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(54) Title: ACTIVATED MULTINUCLEAR TRANSITION METAL CATALYST COMPOSITIONS

(57) Abstract: The present invention is an activated catalyst composition produced by contacting A) a multinuclear transition metal compound with B) a mononuclear transition metal compound. This activated catalyst composition can be used in polymerization reactions to enable higher polymerization conversions when compared to the use of multinuclear transition metal compounds alone.

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ACTIVATED MULTINUCLEAR TRANSITION METAL CATALYST COMPOSITIONS

Cross Reference Statement

This application claims the benefit of U.S. Provisional Application No. _60/476,264, filed June 5, 2003.

Background of the Invention

The present invention relates to activated multinuclear transition metal catalyst compositions and their use in polymerization reactions. More particularly, this invention relates to improved activated catalyst compositions comprising a Group 4 metal complex containing multiple transition metals.

Numerous Group 4 metal compounds containing one or more cyclopentadienyl ligands or multi-ring derivatives of such cyclopentadienyl ligands (also known as metallocenes), their preparation, methods of activation, active catalysts formed therefrom including cationic catalysts, and methods of use are previously known in the art. Such compounds are capable of preparing polymers of addition polymerizable monomers, especially olefins, including vinylaromatic monomers in high yields and/or narrow molecular weight distributions. Examples include United States Patents (US-A-) 5,045,517, 5,196,490 and 5,536,797 wherein titanium containing compounds that are highly selective for the production of syndiotactic polymers of vinyl aromatic monomers are disclosed. Multinuclear, especially binuclear, transition metal compounds useful as catalyst components are disclosed in US-A-5,892,079.

US-A-5,045,517 and US-A-5,196,490 disclose a process for preparing syndiotactic polymers of vinyl aromatic monomers using, as a catalyst, the reaction product of polymethylaluminoxane and a titanium (IV) complex corresponding to the formula $CpTiX_3$. Cp and X are defined at column 1, lines 32-45. Illustrative $CpTiX_3$ complexes include cyclopentadienyltitanium tris(phenoxide), cyclopentadienyltitanium tris(ethoxide), indenyltitanium tris(dimethylamide), cyclopentadienyltitanium tris(dimethylamide), pentamethylcyclopentadienyltitanium tris(phenoxide) and cyclopentadienyltitanium phenoxy dichloride.

US-A-5,536,797 teaches preparation of polymers of prochiral olefin monomers having high stereo-regularity (for example, high syndiotactic polymers) and a molecular weight less than 500,000 using an octahydrofluorenyltitanium metal complex or a ring substituted octahydrofluorenyltitanium metal complex in the +2, +3 or +4 formal oxidation state and an activating cocatalyst or activating technique. Examples of such metal complexes include octahydrofluorenyltitanium (IV) trichloride; octahydrofluorenyltitanium (IV) trimethoxide; octahydrofluorenyltitanium (IV) triphenoxide; octahydrofluorenyltitanium (IV) dichloride phenoxide; octahydrofluorenyltitanium (III) dimethoxide; octahydrofluorenyltitanium (III) methyl

(2-dimethylaminobenzyl); octahydrofluorenyltitanium (II) allyl (s-cis-1,4-diphenylbutadiene); octahydrofluorenyltitanium (II) 2,4-dimethylpentadienyl. Additional complexes that are variously substituted as herein defined will be readily apparent to the skilled artisan. A number of boron compounds suitable for use as an activating cocatalyst are listed at column 5, line 63 through column 7, line 43.

US-A-5,892,079 provides a number of novel metallocene catalysts at column 4, line 20 through column 5, line 20. Specific metallocene catalyst examples include those found in columns 10-16.

Despite the advance in the art occasioned by the foregoing patented products new catalyst compositions having favorable catalytic properties are still sought, especially in attaining higher polymerization conversions and improved molecular properties.

Summary of the Invention

The present invention is an activated catalyst composition produced by contacting A) a multinuclear transition metal compound with B) a mononuclear transition metal compound.

This activated catalyst composition can be used in polymerization reactions to enable higher polymerization conversions when compared to the use of multinuclear transition metal compounds alone.

Detailed Description of the Invention

All reference to the Periodic Table of the Elements herein refers to the Periodic Table of the Elements, published and copyrighted by CRC Press, Inc., 2001. Also, any reference to a Group or Groups is to the Group or Groups as reflected in this Periodic Table of the Elements using the IUPAC system for numbering groups. For purposes of United States patent practice, the contents of any patent or patent application is hereby incorporated by reference in its entirety, especially with respect to the disclosure of analytical or synthetic techniques and general knowledge in the art.

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.

The term "polymer" includes both homopolymers, that is, polymers prepared from a single reactive compound, and copolymers, that is, polymers prepared by reaction of at least two polymer forming reactive, monomeric compounds. The term “syndiotactic” means a polymer of one or more monomers capable of forming enantiomers wherein the syndiotacticity at a racemic diad in the ^{13}C nuclear magnetic resonance spectrum thereof is at least seventy five percent, or the syndiotacticity at a racemic pentad in the ^{13}C nuclear magnetic resonance spectrum thereof is at least thirty percent.

The multinuclear transition metal compound used in the catalyst composition of the present invention is any compound described by Formula (I).

$$MR^1_m[-R^2-]_p[M_qR^3_r]_n \qquad (I)$$

wherein:

M is independently a metal of Group 4 or the Lanthanide Series of the Periodic Table and is preferably titanium (Ti), zirconium (Zr) or hafnium (Hf);

R^1 is independently in each occurrence a C_{1-50} (1 to 50 carbon atoms, “C” representing carbon and the subscript showing the range of atoms of the element so modified) hydrocarbon group, π-coordinated hydrocarbyl ligand, or a boron (B), silicon (Si), nitrogen (N), phosphorus (P), or oxygen (O) substituted derivative thereof, wherein any R^1 group may optionally contain one or more halo-, halocarbyl-, halohydrocarbyl-, tri(hydrocarbyl)silyl-, or tri(hydrocarbyl)silylhydrocarbyl-, substituents. Preferably R^1 is a cyclopentadienyl, pentamethylcyclopentadienyl, indenyl, benzindenyl, fluorenyl, or octahydrofluorenyl group; or substituted groups thereof; and more preferably R^1contains no metal atoms;

