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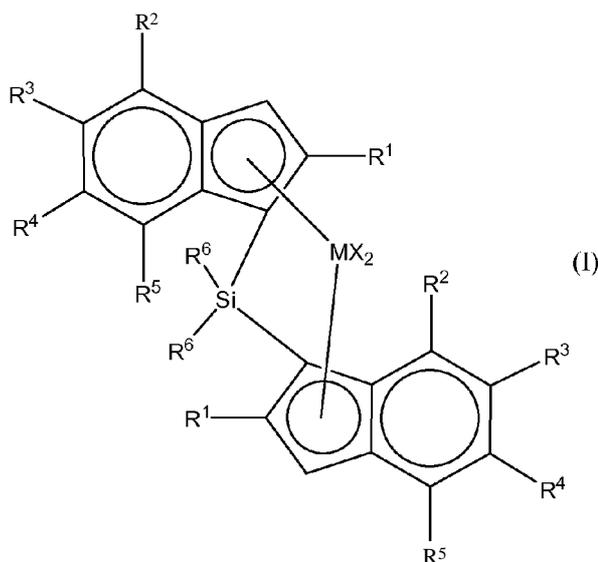
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(54) Title: ETHYLENE COPOLYMERS



(57) Abstract: A process for copolymerizing ethylene, comprising the step of contacting ethylene, one or more non-conjugated cyclic diene and optionally one or more alpha olefins of formula $\text{CH}_2=\text{CHT}$ wherein T is a $\text{C}_1\text{-C}_{20}$ alkyl radical under polymerization conditions in the presence of a catalyst system obtainable by contacting: A) a metallocene compound of formula (I) wherein: M is titanium zirconium or hafnium; X, equal to or different from each other, is a hydrogen atom, a halogen atom, a hydrocarbon group optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; R^1 are $\text{C}_1\text{-C}_{40}$ hydrocarbon radical; R^2 , and R^5 are hydrogen atoms, or $\text{C}_1\text{-C}_{20}$ hydrocarbon radicals; R^6 , equal to or different from each other, are $\text{C}_1\text{-C}_{20}$ hydrocarbon radicals; R^3 and R^4 , form together a condensed saturated or unsaturated $\text{C}_3\text{-C}_7$ -membered ring; B) an alumoxane or a compound capable of forming an alkyl metallocene cation; and optionally C) an organo aluminum compound.

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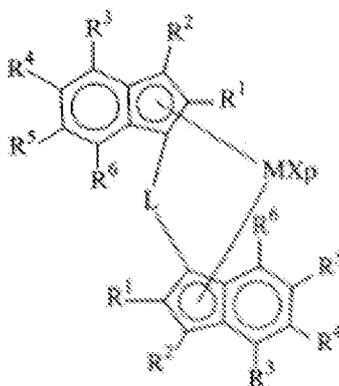
Title**Ethylene copolymers**

The present invention relates to a process for obtaining copolymers containing derived units of ethylene and non conjugated cyclic diene and optionally containing derived units of one or more alpha olefins of formula $\text{CH}_2=\text{CHT}$ wherein T is a $\text{C}_i\text{-C}_{20}$ alkyl radical. Said copolymers being obtained by using a class of metallocene compounds having a specific substitution pattern.

Polymers based on non-conjugated cyclic dienes such as ethylene/propylene/ethylidene norbornene copolymers are those which are vulcanizable, are superior in weatherability, heat resistance and ozone resistance and are used for automobile industrial parts, industrial rubber products, insulating materials, civil and construction materials and rubber products such as gummed clothes and also widely used for materials to be blended with plastics such as a polypropylene and polystyrene.

However when non-conjugated cyclic dienes are polymerized the polymerization activity is low, furthermore the polymer obtained has low molecular weight and low content of non-conjugated cyclic dienes derived units since this class of comonomer is not easy to polymerize.

WO 2004/050724 relates to a class of metallocene compounds having formula:



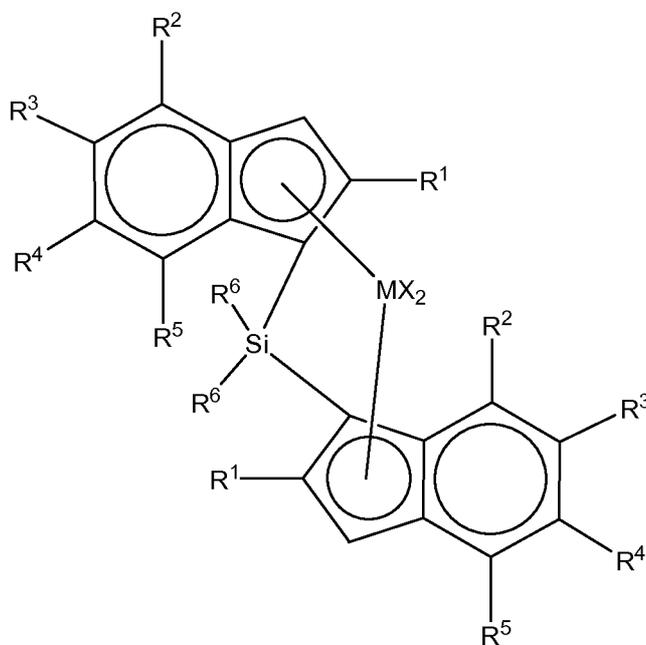
Wherein in particular R^4 and R^5 , form together a condensed saturated or unsaturated $\text{C}_3\text{-C}_7$ -membered ring. However this document is completely silent about the use of non conjugated cyclic diene as comonomers.

