615113

COMMONWEALTH OF AUSTRALIA

Patents Act 1952-1969

CONVENTION APPLICATION FOR A PATENT

(1) Here insert (in full) Name or Names of Applicant or Applicants, followed by Address (es).

I/We (1) HOECHST AKTIENGESELLSCHAFT

OF 50 Bruningstrasse, D-6230 Frankfurt/Main 80, Federal Republic of Germany

hereby apply for the grant of a Patent for an invention entitled: (2)

(2) Here insert Title of Invention.

PROCESS FOR THE PREPARATION OF AN ETHYLENE/PROPYLENE COPOLYMER

(3) Here insert number(s) of basic application(s)

which is described in the accompanying complete specification. This application is a Convention application and is based on the application numbered (3)

P38 36 059.4

(4) Here insert Name of basic Country or Countries, and basic date or dates

for a patent or similar protection made in (4) Federal Republic of Germany on 22nd October 1988

FO11731

20/10/89

Our address for service is Watermark Patent & Trademark Attorneys

50 Queen Street, Melbourne, Victoria, Australia.

DATED this 19th day of October 1989

(5) Signature (s) of Applicant (s) or Seal of Company and Signatures of its Officers as prescribed by its Articles of Association.

(5) HOECHST AKTIENGESELLSCHAFT

by

D. B. Mischlewski

Registered Patent Attorneys

To:

THE COMMISSIONER OF PATENTS.

Edwd. Waters & Sons, Melbourne.

Form 7

COMMONWEALTH OF AUSTRALIA

Patents Act 1952

DECLARATION IN SUPPORT OF A CONVENTION APPLICATION UNDER PART XVI. FOR A PATENT.

In support of the Convention application made under Part XVI. of the Patents Act 1952 by HOECHST AKTIENGESELLSCHAFT of 50, Brüningstrasse, D-6230 Frankfurt/Main 80, Federal Republic of Germany for a patent for an invention entitled:

Procress for the preparation of an ethylene/propylene copolymer

We, Günter Isenbruck, Biebricher Allee 173, D-6200 Wiesbaden,
Franz Lapice, Sandweg 2,D-6233 Kelkheim(Taunus),
Federal Republic of Germany
do solemnly and sincerely declare as follows:

1. We are authorized by HOECHST AKTIENGESELLSCHAFT the applicant for the patent to make this declaration on its behalf.

2. The basic application as defined by Section 141 of the Act was made in the Federal Republic of Germany
under No. P 38 36 059.4 on Oktober 22, 1988
by HOECHST AKTIENGESELLSCHAFT

3.
a) Martin Antberg, Sachsenring 10, D-6238 Hofheim am Taunus
b) Walter Spaleck, Sulzbacher Straße 63, D-6237 Liederbach
c) Jürgen Rohrmann, Die Ritterwiesen 10, D-6237 Liederbach
d) Hartmut Lüker, Königsteiner Straße 13, D-6238 Hofheim am Taunus
e) Andreas Winter, Gundelhardtstraße 2, D-6233 Kelkheim(Taunus)
a) - e) Federal Republic of Germany
is/are the actual inventor(s) of the invention and the facts upon which HOECHST AKTIENGESELLSCHAFT
is entitled to make the application are as follows:
The said HOECHST AKTIENGESELLSCHAFT
is the assignee of the said
Martin Antberg, Walter Spaleck, Jürgen Rohrmann, Hartmut Lüker, Andreas Winter

4. The basic application referred to in paragraph 2 of this Declaration was the first application made in a Convention country in respect of the invention the subject of the application.

