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AUSTRALIA 659218

Patents Act 1990

PATENT REQUEST: STANDARD PATENT/PATENT OF ADDITION

We, being the person identified below as the Applicant, request the grant of a patent to the person identified below as the Nominated Person, for an invention described in the accompanying standard complete specification.

Full application details follow.

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[70] Nominated Person: HOECHST AKTIENGESELLSCHAFT

Address: D-6230 FRANKFURT/MAIN 80, FEDERAL REPUBLIC OF GERMANY

[54] invention Title: PROCESS FOR THE PREPARATION OF AN OLEFIN POLYMER USING METALLOCENES HAVING SPECIFICALLY SUBSTITUTED INDENYL LIGANDS

[72] Name(s) of actual inventor(s): ANDREAS WINTER, MARTIN ANTBERG, VOLKER DOLLE, JURGEN ROHRMANN AND WALTER SPALECK

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BASIC CONVENTION APPLICATION(S) DETAILS

[31] Application Number	[33] Country	Country Code	[32] Date of Application
P41 34 088.4	GERMANY	DE	15TH OCTOBER 1991

Drawing number recommended to accompany the abstract .....

By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

.....

DARRYL B. MISCHLEWSKI

Registered Patent Attorney

DATED this 13th day of October 1992

F038141 14/10/92

P/00/008b 12/11/91
Section 29 (1)
Regulation 3.1 (2)

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NOTICE OF ENTITLEMENT

We, **HOECHST AKTIENGESELLSCHAFT** of, D-6230 Frankfurt/Main 80, Federal Republic of Germany, being the applicant in respect of Application No. **26395/92** state the following:-

The Person nominated for the grant of the patent has entitlement from the actual inventors by virtue of an employment agreement between the inventors and the nominated person.

The person nominated for the grant of the patent is the applicant of the basic application listed on the patent request form.

The basic application listed on the request form is the first application made in a Convention country in respect of the invention.

HOECHST AKTIENGESELLSCHAFT
By our Patent Attorneys,
WATERMARK PATENT & TRADEMARK ATTORNEYS

..... 2 March 1995

Karen J. Sinclair
Registered Patent Attorney

AU9226395

(12) PATENT ABRIDGMENT (11) Document No. AU-B-26395/92
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 659218

(54) Title
PROCESS FOR THE PREPARATION OF AN OLEFIN POLYMER USING METALLOCENES HAVING SPECIFICALLY SUBSTITUTED INDENYL LIGANDS

International Patent Classification(s)
(51)[5] **C08F 004/642** **C08F 004/68** **C08F 004/69** **C08F 004/646**

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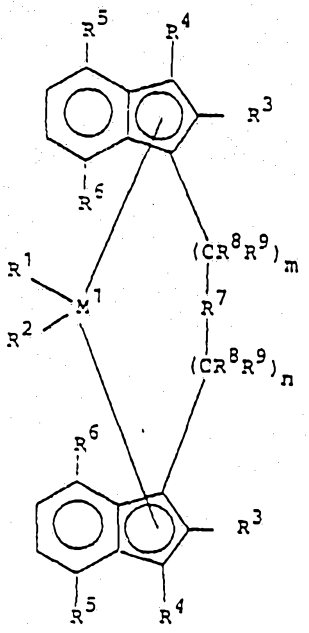
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(56) Prior Art Documents
AU 21254/92 C08F 4/622 4/623 4/74
AU 11216/92 C08F 4/622 4/623 4/74
AU 91591/91 C08F 4/622 4/623 4/74

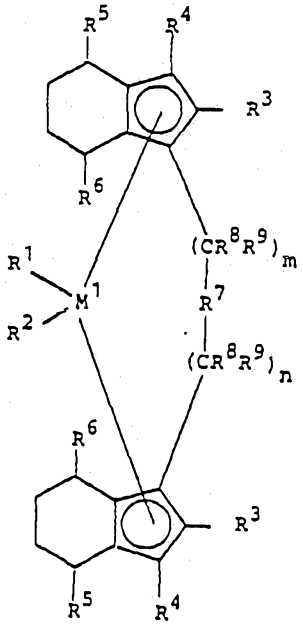
(57) Claim

1. A process for the preparation of an olefin polymer by polymerization or copolymerization of an olefin of the formula R^a-CH=CH-R^b, in which R^a and R^b are identical or different and are a hydrogen atom or a hydrocarbon radical having 1 to 14 carbon atoms, or R^a and R^b, together with the atoms joining them, can form a ring, at a temperature of -60 to 200°C, under a pressure of 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst which is formed from a metallocene as the transition metal compound and a cocatalyst, wherein the metallocene is a compound of the formula I or Ia

.../2



(I)



(Ia)

in which

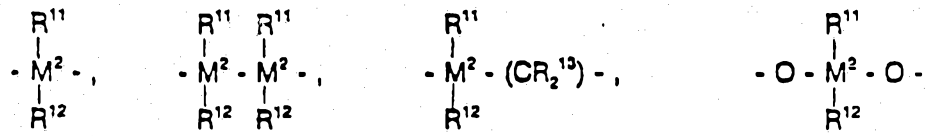
M^1 is a metal of group IVb, Vb or VIb of the periodic table (American nomenclature, chemical abstract service, 1986),

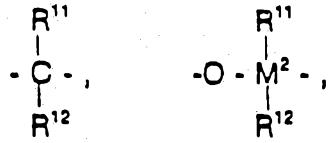
R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group, a C_8-C_{40}-arylalkenyl group or a halogen atom,

R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, which can be halogenated, a C_6-C_{10}-aryl group or an $-NR_2^{10}$, $-SR^{10}$, $-OSiR_3^{10}$, $-SiR_3^{10}$ or $-PR_2^{10}$ radical, in which R^{10} is a halogen atom, a C_1-C_{10}-alkyl group or a C_6-C_{10}-aryl group,

R^5 and R^6 are identical or different and have the meaning given for R^3 and R^4, with the proviso that R^5 and R^6 are not hydrogen,

R^7 is





$=BR^{11}$, $=AlR^{11}$, -Ge-, -Sn-, -O-, -S-, =SO, $=SO_2$, $=NR^{11}$, =CO, $=PR^{11}$ or $P(O)R^{11}$,

in which

R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a C_6-C_{10}-fluoroaryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^{11} and R^{12} or R^{11} and R^{13}, in each case with the atoms joining them, form a ring, and

M^2 is silicon, germanium or tin,

R^8 and R^9 are identical or different and have the meaning given for R^{11} and

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2.

P/00/011 28/5/91
Regulation 3.2(2)

AUSTRALIA

Patents Act 1990

659218

ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT

Application Number:

Lodged:

Invention Title: PROCESS FOR THE PREPARATION OF AN OLEFIN POLYMER USING METALLOCENES HAVING SPECIFICALLY SUBSTITUTED INDENYL LIGANDS

The following statement is a full description of this invention, including the best method of performing it known to :-US

HOECHST AKTIENGESELLSCHAFT HOE 91/F 322 Dr.LO/sch

Description

Process for the preparation of an olefin polymer using metallocenes having specifically substituted indenyl ligands

The invention relates to a process for the preparation of olefin polymers and copolymers using metallocenes having specifically substituted indenyl ligands.

The use of chiral metallocenes as catalyst components in olefin polymerization is known and leads to highly isotactic polyolefins of high crystallinity and high melting points (cf. Angew. Chem. 97 (1985) 507 and DE-P 40 35 886.0).

The use of non-chiral metallocenes gives atactic polymers which are of only limited industrial importance because of their unbalanced and inadequate product properties.

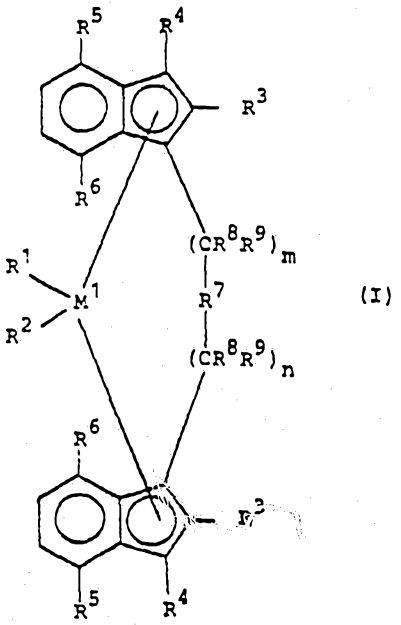
Products which have a profile of properties which lies between these two extremes are of great interest.