WO 2005/058916 relates to a similar class of metallocene compounds wherein preferably the indenyl ring is substituted in position 4 with a phenyl moiety. Even this document is silent about the possibility to use non conjugated cyclic diene as comonomers.

The applicant find a class of bridged metallocene compound having a particular substitution pattern able to give in high yields ethylene optionally an alpha olefin, and non conjugated cyclic diene copolymers having an high molecular weight and a relatively high non conjugated cyclic diene derived units content, without using an high concentration of non conjugated cyclic diene in the polymerization bath.

An object of the present invention is a process for copolymerizing ethylene comprising the step of contacting ethylene, one or more non-conjugated cyclic diene and optionally one or more alpha olefins of formula $\text{CH}_2=\text{CHT}$ wherein T is a C1-C20 alkyl radical under polymerization conditions in the presence of a catalyst system obtainable by contacting:

A) a metallocene compound of formula (I)



(I)

Wherein:

M is titanium zirconium or hafnium; preferably M is zirconium

X, equal to or different from each other, is a hydrogen atom, a halogen atom, a R, OR, OSO₂CF₃, OCOR, SR, NR₂ or PR₂ group wherein R is a linear or branched, cyclic or acyclic, C₁-C₄₀-alkyl, C₂-C₄₀ alkenyl, C₂-C₄₀ alkynyl, C₆-C₄₀-aryl, C₇-C₄₀-alkylaryl or C₇-C₄₀-arylalkyl radical; optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; or two X groups can be joined together to form a group OR'O wherein R' is a C₁-C₂₀-alkylidene, C₆-C₂₀-arylidene, C₇-C₂₀-alkylarylidene, or C₇-C₂₀-arylalkylidene radical; preferably X is a

hydrogen atom, a halogen atom or R group; more preferably X is chlorine or a methyl radical;

R¹, equal to each other, are C1-C40 hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R¹ is a linear Ci-Cio -alkyl radical; more preferably R¹, is a methyl, ethyl or isopropyl radical;

R², and R⁵, equal to or different from each other, are hydrogen atoms, or C1-C20 alkyl radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R², and R⁵ are hydrogen atoms.

R⁶, equal to or different from each other, are C1-C40 hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R⁶, equal to or different from each other are , Ci-C4o -alkyl, C2-C40 alkenyl, C2-C40 alkynyl, C6-C4o-aryl, C7-C4o-alkylaryl or C7-C4o-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably R⁶, equal to or different from each other are Ci-C4o -alkyl, such as methyl, ethyl or isopropyl;

R³ and R⁴, form together a condensed saturated or unsaturated C3-C7 -membered ring preferably a C4-C6 -membered ring, optionally containing heteroatoms belonging to groups 13-16 of the Periodic Table of the Elements; every atom forming said ring being substituted with R⁷ radicals; that means that the valence of each atom forming said ring is filled with R⁷ groups, wherein R⁷, equal to or different from each other, are hydrogen atoms or C1-C40 hydrocarbon radicals optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; preferably R⁷ are hydrogen atoms or Ci-C4o -alkyl, C2-C40 alkenyl, C2-C40 alkynyl, C6-C4o-aryl, C7-C4o-alkylaryl or C7-C4o-arylalkyl radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; more preferably R⁷ is a hydrogen atom or a Ci-C2o -alkyl radical; even more preferably it is a hydrogen atom or a methyl or ethyl radical;

B) an alumoxane or a compound capable of forming an alkyl metallocene cation; and optionally

(C) an organo aluminum compound.

Preferably the metallocene of formula (I) is in the racemic form

The non-conjugated cyclic diene of the present invention is a cyclic compound having two unsaturated bonds. This non-conjugated cyclic diene is preferably a hydrocarbon cyclic compound having preferably 6 to 20 carbon atoms and more preferably 6 to 12 carbon atoms.

