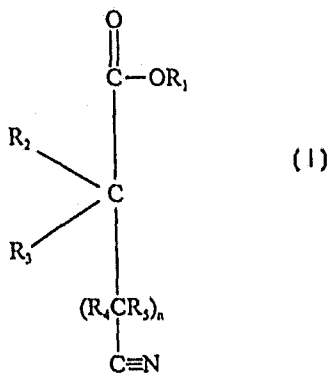




<p>(51) International Patent Classification ⁶ : C08F 10/00</p>	<p>A1</p>	<p>(11) International Publication Number: WO 99/11677 (43) International Publication Date: 11 March 1999 (11.03.99)</p>
<p>(21) International Application Number: PCT/EP98/05160 (22) International Filing Date: 14 August 1998 (14.08.98) (30) Priority Data: 97202707.2 3 September 1997 (03.09.97) EP (71) Applicant: MONTELL TECHNOLOGY COMPANY B.V. [NL/NL]; Hoeksteen 66, NL-2132 MS Hoofddorp (NL). (72) Inventors: MORINI, Giampiero; Via Giotto, 36, I-35100 Padova (IT). GULEVICH, Yuri, V.; Apartment H, 103 Deerfield Road, Elkton, MD 21921 (US). BALBONTIN, Giulio; Via Ugo Bassi, 17A, I-44100 Ferrara (IT). (74) Agent: ZANOLI, Enrico; Montell Italia S.p.A., Via Pergolesi, 25, I-20124 Milano (IT).</p>	<p>(81) Designated States: AU, BR, CA, CN, JP, KR, RU, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>	

(54) Title: COMPONENTS AND CATALYSTS FOR THE POLYMERIZATION OF OLEFINS



(57) Abstract

The invention relates to solid catalyst components for the polymerization of olefins $\text{CH}_2=\text{CHR}$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising Ti, Mg, halogen and an electron donor compound selected from cyanoesters of formula (1); wherein R_1 is a C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl group; n is 0, 1, 2 or 3; R_2 , R_3 , R_4 and R_5 are independently selected from hydrogen or C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl groups; two or more of R_2 and R_3 , and R_4 and R_5 , can be joined to form a cycle. Said catalyst components when used in the polymerization of olefins are characterized by an excellent response to hydrogen and capability to produce polymers with broad Molecular Weight Distribution.

“COMPONENTS AND CATALYSTS FOR THE POLYMERIZATION OF OLEFINS”

The present invention relates to catalyst components for the polymerization of olefins, to the catalysts obtained therefrom and to the use of said catalysts in the polymerization of olefins $\text{CH}_2=\text{CHR}$ in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms. In particular the present invention relates to catalyst components, suitable for the stereospecific polymerization of olefins, comprising titanium, Mg, halogen and an electron donor compound selected from cyanoesters having a particular formula. Said catalyst components when used in the polymerization of olefins, and in particular of propylene, are characterized by an excellent response to hydrogen and are also capable to give polymers with very broad molecular weight distribution.

Many patent applications have been filed in the field of the so-called high-yield polymerization catalysts, in particular regarding the catalysts for the polymerization of propylene. Typically, said catalysts comprise a solid catalyst component, constituted by a magnesium dichloride on which are supported a titanium compound and an internal electron donor compound (usually an ester of a phthalic acid), an Al-alkyl compound and an external donor (usually a silicon compound). The above catalyst systems, although capable of providing propylene polymers with high stereoregularity and in high yields, are also characterized by a poor capability of response to hydrogen. In other words, very high concentrations of hydrogen, used as molecular weight regulator, are necessary in order to obtain polymers with low molecular weight. The low molecular weight polymers are requested in applications where high fluidity in the molten state and good mechanical properties are necessary. The production of webs for non-woven fabrics, which is carried out by melt blown or spun bonded processes, is an example of such applications. In some cases, the molecular weights required for the

propylene polymers are so low that, to produce them, the prior art catalyst systems would require a pressure of hydrogen well above the operative limit of conventional bulk polymerization plants. In these cases, such low molecular weight polymers are obtained by visbreaking of the high molecular weight polymers at high temperatures (200°-300°C) and in the presence of free radical generators such as organic peroxides.