There was thus the object of discovering a suitable process and a suitable catalyst system which allows the preparation of polymers of reduced crystallinity, increased impact strength, increased transparency, high flowability at the processing temperature, low molecular weight and reduced melting point.

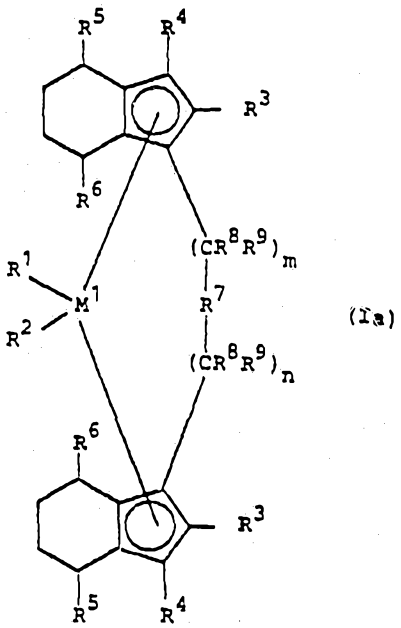
The main applications of such polymers are plasticizer and lubricant recipes, hot melt adhesive, coatings, sealings, insulations, plugging compositions or sound-proofing materials.

The invention thus relates to a process for the preparation of an olefin polymer by polymerization or

copolymerization of an olefin of the formula R^a-CH=CH-R^b, in which R^a and R^b are identical or different and are a hydrogen atom or a hydrocarbon radical having 1 to 14 carbon atoms, or R^a and R^b, together with the atoms joining them, can form a ring, at a temperature of -60 to 200°C, under a pressure of 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst which is formed from a metallocene as the transition metal compound and a cocatalyst, wherein the metallocene is a compound of the formula I or Ia



(I)



(Ia)

in which

M^1 is a metal of group IVb, Vb or VIb of the periodic table,

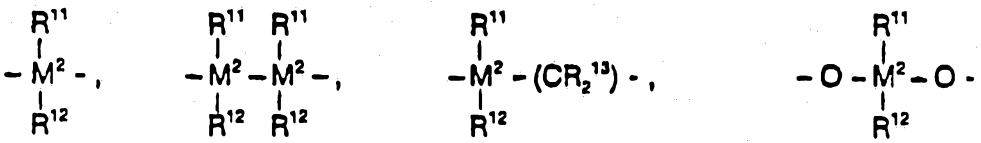
R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group, a C_8-C_{40}-arylalkenyl group or a halogen atom,

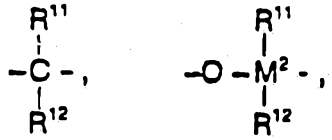
R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, which can be halogenated, a C_6-C_{10}-aryl group or an -NR_2^{10},

$-SR^{10}$, $-OSiR_3^{10}$, $-SiR_3^{10}$ or $-PR_2^{10}$ radical, in which R^{10} is a halogen atom, a C_1-C_{10}-alkyl group or a C_6-C_{10}-aryl group,

R^5 and R^6 are identical or different and have the meaning given for R^3 and R^4, with the proviso that R^5 and R^6 are not hydrogen,

R^7 is





=BR^{11}, =ALR^{11}, -Ge-, -Sn-, -O-, S-, =SO, =SO_2, =NR^{11}, =CO, =PR^{11} or $P(O)R^{11}$,

in which

R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a C_6-C_{10}-fluoroaryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^{11} and R^{12} or R^{11} and R^{13}, in each case with the atoms joining them, form a ring, and

M^2 is silicon, germanium or tin,

R^8 and R^9 are identical or different and have the meaning given for R^{11} and

m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2.

Alkyl is straight-chain or branched alkyl. Halogen (halogenated) is fluorine, chlorine, bromine or iodine,

preferably fluorine or chlorine.

The catalyst to be used for the process according to the invention comprises a cocatalyst and a metallocene of the formula I or Ia.

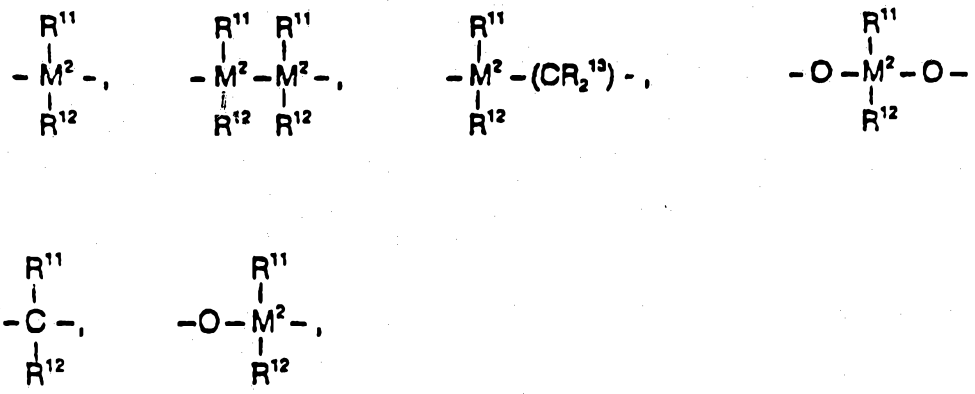
In formula I or Ia, M^1 is a metal of group IVb, Vb or VIb of the periodic table, for example titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum or tungsten, preferably zirconium, hafnium and titanium.

R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-, preferably C_1-C_3-alkyl group, a C_1-C_{10}-, preferably C_1-C_3-alkoxy group, a C_6-C_{10}-, preferably C_6-C_8-aryl group, a C_6-C_{10}-, preferably C_6-C_8-aryloxy group, a C_2-C_{10}-, preferably C_2-C_4-alkenyl group, a C_7-C_{40}-, preferably C_7-C_{10}-arylalkyl group, a C_7-C_{40}-, preferably C_7-C_{12}-alkylaryl group, a C_8-C_{40}-, preferably C_8-C_{12}-arylalkenyl group or a halogen atom, preferably chlorine.

R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, preferably a fluorine, chlorine or bromine atom, a C_1-C_{10}-, preferably C_1-C_4-alkyl group, which can be halogenated, a C_6-C_{10}-, preferably C_6-C_8-aryl group or an $-NR_2^{10}$, $-SR^{10}$, $-OSiR_3^{10}$, $-SiR_3^{10}$ or $-PR_2^{10}$ radical, in which R^{10} is a halogen atom, preferably a chlorine atom, or a C_1-C_{10}-, preferably C_1-C_3-alkyl group or C_6-C_{10}-, preferably C_6-C_8-aryl group. R^3 and R^4 are particularly preferably hydrogen or methyl.

R^5 and R^6 are identical or different, preferably identical, and have the meaning given for R^3 and R^4, with the proviso that R^5 and R^6 cannot be hydrogen. R^5 and R^6 are preferably (C_1-C_4)-alkyl, which can be halogenated, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl or trifluoromethyl, in particular methyl.

R^7 is



$=BR^{11}$, $=AlR^{11}$, -Ge-, -Sn-, -O-, -S-, =SO, $=SO_2$, $=NR^{11}$, =CO, $=PR^{11}$ or $P(O)R^{11}$,

in which R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-, preferably C_1-C_4-alkyl group, in particular a methyl group, a C_1-C_{10}-fluoroalkyl group, preferably a CF_3- group, a C_6-C_{10}-, preferably C_6-C_8-aryl group, a C_6-C_{10}-fluoroaryl group, preferably a pentafluorophenyl group, a C_1-C_{10}-, preferably C_1-C_4-alkoxy group, in particular a methoxy group, a C_2-C_{10}-, preferably C_2-C_4-alkenyl group, a C_7-C_{40}-, preferably C_7-C_{10}-arylalkyl group, a C_8-C_{40}-, preferably C_8-C_{12}-arylalkenyl group or a C_7-C_{40}-, preferably C_7-C_{12}-alkylaryl group, or R^{11} and R^{12} or R^{11} and R^{13}, in each case together with the atoms joining them, form a ring.