Examples of the non-conjugated cyclic diene of the present invention may include, though not particularly limited to, bicyclo [2.2.1]hept-2-ene derivatives having an alkylidene group such as 5-ethylidenebicyclo[2.2.1]hept-2-ene (5-ethylidene-2-norbornene), 5-ethylidene-6-methylbicyclo[2.2.1]hept-2-ene, 5-ethylidene-6-ethylbicyclo[2.2.1]hept-2-ene, 5-ethylidene-6-isopropylbicyclo[2.2.1]hept-2-ene, 5-ethylidene-6-butylbicyclo[2.2.1]hept-2-ene, 5-n-propylidenebicyclo[2.2.1]hept-2-ene, 5-n-propylidene-6-methylbicyclo[2.2.1]hept-2-ene, 5-n-propylidene-6-ethylbicyclo[2.2.1]hept-2-ene, 5-n-propylidene-6-isopropylbicyclo[2.2.1]hept-2-ene, 5-n-propylidene-6-butylbicyclo[2.2.1]hept-2-ene, 5-isopropylidenebicyclo[2.2.1]hept-2-ene, 5-isopropylidene-6-methylbicyclo [2.2.1]hept-2-ene, 5-isopropylidene-6-ethylbicyclo [2.2.1]hept-2-ene, 5-isopropylidene-6-isopropylbicyclo[2.2.1]hept-2-ene and 5-isopropylidene-6-butylbicyclo[2.2.1]hept-2-ene; bicyclo[2.2.1]hept-2-ene derivatives having an alkenyl group such as 5-ethenylbicyclo[2.2.1]hept-2-ene(5-vinyl-2-norbornene), 5-propenylbicyclo[2.2.1] hept-2-ene and 5-butenylbicyclo[2.2.1]hept-2-ene; dicyclopentadiene, cyclooctadiene, and 4-vinyl-1-cyclohexene. Among these groups, bicyclo[2.2.1]hept-2-ene derivatives having a Ci-Cio alkylidene group as substituent and bicyclo[2.2.1]hept-2-ene derivatives having a Ci-Cio alkenyl group as substituent are preferable. Particularly preferred are 5-ethylidene-2-norbornene (E/Z-5-ethylidenebicyclo[2.2.1]hept-2-ene) and 5-vinyl-2-norbornene are most preferable.

Examples of alpha olefins of formula $\text{CH}_2=\text{CHT}$ wherein T is a Ci-C₂₀ alkyl radical are propylene, 1-butene, 1-pentene, 2-methyl-1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecacene. Preferred alpha olefin is propylene or 1-butene.

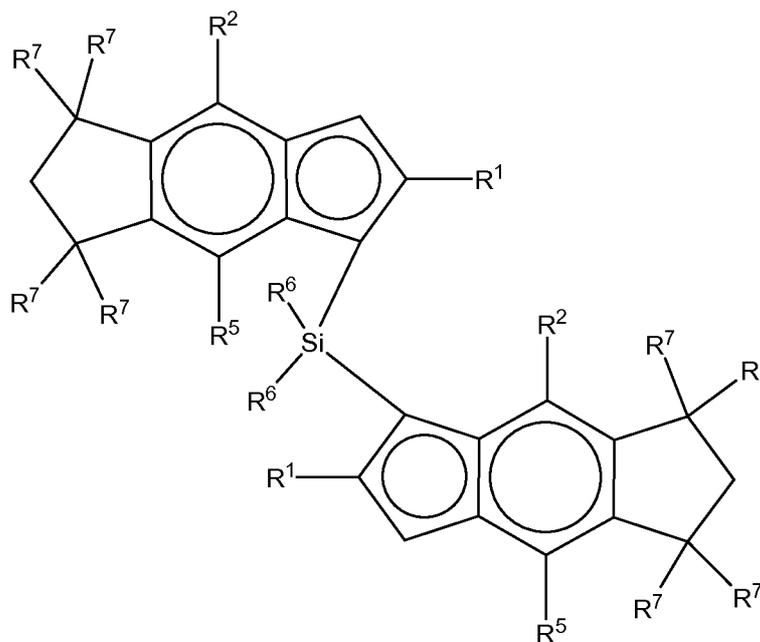
Preferably an object of the present invention is a process for copolymerizing ethylene, one or more non-conjugated cyclic diene and one or more alpha olefins of formula $\text{CH}_2=\text{CHT}$ wherein T is a Ci-C₂₀ alkyl radical comprising the step of contacting ethylene, one or more non-conjugated cyclic diene and one or more alpha olefins of formula $\text{CH}_2=\text{CHT}$.

The process according to the present invention can be carried out in a gas phase, or in a liquid phase in the presence or absence of an inert hydrocarbon solvent. The hydrocarbon solvent can either be aromatic such as toluene, or aliphatic such as propane, hexane, heptane, isobutane or cyclohexane. When the process is carried out in a liquid phase it can be in slurry, or in solution. Preferably the copolymers of the present invention are obtained by a solution process, i.e. a process carried out in liquid phase wherein the polymer is completely or partially soluble in the reaction medium.

As a general rule, the polymerization temperature is generally comprised between -100°C and $+200^{\circ}\text{C}$ preferably comprised between 0° and 160°C , more preferably between 30°C and 90°C .

The polymerization pressure is generally comprised between 0,5 and 100 bar.

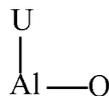
Preferably the metallocene compound A) has formula (II)



(II)

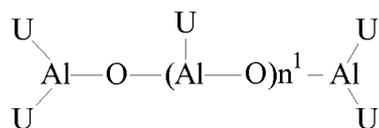
Wherein R^1 , R^2 , R^5 , R^6 and R^7 have the meaning specified above; more preferably R^7 are hydrogen atoms.