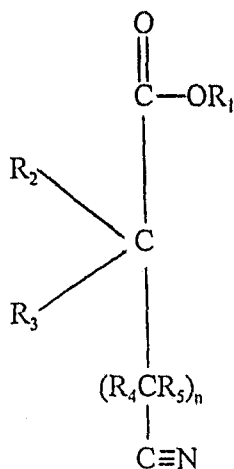
Moreover, the propylene polymers obtained with the above mentioned catalyst systems usually have a narrow molecular weight distribution (MWD) as compared for example with polyolefins prepared by using the conventional catalysts comprising a titanium trichloride based catalyst component. The narrow MWD causes a worsening of the processability of the polymers which involves a decrease of the quality of the products in applications such as molding or thermoforming. One of the approaches that have been tried to broaden the MWD comprises carrying out the polymerization in at least two steps under different polymerization conditions. However, these multisteps processes require a more complicated and sophisticated polymerization operation which increases the cost of the polymerization process.

Accordingly, there is still a need of a polymerization catalyst system with a good response to hydrogen and also capable of producing polymers with broad MWD.

It has now surprisingly been found that if specific cyanoesters are used as internal donor, catalyst components capable to give an excellent response to hydrogen are obtained. Very surprisingly said catalyst components, differently from what is known in the art, couple this feature with the capability of producing polymers with broad molecular weight distribution.

It is therefore an object of the present invention to provide a solid catalyst component for the polymerization of olefins $\text{CH}_2=\text{CHR}$ in which R is hydrogen or a hydrocarbyl radical

with 1 - 12 carbon atoms, comprising Ti, Mg, halogen and an electron donor compound selected from cyanoesters of formula (I):



wherein R_1 is a C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl group; n is 0, 1, 2 or 3; R_2 , R_3 , R_4 and R_5 are independently selected from hydrogen or C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl groups; two or more of R_2 and R_3 , and R_4 and R_5 , can be joined to form a cycle.

Preferably R_1 is a C_1 - C_4 linear alkyl group. In particular, R_1 is preferably selected from methyl or ethyl.

Among the compounds of formula (I) particularly preferred are those compounds in which n is 0. In this case one particularly preferred class is that in which one of R_2 or R_3 is hydrogen and the other is selected from C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl group and in particular from C_1 - C_8 branched alkyl groups. Specific examples of preferred compounds of this latter class are methyl 2-*i*-butyl-cyanoacetate, ethyl 2-*i*-butyl-cyanoacetate, ethyl 2-*i*-propyl-cyanoacetate, ethyl 2-(1,2-dimethyl-propyl)-cyanoacetate, ethyl 2-*t*-butyl-cyanoacetate.

Among the compounds in which n is 0 particularly preferred is the class in which both R_2 and R_3 are selected from C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl groups in which R_2 and R_3 can also form a cycle. Particularly preferred are the compounds in which both R_2 and R_3 , equal or different to each other, are selected from C_1 - C_8 linear or branched alkyl or aryl groups. Specific examples of preferred compounds of this class are ethyl 2,2-di-n-butyl-cyanoacetate, ethyl 2-i-butyl-2-n-butyl-cyanoacetate, ethyl 2,2-di-i-butyl-cyanoacetate, ethyl 2-i-butyl-2-i-propyl-cyanoacetate, ethyl 2,2-di-i-propyl-cyanoacetate, ethyl 2,2-di-benzyl ethyl-cyanoacetate.

As explained above, the catalyst component comprises, in addition to the above electron donor, Ti, Mg and halogen. In particular, the catalyst component comprises a titanium compound, having at least a Ti-halogen bond, and the above mentioned electron donor compound supported on a Mg halide. The magnesium halide is preferably $MgCl_2$ in active form that is widely known from the patent literature as a support for Ziegler-Natta catalysts. Patents USP 4,298,718 and USP 4,495,338 were the first to describe the use of these compounds in Ziegler-Natta catalysis. It is known from these patents that the magnesium dihalides in active form used as support or co-support in components of catalysts for the polymerization of olefins are characterized by X-ray spectra in which the most intense diffraction line that appears in the spectrum of the non-active halide is diminished in intensity and is replaced by a halo whose maximum intensity is displaced towards lower angles relative to that of the more intense line.