R^2 is independently in each occurrence R^1, a hydride, or a hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido, trihydrocarbylsilyl, or halo group of up to 20 nonhydrogen atoms;

R^3 is independently in each occurrence R^1, R^2, or a divalent ligand group selected from O, NR^5, PR^5, O-R^4-O, NR^5-R^4-NR^5, and PR^5-R^4-PR^5, which is shared by two metal centers, M, in the form of a μ-bridged structure;

R^4 is a divalent ligand group of up to 30 atoms, not counting hydrogen, preferably C_{1-10} alkylene;

R^5 is an anionic ligand group of up to 30 atoms, not counting hydrogen, preferably C_{1-6} alkyl; and

m is 1, 2, or 3;

n is an integer greater than or equal to (≥) 1;

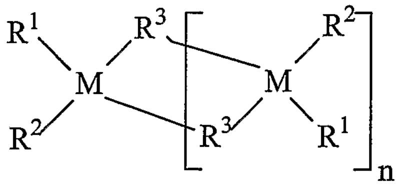
p is equal to 4-m;

q is an integer ≥1; and

r is an integer ≥1.

In a preferred embodiment, n is ≥1, but less than (<) 100, q is ≥1, but <100, and r is ≥1, but <100.

In one embodiment, the multinuclear transition metal compound may be of the formula:



(II)

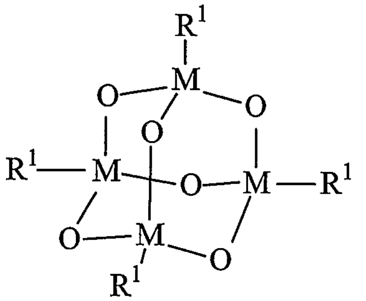
;

wherein,

R^1, R^2, R^3, and n are as defined previously or when n is ≥2, two R^2 groups on different metal centers may together form an R^3 group; and

M is independently in each occurrence a group 4 metal, preferably Ti;

The metal compounds preferably are Group 4 metalloxanes having an "adamantane like" structure corresponding to the formula:



(III)

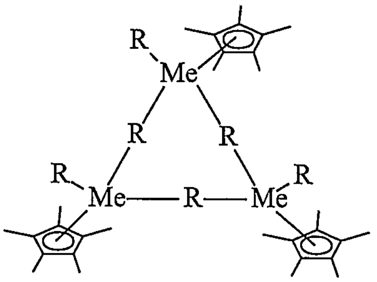
;

wherein,

M and R^1 are as previously defined with respect to compounds of formula (I).

Preferred metal complexes are those complexes of formula (III) wherein M in each occurrence is Ti, and R^1 independently in each occurrence is η^5-pentamethylcyclopentadienyl or η^5-octahydrofluorenyl.

Additional multinuclear transition metal compounds useful in the catalyst composition of the present invention include the following:



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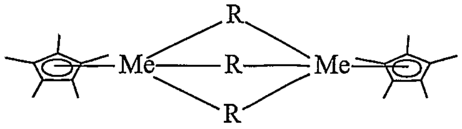

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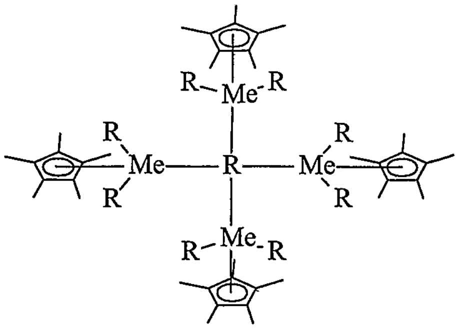

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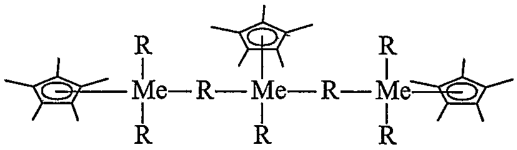


(VII)

The foregoing metal complexes are conveniently prepared by standard metallation and ligand exchange procedures involving a source of the transition metal and the various ligand sources. The metalloxanes in particular are prepared by reaction of the corresponding monocyclopentadienyl metal trialkoxide with water. The complexes may be prepared using standard dry box synthetic techniques.

The multinuclear transition metal compounds may also be supported on a support material and used in olefin polymerization processes in a slurry or in the gas phase upon activation.

The catalyst composition of the present invention additionally comprises a mononuclear transition metal compound of formula VIII:

$$M'X_s \qquad \text{(VIII)}$$

wherein:

M' is independently a metal of Group 4 or the Lanthanide Series of the Periodic Table, or a mixture thereof; preferably Ti, Zr, or Hf;

X is independently a halide (that is, bromine, fluorine, chlorine, or iodine), preferably chlorine; and

s is 2, 3 or 4, preferably 4.

Preferably the mononuclear transition metal compound is titanium tetrachloride. Mononuclear transition metal compounds are well known by those skilled in the art and are typically commercially available. Methods of making such compounds are also well known by those skilled in the art.

The multinuclear transition metal compound of A) and mononuclear transition metal compound of B) are typically used in molar ratios (B:A) of from (5n):1 to (0.05n):1, and preferably from (4n):1 to (0.1n):1.; wherein n is as defined in Formula I.

The two components used to produce the activated catalyst composition of the present invention can be combined prior to use, or can be added independently within a reaction process.

The activated catalyst composition of the present invention can be used in polymerization processes with polymerizable monomers or mixtures thereof by contacting said monomer or mixture of monomers with the activated catalyst composition under polymerization conditions. Preferred polymerizable monomers are C_{8-20} vinylaromatic monomers, especially styrene, o-, m- or p- C_{1-4} alkyl- substituted styrenes, and mixtures thereof, which form highly syndiotactic polymers. Polymers prepared by the foregoing invented process are usefully employed for injection molding and other applications.

The activated catalyst composition of the present invention can also be used in combination with other components which are beneficial to the polymer product being produced. Such compounds include additional cocatalysts useful in polymerization reactions.