Alumoxanes used as component B) can be obtained by reacting water with an organo-aluminium compound of formula H_jAlU_{3-j} or $H_jAl_2U_{6-j}$, where U substituents, same or different, are hydrogen atoms, halogen atoms, C_1-C_{20} -alkyl, C_3-C_{20} -cycloalkyl, C_6-C_{20} -aryl, C_7-C_{20} -aryllalkyl radical, optionally containing silicon or germanium atoms with the proviso that at least one U is different from halogen, and j ranges from 0 to 1, being also a non-integer number. In this reaction the molar ratio of Al/water is preferably comprised between 1:1 and 100:1. The molar ratio between aluminium and the metal of the metallocene generally is comprised between about 10:1 and about 20000:1, and more preferably between about 100:1 and about 5000:1. The alumoxanes used in the catalyst according to the invention are considered to be linear, branched or cyclic compounds containing at least one group of the type:



wherein the substituents U, same or different, are described above.

In particular, alumoxanes of the formula:



can be used in the case of linear compounds, wherein n^1 is 0 or an integer from 1 to 40 and the substituents U are defined as above, or alumoxanes of the formula:



can be used in the case of cyclic compounds, wherein n^2 is an integer from 2 to 40 and the U substituents are defined as above. Examples of alumoxanes suitable for use according to the present invention are methylalumoxane (MAO), tetra-(isobutyl)alumoxane (TIBAO), tetra-(2,4,4-trimethyl-pentyl)alumoxane (TIOAO), tetra-(2,3-dimethylbutyl)alumoxane (TDMBAO) and tetra-(2,3,3-trimethylbutyl)alumoxane (TTMBAO). Particularly interesting cocatalysts are those described in WO 99/21899 and in WOO 1/2 1674 in which the alkyl and aryl groups have specific branched patterns. Non-limiting examples of aluminium compounds according to WO 99/21899 and WOO 1/2 1674 are:

tris(2,3,3-trimethyl-butyl)aluminium, tris(2,3-dimethyl-hexyl)aluminium, tris(2,3-dimethyl-butyl)aluminium, tris(2,3-dimethyl-pentyl)aluminium, tris(2,3-dimethyl-heptyl)aluminium, tris(2-methyl-3-ethyl-pentyl)aluminium, tris(2-methyl-3-ethyl-hexyl)aluminium, tris(2-methyl-3-ethyl-heptyl)aluminium, tris(2-methyl-3-propyl-hexyl)aluminium, tris(2-ethyl-3-methyl-butyl)aluminium, tris(2-ethyl-3-methyl-pentyl)aluminium, tris(2,3-diethyl-pentyl)aluminium, tris(2-propyl-3-methyl-butyl)aluminium, tris(2-isopropyl-3-methyl-butyl)aluminium, tris(2-isobutyl-3-methyl-pentyl)aluminium, tris(2,3,3-trimethyl-pentyl)aluminium, tris(2,3,3-trimethyl-hexyl)aluminium, tris(2-ethyl-3,3-dimethyl-butyl)aluminium, tris(2-ethyl-3,3-dimethyl-pentyl)aluminium, tris(2-isopropyl-3,3-dimethyl-butyl)aluminium, tris(2-trimethylsilyl-propyl)aluminium, tris(2-methyl-3-phenyl-butyl)aluminium, tris(2-ethyl-3-phenyl-butyl)aluminium, tris(2,3-dimethyl-3-phenyl-butyl)aluminium, tris(2-phenyl-propyl)aluminium, tris[2-(4-fluoro-

phenyl)-propyl] aluminium, tris[2-(4-chloro-phenyl)-propyl]aluminium, tris[2-(3-isopropyl-phenyl)-propyl]aluminium, tris(2-phenyl-butyl)aluminium, tris(3-methyl-2-phenyl-butyl)aluminium, tris(2-phenyl-pentyl)aluminium, tris[2-(pentafluorophenyl)-propyl]aluminium, tris[2,2-diphenyl-ethyl] aluminium

and tris[2-phenyl-2-methyl-propyl] aluminium, as well as the corresponding compounds wherein one of the hydrocarbyl groups is replaced with a hydrogen atom, and those wherein one or two of the hydrocarbyl groups are replaced with an isobutyl group.

Amongst the above aluminium compounds, trimethylaluminium (TMA), triisobutylaluminium (TIBAL), tris(2,4,4-trimethyl-pentyl)aluminium (TIOA), tris(2,3-dimethylbutyl)aluminium (TDMBA) and tris(2,3,3-trimethylbutyl)aluminium (TTMBA) are preferred.