The preferred titanium compounds used in the catalyst component of the present invention are $TiCl_4$ and $TiCl_3$, furthermore, also Ti-haloalcoholates of formula $Ti(OR)_{n-y}X_y$, where n is the valence of titanium and y is a number between 1 and n, can be used.

The preparation of the solid catalyst component can be carried out according to several methods.

According to one of these methods, the magnesium dichloride in an anhydrous state and the electron donor compound of formula (I) are milled together under conditions in which activation of the magnesium dichloride occurs. The so obtained product can be treated one or more times with an excess of TiCl_4 at a temperature between 80 and 135°C. This treatment is followed by washings with hydrocarbon solvents until chloride ions disappeared. According to a further method, the product obtained by co-milling the magnesium chloride in an anhydrous state, the titanium compound and the electron donor compound of formula (I) is treated with halogenated hydrocarbons such as 1,2-dichloroethane, chlorobenzene, dichloromethane etc. The treatment is carried out for a time between 1 and 4 hours and at temperature of from 40°C to the boiling point of the halogenated hydrocarbon. The product obtained is then generally washed with inert hydrocarbon solvents such as hexane.

According to another method, magnesium dichloride is preactivated according to well known methods and then treated with an excess of TiCl_4 at a temperature of about 80 to 135°C which contains, in solution, an electron donor compound of formula (I). The treatment with TiCl_4 is repeated and the solid is washed with hexane in order to eliminate any non-reacted TiCl_4 .

A further method comprises the reaction between magnesium alcoholates or chloroalcoholates (in particular chloroalcoholates prepared according to U.S. 4,220,554) and an excess of TiCl_4 comprising the electron donor compound of formula (I) in solution at a temperature of about 80 to 120°C.

According to a preferred method, the solid catalyst component can be prepared by

reacting a titanium compound of formula $Ti(OR)_{n-y}X_y$, where n is the valence of titanium and y is a number between 1 and n, preferably $TiCl_4$, with a magnesium chloride deriving from an adduct of formula $MgCl_2 \cdot pROH$, where p is a number between 0,1 and 6, preferably from 2 to 4, and R is a hydrocarbon radical having 1-18 carbon atoms. The adduct can be suitably prepared in spherical form by mixing alcohol and magnesium chloride in the presence of an inert hydrocarbon immiscible with the adduct, operating under stirring conditions at the melting temperature of the adduct (100-130°C). Then, the emulsion is quickly quenched, thereby causing the solidification of the adduct in form of spherical particles. Examples of spherical adducts prepared according to this procedure are described in USP 4,399,054. The so obtained adduct can be directly reacted with the Ti compound or it can be previously subjected to thermal controlled dealcoholation (80-130°C) so as to obtain an adduct in which the number of moles of alcohol is generally lower than 2.8 preferably between 0,1 and 2,5. The reaction with the Ti compound can be carried out by suspending the adduct (dealcoholated or as such) in cold $TiCl_4$ (generally 0°C); the mixture is heated up to 80-130°C and kept at this temperature for 0,5-2 hours. The treatment with $TiCl_4$ can be carried out one or more times. The electron donor compound of formula (I) can be added during the treatment with $TiCl_4$. The treatment with the electron donor compound can be repeated one or more times.

The preparation of catalyst components in spherical form is described for example in European Patent Applications EP-A-395083, EP-A-553805, and EP-A-553806.

The solid catalyst components obtained according to the above method show a surface area (by B.E.T. method) generally between 20 and 500 m^2/g and preferably between 50 and 400 m^2/g , and a total porosity (by B.E.T. method) higher than 0,2 cm^3/g preferably between 0.2 and 0,6 cm^3/g .