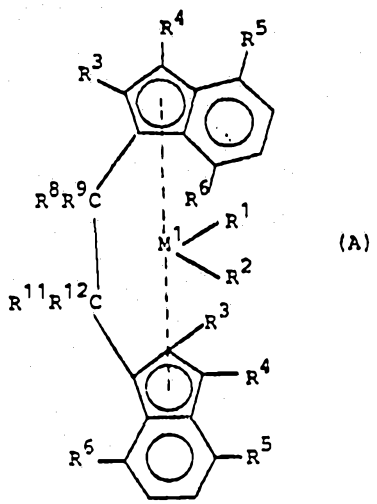
M^2 is silicon, germanium or tin, preferably silicon and germanium.

R^7 is preferably $=CR^{11}R^{12}$, $=SiR^{11}R^{12}$, $=GeR^{11}R^{12}$, -O-, -S-, =SO, $=PR^{11}$ or $=P(O)R^{11}$.

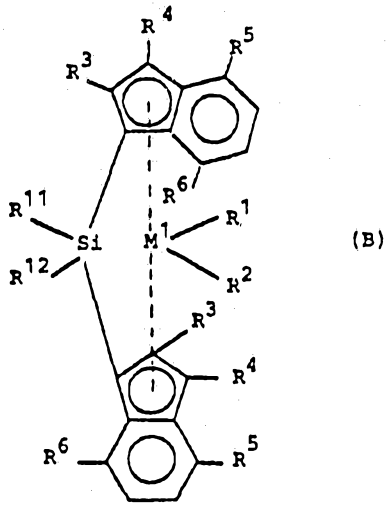
R^8 and R^9 are identical or different and have the meaning given for R^{11}.

m and n are identical or different and are zero, 1 or 2, preferably zero or 1, m plus n being zero, 1 or 2, preferably zero or 1.

The particularly preferred metallocenes are thus the compounds of the formulae A and B and hydrogenated forms thereof in the sense of formula Ia



(A)



(B)

where

M^1 = Zr or Hf; R^1 and R^2 = (C_1-C_3)-alkyl or chlorine; R^3 and R^4 = hydrogen or (C_1-C_4)-alkyl; R^5 and R^6 = (C_1-C_4)-alkyl, which can be halogenated, and R^8, R^9, R^{11} and R^{12} have the abovementioned meanings, in particular the compounds I and Ia described in the embodiment examples.

The chiral metallocenes are preferably employed as a racemate. However, the pure R- or S-form can also be used. An optically active polymer can be prepared using these pure stereoisomeric forms. However, the meso-form of the metallocenes should be removed, since the polymerization-active center (the metal atom) in these compounds is no longer chiral because of mirror symmetry at the central metal and therefore cannot generate a highly isotactic polymer. If the meso-form is not removed, atactic polymer is also formed, in addition to isotactic polymer. For certain uses - flexible shaped articles, for example - this may be entirely desirable.

The separation of the stereoisomers is known in principle.

The metallocenes described above can be prepared in accordance with the following equation:

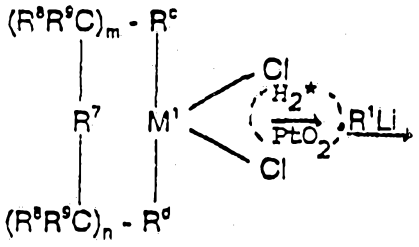
$$H_2R^c + \text{ButylLi} \longrightarrow HR^cLi$$

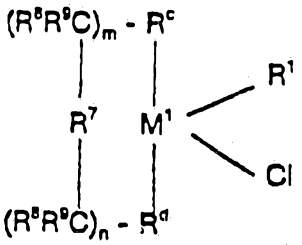
$$H_2R^d + \text{ButylLi} \longrightarrow HR^dLi$$

$$\xrightarrow{X\text{-}(CR^8R^9)_m\text{-}R^7\text{-}(CR^8R^9)_n\text{-}X}$$

$$HR^c\text{-}(CR^8R^9)_m\text{-}R^7\text{-}(CR^8R^9)_n\text{-}R^dH \xrightarrow{2\ \text{Butyl Li}}$$

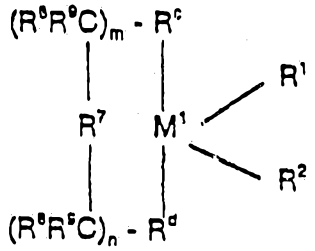
$$LiR^c\text{-}(CR^8R^9)_m\text{-}R^7\text{-}(CR^8R^9)_n\text{-}R^dLi \xrightarrow{M^1Cl_4}$$



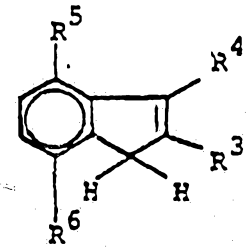


(* additional hydrogenation step for compounds of the formula Ia; cf. Embodiment Example V)

$R^2Li \longrightarrow$



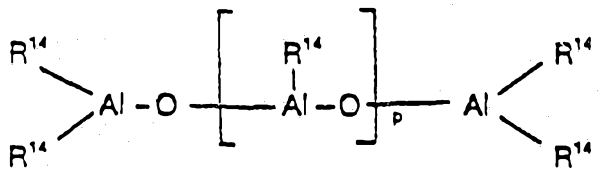
X = Cl, Br, I, O-Tosyl; $H_2R^c_1$ = H_2R^d



5 The preparation processes are known from the literature; cf. Journal of Organometallic Chem. 288 (1985) 63-67, EP-A 320 762 and the embodiment examples.

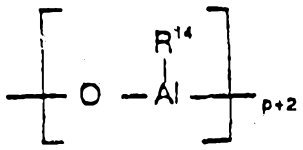
The starting compounds H_2R^c and H_2R^d are prepared in accordance with Bull. Soc. Chim. Fr. 6 (1969) 1981 and the embodiment examples.

According to the invention, an aluminoxane of the formula (II)



(II)

for the linear type, and/or of the formula (III)



(III)

for the cyclic type, in which, in the formulae (II) and (III), the radicals R^{14} can be identical or different and are a C_1-C_6-alkyl group, a C_6-C_{18}-aryl group, benzyl or hydrogen and p is an integer from 2 to 50, preferably 10 to 35, is preferably used as the cocatalyst.

Preferably, the radicals R^{14} are identical and are methyl, isobutyl, phenyl or benzyl, particularly preferably methyl.

If the radicals R^{14} are different, they are preferably methyl and hydrogen, or alternatively methyl and isobutyl, the compounds preferably containing hydrogen or, respectively, isobutyl to the extent of 0.01 - 40% (number of radicals R^{14}).

The aluminoxane can be prepared in various ways by known processes. One of the methods is, for example, to react an aluminum-hydrocarbon compound and/or a hydrido-

aluminum-hydrocarbon compound with water (gaseous, solid, liquid or bonded - for example as water of crystallization) in an inert solvent (such as, for example, toluene). To prepare an aluminoxane having different alkyl groups R^{14}, two different aluminum trialkyls (AlR_3 + AlR'_3) corresponding to the desired composition are reacted with water (cf. S. Pasynkiewicz, Polyhedron 9 (1990) 429 and EP-A 302 424).

The precise structure of the aluminoxanes II and III is not known.

Regardless of the type of preparation, all aluminoxane solutions have the common feature of a varying content of unreacted aluminum starting compound, which is present in the free form or as an adduct.

It is possible to preactivate the metallocene with an aluminoxane of the formula (II) and/or (III) before use in the polymerization reaction. By this procedure, the polymerization activity is significantly increased and the grain morphology is improved.