Non-limiting examples of compounds able to form an alkylmetallocene cation are compounds of formula O^+E^- , wherein D^+ is a Brønsted acid, able to donate a proton and to react irreversibly with a substituent X of the metallocene of formula (I) and E^- is a compatible anion, which is able to stabilize the active catalytic species originating from the reaction of the two compounds, and which is sufficiently labile to be able to be removed by an olefinic monomer. Preferably, the anion E^- comprises of one or more boron atoms. More preferably, the anion E^- is an anion of the formula $BAr_4^{(-)}$, wherein the substituents Ar which can be identical or different are aryl radicals such as phenyl, pentafluorophenyl or bis(trifluoromethyl)phenyl. Tetrakis-pentafluorophenyl borate is particularly preferred examples of these compounds are described in WO 91/02012. Moreover, compounds of the formula BAr_3 can conveniently be used. Compounds of this type are described, for example, in the published International patent application WO 92/00333. Other examples of compounds able to form an alkylmetallocene cation are compounds of formula BAr_3P wherein P is a substituted or unsubstituted pyrrol radicals. These compounds are described in WO01/62764. Other examples of cocatalyst can be found in EP 775707 and DE 19917985. Compounds containing boron atoms can be conveniently supported according to the description of DE-A-19962814 and DE-A-19962910. All these compounds containing boron atoms can be used in a molar ratio between boron and the metal of the metallocene comprised between about 1:1 and about 10:1; preferably 1:1 and 2.1; more preferably about 1:1.

Non limiting examples of compounds of formula D^+E^- are:

Tributylammoniumtetrakis(pentafluorophenyl)aluminate,

Tributylammoniumtetrakis(3,5-bis(trifluoromethyl)phenyl)borate,

Tributylammoniumtetrakis(4-fluorophenyl)borate,
N,N-Dimethylbenzylammonium-tetrakis(pentafluorophenyl)borate,
N,N-Dimethylhexylammonium-tetrakis(pentafluorophenyl)borate,
N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)borate,
N,N-Dimethylaniliniumtetrakis(pentafluorophenyl)aluminate,
Di(propyl)ammoniumtetrakis(pentafluorophenyl)borate,
Di(cyclohexyl)ammoniumtetrakis(pentafluorophenyl)borate,
Triphenylcarbeniumtetrakis(pentafluorophenyl)borate,
Triphenylcarbeniumtetrakis(pentafluorophenyl)aluminate,
Ferroceniumtetrakis(pentafluorophenyl)borate,
Ferroceniumtetrakis(pentafluorophenyl)aluminate.

Organic aluminum compounds used as compound C) are those of formula H_jAlU_{3-j} or $H_jAl_2U_{6-j}$ described above. The catalysts of the present invention can also be supported on an inert carrier. This is achieved by depositing the metallocene compound A) or the product of the reaction thereof with the component B), or the component B) and then the metallocene compound A) on an inert support such as, for example, silica, alumina, Al-Si, Al-Mg mixed oxides, magnesium halides, styrene/divinylbenzene copolymers, polyethylene or polypropylene. The supportation process is carried out in an inert solvent such as hydrocarbon for example toluene, hexane, pentane or propane and at a temperature ranging from 0°C to 100°C, preferably the process is carried out at a temperature ranging from 25°C to 90°C or the process is carried out at room temperature.

A suitable class of supports which can be used is that constituted by porous organic supports functionalized with groups having active hydrogen atoms. Particularly suitable are those in which the organic support is a partially crosslinked styrene polymer. Supports of this type are described in European application EP-633272. Another class of inert supports particularly suitable for use according to the invention is that of polyolefin porous prepolymers, particularly polyethylene.

A further suitable class of inert supports for use according to the invention is that of porous magnesium halides such as those described in International application WO 95/32995.

The polymer obtained with the present invention have preferably an ethylene derived units content ranging from 25.0 to 99.5 % by weight; a content of non-conjugated cyclic diene derived units ranging from 0.5 to 15.0 % by weight, preferably from 1.0 to 10.0 % by weight. Preferably the ethylene derived units content ranges from 30.0 to 75.0 % by weight, the non-conjugated

cyclic diene derived units ranging from 2.0 to 10.0 % by weight the and a content of alpha olefins of formula $\text{CH}_2=\text{CHT}$ derived units ranging from 23.0 to 60.0 % by weight. More preferably the ethylene derived units content ranges from 50.0 to 70.0 % by weight, the non-conjugated cyclic diene derived units ranges from 3.5 to 9.0 % by weight the and a content of alpha olefins of formula $\text{CH}_2=\text{CHT}$ derived units ranges from 21.0 to 55.0 % by weight.

The following examples are for illustrative purpose and do not intend to limit the scope of the invention.

Examples

Measure of Ethylene, propylene and non-conjugated diene content

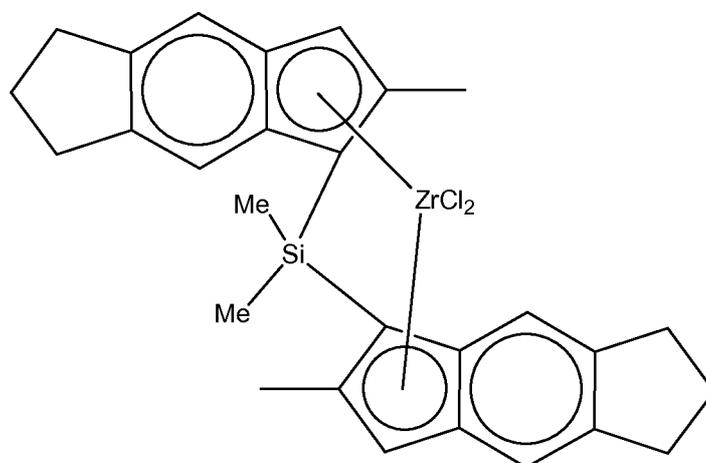
ENB content was determined with Infrared spectroscopy by using a method based on a calibration straight line obtained by using the absorption bands in the region between 4482 cm⁻¹ and 3950 cm⁻¹ and the absorption band at 1688 cm⁻¹.