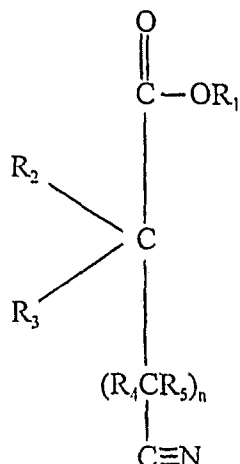
A further method to prepare the solid catalyst component of the invention comprises halogenating magnesium dihydrocarbyloxy compounds, such as magnesium dialkoxide or diaryloxy, with solution of $TiCl_4$ in aromatic hydrocarbon (such as toluene, xylene etc.) at temperatures between 80 and 130°C. The treatment with $TiCl_4$ in aromatic hydrocarbon solution can be repeated one or more times, and the electron donor compound of formula (I) is added during one or more of these treatments.

In any of these preparation methods the desired electron donor compound of formula (I) can be added as such or, in an alternative way, it can be obtained *in situ* by using an appropriate precursor capable to be transformed in the desired electron donor compound by means, for example, of known chemical reactions such as esterification, transesterification etc. Generally, the electron donor compound of formula (I) is used in molar ratio with respect to the $MgCl_2$ of from 0.1 to 1 preferably from 0.05 to 0.5.

The solid catalyst component according to the present invention are converted into catalysts for the polymerization of olefins by reacting them with organoaluminum compounds according to known methods.

In particular, it is an object of the present invention a catalyst for the polymerization of olefins $CH_2=CHR$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:

- (i) a solid catalyst component comprising a Ti, Mg, halogen and an electron donor compound selected from cyanoesters of formula (I):

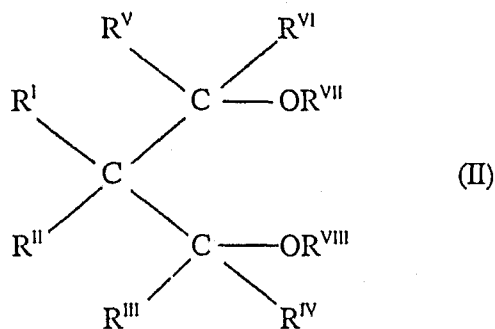


wherein R_1 is a C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl group; n is 0, 1, 2 or 3; R_2 , R_3 , R_4 and R_5 are independently selected from hydrogen or C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl group; two or more of R_2 and R_3 , and R_4 and R_5 , can be joined to form a cycle;

- (ii) an alkylaluminum compound and, optionally
- (iii) an electron-donor compound (external donor).

The alkyl-Al compound (ii) is preferably chosen among the trialkyl aluminum compounds such as for example triethylaluminum, triisobutylaluminum, tri-*n*-butylaluminum, tri-*n*-hexylaluminum, tri-*n*-octylaluminum. It is also possible to use mixtures of trialkylaluminum compounds with alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides such as AlEt_2Cl and $\text{Al}_2\text{Et}_3\text{Cl}_3$.

The external donor (iii) can be of the same type or it can be different from the internal donor of formula (I). Suitable external electron-donor compounds include silicon compounds, ethers, esters such as ethyl 4-ethoxybenzoate, amines, heterocyclic compounds and particularly 2,2,6,6-tetramethyl piperidine, ketones and the 1,3-diethers of the general formula (II):



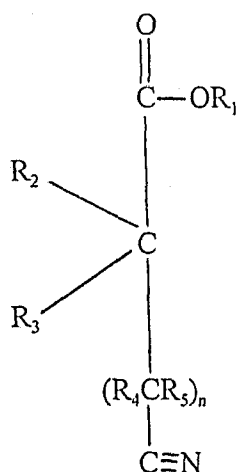
wherein R^I , R^{II} , R^{III} , R^{IV} , R^V and R^{VI} equal or different to each other, are hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R^{VII} and R^{VIII} , equal or different from each other, have the same meaning of R^I - R^{VI} except that they cannot be hydrogen; one or more of the R^I - R^{VIII} groups can be linked to form a cycle. Particularly preferred are the 1,3-diethers in which R^{VII} and R^{VIII} are selected from C_1 - C_4 alkyl radicals.