Suitable cocatalysts useful in combination with the present activated catalyst composition of the present invention are those compounds capable of abstraction of a substituent therefrom to form an inert, non-interfering counter ion, or that form a zwitterionic or other catalytically active derivative of the metal complex. Suitable cocatalysts for use herein include Lewis acids, such as alumoxanes, including trialkylaluminum, tris(fluoroaryl)aluminum and tris(fluoroaryl)boron modified alumoxanes, or perfluorinated tri(aryl)boron compounds, and most especially methylalumoxane (MAO) or tris(pentafluorophenyl)borane; nonpolymeric, compatible, noncoordinating, ion forming compounds (including the use of such compounds under oxidizing conditions), especially ammonium-, phosphonium-, oxonium-, carbonium-, silylium-, sulfonium-, or ferrocenium- salts of compatible, noncoordinating anions. A combination of the foregoing cocatalysts may be employed as well.

More particularly, suitable ion forming compounds useful as cocatalysts in one embodiment of the present invention comprise a cation which is a Bronsted acid capable of donating a proton, and a compatible, noncoordinating anion, A^-. Preferred anions are those containing a single coordination complex comprising a charge-bearing metal or metalloid core which anion is capable of balancing the charge of the active catalyst species (the metal cation) which may be formed when the two components are combined. Also, said anion should be sufficiently labile to be displaced by olefinic, diolefinic and acetylenically unsaturated compounds or other neutral Lewis bases such as ethers or nitriles. Suitable metals include, but are not limited to, aluminum (Al), gold and platinum. Suitable metalloids include, but are not limited to, B, P, and Si. Compounds containing anions which comprise coordination complexes containing a single metal or metalloid atom are, of course, well known and many, particularly such compounds containing a single boron atom in the anion portion, are available commercially.

Preferably such cocatalysts may be represented by the following general formula:

$$(L^*\text{-}H)^+_d\,(A)^{d-n} \qquad (X)$$

wherein:

L* is a neutral Lewis base;

$(L^*\text{-}H)^+$ is a Bronsted acid;

A^{d-} is a noncoordinating, compatible anion having a charge of d-, and

d is an integer from 1 to 3.

More preferably A^{d-} corresponds to the formula: $[M'Q_4]^-$; (XI)

wherein:

M' is B or Al in the +3 formal oxidation state; and

Q independently each occurrence is selected from hydride, dialkylamido, halide, hydrocarbyl, hydrocarbyloxide, halosubstituted-hydrocarbyl, hydroxy- substituted hydrocarbyl, halosubstituted hydrocarbyloxy, and halo- substituted silylhydrocarbyl radicals (including perhalogenated hydrocarbyl- perhalogenated hydrocarbyloxy- and perhalogenated silylhydrocarbyl radicals), said Q having up to 20 carbons with the proviso that in not more than one occurrence is Q halide. Examples of suitable hydrocarbyloxide Q groups are disclosed in US-A-5,296,433.

In a more preferred embodiment, d is one, that is, the counter ion has a single negative charge and is A^-. Cocatalysts comprising B which are particularly useful in the preparation of catalysts of this invention may be represented by the following general formula:

$$(L^*\text{-}H)^+(BQ_4)^-; \qquad (XII)$$

wherein:

L* is as previously defined;

B is boron in a formal oxidation state of 3; and

Q is a hydrocarbyl-, hydrocarbyloxy-, fluorinated hydrocarbyl-, fluorinated hydrocarbyloxy-, or fluorinated silylhydrocarbyl- group of up to 20 nonhydrogen atoms, with the proviso that in not more than one occasion is Q hydrocarbyl.

Most preferably, Q is each occurrence a fluorinated aryl group, especially, a pentafluorophenyl group.

Illustrative, but not limiting, examples of B compounds which may be used as an cocatalyst in the preparation of the improved catalysts of this invention are

tri-substituted ammonium salts such as:

trimethylammonium tetrakis(pentafluorophenyl) borate,

triethylammonium tetrakis(pentafluorophenyl) borate,
tripropylammonium tetrakis(pentafluorophenyl) borate,
tri(n-butyl)ammonium tetrakis(pentafluorophenyl) borate,
tri(sec-butyl)ammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-N-dodecylammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-N-octadecylammonium tetrakis(pentafluorophenyl) borate,
N-methyl-N,N-didodecylammonium tetrakis(pentafluorophenyl) borate,
N-methyl-N,N-dioctadecylammonium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-dimethylanilinium n-butyltris(pentafluorophenyl) borate,
N,N-dimethylanilinium benzyltris(pentafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(4-(t-butyldimethylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(4-(triisopropylsilyl)-2, 3, 5, 6-tetrafluorophenyl) borate,
N,N-dimethylanilinium pentafluorophenoxytris(pentafluorophenyl) borate,
N,N-diethylanilinium tetrakis(pentafluorophenyl) borate,
N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(pentafluorophenyl) borate,
trimethylammonium tetrakis(2,3,4,6-tetrafluorophenyl)borate,
triethylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
tripropylammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
tri(n-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
dimethyl(t-butyl)ammonium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
N,N-dimethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate,
N,N-diethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate, and
N,N-dimethyl-2,4,6-trimethylanilinium tetrakis(2,3,4,6-tetrafluorophenyl) borate;
disubstituted ammonium salts such as:
di-(i-propyl)ammonium tetrakis(pentafluorophenyl) borate, and
dicyclohexylammonium tetrakis(pentafluorophenyl) borate;
trisubstituted phosphonium salts such as:
triphenylphosphonium tetrakis(pentafluorophenyl) borate,
tri(o-tolyl)phosphonium tetrakis(pentafluorophenyl) borate, and
tri(2,6-dimethylphenyl)phosphonium tetrakis(pentafluorophenyl) borate;
disubstituted oxonium salts such as:
diphenyloxonium tetrakis(pentafluorophenyl) borate,
di(o-tolyl)oxonium tetrakis(pentafluorophenyl) borate, and
di(2,6-dimethylphenyl)oxonium tetrakis(pentafluorophenyl) borate;

disubstituted sulfonium salts such as:
diphenylsulfonium tetrakis(pentafluorophenyl) borate,
di(o-tolyl)sulfonium tetrakis(pentafluorophenyl) borate, and
bis(2,6-dimethylphenyl)sulfonium tetrakis(pentafluorophenyl) borate.