The preactivation of the transition metal compound is carried out in solution. Preferably, for this, the metallocene is dissolved in a solution of the aluminoxane in an inert hydrocarbon. An aliphatic or aromatic hydrocarbon is a suitable inert hydrocarbon. Toluene is preferably used.

The concentration of the aluminoxane in the solution is in the range from about 1% by weight up to the saturation limit, preferably from 5 to 30% by weight, in each case based on the total solution. The metallocene can be employed in the same concentration, but is preferably employed in an amount of 10^{-4} - 1 mol per mole of aluminoxane. The preactivation time is 5 minutes to 60 hours, preferably 5 to 60 minutes. The preactivation is carried out at a temperature of -78°C to 100°C,

preferably 0 to 70°C.

The metallocene can also be prepolymerized or applied to a support. The (or one of the) olefin(s) employed in the polymerization is(are) preferably used for the prepolymerization.

Suitable supports are, for example, silica gels, aluminum oxides, solid aluminoxane or other inorganic support materials. A polyolefin powder in finely divided form is also a suitable support material.

According to the invention, compounds of the formulae $R_xNH_{4-x}BR'_4$, $R_xPH_{4-x}BR'_4$, $R_3CBR'_4$ or BR'_3 can be used as suitable cocatalysts instead of or as well as an aluminoxane. In these formulae, x is a number from 1 to 4, preferably 3, the radicals R are identical or different, preferably identical, and are C_1-C_{10}-alkyl or C_6-C_{18}-aryl, or 2 radicals R, together with the atom joining them, form a ring, and the radicals R' are identical or different, preferably identical, and are C_6-C_{18}-aryl, which can be substituted by alkyl, haloalkyl or fluorine.

In particular, R is ethyl, propyl, butyl or phenyl and R' is phenyl, pentafluorophenyl, 3,5-bistrifluoromethylphenyl, mesityl, xylyl or tolyl (cf. EP-A 277 003, EP-A 277 004 and EP-A 426 638).

If the abovementioned cocatalysts are used, the actual (active) polymerization catalyst comprises the reaction product of the metallocene and one of the compounds mentioned. This reaction product is therefore preferably prepared outside the polymerization reactor in a separate step using a suitable solvent.

In principle, any compound which, on the basis of its Lewis acidity, can convert the neutral metallocene into a cation and stabilize this ("labile coordination") is suitable according to the invention as the cocatalyst.

Moreover, the cocatalyst or the anion formed from it should not undergo further reactions with the metallocene cation formed (cf. EP-A 427 697).

To remove catalyst poisons present in the olefin, purification with an aluminumalkyl, for example $AlMe_3$ or $AlEt_3$, is advantageous. This purification either can be carried out in the polymerization system itself, or the olefin is brought into contact with the Al compound before addition into the polymerization system, and is then separated off again.

The polymerization or copolymerization is carried out in a known manner in solution, in suspension or in the gas phase, continuously or discontinuously, in one or more stages, at a temperature of -60 to 200°C, preferably 30 to 80°C. Olefins of the formula R^a-CH=CH-R^b are polymerized or copolymerized. In this formula, R^a and R^b are identical or different and are a hydrogen atom or an alkyl radical having 1 to 14 carbon atoms. However, R^a and R^b can also form a ring with the C atoms joining them. Examples of such olefins are ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, norbornene or norbonadiene. In particular, propylene and ethylene are polymerized.

Hydrogen is added, if necessary, as a molecular weight regulator and/or to increase the activity. The overall pressure in the polymerization system is 0.5 to 100 bar. Polymerization in the pressure range of 5 to 64 bar, which is of particular interest industrially, is preferred.

In this procedure, the metallocene is used in a concentration, based on the transition metal, of 10^{-3} to 10^{-8}, preferably 10^{-4} to 10^{-7}, mol of transition metal per dm^3 of solvent or per dm^3 of reactor volume. The aluminoxane is used in a concentration of 10^{-5} to 10^{-1} mol, preferably 10^{-4} to 10^{-2} mol, per dm^3 of solvent or per dm^3 of reactor

volume. The other cocatalysts mentioned are used in amounts which are approximately equimolar to that of the metallocene. In principle, however, higher concentrations are also possible.

If the polymerization is carried out as suspension or solution polymerization, an inert solvent customary for the Ziegler low pressure process is used. For example, the polymerization is carried out in an aliphatic or cycloaliphatic hydrocarbon; examples of such which may be mentioned are propane, butane, pentane, hexane, heptane, isooctane, cyclohexane and methylcyclohexane.

Furthermore, a gasoline or hydrogenated diesel oil fraction can be used. Toluene can also be used. The polymerization is preferably carried out in the liquid monomer.

If inert solvents are used, the monomers are metered into the reaction in gaseous or liquid form.

The polymerization can be of any duration, since the catalyst system to be used according to the invention exhibits only a slight decrease in polymerization activity with respect to time.

The process according to the invention is distinguished by the fact that the metallocenes described preferentially produce, in the temperature range of industrial interest of between 30 and 80°C and at a high polymerization activity, polymers having the desired spectrum of properties.

Moreover, it has been found, surprisingly, that olefins such as propylene or higher molecular weight homologs can be polymerized using the metallocenes I and Ia to give polymers of low molecular weight, but the behavior of these metallocenes toward ethylene is completely different - very high molecular weight polyethylenes are

formed with an excellent activity.

The following examples are intended to illustrate the invention in more detail.

In the examples:

VN = viscosity number in cm^3/g

M_w = weight-average molecular weight in g/mol } determined by gel permeation chromatography

M_w/M_n = molecular weight dispersity } determined by gel permeation chromatography

m.p. = melting point determined by differential scanning calorimetry (20°C/minute heating up/-cooling down rate)

II = isotactic index (II = mm + 1/2 mr), determined by ^{13}C-NMR spectroscopy

BD = polymer bulk density in g/dm^3

Synthesis of the metallocenes used in the examples:

I. rac-[Dimethylsilylbis{1-(4,7-dimethylindenyl)}]-zirconium dichloride

1. 4,7-Dimethylindene

23 g (1.0 mol) of sodium were dissolved in portions in 250 ml of absolute methanol. A mixture of 45.6 g (0.40 mol) of 2,5-hexanedione and 39.7 g (0.60 mol) of cyclopentadiene was then added dropwise at 0°C in the course of 1 hour. After the mixture had been stirred at room temperature for 1 hour, 50 ml of water were added and the mixture was extracted with about 2 l of diethyl ether. The residue which remained after the solvent had been stripped off was chromatographed on 1.4 kg of silica gel 60. 38 g (65%) of 4,7-dimethylindene (yellowish oil) were eluted with hexane/methylene chloride (10:1).

2. bis{1-(4,7-Dimethylindenyl)}-dimethylsilane

7.0 g (48.5 mmol) of 4,7-dimethylindene were dissolved in 60 ml of diethyl ether, and 19.4 ml (48.5 mmol) of a 2.5 M solution of butyllithium in hexane were added under an Ar atmosphere. After a short time, a white precipitate separated out and was dissolved again by addition of 4 ml of tetrahydrofuran. After the solution had been stirred at room temperature for 2 hours, it was slowly added dropwise to a solution of 3.1 g (24.3 mmol) of dimethyldichlorosilane in 15 ml of diethyl ether. After the mixture had been stirred for 19 hours, it was poured onto ice-water and extracted several times with ether. The combined ether extracts were washed with water and dried over sodium sulfate. The yellow oil which remained after the solvent had been stripped off under reduced pressure was chromatographed on 350 g of silica gel 60. 3.1 g (37%) of the product (white powder, 2 isomers, melting point 67°C) were eluted using a mobile phase mixture of hexane/methylene chloride (20:1).