Another class of preferred external donor compounds is that of silicon compounds of formula $R_a^6 R_b^7 Si(OR^8)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^6 , R^7 , and R^8 , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms. Particularly preferred are the silicon compounds in which a is 1, b is 1, c is 2, at least one of R^6 and R^7 is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms optionally containing heteroatoms and R^8 is a C_1 - C_{10} alkyl group, in particular methyl. Examples of such preferred silicon compounds are methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane, 2-ethylpiperidinyl-2-t-butyldimethoxysilane and 1,1,1-trifluoropropyl-2-ethylpiperidinyl-dimethoxysilane. Moreover, are also preferred the silicon compounds in which a is 0, c is 3, R^7 is a branched alkyl or cycloalkyl group, optionally containing heteroatoms, and R^8 is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyldimethoxysilane and hexyltrimethoxysilane.

The electron donor compound (iii) is used in such an amount to give a molar ratio between the organoaluminum compound and said electron donor compound (iii) of from 0.1 to 500, preferably from 1 to 300 and more preferably from 3 to 100. As previously indicated, when used in the polymerization of olefins, and in particular of propylene, the catalysts of the invention allow to obtain, with acceptable yields and isotactic indexes (expressed by xylene insolubility X.I.), a response to hydrogen concentrations (expressed by the high values of Melt Index "L") and a MWD (expressed by the values of the Polydispersity Index "PI") higher than those of the catalysts of the prior art.

Therefore, it constitutes a further object of the present invention a process for the (co)polymerization of olefins $\text{CH}_2=\text{CHR}$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, carried out in the presence of a catalyst comprising the product of the reaction between:

a solid catalyst component comprising Ti, Mg, halogen and an electron donor compound selected from cyanoesters of formula (I):



wherein R_1 is a C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl group; n is 0, 1, 2 or 3; R_2 , R_3 , R_4 and R_5 are

independently selected from hydrogen or C₁-C₂₀ linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl group; two or more of R₂ and R₃, and R₄ and R₅, can be joined to form a cycle;

- (ii) an alkylaluminum compound and,
- (iii) an electron-donor compound (external donor).

The polymerization process can be carried out according to known techniques for example slurry polymerization using as diluent an inert hydrocarbon solvent, or bulk polymerization using the liquid monomer (for example propylene) as a reaction medium. Moreover, it is possible to carry out the polymerization process in gas-phase operating in one or more fluidized or mechanically agitated bed reactors.

The polymerization is generally carried out at temperature of from 20 to 150°C, preferably of from 40 to 80°C. When the polymerization is carried out in gas-phase the operating pressure is generally between 0.5 and 5 MPa, preferably between 1 and 4 MPa. In the bulk polymerization the operating pressure is generally between 1 and 8 MPa preferably between 1.5 and 5 MPa.

The following examples are given in order to better illustrate the invention without limiting it.

CHARACTERIZATIONS

The cyanoacetates according to formula (I) used in the present invention can be prepared, for example, by reaction of ethyl cyanoacetate with alkyl halides in the presence of a base such as sodium ethoxide. According to another synthesis, monosubstituted cyanoacetates are obtained by reacting ethyl cyanoacetate with a ketone or with an aldehyde (Knoevenagel condensation) to give unsaturated cyanoacetates that can be reduced with H₂ in the presence of Pd or Pt based

catalysts. Alternatively, the unsaturated cyanoacetate can be reacted with Grignard reagents in the presence of CuCl.

Propylene general polymerization procedure

In a 4 liter autoclave, purged with nitrogen flow at 70°C for one hour, 80 ml of anhydrous hexane containing 10 mg of solid catalyst component, 7 mmoles of AlEt₃ and 0.35 mmoles of dicyclopentylidimethoxysilane were introduced in propylene flow at 30°C. The autoclave was closed, 3 NL of hydrogen were added and then, under stirring, 1.2 Kg of liquid propylene were fed. The temperature was raised to 70°C in five minutes and the polymerization was carried out at this temperature for two hours. The unreacted propylene was removed, the polymer was recovered and dried at 70°C under vacuum for three hours, and then it was weighed and fractionated with o-xylene to determine the amount of the xylene insoluble (X.I.) fraction at 25°C.

Determination of X.I.

2.5 g of polymer were dissolved in 250 ml of o-xylene under stirring at 135°C for 30 minutes, then the solution was cooled to 25°C and after 30 minutes the insoluble polymer was filtered. The resulting solution was evaporated in nitrogen flow and the residue was dried and weighed to determine the percentage of soluble polymer and then, by difference, the X.I. %.