Preferred $(L^*\text{-}H)^+$ cations are N,N-dimethylanilinium, tributylammonium, N-methyl-N,N-di(dodecyl)ammonium, N-methyl-N,N-di(tetradecyl)ammonium, N-methyl-N,N-di(hexadecyl)ammonium, N-methyl-N,N-di(octadecyl)ammonium, and mixtures thereof. The latter three cations are the primary ammonium cations derived from a commercially available mixture of C_{14-18} tallow amines, and are collectively referred to as bis-hydrogenated tallowalkyl methylammonium cation. The resulting ammonium salt of the tetrakis(pentafluorophenyl)borate anion accordingly is know as bis-hydrogenated tallowalkyl methylammonium tetrakis(pentafluorophenyl)borate.

Another suitable ion forming, cocatalyst comprises a salt of a cationic oxidizing agent and a noncoordinating, compatible anion represented by the formula:

$$(Ox^{e+})_d(A^{d-})_e. \qquad \text{(XIII)}$$

wherein:

Ox^{e+} is a cationic oxidizing agent having a charge of e+;

e is an integer from 1 to 3; and

A^{d-} and d are as previously defined.

Examples of cationic oxidizing agents include: ferrocenium, hydrocarbyl-substituted ferrocenium, Ag^+ or Pb^{+2}. Preferred embodiments of A^{d-} are those anions previously defined with respect to the Bronsted acid containing cocatalysts, especially tetrakis(pentafluorophenyl)borate.

Another suitable ion forming, cocatalyst comprises a compound which is a salt of a carbenium ion and a noncoordinating, compatible anion represented by the formula:

$$©^+ A^- \qquad \text{(XIV)}$$

wherein:

$©^+$ is a C_{1-20} carbenium ion; and

A^- is as previously defined. A preferred carbenium ion is the trityl cation,that is, triphenylmethylium.

A further suitable ion forming, cocatalyst comprises a compound which is a salt of a silylium ion and a noncoordinating, compatible anion represented by the formula:

$$R'_3Si^+ A^- \qquad \text{(XV)}$$

wherein:

$R'$is C_{1-10} hydrocarbyl, and A^- are as previously defined.

Preferred silylium salt cocatalysts are trimethylsilylium tetrakispentafluorophenylborate, triethylsilylium tetrakispentafluorophenylborate and ether substituted adducts thereof.

Certain complexes of alcohols, mercaptans, silanols, and oximes with tris(pentafluorophenyl)borane are also effective catalyst activators and may be used according to the present invention. Such cocatalysts are disclosed in US-A-5,296,433.

Another class of suitable catalyst activators which may be used in addition to the multinuclear and mononuclear transition metal compounds of the composition of the present invention are expanded anionic compounds corresponding to the formula:

$$(A^{1+a^1})_{b^1}(Z^1J^1_{j^1})^{-c^1}_{d^1}, \qquad \text{(XVI)}$$

wherein:

A^1 is a cation of charge $+a^1$,

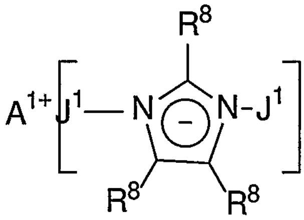
Z^1 is an anion group of from 1 to 50, preferably 1 to 30 atoms, not counting hydrogen atoms, further containing two or more Lewis base sites;

J^1 independently each occurrence is a Lewis acid coordinated to at least one Lewis base site of Z^1, and optionally two or more such J^1 groups may be joined together in a moiety having multiple Lewis acidic functionality,

j^1 is a number from 2 to 12 and

a^1, b^1, c^1, and d^1 are integers from 1 to 3, with the proviso that $a^1 \times b^1$ is equal to $c^1 \times d^1$.

The foregoing cocatalysts (illustrated by those having imidazolide, substituted imidazolide, imidazolinide, substituted imidazolinide, benzimidazolide, or substituted benzimidazolide anions) may be depicted schematically as follows:



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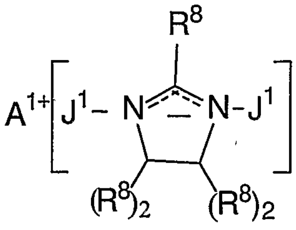

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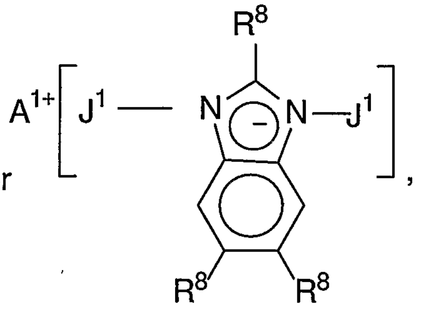

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(XVII) (XVIII) (XIX)

wherein:

A^{1+} is a monovalent cation as previously defined, and preferably is a trihydrocarbyl ammonium cation, containing one or two C_{10-40} alkyl groups, especially the methylbis(tetradecyl)ammonium- or methylbis(octadecyl)ammonium- cation,

R^8, independently each occurrence, is hydrogen or a halo, hydrocarbyl, halocarbyl, halohydrocarbyl, silylhydrocarbyl, or silyl, (including mono-, di- and tri(hydrocarbyl)silyl) group of up to 30 atoms not counting hydrogen, preferably C_{1-20} alkyl, and

J^1 is tris(pentafluorophenyl)borane or tris(pentafluorophenyl)aluminane.