Ethylene and propylene content were obtained with a method based on Near Infrared absorption bands at 5669cm⁻¹ and 5891 cm⁻¹, the resulting value is then corrected for the ENB content.

The measures are carried out on a film sample obtained by molding the raw polymer with a hydraulic press (0.2 - 3 Kg/cm²) for about 30 seconds at either 160 °C (ethylene/propylene determination) or 180 °C (ENB determination) using an aluminium spacer of fixed thickness (0.1 - 0.2 mm).

Compounds

Synthesis of Me₂Si[2-Me-5,6(cyclotrymethylen)indenyl]₂ZrCl₂ [Al]



6-methyl-1,2,3,5 tetrahydro-s-indacene has been synthesized according to the procedure reported on WO 2009/080438.

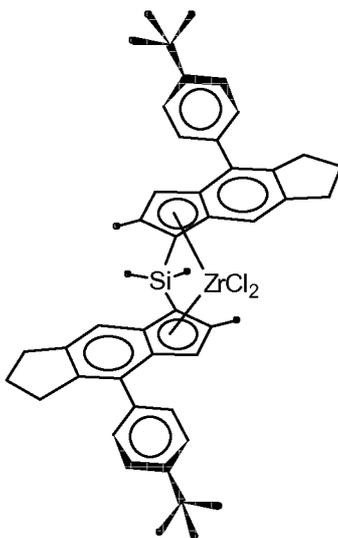
Rac-dimethyl-bis-(2-methyl-1,5,6,7-tetrahydro -s-indacen-1-yl)-silane has been synthesized according to the procedure described in WO 2004/050724 by using 6-methyl-1,2,3,5 tetrahydro-s-indacene instead of 1,1,3,3,6-Pentamethyl-1,2,3,5-tetrahydro-s-indacene.

Me₂Si[2-Me-5,6(cyclotrymethylen)indenyl]₂ZrCl₂ has been synthesized according to the procedure described in WO 2004/050724 by using rac-dimethyl-bis-(2 -methyl- 1,5,6,7-

tetrahydro-s-indacen-1-yl)-silane instead of rac-dimethyl-bis-(2,5,5,7,7-pentamethyl-1,5,6,7-tetrahydro-s-indacen-1-yl)-silane.

rac- μ -{bis- $[\eta^5$ -2-methyl-4-(4-*tert*-butylphenyl)-1,5,6,7-tetrahydro-s-indacen-1-yl]dimethylsilanediyl}dichlorozirconium (IV). (C-1)

rac- μ -{bis- $[\eta^5$ -2-methyl-4-(4-*tert*-butylphenyl)-1,5,6,7-tetrahydro-s-indacen-1-yl]dimethylsilanediyl}dichlorozirconium has been synthesized according to the procedure described in WO2006/097497



$\text{Al}(\text{i-Bu})_3$ (TIBA) and methylalumoxane (MAO, Chemtura 30%wt/wt in toluene) were used as received.

Preparation of the catalyst system

A weighted amount of metallocene is transferred in a Schlenk flask under nitrogen. The solid is then dissolved in a quantity of MAO/TIBA toluene/cyclohexane solution (MAO/TIBA = 2 molar) to obtain a final Al/Zr ratio equal to 600 mol/mol. The MAO/TIBA solution is obtained by mixing a solution of MAO in Toluene with a cyclohexane solution of TIBA (Al = 4 g/l).

This activated metallocene solution is maintained at room temperature under stirring for 12 h. After this, it can be used in polymerization and it maintains the initial polymerization over at least a week.

Examples 1-3

In a 4.5 litre jacketed stainless-steel autoclave is purged with nitrogen flow at 70 °C for one hour. Then, at 30 °C, 1300 g. of technical iso-hexane, 5-ethenylbicyclo[2.2.1]hept-2-ene(5-vinyl-2-norbornene) (ENB) (amount reported in Table 1) and 4 mmol of MAO/TIBA cyclohexane solution (MAO/TIBA = 2 molar) are introduced in the autoclave.

The autoclave is closed and the temperature is raised to 58 °C and ethylene and propylene (amounts reported in Table 1) are added.

A measured amount (Table 1) of activated metallocene catalyst system solution is added to 5 mL of technical iso-hexane and then injected in the autoclave by nitrogen overpressure.

The internal pressure is kept constant for the entire polymerization test by feeding an ethylene/propylene mixture having nearly the same weight ratio of the terpolymer under production. On table 1 the polymerization conditions are reported.