3. rac-[Dimethylsilylbis{1-(4,7-dimethylindenyl)}]-zirconium dichloride

4.0 ml (10 mmol) of a 2.5 M solution of butyllithium in hexane were added to a solution of 1.5 g (4.86 mmol) of the ligand system in 15 ml of diethyl ether at room temperature, and the mixture was stirred for 5 hours, until the evolution of gas had ended. The yellow solution was evaporated and the residue was washed with hexane in order to remove excess butyllithium. After drying under an oilpump vacuum at 40 - 50°C, the dilithium salt was added to a suspension of 1.08 g (4.3 mmol) of zirconium tetrachloride in 10 ml of methylene chloride at -78°C. After the mixture had been warmed up overnight, the orange-colored suspension was filtered over a G4 frit. The orange-colored filtrate was evaporated. 1.58 g (72%) of the complex were obtained as a mixture of the racemic form and the meso-form in a ratio of 5:1. The pure racemate was obtained in the form of large orange crystals by recrystallization from methylene chloride.

^{1}H-NMR of the racemate ($CDCl_3$): 7.07 (d,2,β-H), 6.75-7.05 (m,4,aromatic-H), 6.17 (d,2,α-H), 2.53 (s,6,CH_3), 2.38 (s,6,CH_3), 1.14 (s,6,$Si(CH_3)_2$).

II. rac-[1,2-Ethanediylbis{1-(2-methyl-4,7-dimethyl-indenyl)}]zirconium dichloride

1. 4,7-Dimethyl-2-indanone

8.2 g (57 mmol) of 4,7-dimethylindene (for the preparation, see Example I) were added dropwise to a mixture of 34 ml of formic acid and 8 ml (80 mmol) of H_2O_2 (35% strength) at 35-40°C in the course of 80 minutes, while stirring vigorously (exothermic reaction). After the mixture had been stirred overnight, the formic acid was stripped off under reduced pressure (40°C/20 mm Hg). 200 ml of 7% strength sulfuric acid were added to the orange-colored oil which remained, and the mixture was distilled. The product was distilled over with a total of 800 ml of water, the water constantly being topped up. The product partly precipitated as a solid in the condenser and was transferred to the receiver by brief heating. The aqueous distillate was neutralized with a saturated sodium carbonate solution and extracted with ether. The organic phase was dried over sodium sulfate and concentrated, whereupon the product crystallized. 5.6 g (62%) of the indanone were obtained in the form of colorless needles.

2. 2,4,7-Trimethylindene

20 ml (60 mmol) of a 3M solution of methylmagnesium bromide in diethyl ether were slowly added to a solution of 5.5 g (34.3 mmol) of the indanone in 100 ml of diethyl ether such that the solvent boiled gently. After the mixture had been boiled under reflux for 1 hour, the white suspension was stirred overnight. The mixture was poured onto ice acidified with HCl, and extracted with diethyl ether. After the extract had been dried over sodium sulfate, the solvent was stripped off completely.

The solid was suspended in 170 ml of toluene, 0.65 g (3.14 mmol) of p-toluenesulfonic acid was added and the mixture was heated under reflux for 1.5 hours. After water had been added, the organic phase was isolated, dried over sodium sulfate and evaporated completely. The residue was chromatographed on 350 g of silica gel 60. 3.0 g (60%) of 2,4,7-trimethylindene (white solid) were eluted using hexane/methylene chloride 10:1.

3. 1,2-bis{1-(2,4,7-Trimethylindenyl)}ethane

4.2 ml (10.5 mmol) of a 2.5 M butyllithium solution in hexane were added to a solution of 1.7 g (10.5 mmol) of 2,4,7-trimethylindene in 50 ml of tetrahydrofuran at room temperature, and the mixture was stirred at 40°C for 1 hour. 0.98 g (5.25 mmol) of dibromoethane was added at -78°C. The mixture was warmed to room temperature overnight, poured onto ice-water containing hydrochloric acid (pH 2) and extracted with diethyl ether. The ether phase was washed with $NaHCO_3$ solution and NaCl solution and dried over magnesium sulfate. When the ether extract was concentrated, 350 mg of the product crystallized in the form of a colorless crystalline powder (2 isomers). 430 mg of unused 2,4,7-trimethylindene and a further 50 mg of the product were obtained by chromatography of the mother liquor on silica gel 60 using hexane/methylene chloride (10:1). The total yield was 22%.

4. rac-[1,2-Ethanediylbis{1-(2,4,7-trimethylindenyl)}]-zirconium dichloride

1.4 ml (3.5 mmol) of a 2.5 M butyllithium solution in hexane were added to a solution of 400 mg (1.16 mmol) of the chelating ligand in 60 ml of diethyl ether at room temperature, a red-orange coloration starting. After the mixture had been stirred at room temperature for 2-3 hours, 20 ml of hexane were added. The precipitate was isolated by decanting the supernatant solution, washed with hexane and dried under an oilpump vacuum for

3-4 hours. The dilithium salt was then added to a suspension of 240 mg (1.03 mmol) of zirconium tetrachloride in 15 ml of methylene chloride at -78°C. After the mixture had been warmed to room temperature, the orange suspension was filtered over a G4 frit and the solid was washed with methylene chloride. The filtrate was concentrated to dryness under an oilpump vacuum. 120 mg (24%) of the complex were obtained as an orange powder. ^{1}H-NMR of the racemate ($CDCl_3$): 6.8-7.1 (m,4,aromatic-H), 6.30 (s,2,β-H), 3.3-3.5 (m,4,C_2H_4), 2.60 (s,6,CH_3), 2.27 (s,6,CH_3), 1.57 (s,6,CH_3).

III. rac-[Dimethylsilylbis{1-(3,4,7-trimethylindenyl)}]-zirconium dichloride

1. 3,4,7-Trimethylindene

A mixture of 12 g (150 mmol) of methylcyclopentadiene and 17.1 g (150 mmol) of 2,5-hexanedione was added dropwise to a solution of 8.6 g (975 mmol) of sodium in 200 ml of methanol at 0°C in the course of 1 hour. After stirring at room temperature for 18 hours, the dark red mixture was poured onto ice-water and extracted with ether. After the extract had been dried over sodium sulfate, the solvent was stripped off and the oil which remained was chromatographed on 600 g of silica gel 60. Using hexane as the mobile phase, first 3.2 g (13%) of 3,4,7-trimethylindene and then 1.5 g (6%) of 2,4,7-trimethylindene were eluted in close succession. Subsequent recrystallization from hexane gave the pure products.

2. bis{1-(3,4,7-Trimethylindenyl)}dimethylsilane

8.1 ml (20.2 mmol) of a 2.5 M butyllithium solution in hexane were added to a solution of 3.2 g (20.2 mmol) of 3,4,7-trimethylindene in 40 ml of tetrahydrofuran at 0°C, and the mixture was heated under reflux for a further hour and then added to a solution of 1.3 g (10.1 mmol) of dimethyldichlorosilane in 10 ml of tetrahydrofuran at

room temperature. The red suspension was stirred at room temperature for 17 hours and was heated at the boiling point under reflux for a further 4 hours. The mixture was poured onto ice and extracted with ether. The ether extracts were combined, dried over sodium sulfate and evaporated to dryness. Recrystallization from hexane gave 1.4 g (37%) of the product in the form of beige-colored crystals (isomers).

3. rac-[Dimethylsilylbis{1-(3,4,7-dimethylindenyl)}]-zirconium dichloride

3.4 ml (8.4 mmol) of a 2.5 M butyllithium solution in hexane were added to a solution of 1.4 g (3.8 mmol) of the ligand system in 25 ml of diethyl ether at 0°C. After the mixture had been stirred at room temperature for 2-3 hours, it was concentrated to 15 ml and the precipitate was filtered over a G4 frit. After being washed with hexane, it was dried under an oilpump vacuum. The pale beige dilithium salt was added to 800 mg (3.5 mmol) of zirconium tetrachloride in 20 ml of methylene chloride at -78°C. The mixture was warmed to room temperature in the course of 3-4 hours and filtered over a G4 frit. 20 ml of hexane were added to the filtrate and the mixture was concentrated to a volume of 10 ml. 500 mg of the complex (pure racemate) crystallized at -35°C. ^{1}H-NMR ($CDCl_3$): 6.6-6.9 (m,4,aromatic-H), 5.75 (s,2,α-H), 2.50 (s,6,CH_3), 2.45 (s,6,CH_3), 2.40 (s,6,CH_3), 1.07 (s,6,Si-CH_3).