Examples of these catalyst activators include the trihydrocarbylammonium-, especially, methylbis(tetradecyl)ammonium- or methylbis(octadecyl)ammonium- salts of: bis(tris(pentafluorophenyl)borane)imidazolide, bis(tris(pentafluorophenyl)borane)-2-undecylimidazolide, bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolide, bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolide, bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolide, bis(tris(pentafluorophenyl)borane)imidazolinide, bis(tris(pentafluorophenyl)borane)-2-undecylimidazolinide, bis(tris(pentafluorophenyl)borane)-2-heptadecylimidazolinide, bis(tris(pentafluorophenyl)borane)-4,5-bis(undecyl)imidazolinide, bis(tris(pentafluorophenyl)borane)-4,5-bis(heptadecyl)imidazolinide, bis(tris(pentafluorophenyl)borane)-5,6-dimethylbenzimidazolide, bis(tris(pentafluorophenyl)borane)-5,6-bis(undecyl)benzimidazolide, bis(tris(pentafluorophenyl)alumane)imidazolide, bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolide, bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolide, bis(tris(pentafluorophenyl)alumane)imidazolinide, bis(tris(pentafluorophenyl)alumane)-2-undecylimidazolinide, bis(tris(pentafluorophenyl)alumane)-2-heptadecylimidazolinide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(undecyl)imidazolinide, bis(tris(pentafluorophenyl)alumane)-4,5-bis(heptadecyl)imidazolinide, bis(tris(pentafluorophenyl)alumane)-5,6-dimethylbenzimidazolide, and bis(tris(pentafluorophenyl)alumane)-5,6-bis(undecyl)benzimidazolide.

A further class of additional suitable activating cocatalysts which may be used in the composition of the present invention include cationic Group 13 salts corresponding to the formula:

$$[M''Q^1_2L'_{l'}]^+ (Ar^f_3M'Q^2)^- \qquad (XX)$$

wherein:

M" is Al, gallium, or indium;

M' is B or Al;

Q^1 is C_{1-20} hydrocarbyl, optionally substituted with one or more groups which independently each occurrence are hydrocarbyloxy, hydrocarbylsiloxy, hydrocarbylsilylamino, di(hydrocarbylsilyl)amino, hydrocarbylamino, di(hydrocarbyl)amino, di(hydrocarbyl)phosphino, or hydrocarbylsulfido groups having from 1 to 20 atoms other than hydrogen, or, optionally, two or more Q^1 groups may be covalently linked with each other to form one or more fused rings or ring systems;

Q^2 is an alkyl group, optionally substituted with one or more cycloalkyl or aryl groups, said Q^2 having from 1 to 30 carbons;

L' is a monodentate or polydentate Lewis base, preferably L' is reversibly coordinated to the metal complex such that it may be displaced by an olefin monomer, more preferably L' is a monodentate Lewis base;

l' is a number greater than zero indicating the number of Lewis base moieties, L', and

Ar^f independently each occurrence is an anionic ligand group; preferably Ar^f is selected from the group consisting of halide, C_{1-20} halohydrocarbyl, and Q^1 ligand groups, more preferably Ar^f is a fluorinated hydrocarbyl moiety of from 1 to 30 carbon atoms, most preferably Ar^f is a fluorinated aromatic hydrocarbyl moiety of from 6 to 30 carbon atoms, and most highly preferably Ar^f is a perfluorinated aromatic hydrocarbyl moiety of from 6 to 30 carbon atoms.

Examples of the foregoing Group 13 metal salts are aluminium tris(fluoroaryl)borates or gallicinium tris(fluoroaryl)borates corresponding to the formula:

$$[M''Q^1_2L'_{l'}]^+ (Ar^f_3BQ^2)^-, \qquad \text{(XXI)}$$

wherein M" is aluminum or gallium; Q^1 is C_{1-20} hydrocarbyl, preferably C_{1-8} alkyl; Ar^f is perfluoroaryl, preferably pentafluorophenyl; and Q^2 is C_{1-8} alkyl, preferably C_{1-8} alkyl. More preferably, Q^1 and Q^2 are identical C_{1-8} alkyl groups, most preferably, methyl, ethyl or octyl.

The foregoing activating cocatalysts may also be used in any combination. An especially preferred combination is a mixture of a tri(hydrocarbyl)aluminum or tri(hydrocarbyl)borane compound having from 1 to 4 carbons in each hydrocarbyl group or an ammonium borate with an oligomeric or polymeric alumoxane compound.

The molar ratio of the amount of metal in the activated catalyst composition of the present invention to additional cocatalyst, if employed, preferably ranges from 1:10,000 to 100:1, more preferably from 1:5000 to 10:1, most preferably from 1:1000 to 1:1. Alumoxane, when used by itself as an activating cocatalyst, is employed in large quantity, generally at least 50 times the quantity of the amount of metal in the activated catalyst composition on a molar basis. Tris(pentafluorophenyl)-borane, where used as an additional activating cocatalyst is employed in a molar ratio to the amount of metal in the activated catalyst composition of from 0.5:1 to 10:1, more preferably from 1:1 to 6:1 most preferably from 1:1 to 5:1. The remaining activating cocatalysts are, if used, generally employed in approximately equimolar quantity to the amount of metal in the activated catalyst composition.

The most preferred activating cocatalysts are methylalumoxanes, including tri(C_{3-12} alkyl)aluminum modified alumoxanes, trispentafluorophenylborane and a mixture of long chain ammonium salts of tetrakis(pentafluorophenyl)borate, especially N,N-dioctadecyl-N-methylammonium tetrakpentafluorophenylborate, N-methyl-N,N-di(hexadecyl)ammonium tetrakpentafluorophenylborate and N,N-ditetradecyl-N-methylammonium tetrakpentafluorophenylborate. The latter mixture of borate salts is derived from hydrogenated tallow amine, and is referred to as bis-hydrogenated tallowalkyl methylammonium tetrakis(pentafluorophenyl)borate.

Additional components, such as scavengers, especially trialkylaluminum compounds, dialkylaluminum alkoxides, dialkylaluminum N,N-di(hydrocarbyl)amides, alkylaluminum dialkoxide compounds and hydroxyl containing compounds, especially triphenylmethanol, and the reaction products of such hydroxyl containing compounds with alkylaluminum compounds, may be included in the catalyst composition of the invention if desired. A particularly preferred scavenger is triisobutylaluminum (TIBA). Generally such additional components are present in the reaction mixture in molar ratios from 1:1 to 500:1 based on the amount of metal in the activated catalyst composition, preferably from 10:1 to 100:1.