Determination of Polydispersity Index "P.I."

This property is strictly connected with the molecular weight distribution of the polymer under examination. In particular it is inversely proportional to the creep resistance of the polymer in the molten state. Said resistance called modulus separation at low modulus value (500 Pa), was determined at a temperature of 200°C by using a parallel plates rheometer model RMS-800 marketed by RHEOMETRICS (USA), operating at an oscillation frequency which increases

from 0.1 rad/sec to 100 rad/second. From the modulus separation value, one can derive the P.I. by way of the equation:

$$P.I. = 54.6 * (\text{modulus separation})^{-1.76}$$

in which the modulus separation is defined as:

$$\text{modulus separation} = \text{frequency at } G' = 500\text{Pa} / \text{frequency at } G'' = 500\text{Pa}$$

wherein G' is storage modulus and G'' is the loss modulus.

Determination of Melt Index

ASTM D 1238 condition "L"

EXAMPLES

Examples 1-12

Preparation of Solid Catalyst Components

Into a 500 ml four-necked round flask, purged with nitrogen, 225 ml of TiCl_4 were introduced at 0°C . While stirring, 10.3 g of microspheroidal $\text{MgCl}_2 \cdot 2.1\text{C}_2\text{H}_5\text{OH}$ (obtained by partial thermal dealcoholation of an adduct prepared as described in Ex. 2 of USP 4,399,054 but operating at 3,000 rpm instead of 10,000) were added. The flask was heated to 40°C and 9 mmoles of cyanoester were thereupon added. The temperature was raised to 100°C and maintained for two hours, then the stirring was discontinued, the solid product was allowed to settle and the supernatant liquid was siphoned off.

200 ml of fresh TiCl_4 were added, the mixture was reacted at 120°C for one hour and then the supernatant liquid was siphoned off. The solid was washed six times with anhydrous hexane (6 x 100 ml) at 60°C and then dried under vacuum: the cyanoesters used, the amount of Ti (wt%) and of cyanoesters (wt%) contained in the solid catalyst component are reported in table 1. The polymerization results are reported in table 2.

COMPARATIVE EXAMPLES 1-2

Preparation of Solid Catalyst Component

The catalyst components have been prepared according to the same procedure of the examples 1-12 except for the fact that donors different from cyanoesters of formula (I) were used. The donors used, the amount of Ti (wt%) and of donors (wt%) contained in the solid catalyst component are reported in table 1. The polymerization results are reported in table 2.

EXAMPLE 13

The same solid catalyst component and polymerization procedure of example 7 have been used with the only difference that 2.3 mmoles of 4-ethoxy ethyl-benzoate was used as external donor instead of dicyclopentyl dimethoxysilane.

COMPARATIVE EXAMPLE 3

The same polymerization procedure according to Example 13 was carried out but using the catalyst component of comparison example 2.

Table 1

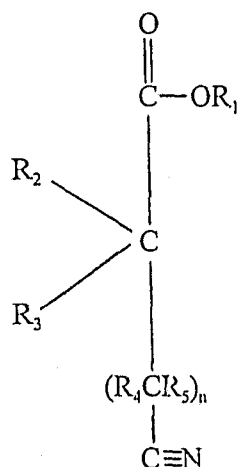
Solid catalyst component preparation		Solid catalyst component composition	
Ex n.	Donor type	Ti	Donor
		wt. %	wt %
1	methyl 2-i-butyl-cyanoacetate	4.7	3.6
2	ethyl 2-i-butyl-cyanoacetate	3.7	10.6
3	ethyl 2-i-propyl-cyanoacetate	4.5	12.5
4	ethyl 2-t-butyl-cyanoacetate	2.8	10.4
5	ethyl 2,2di-n-butyl-cyanoacetate	5.5	9.9
6	ethyl 2-i-butyl-2-n-butyl-cyanoacetate	5.1	9.1
7	ethyl 2,2di-i-butyl-cyanoacetate	4.7	6.4
8	ethyl 2-i-propyl-2-n-butyl-cyanoacetate	5.0	9.8
9	ethyl 2-i-butyl-2-i-propyl-cyanoacetate	4.1	7.9
10	ethyl 2,2di-i-propyl-cyanoacetate	3.9	9.0
11	ethyl 2,2di-benzyl-cyanoacetate	4.8	10.9
12	ethyl 3,3-dimethyl-4-cyanobutyrate	3.4	3
comp.1	di-isobutyl phthalate	2.5	7.4
comp.2	ethyl benzoate	3.5	9.1
13	ethyl 2,2di-i-butyl-cyanoacetate	4.7	6.4
comp.3	ethyl benzoate	3.5	9.1