IV. rac-[1,2-Ethanediylbis{1-(4,7-dimethylindenyl)}]-zirconium dichloride

1. 1,2-bis(4,7-Dimethylindenyl)ethane

27 ml (43.2 mmol) of a 1.6 M solution of butyllithium in hexane were added dropwise to 6.19 g (42.9 mmol) of 4,7-dimethylindene in 150 ml of tetrahydrofuran under an Ar atmosphere, and the mixture was stirred at 60°C for

1.5 hours. It was cooled to -78°C, 1.86 ml (21.5 mmol) of 1,2-dibromoethane were added and stirring was continued at room temperature for 2 hours. The reaction mixture was poured onto 2 N aqueous HCl and the organic phase was separated off, washed with saturated aqueous $NaHCO_3$ solution and NaCl solution in succession and dried ($MgSO_4$). The oil which remained after the solvent had been stripped off under reduced pressure was taken up in hexane and the precipitate formed was separated off. After drying under an oilpump vacuum, 4.2 g (62%) of product were obtained.

2. rac-[1,2-Ethanediylbis{1-(4,7-dimethyl-indenyl)}]-zirconium dichloride

2.14 g (6.8 mmol) of the ligand system were dissolved in 80 ml of tetrahydrofuran, 8.7 ml (13.9 mmol) of a 1.6 M solution of butyllithium in hexane were added dropwise at room temperature in the course of 15 minutes, while stirring with a magnetic stirrer, and the mixture was stirred at 50°C for 1 hour, until the evolution of gas had ended. The solvent was removed under an oilpump vacuum and the residue was washed with hexane in order to remove excess butyllithium. After drying under an oilpump vacuum, the dilithium salt, dissolved in 100 ml of tetrahydrofuran, and 2.65 g (7.1 mmol) of $ZrCl_4 \cdot 2THF$, dissolved in 100ml of tetrahydrofuran, were simultaneously added dropwise to 50 ml of tetrahydrofuran in the course of 1 hour. After the mixture had been stirred overnight, the solvent was removed under reduced pressure, the residue was taken up in toluene, the mixture was filtered and the solvent was removed. The residue was stirred with n-pentane for consolidation and crystallized from toluene at -35°C. 1.9 g (59%) of the complex were obtained as a mixture of the racemic form and the meso-form in a ratio of 3:1. The pure racemate was obtained by recrystallization from toluene/ pentane. ^{1}H-NMR of the racemate ($CDCl_3$): 6.80 (d,2,β-H), 6.70-7.00 (m,4,aromatic-H), 6.30 (2,d,α-H), 3.50-4.30 (m,4,$2CH_2$),

2.73 (s,3,CH_3), 2.30 (s,3,CH_3).

V. rac-[1,2-Ethanediylbis{1-(4,7-dimethyl-4,5,6,7-tetrahydroindenyl)}]zirconium dichloride

1.47 g (3.1 mmol) of CH_2CH_2 (4,7-Me_2-Ind)$_2ZrCl_2$ were dissolved in 70 ml of methylene chloride, 100 mg of PtO_2 were added and hydrogenation was carried out at room temperature under an increased pressure of 100 bar for 24 hours. After filtration, the solvent was removed in vacuo and the residue was recrystallized from hexane/toluene. 1.0 g (67%) of yellow crystals was obtained. ^{1}H-NMR of the racemate ($CDCl_3$): 6.60 (d,2,β-H), 5.85 (2,d,α-H), 2.30-3.30 (m,16,CH_2 and CH), 1.45 (d,3,CH_3), 1.35 (d,3,CH_3).

VI. rac-[1,2-Butanediylbis{1-(4,7-dimethylindenyl)}]-zirconium dichloride

1. 1,2-bis(4,7-Dimethylindenyl)butane

52 ml (83.2 mmol) of a 1.6 M solution of butyllithium in hexane were added dropwise to 11.8 g (92 mmol) of 4,7-dimethylindene in 200 ml of tetrahydrofuran at room temperature under an Ar atmosphere, and the mixture was stirred at 60°C for 1 hour. It was cooled to -78°C, 5 ml (40 mmol) of 1,2-dibromobutane were added, and stirring was continued overnight at room temperature. The reaction mixture was poured onto 2 N aqueous HCl and the organic phase was separated off, washed with saturated aqueous $NaHCO_3$ solution and NaCl solution in succession and dried ($MgSO_4$). The oil which remained after the solvent had been stripped off under reduced pressure was chromatographed on 350 g of silica gel (hexane). After drying under an oilpump vacuum, 1.4 g (10%) of product were obtained.

2. rac-[1,2-Butanediylbis{1-(4,7-dimethylindenyl)}]-zirconium dichloride

1.4 g (4 mmol) of the ligand system were dissolved in 50 ml of tetrahydrofuran, 5.1 ml (18.2 mmol) of a 1.6 M solution of butyllithium in hexane were added dropwise at room temperature in the course of 15 minutes while stirring with a magnetic stirrer, and the mixture was stirred at 60°C for 1.5 hours until the evolution of gas had ended. The solvent was removed under an oilpump vacuum and the residue was washed with hexane in order to remove excess butyllithium. After drying under an oilpump vacuum, the dilithium salt was added in portions to 1.55 g (4.1 mmol) of $ZrCl_4 \cdot 2THF$ in 100ml of tetrahydrofuran in the course of 50 minutes and stirring was continued for 3.5 hours. After the mixture had been filtered and the solvent had been removed, the residue was extracted with toluene/hexane, the extract was filtered and the solvent was removed. The residue was stirred with n-pentane for consolidation and crystallized from toluene at -35°C. 0.72 g (35%) of the complex was obtained as a mixture of the racemic form and the meso-form. The pure racemate was obtained by recrystallization from toluene/pentane. ^{1}H-NMR of the racemate ($CDCl_3$): 6.80 (d,2,β-H), 6.70-7.00 (m,4,aromatic-H), 6.25 (2,d,α-H), 3.50-4.30 (m,5,$2CH_2$ and CH), 2.70 (s,3,CH_3), 2.35 (s,3,CH_3), 1.1 (t,3,CH_3).

Polymerization Examples

Example 1

A dry 16 dm^3 reactor was flushed with nitrogen, and 10 dm^3 of liquid propylene were introduced. 30 cm^3 of a toluene solution of methylaluminoxane (corresponding to 40 mmol of Al, average degree of oligomerization n = 20) were then added and the batch was stirred at 30°C for 15 minutes.

In parallel, 9.9 mg (0.02 mmol) of rac-dimethylsilyl (4,7-dimethyl-1-indenyl)$_2$zirconium dichloride were dissolved in 15 cm^3 of a toluene solution of methyl-aluminoxane (20 mmol of Al) and preactivated by being

left to stand for 15 minutes. The solution was then introduced into the reactor, the mixture was heated up to 70°C (10°C/minute) by supplying heat, and the polymerization system was kept at 70°C, by cooling, for 1 hour. The polymerization was stopped by gassing off the excess monomer. 1.39 kg of polypropylene were obtained. The activity of the metallocene was thus 140.4 kg of polypropylene/g of metallocene × hour.

VN = 20 cm^3/g, M_w = 12,500 g/mol, M_w/M_n = 2.1, m.p. = 128°C, BD = 500 g/dm^3, II = 90%.

Example 2

Example 1 was repeated at a polymerization temperature of 50°C. 0.65 kg of polypropylene, corresponding to 65.7 kg of polypropylene/g of metallocene × hour, was obtained.

VN = 30 cm^3/g, M_w = 14,500 g/mol, M_w/M_n = 2.1, m.p. = 134°C, BD = 422 g/dm^3, II = 95%.

Example 3

Example 1 was repeated with twice the amount of metallocene at a polymerization temperature of 30°C. 0.28 kg of polypropylene, corresponding to 14.9 kg of polypropylene/g of metallocene × hour, was obtained.