The activated catalyst composition of the present invention may be used in the polymerization of ethylenically unsaturated monomers having from 2 to 20 carbon atoms either alone or in combination. Preferred monomers include monovinylidene aromatic monomers, 4-vinylcyclohexene, vinylcyclohexane, norbornadiene and C_{2-10} aliphatic α-olefins (especially ethylene, propylene, isobutylene, 1-butene, 1-hexene, 3-methyl-1-pentene, 4-methyl-1-pentene, and 1-octene), C_{4-40} dienes, and mixtures thereof. Of the dienes typically used to prepare ethylene/propylene/diene monomer polymers (EPDMs), the particularly preferred dienes are 1,4-hexadiene (HD), 5-ethylidene-2-norbornene (ENB), 5-vinylidene-2-norbornene (VNB), 5-methylene-2-norbornene (MNB), and dicyclopentadiene (DCPD). The especially preferred dienes are 5-ethylidene-2-norbornene (ENB) and 1,4-hexadiene (HD). Most preferred monomers are ethylene, mixtures of ethylene, propylene and ethylidenenorbornene, mixtures of ethylene and a C_{4-8} α-olefin, especially 1-butene, 1-hexene or 1-octene, styrene, and mixtures of styrene and p-methylstyrene.

In general, the polymerization may be accomplished at conditions well known in the prior art for Ziegler-Natta or Kaminsky-Sinn type polymerization reactions, that is, temperatures from 0 to 250 degrees centigrade (°C), preferably 30 to 200 °C and pressures from atmospheric to $\geq$30,000 atmospheres. Suspension, solution, slurry, gas phase, solid state powder polymerization or other process condition may be employed if desired. A support for the multinuclear transition metal compound of the activated catalyst composition, especially silica, alumina, or a polymer (especially poly(tetrafluoroethylene) or a polyolefin) may be employed, and desirably is employed when the activated multinuclear transition metal catalyst composition is used in a gas phase polymerization process. The support is preferably employed in an amount to provide a weight ratio of the multinuclear transition metal catalyst composition to support from 1:100,000 to 1:10, more preferably from 1:50,000 to 1:20, and most preferably from 1:10,000 to 1:30.

In most polymerization reactions the molar ratio of the amount of metal in the activated catalyst composition to polymerizable compounds employed is from 10^{-12}:1 to 10^{-1}:1, more preferably from 10^{-9}:1 to 10^{-5}:1.

Suitable solvents for polymerization are inert liquids. Examples include straight and branched-chain hydrocarbons such as isobutane, butane, pentane, hexane, heptane, octane, and mixtures thereof; cyclic and alicyclic hydrocarbons such as cyclohexane, cycloheptane, methylcyclohexane, methylcycloheptane, and mixtures thereof; perfluorinated hydrocarbons such as perfluorinated C_{4-10} alkanes, and the like and aromatic and alkyl-substituted aromatic compounds such as benzene, toluene, xylene, ethylbenzene and the like. Suitable solvents also include liquid olefins which may act as monomers or comonomers including ethylene, propylene, butadiene, cyclopentene, 1-hexene, 1-hexane, 4-vinylcyclohexene, vinylcyclohexane, 3-methyl-1-pentene, 4-methyl-1-pentene, 1,4-hexadiene, 1-octene, 1-decene, styrene, divinylbenzene, allylbenzene, vinyltoluene (including all isomers alone or in admixture), and the like. Mixtures of the foregoing are also suitable.

The activated catalyst composition of the present invention may be utilized in combination with at least one additional homogeneous or heterogeneous polymerization catalyst in the same or separate reactors connected in series or in parallel to prepare polymer blends having desirable properties.

The activated catalyst composition may be prepared as a homogeneous catalyst by addition of the requisite components to a solvent. The activated catalyst composition may also be prepared and employed as a heterogeneous catalyst by adsorbing the requisite components on a catalyst support material such as silica gel, alumina or other suitable inorganic support material. When prepared in heterogeneous or supported form, it is preferred to use silica as the support material. The heterogeneous form of the catalyst system is desirably employed in a slurry or gas phase polymerization. As a practical limitation, slurry polymerization takes place in liquid diluents in which the polymer product is substantially insoluble. Preferably, the diluent for slurry polymerization is one or more hydrocarbons with < 5 carbon atoms. If desired, saturated hydrocarbons such as ethane, propane or butane may be used in whole or part as the diluent. Likewise the α-olefin monomer or a mixture of different α-olefin monomers may be used in whole or part as the diluent. Most preferably the diluent comprises in at least major part the α-olefin monomer or monomers to be polymerized.

In contrast, solution polymerization conditions utilize a solvent for the respective components of the reaction, particularly the resulting polymer, at the temperature of operation. Preferred solvents include mineral oils and the various hydrocarbons which are liquid at reaction temperatures. Illustrative examples of useful solvents include alkanes such as pentane, iso-pentane, hexane, heptane, octane and nonane, as well as mixtures of alkanes including kerosene and Isopar E™, available from Exxon Chemicals Inc.; cycloalkanes such as cyclopentane and cyclohexane; and aromatics such as benzene, toluene, xylenes, ethylbenzene and diethylbenzene.

At all times, the individual ingredients as well as the recovered activated catalyst components must be protected from oxygen and moisture. Therefore, the activated catalyst components and activated catalyst composition must be prepared and recovered in an oxygen and moisture free environment. Preferably, therefore, the syntheses are performed in the presence of a dry, inert gas such as, for example, nitrogen.

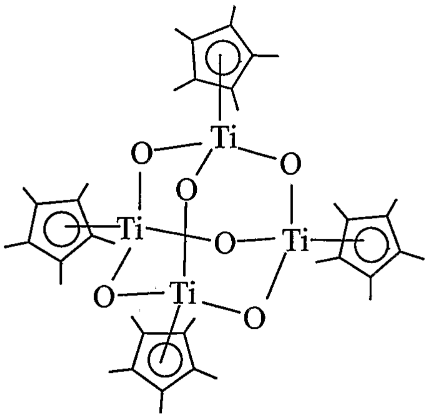
Generally the polymerization of olefin monomers is carried out with a differential pressure from 10 to 1000 pounds per square in (psi) (70 to 7000 kilopascals (kPa)), most preferably from 40 to 400 psi (30 to 300 kPa). The polymerization is generally conducted at a temperature of from 25 to 200 °C, preferably from 75 to 170 °C, and most preferably from greater than 95 to 160 °C. Generally polymerization of vinylaromatic monomers is conducted in a solid, powder bed polymerization reactor at temperatures from 25 to 120°C, preferably from 50 to 90 °C under conditions to avoid substantial formation of atactic vinylaromatic polymer.