After 30 minutes the bottom discharge valve is opened and the terpolymer solution is discharged from the autoclave into a heated steel tank and monomers and solvent are removed by feeding for 10 min hot water steam.

The terpolymer was recovered and carefully dried at 70 °C under vacuum for 8 hours, the characterization data are reported in Table 2.

Table 1

Ex	Metallocene(mg)	Al _{tot} /Zr Molar ratio	T. pol. °C	Ethylene g	Propylene g	ENB g
1	A1 (1.1)	2625	60	43	108	7
2	A1 (2)	1714	60	35	160	10
3	A1 (1.4)	2191	50	53	125	8
4	A1 (2.4)	1528	50	32	230	11
5	C1 (6.7)	1791	60	46	69	10

* Comparative

Table 2

Ex	Ethylene Wt%	ENB Wt%	Activity Kgpol/gmetallocene *30 min	IV dL/g
1	65	4.5	102	1.89
2	44	4.1	113	1.11
3	68	4.9	85	2.12
4	51	8.1	39	1.67
5*	46	4.1	0.9	1.51

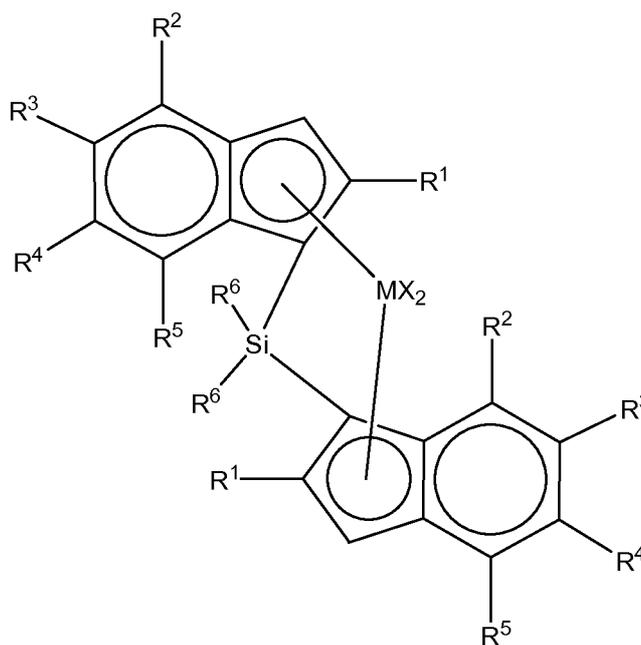
* Comparative

The results of table 2 clearly show that compound A1 has an higher activity with respect to compound CI.

Claims

1. A process for copolymerizing ethylene, comprising the step of contacting ethylene, one or more non-conjugated cyclic diene and optionally one or more alpha olefins of formula $\text{CH}_2=\text{CHT}$ wherein T is a Ci-C_{20} alkyl radical under polymerization conditions in the presence of a catalyst system obtainable by contacting:

A) a metallocene compound of formula (I)



(I)

Wherein:

M is titanium zirconium or hafnium;

X, equal to or different from each other, is a hydrogen atom, a halogen atom, a R, OR, OR'O, OSO_2CF_3 , OCOR , SR, NR_2 or PR_2 group wherein R is a linear or branched, saturated or unsaturated Ci-C_{20} -alkyl, $\text{C}_3\text{-C}_{20}$ -cycloalkyl, $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_7\text{-C}_{20}$ -alkylaryl or $\text{C}_7\text{-C}_{20}$ -arylalkyl radical, optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements; and R' is a Ci-C_{20} -alkylidene, $\text{C}_6\text{-C}_{20}$ -arylidene, $\text{C}_7\text{-C}_{20}$ -alkylarylidene, or $\text{C}_7\text{-C}_{20}$ -arylalkylidene radical;

R^1 , equal to or different from each other, are $\text{C}_1\text{-C}_{40}$ hydrocarbon radical optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

R^2 , and R^5 , equal to or different from each other, are hydrogen atoms, or Ci-C_{20} alkyl radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic

Table of the Elements;

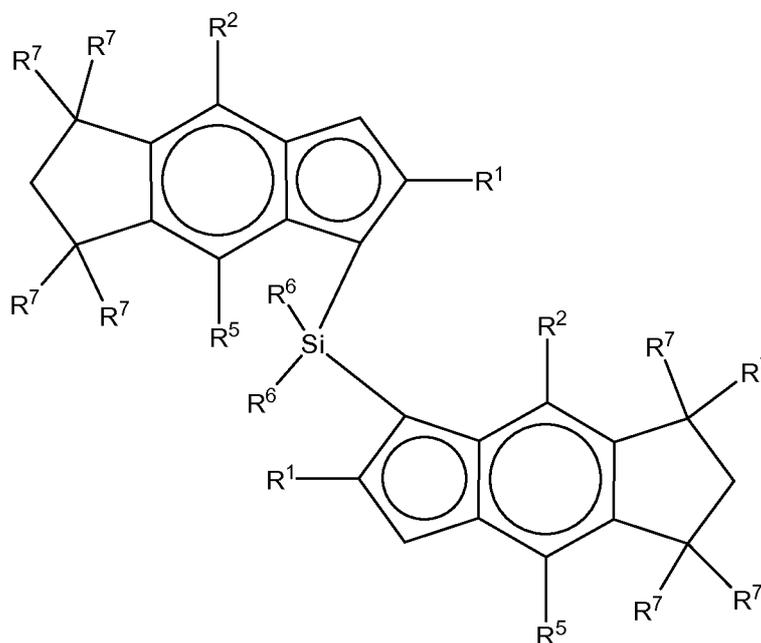
R^6 , equal to or different from each other, are C1-C40 hydrocarbon radicals optionally containing heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