VN = 40 cm^3/g, M_w = 16,000 g/mol, M_w/M_n = 2.3, m.p. = 139°C.

Example 4

Example 1 was repeated, but before the addition of the liquid propylene, 5 Ndm^3 of hydrogen were introduced into the reactor, and the weight of the metallocene was 10.6 mg. 2.52 kg of polymer, corresponding to 237.7 kg of polypropylene/g of metallocene × hour, were obtained.

VN = 21 cm^3/g, M_w = 13,100 g/mol, M_w/M_n = 1.9, m.p. = 131°C.

Example 5

Example 1 was repeated, but 14.7 mg (0.031 mmol) of rac-ethylene(4,7-dimethyl-1-indenyl)$_2$zirconium dichloride were added as the metallocene. 2.92 kg of polypropylene,

corresponding to a metallocene activity of 198.6 kg of polypropylene/g of metallocene × hour, were obtained.
VN = 18 cm^3/g, M_w = 8400 g/mol, M_w/M_n = 2.1, m.p. = 124°C, BD = 411 g/dm^3, II = 90%.

Example 6

Example 5 was repeated at a polymerization temperature of 50°C. 1.38 kg of polymer, corresponding to 93.9 kg of polypropylene/g of metallocene × hour, were obtained.
VN = 17 cm^3/g, M_w = 8100 g/mol, M_w/M_n = 2.0, m.p. = 130°C, BD = 453 g/dm^3.

Example 7

Example 5 was repeated at a polymerization temperature of 30°C. 0.37 kg of polymer, corresponding to 25.2 kg of polypropylene/g of metallocene × hour, was obtained.
VN = 40 cm^3/g, M_w = 32,000 g/mol, M_w/M_n = 2.7, m.p. = 150°C, BD = 347 g/dm^3, II = 94%.

Example 8

Example 1 was repeated, but 14.5 mg of rac-ethylene(4,7-dimethyl-4,5,6,7-tetrahydro-1-indenyl)$_2$zirconium dichloride were used as the metallocene. 1.37 kg of polypropylene, corresponding to a metallocene activity of 94.5 kg of polypropylene/g of metallocene × hour, were obtained.
VN = 23 cm^3/g, M_w = 12,300 g/mol, M_w/M_n = 2.3, m.p. = 121°C, glass stage Tg at -25°C.

Example 9

Example 8 was repeated using 15.0 mg of the metallocene at a polymerization temperature of 50°C. 0.60 kg of polymer, corresponding to 40.0 kg of polypropylene/g of metallocene × hour, was obtained.
VN = 35 cm^3/g, M_w = 24,500 g/mol, M_w/M_n = 2.4, m.p. = 116°C, glass stage Tg at -22°C.

Example 10

Example 1 was repeated, but 15.0 mg of rac-ethylethylene-(4,7-dimethyl-1-indenyl)$_2$zirconium dichloride were used as the metallocene. 1.45 kg of polymer, corresponding to 96.7 kg of polypropylene/g of metallocene × hour, were obtained.

VN = 16 cm^3/g, M_w = 7700 g/mol, M_w/M_n = 1.8, m.p. = 129°C.

Example 11

Example 10 was repeated at a polymerization temperature of 50°C. 0.65 kg of polymer, corresponding to 43.3 kg of polypropylene/g of metallocene × hour, was obtained.

VN = 17 cm^3/g, m.p. = 134°C.

Example 12

Example 1 was repeated, but 15.2 mg of rac-ethylene-(2,4,7-trimethyl-1-indenyl)$_2$zirconium dichloride were employed as the metallocene. 1.49 kg of polymer, corresponding to 98.0 kg of polypropylene/g of metallocene × hour, were obtained.

VN = 44 cm^3/g, M_w = 30,600 g/mol, M_w/M_n = 2.3, m.p. = 145°C.

Example 13

Example 12 was repeated at a polymerization temperature of 50°C. 0.41 kg of polymer, corresponding to 27.0 kg of polypropylene/g of metallocene × hour, was obtained.

VN = 70 cm^3/g, M_w = 61,100 g/mol, M_w/M_n = 2.5, m.p. = 152°C.

Examples 14 to 18

0.75 dm^3 of a hydrocarbon cut (boiling point 100-120°C) was initially introduced into a dry 1.5 dm^3 reactor flushed with nitrogen, and 3.75 cm^3 of a toluene solution of methylaluminoxane (corresponding to 5 mmol of Al, average degree of oligomerization n = 20) were added, while stirring.

0.125 mg of metallocene (Table 1) was dissolved in 1.25 cm^3 of a toluene solution of methylaluminoxane

(1.66 mmol of Al) and was preactivated by being left to stand for 15 minutes. The reactor was heated up to 70°C, and 5 bar of ethylene were forced in, while stirring. The metallocene solution was added through a pressure block, the reactor pressure was kept constant at 5 bar by continuous addition of ethylene gas, and the temperature was kept constant at 70°C by thermostatic control.

After a polymerization time of one hour, while stirring, the reaction was stopped by addition of 5 ml of isopropanol, the reactor was emptied and the polymer was filtered off and dried in vacuo. For the results, see Table 1.

Table 1

Ethylene polymerizations

Example	Metallocene	Yield of PE (g)	VN (cm^3/g)	M_w (g/mol)	M_w/M_n
14	$Me_2Si(3,4,7\text{-}Me_3Ind)_2ZrCl_2$	56	500	326,000	2.4
15	$Ethylethylene(4,7\text{-}Me_2Ind)_2ZrCl_2$	39	599	470,000	2.5
16	$Ethylene(4,7\text{-}Me_2Ind)_2ZrCl_2$	35	910	610,000	2.3
17	$Me_2Si(4,7\text{-}Me_2Ind)_2ZrCl_2$	38	505	344,000	2.1
18	$Ethylene(2,4,7\text{-}Me_3Ind)_2ZrCl_2$	35	480	310,000	2.3

In the table: Me denotes methyl, Ind denotes indenyl, PE denotes polyethylene

Example 19

Example 1 was repeated, but 50 g of ethylene were metered in continuously during the polymerization. 1.44 kg of C_2/C_3 copolymer, corresponding to a metallocene activity of 145.5 kg of copolymer/g of metallocene × hour, were obtained.

VN = 30 cm^3/g, M_w = 15,600, M_w/M_n = 2.2, m.p. 122°C.

Ethylene content 3.1%, according to ^{13}C-NMR, isolated incorporation of the ethylene units.

The melting point can be reduced by ethylene as a comonomer.

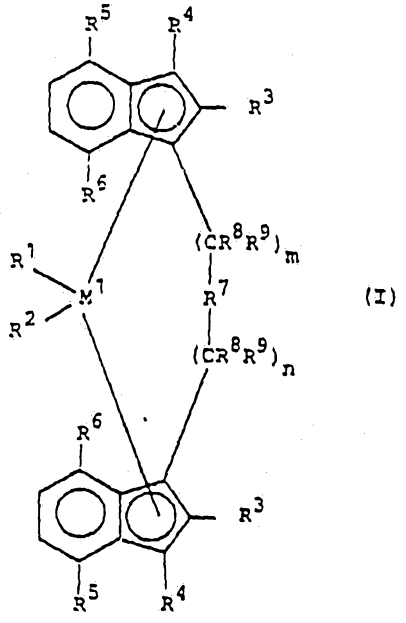
Example 20

Example 1 was repeated, but 16 Ndm^3 of hydrogen were additionally metered into the reactor before addition of the propylene. 1.50 kg of polypropylene, corresponding to a metallocene activity of 151.5 kg of polymer/g of metallocene × hour, were obtained.