Table 2

Example	MFR g/10'	P.I.	Yield KgPP/gCat	X.I. %
1	22	n.d.	12	95.2
2	12	5.5	11	95.4
3	11.4	n.d.	13.5	93.2
4	12.5	5.4	15	93
5	12.7	n.d.	26.6	93.2
6	11	5.	27.5	92.1
7	12	n.d.	23	93.2
8	12.3	4.9	26	93
9	34.6	n.d.	30.2	94.1
10	11	4.9	33	93.7
11	17.8	n.d.	24.3	94
12	16	5	14	95.4
comp.1	5	4.3	50	98
comp.2	6	4.4	25	92
13	34	6.5	15	93
comp.3	2.0	5.3	20	94

CLAIMS

1. A solid catalyst component for the polymerization of olefins $\text{CH}_2=\text{CHR}$ in which R is hydrogen or a hydrocarbyl radical with 1 - 12 carbon atoms, comprising Ti, Mg, halogen and an electron donor compound selected from cyanoesters of formula (I):



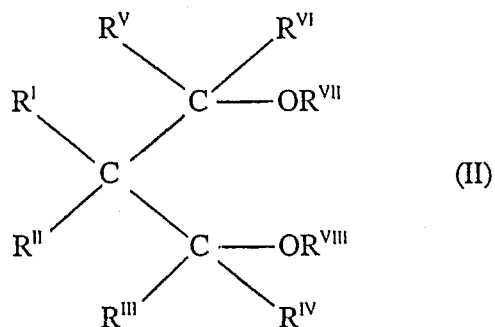
- wherein R_1 is a $\text{C}_1\text{-C}_{20}$ linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl group; n is 0, 1, 2 or 3; R_2 , R_3 , R_4 and R_5 are independently selected from hydrogen or $\text{C}_1\text{-C}_{20}$ linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl groups; two or more of R_2 and R_3 , and R_4 and R_5 , can be joined to form a cycle.
2. A solid catalyst component according to claim 1 in which R_1 is a $\text{C}_1\text{-C}_4$ linear alkyl group.
3. A solid catalyst component according to claim 1 or 2 in which n is 0.
4. A solid catalyst component according to claim 3 in which one of R_2 or R_3 is hydrogen and the other is selected from $\text{C}_1\text{-C}_{20}$ linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl group and in particular from $\text{C}_1\text{-C}_8$ branched alkyl groups.

5. A solid catalyst component according to claim 4 in which the compound of formula (I) is selected from the group consisting of methyl 2-i-butyl-cyanoacetate, ethyl 2-i-butyl-cyanoacetate, ethyl 2-i-propyl-cyanoacetate, ethyl 2-(1,2-dimethyl-propyl)-cyanoacetate, ethyl 2-t-butyl-cyanoacetate.
6. A solid catalyst component according to claim 3 in which both R_2 and R_3 are selected from C_1 - C_{20} linear or branched alkyl, alkenyl, cycloalkyl, cycloalkylalkyl, alkylcycloalkyl, aryl, arylalkyl or alkylaryl group in which R_2 and R_3 can also form a cycle.
7. A solid catalyst component according to claim 6 in which both R_2 and R_3 equal or different to each other, are selected from C_1 - C_8 linear or branched alkyl or aryl groups.
8. A solid catalyst component according to claim 7 in which the compound of formula (I) is selected from the group consisting of ethyl 2,2-di-n-butyl-cyanoacetate, ethyl 2-i-butyl-2-n-butyl-cyanoacetate, ethyl 2,2-di-i-butyl-cyanoacetate, ethyl 2-i-butyl-2-i-propyl-cyanoacetate, ethyl 2,2-di-i-propyl-cyanoacetate, ethyl 2,2-di-benzyl ethyl-cyanoacetate.
9. A solid catalyst component according to claim 1 comprising a titanium compound, having at least a Ti-halogen bond, and the electron donor compound of formula (I) supported on a Mg halide in active form.
10. A solid catalyst component according to claim 1 in which the titanium compound is $TiCl_4$ or $TiCl_3$.
11. A solid catalyst component according to claim 1 having a spherical form, a surface area (by B.E.T. method) between 20 and 400 m^2/g , preferably between 50 and 300 m^2/g , and a total porosity (by B.E.T. method) higher than 0.2 cm^3/g preferably between 0.2 and 0.6 cm^3/g .