R^3 and R^4 , form together a condensed saturated or unsaturated C3-C7-membered ring preferably a C4-C6-membered ring, optionally containing heteroatoms belonging to groups 13-16 of the Periodic Table of the Elements; every atom forming said ring being substituted with R^7 radicals; wherein R^7 , equal to or different from each other, are hydrogen atoms or C1-C40 hydrocarbon radicals, optionally containing one or more heteroatoms belonging to groups 13-17 of the Periodic Table of the Elements;

B) an alumoxane or a compound capable of forming an alkyl metallocene cation; and optionally

(C) an organo aluminum compound.

2. The process according to claim 1 wherein in the compound of formula (I) X is a hydrogen atom, a halogen atom, a OR'O or R group;
3. The process according to claims 1 or 2 wherein in the compound of formula (I) R^1 , equal to or different from each other, is a linear Ci-Cio-alkyl radical;
4. The process according to anyone of claims 1-3 wherein R^2 , and R^5 are hydrogen atoms
5. The process according to anyone of claims 1-4 wherein the metallocene compound A) has formula (II):



(II)

Wherein R^1 , R^2 , R^5 , R^6 and R^7 have the meaning described in claim 1.

6. The process according to claim 5 wherein in the compound of formula (II) R^7 are hydrogen atoms.
7. The process according to anyone of claims 1-6 for copolymerizing ethylene, one or more non-conjugated cyclic diene and one or more alpha olefins of formula $CH_2=CHT$ wherein T is a C1-C20 alkyl radical comprising the step of contacting ethylene, one or more non-conjugated cyclic diene and one or more alpha olefins of formula $CH_2=CHT$ in the presence of the catalyst system of claims 1-6.
8. The process according to anyone of claims 1-7 wherein the non-conjugated cyclic diene is a hydrocarbon compound having 6 to 20 carbon atoms.
9. The process according to claim 8 wherein the non-conjugated cyclic diene is selected from the group consisting of bicyclo[2.2.1]hept-2-ene derivatives having a C1-C10 alkylidene group as substituent and bicyclo[2.2.1]hept-2-ene derivatives having a C1-C10 alkenyl group as substituent.
10. The process according to claim 9 wherein the non-conjugated cyclic diene is selected from 5-ethylidene-2-norbornene (E/Z-5-ethylidenebicyclo[2.2.1]hept-2-ene) and 5-vinyl-2-norbornene.

11. The process according to anyone of claims 1-10 wherein the alpha olefins of formula $\text{CH}_2=\text{CHT}$ are selected from the group consisting of propylene, 1-butene, 1-pentene, 2-methyl-1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene, 1-dodecene.
12. The process according to anyone of claims 1-11 wherein the polymer has an ethylene derived units content ranging from 25.0 to 99.5 % by weight and a content of non-conjugated cyclic diene derived units ranging from 0.5 to 15.0 % by weight.
13. The process according to claim 12 wherein the polymer has content of non-conjugated cyclic diene derived units ranging from 1.0 to 10.0 % by weight.
14. The process according to anyone of claims 1-13 wherein the polymer has an ethylene derived units content ranging from 30.0 to 75.0 % by weight, a non-conjugated cyclic diene derived units ranging from 2.0 to 10.0 % by weight and a content of alpha olefins of formula $\text{CH}_2=\text{CHT}$ derived units ranging from 23.0 to 60.0 % by weight, the sum being 100%.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP201Q/067490

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F21Q/02
ADD.

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)
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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	wo 2006/O97497 AI (BASELL POLYOLEFINE GMBH [DE]; NIFANT EV ILYA E [RU]; IVCHENKO PAVEL V) 21 September 2006 (2006-09-21) cited in the application on page 26; examples A-I page 18, line 4 - line 30 page 20, line 24 - page 21, line 28 -----	1-14
A	wo 2004/050724 AI (BASELL POLYOLEFINE GMBH [DE]; RESCONI LUIGI [IT]; CASCIO INGURGIO ANTO) 17 June 2004 (2004-06-17) cited in the application claims 7-9 ----- -/--	1-14

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

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance	"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
"E" earlier document but published on or after the international filing date	"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
"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)	"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.
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 11 March 2011	Date of mailing of the international search report 28/03/2011
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Lippert, Si grid
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INTERNATIONAL SEARCH REPORT

International application No
PCT/ EP201Q/067490

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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International application No

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