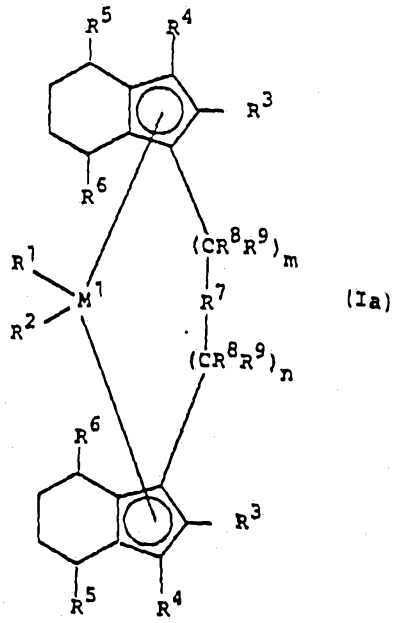
VN = 15 cm^3/g, M_w = 9300 g/mol, M_w/M_n = 2.0, m.p. = 132°C, BD = 520 g/dm^3, II = 92%.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the preparation of an olefin polymer by polymerization or copolymerization of an olefin of the formula R^a-CH=CH-R^b, in which R^a and R^b are identical or different and are a hydrogen atom or a hydrocarbon radical having 1 to 14 carbon atoms, or R^a and R^b, together with the atoms joining them, can form a ring, at a temperature of -60 to 200°C, under a pressure of 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst which is formed from a metallocene as the transition metal compound and a cocatalyst, wherein the metallocene is a compound of the formula I or Ia



(I)



(Ia)

in which

M^1 is a metal of group IVb, Vb or VIb of the periodic table (American nomenclature, chemical abstract service, 1986),

R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl

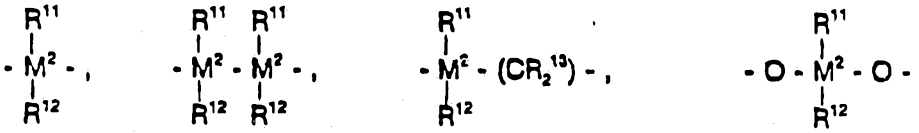
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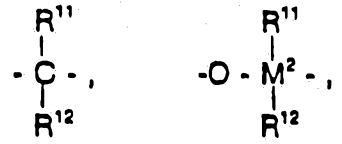
group, a C_8-C_{40}-arylalkenyl group or a halogen atom,

R^3 and R^4 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, which can be halogenated, a C_6-C_{10}-aryl group or an $-NR_2^{10}$, $-SR^{10}$, $-OSiR_3^{10}$, $-SiR_3^{10}$ or $-PR_2^{10}$ radical, in which R^{10} is a halogen atom, a C_1-C_{10}-alkyl group or a C_6-C_{10}-aryl group,

R^5 and R^6 are identical or different and have the meaning given for R^3 and R^4, with the proviso that R^5 and R^6 are not hydrogen,

R^7 is





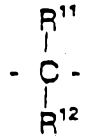
$=BR^{11}$, $=AlR^{11}$, $-Ge-$, $-Sn-$, $-O-$, $-S-$, $=SO$, $=SO_2$, $=NR^{11}$, $=CO$, $=PR^{11}$ or $P(O)R^{11}$,

in which

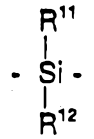
R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a C_6-C_{10}-fluoroaryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^{11} and R^{12} or R^{11} and R^{13}, in each case with the atoms joining them, form a ring, and

M^2 is silicon, germanium or tin,
R^8 and R^9 are identical or different and have the meaning given for R^{11} and
m and n are identical or different and are zero, 1 or 2, m plus n being zero, 1 or 2.

2. A process as claimed in claim 1, wherein, in formula I or Ia, M^1 is Zr or Hf, R^1 and R^2 are identical or different and are (C_1-C_3)-alkyl or chlorine, R^3 and R^4 are identical or different and are hydrogen or (C_1-C_4)-alkyl, R^5 and R^6 are identical or different and are (C_1-C_4)-alkyl, which can be halogenated, R^7 is a radical



or



and m plus n is zero or 1.

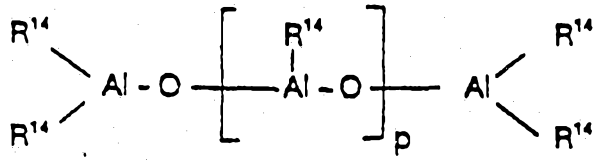
3. The process as claimed in claim 1 or 2, wherein, in formula I or Ia, the substituents R^5 and R^6 are identical.

4. The process as claimed in one or more of claims 1 to 3, wherein
rac-[dimethylsilylbis{1-(4,7-dimethylindenyl)}]-zirconium dichloride,
rac-[1,2-ethanediylbis{1-(2-methyl-4,7-dimethyl-indenyl)}]zirconium dichloride,
rac-[dimethylsilylbis{1-(3,4,7-trimethylindenyl)}]-zirconium dichloride,
rac-[1,2-ethanediylbis{1-(4,7-dimethylindenyl)}]-zirconium dichloride,
rac-(1,2-ethanediylbis{1-(4,7-dimethyl-4,5,6,7-

tetrahydroindenyl)}]zirconium dichloride or
rac-[1,2-butanediylbis{1-(4,7-dimethylindenyl)}]-zirconium dichloride

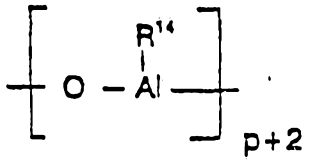
is used as the metallocene of the formula I or Ia.

5. The process as claimed in one or more of claims 1 to 4, wherein an aluminoxane of the formula (II)



(II)

for the linear type, and/or of the formula (III)



(III)

for the cyclic type, in which, in the formulae (II) and (III), the radicals R^{14} are identical or different and are a C_1-C_6-alkyl group, a C_6-C_{18}-aryl group, benzyl or hydrogen and p is an integer from 2 to 50, is used as the cocatalyst.

6. The process as claimed in one or more of claims 1 to 5, wherein methylaluminoxane is used as the cocatalyst.

7. The process as claimed in claim 5 or 6, wherein the metallocene of the formula I or Ia is preactivated with an aluminoxane of the formula II and/or III before use in the polymerization reaction.

8. The use of a metallocene of the formula I or Ia as claimed in one or more of claims 1 to 4 as a catalyst in olefin polymerization.

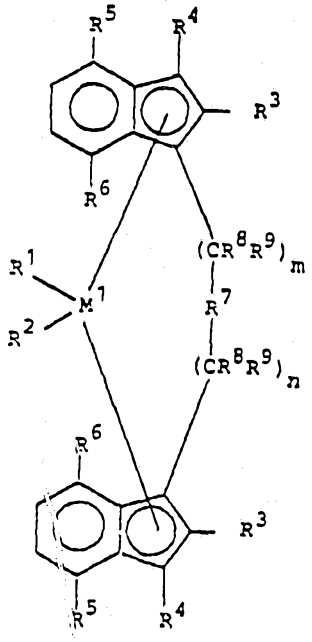
DATED this 13th day of October 1992.
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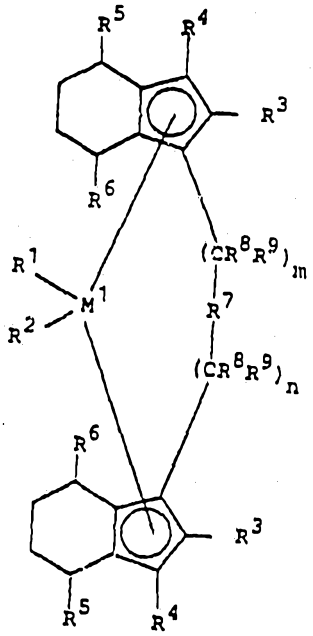
Abstract of the Disclosure:

Process for the preparation of an olefin polymer using metallocenes having specifically substituted indenyl ligands

A very active catalyst system for olefin polymerization comprises a cocatalyst, preferably an aluminoxane, and a metallocene of the formula I or Ia



(I)



(Ia)

in which, preferably, M^1 is Zr or Hf, R^1 and R^2 are alkyl or halogen, R^3 and R^4 are hydrogen or alkyl, R^5 and R^6 are alkyl, $-(CR^8R^9)_m-R^7-(CR^8R^9)_n$ is a chain with one or more members, in which R^7 can also be a (substituted) heteroatom, and m+n is zero or 1.