12. A catalyst for the polymerization of olefins $\text{CH}_2=\text{CHR}$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, comprising the product of the reaction between:
- (i) the solid catalyst component according to one of the claims 1-12;
 - (ii) an alkylaluminum compound and, optionally
 - (iii) an electron-donor compound (external donor).
13. Catalyst according to claim 12 in which the alkylaluminum compound (ii) is a trialkyl aluminum compound.
14. Catalyst according to claim 13 in which the trialkyl aluminum compound is selected from the group consisting of triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum.
15. Catalyst according to claim 12 in which the external donor (iii) is a silicon compound of formula $\text{R}_a^6\text{R}_b^7\text{Si}(\text{OR}^8)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4, R^6 , R^7 , and R^8 , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms optionally containing heteroatoms.
16. Catalyst according to claim 15 in which a is 1, b is 1, c is 2, at least one of R^6 and R^7 is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms, optionally containing heteroatoms, and R^8 is a C_1 - C_{10} alkyl group preferably methyl.
17. Catalyst according to claim 15 in which a is 0, c is 3, R^7 is a branched alkyl or cycloalkyl group, optionally containing heteroatoms, and R^8 is methyl.
18. Catalyst according to claim 16 in which the silicon compound is selected from the group consisting of methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyl dimethoxysilane, dicyclopentyldimethoxysilane 2-ethylpiperidinyl-2-t-

butyldimethoxysilane and 1,1,1-trifluoropropyl-2-ethylpiperidinyl-dimethoxysilane.

19. Catalyst according to claim 17 in which the silicon compound is selected from the group consisting of cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and hexyltrimethoxysilane.
20. Catalyst according to claim 12 in which the external donor (iii) is selected from the 1,3-diethers of the general formula (II):



wherein R^I , R^{II} , R^{III} , R^{IV} , R^V and R^{VI} equal or different to each other, are hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R^{VII} and R^{VIII} , equal or different from each other, have the same meaning of R^I - R^{VI} except that they cannot be hydrogen; one or more of the R^I - R^{VIII} groups can be linked to form a cycle.

21. Process for the (co)polymerization of olefins $CH_2=CHR$, in which R is hydrogen or a hydrocarbyl radical with 1-12 carbon atoms, carried out in the presence of the catalyst according to any of the claims 12-20.
22. Use of the compounds of formula (I) according to claim 1 as electron donors in a catalyst for the polymerization of olefins.
23. Use of the compounds of formula (I) according to claim 1 as internal electron donors in a catalyst component for the polymerization of olefins.

INTERNATIONAL SEARCH REPORT

I. national Application No

PCT/EP 98/05160

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C08F10/00		
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 6 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)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YANO, T. ET AL: "Supported catalysts for olefin polymerization. The role of the third component" EUR. POLYM. J. (1986), 22(8), 637-41 CODEN: EUPJAG;ISSN: 0014-3057, XP002087507 see page 638, paragraph 4 see page 639; example 8; table 2	1
A	EP 0 704 424 A (SHOWA DENKO KK) 3 April 1996 see example 5 see claim 9	1
A	GB 2 057 469 A (SUMITOMO CHEMICAL CO) 1 April 1981 see claims 1,2,44	1
<input type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> 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	Date of mailing of the international search report	
14 December 1998	12/01/1999	
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HP Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Fischer, B	

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Information on patent family members

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