The polymerization may be carried out as a batchwise or a continuous polymerization process. A continuous process is preferred, in which event the catalyst composition or the individual components thereof, monomer(s), and optionally solvent are continuously supplied to the reaction zone and polymer product continuously or semi-continuously removed therefrom.

The skilled artisan will appreciate that the invention disclosed herein may be practiced in the absence of any component which has not been specifically disclosed. The following examples are provided as further illustration of the invention and are not to be construed as limiting. Unless stated to the contrary all parts and percentages are expressed on a weight basis.

Examples

Preparation of Tetrakis(pentamethylcyclopentadienyl)titanoxane (CP-MTMC)

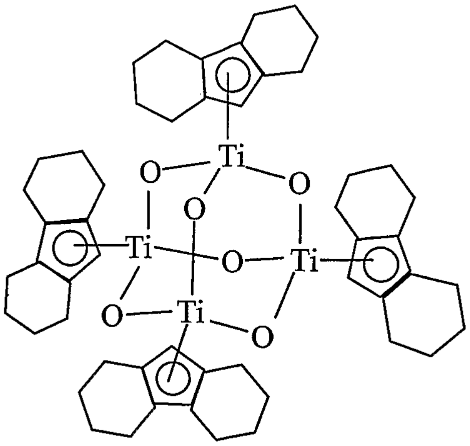


To a crimp sealed ampoule equipped with a stirring bar under nitrogen atmosphere, 5 grams (g) (18.1 millimoles (mmol)) of η^5-pentamethylcyclopentadienyltitanium trimethoxide is added. Then, 10 g, (0.556 mol) of degassed distilled water are slowly added by syringe at room temperature. After a complete reaction, the mixture is filtered under air and dried under vacuum at room temperature for three days. The desired product is recovered as a light yellow powder. Yield 3.47 g, 93 percent. After preparing crystals, the product is subjected to analysis by X-ray crystallography.

Activation

To an ampoule equipped with a stirring bar under argon atmosphere in a glove box, 0.2299 g (0.278 mmol) of CP-MTMC is dissolved in 20 milliliters (ml) of degassed toluene. Titanium tetrachloride ($TiCl_4$) (0.1897 g (1.00 mmol)) dissolved in 5 ml of toluene is added dropwise to the stirred solution at room temperature (nominally 25 °C). After completion of the reaction, stirring is continued for 15 minutes. The red-orange solution is separated from the precipitate by filtration, and dried under reduced pressure to a red-orange powder.

Preparation of Tetrakis(octahydrofluorenyl)titanoxane ([656]-MTMC)



In a glass flask under an inert atmosphere, 5 g (15.9 mmol) of η^5-octahydrofluorenyl-titanium trimethoxide are dissolved in 150 ml of degassed acetone. While refluxing 40 ml (2.22 mol) of degassed distilled water is added slowly by syringe. After completion of the addition, refluxing is continued for 30 minutes. The light yellow precipitate that formed is separated, washed with a 15:4 volume mixture of acetone and water and dried under reduced pressure. The desired product is recovered as a light yellow powder. Yield 3.50 g, 90 percent.

Activation

To an ampoule equipped with a stirring bar under argon atmosphere in a glove box, 0.17865 g (0.182 mmol) of [656]-MTMC are dissolved in 10 ml of degassed toluene. $TiCl_4$ (0.1265 g (0.667 mmol)) dissolved in 5 ml of toluene is added dropwise to the stirred solution at room temperature. After completion of the reaction, stirring is continued for 15 minutes. The red-orange solution is separated from the precipitate by filtration, and dried under reduced pressure to a red-orange powder.

Styrene Polymerization

All preparations are carried out under inert gas atmosphere. Catalyst premix solutions are prepared in a 10 ml glass flask by combining 3.59 ml of 1.52 Molar methylalumoxane (MAO) solution in toluene, 3.00 ml of a 1 Molar solution of triisobutylaluminum (TIBA) in toluene, and the corresponding amount of the titanium compound:

9.8 mg of activated [656-MTMC] (0.030 mmol Ti);

8.0 mg non-activated [656]-MTMC (0.033 mmol Ti),

8.7 mg of activated Cp-MTMC (0.030 mmol Ti), or

6.9 mg non-activated Cp-MTMC (0.033 mmol Ti)

and sufficient additional toluene to 10 ml volume.

Styrene polymerizations are conducted in glass ampoules charged with 10 ml of deoxygenated styrene that had been passed through activated alumina and hydrogenated using palladium (Pd) on alumina to remove impurities. The flasks are capped with a septum, crimp sealed and placed in a water bath at the desired temperature for 10 minutes to equilibrate. Polymerization is initiated by addition of 145.5 microliters (µl) the desired catalyst premix solution via microliter syringe. After polymerization for the desired time, the reaction is quenched by addition of methanol. The resulting polymer is isolated and dried under vacuum for 30 minutes at 150 °C followed by 35 minutes at 250 °C. Results are contained in Table 1.

Table 1

Run	Comp. A	Comp. B (activator)	Molar ratio B/A	Polymn. time (min)	Conversion (percent)	Tg (°C)	T_m (°C)	Mw (g/mol) x1000
1	[656]-MTMC	$TiCl_4$	3.7	60	70.3	99	268	830
2*	[656]-MTMC	-		60	12.9	99	268	1260
3	[656]-MTMC	$TiCl_4$	3.7	30	43.5	99	268	1040
4*	[656]-MTMC	-		30	12.7	100	268	1500
5	CP-MTMC	$TiCl_4$	3.6	60	17.9	99	268	971
6*	CP-MTMC	-		60	14.3	100	268	1530
7	CP-MTMC	$TiCl_4$	10.8	60	15.1	100	267	1140
8*	CP-MTMC	$Ti(OMe)_4$	10.8	60	3.7	-	268	-

* comparative example

Glass transition temperature (Tg) is determined by Differential Scanning Calorimetry (DSC) and the weight average molecular weight (Mw) is determined by size-exclusion chromatography (SEC). T_m is the melting temperature.

