einem Succinat und Kombinationen davon ausgewählt ist.

- 5 7. Katalysatorzusammensetzung nach Anspruch 1, die ein Mitglied ausgewählt aus der Gruppe bestehend aus einem externen Elektronendonator, einem gemischten externen Elektronendonator, einem Aktivitätsbegrenzer und Kombinationen davon umfasst.
- 10 8. Katalysatorzusammensetzung nach Anspruch 7, wobei der externe Elektronendonator ein Alkoxy silan umfasst.
- 15 9. Katalysatorzusammensetzung nach Anspruch 8, die einen Aktivitätsbegrenzer umfasst, der aus der Gruppe bestehend aus einem Carboxylsäureester, einem Diether, einem Polyalkenglycol, einem Diolester und Kombinationen davon ausgewählt ist.
- 10. Verfahren zur Herstellung eines olefinbasierten Polymers, bei dem ein Olefin unter Polymerisationsbedingungen mit einer Katalysatorzusammensetzung, die ein Adamantandicarboxylat umfasst, in Kontakt gebracht wird und ein olefinbasiertes Polymer gebildet wird.

Revendications

- 20 1. Composition de catalyseur comprenant :
- 25 une combinaison de fraction de magnésium, d'une fraction de titane et d'un donneur d'électrons interne, comprenant un adamantanedicarboxylate ; et un co-catalyseur.
- 2. Composition de catalyseur selon la revendication 1, dans laquelle l'adamantanedicarboxylate a la structure (III) :

(III)



35 où R₁-R₂ sont les mêmes ou différents, chacun de R₁ et R₂ est sélectionné dans le groupe consistant en un groupe hydrocarbyle substitué ayant 1 à 20 atomes de carbone, un groupe hydrocarbyle non substitué ayant 1 à 20 atomes de carbone et leurs combinaisons.

- 40 3. Composition de catalyseur selon la revendication 2, dans laquelle au moins un parmi R₁ et R₂ est un groupe alkyle primaire.
- 45 4. Composition de catalyseur selon l'une quelconque des revendications 2 - 3, dans laquelle R₁ et R₂ ont les mêmes ou différents, et chacun est sélectionné dans le groupe consistant en un groupe alkyle C₁-C₆.
- 50 5. Composition de catalyseur selon l'une quelconque des revendications 2 à 4, dans laquelle R₁ et R₂ sont les mêmes ou différents et chacun est sélectionné dans le groupe consistant en un groupe méthyle, un groupe éthyle, un groupe n-propyle, un groupe isopropyle, un groupe n-butyle, un groupe isobutyle, un groupe sec-butyle, un groupe pentyle, un groupe n-hexyle et leurs combinaisons.

6. Composition de catalyseur selon la revendication 1, dans laquelle le donneur d'électrons interne comprend un composant de donneur d'électrons sélectionné dans le groupe consistant en un benzoate, un phtalate, un diéther, un ester de diol, un ester de silyl diol, un succinate et leurs combinaisons.

5 7. Composition de catalyseur selon la revendication 1, comprenant un élément sélectionné dans le groupe consistant en un donneur d'électrons externe, un donneur d'électrons externe mélange, un agent de limitation de l'activité et leurs combinaisons.

10 8. Composition de catalyseur selon la revendication 7, dans laquelle le donneur d'électrons externe comprend un alkoxy silane.

15 9. Composition de catalyseur selon la revendication 8, comprenant un agent de limitation d'activité sélectionné dans le groupe consistant en un ester d'acide carboxylique, un diéther, un poly(alcène glycol), un ester de diol et leurs combinaisons.

10. Procédé de production d'un polymère à base d'oléfine, comprenant :

mettre en contact, sous des conditions de polymérisation, une oléfine avec une composition de catalyseur comprenant un adamantanedicarboxylate ; et
20 former un polymère à base d'oléfine.

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REFERENCES CITED IN THE DESCRIPTION

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