CLAIMS:

1. An activated catalyst composition produced by contacting:

A) a multinuclear transition metal compound of the formula:

$$MR^1_m[-R^2-]_p[M_qR^3_r]_n$$

wherein:

M is independently a metal of Group 4 or the Lanthanide Series of the Periodic Table;

R^1 is independently in each occurrence a C_{1-50} hydrocarbon group, π-coordinated hydrocarbyl ligand, or a boron, silicon, nitrogen, phosphorus, or oxygen substituted derivative thereof, wherein any R1 group may optionally contain one or more halo-, halocarbyl-, halohydrocarbyl-, tri(hydrocarbyl)silyl-, or tri(hydrocarbyl)silylhydrocarbyl-, substituents;

R^2 is independently in each occurrence R^1, a hydride, or a hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido, trihydrocarbylsilyl, or halo group of up to 20 nonhydrogen atoms;

R^3 is independently in each occurrence R^1, R^2, or a divalent ligand group selected from O, NR^5, PR^5, O-R^4-O, NR^5-R^4-NR^5, and PR^5-R^4-PR^5, which is shared by two metal centers, M, in the form of a μ-bridged structure~~;~~

R^4, is a divalent ligand group of up to 30 atoms, not counting hydrogen;

R^5 is an anionic ligand group of up to 30 atoms, not counting hydrogen; and

m is 1, 2, or 3;

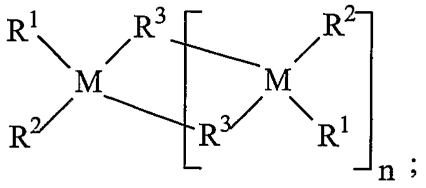
n is an integer greater than or equal to 1;

p is equal to 4-m;

q is an integer greater than or equal to 1; and

r is an integer greater than or equal to 1.

2. The activated catalyst composition of Claim 1, wherein the multi-nuclear transition metal compound corresponds to the formula:



;

wherein,

R^1 is independently in each occurrence a C_{1-50} hydrocarbon group, π-coordinated hydrocarbyl ligand, or a boron, silicon, nitrogen, phosphorus, or oxygen substituted derivative thereof, wherein any R1 group may optionally contain one or more halo-, halocarbyl-, halohydrocarbyl-, tri(hydrocarbyl)silyl-, or tri(hydrocarbyl)silylhydrocarbyl-, substituents;

R^2 is independently in each occurrence R^1, a hydride, or a hydrocarbyl, hydrocarbyloxy, di(hydrocarbyl)amido, trihydrocarbylsilyl, or halo group of up to 20 nonhydrogen atoms;

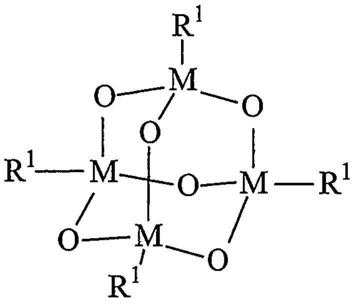
R^3 is independently in each occurrence R^1, R^2, or a divalent ligand group selected from O, NR^5, PR^5, O-R^4-O, NR^5-R^4-NR^5, and PR^5-R^4-PR^5, which is shared by two metal centers, M, in the form of a μ-bridged structure~~;~~

n is an integer greater than or equal to 1;

and when n is 2 or greater, two R^2 groups on different metal centers may together form an R^3 group; and

M is independently in each occurrence a group 4 metal.

3. The activated catalyst composition of Claim 2, wherein the multinuclear transition metal compound corresponds to the formula:



wherein

M is independently a metal of Group 4 or the Lanthanide Series of the Periodic Table; and R^1 is independently in each occurrence a $C_{1\text{-}50}$ hydrocarbon group, π-coordinated hydrocarbyl ligand, or a boron, silicon, nitrogen, phosphorus, or oxygen substituted derivative thereof, wherein any R1 group may optionally contain one or more halo-, halocarbyl-, halohydrocarbyl-, tri(hydrocarbyl)silyl-, or tri(hydrocarbyl)silylhydrocarbyl-, substituents.

4. The activated catalyst composition of Claim 3, wherein M in each occurrence is Ti, and R^1 independently in each occurrence is η^5-pentamethylcyclopentadienyl or η^5-octahydrofluorenyl.

5. The activated catalyst composition of Claim 1 wherein the mononuclear transition metal compound is titanium tetrachloride.

6. The activated catalyst composition of Claim 1 wherein the ratio of B:A is from (5n):1 to (0.05n):1.

7. A process for polymerization of polymerizable monomers or mixtures thereof comprising contacting said monomer or mixture of monomers with an activated catalyst composition of claim 1 under polymerization conditions.

8. A process according to claim 7 wherein the molar ratio of the amount of metal in the activated catalyst composition to cocatalyst is from 1:0.01 to 1:10,000.

9. A process according to claim 7 additionally comprising an activating cocatalyst comprising methylalumoxane, N-methyl-N,N-dioctadecylammonium

tetrakis(pentafluorophenyl)borate, or bis-hydrogenated tallow alkyl methylammonium tetrakis(pentafluorophenyl)borate.

10. The process of claim 7 wherein the polymerizable monomer is styrene, p-methylstyrene, or a mixture thereof.

11. The process of claim 10 wherein a syndiotactic polymer is prepared.

INTERNATIONAL SEARCH REPORT

International Application No
[illegible]CT/US2004/013976

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08F12/08 C08F4/64 C07F17/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08F

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

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

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3 316 233 A (FEAY DARRELL C) 25 April 1967 (1967-04-25) example 20	1-11
Y	EP 1 101 774 A (SAMSUNG ELECTRONICS CO LTD) 23 May 2001 (2001-05-23) paragraph ‘0031! examples 5-12; tables 1,2 paragraph ‘0050!	1-11
X	WO 00/07726 A (EQUISTAR CHEM LP) 17 February 2000 (2000-02-17) examples 3-6; tables 1,2	1-9

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 13 October 2004	Date of mailing of the international search report 20/10/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Authorized officer Parry, J

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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