DECLARED at Frankfurt/Main, Federal Republic of Germany
this 11th day of September, 1989

To the Commissioner of Patents

HOECHST AKTIENGESELLSCHAFT

ppa. Isenbruck
Prokurist

i.V. Lapice
Authorized Signatory

PAT 510

(12) PATENT ABRIDGMENT (11) Document No. AU-B-43563/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 615113

(54) Title
PROCESS FOR THE PREPARATION OF AN ETHYLENE/PROPYLENE COPOLYMER CONTAINING LESS THAN 15MOL% OF PROPYLENE UNITS

International Patent Classification(s)
(51)[4] C08F 210/02

(21) Application No. : 43563/89 (22) Application Date : 20.10.89

(30) Priority Data

(31) Number (32) Date (33) Country
3836059 22.10.88 DE FEDERAL REPUBLIC OF GERMANY

(43) Publication Date : 26.04.90

(44) Publication Date of Accepted Application : 19.09.91

(71) Applicant(s)
HOECHST AKTIENGESELLSCHAFT

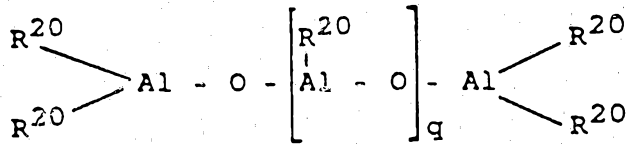
(72) Inventor(s)
MARTIN ANTBERG; WALTER SPALECK; JURGEN ROHRMANN; HARTMUT LUKER; ANDREAS WINTER

(74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122

(56) Prior Art Documents
AU 469950 24973/71 C08F 210/02
AU 483409 76827/74 C08F 210/02

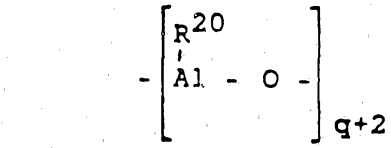
(57) Claim

1. A process for the preparation of an ethylene/propylene copolymer containing less than 15 mol% of propylene units, relative to the entire polymer, by polymerization of ethylene and propylene in ~~a suspending agent~~ liquid propylene, at a temperature of -60 to 90°C, at a pressure of 0.5 to 150 bar, in the presence of a catalyst which consists of a metallocene and an aluminoxane of the formula IV



(IV)

in the case of the linear type and/or of the formula V



(V)

in the case of the cyclic type, in which in formulae IV and V R^{20} is a C_1-C_6-alkyl group and q is an integer from 2 to 50,

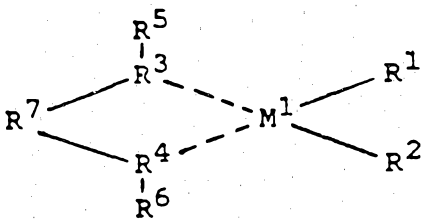
which comprises carrying out the polymerization in liquid

.../2

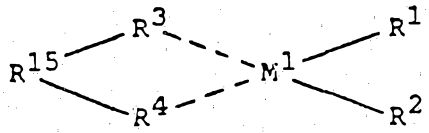
propylene as suspending agent. in which the ratio of the partial pressure P_{C2} of ethylene in the gas phase to the partial pressure P_{C3} of propylene in the gas phase

$$\frac{P_{C2}}{P_{C3}} \text{ is greater than } 0.6$$

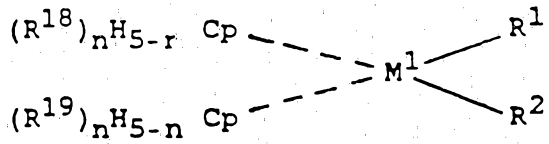
and the metallocene is a compound of the formulae I, II or III



(I),



(II),



(III),

in which in formulae I, II and III

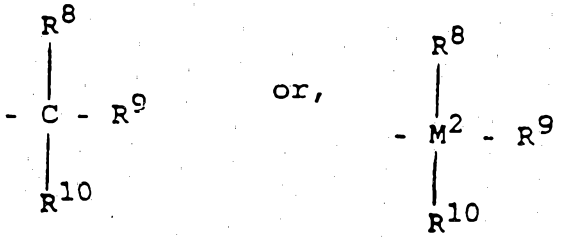
M^1 is a metal from group IVb, Vb or VIb of the periodic table,

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 an indenyl or tetrahydroindenyl radical in which the five-membered rings of the radicals R^3 and R^4 form a sandwich structure with the central atom M^1,

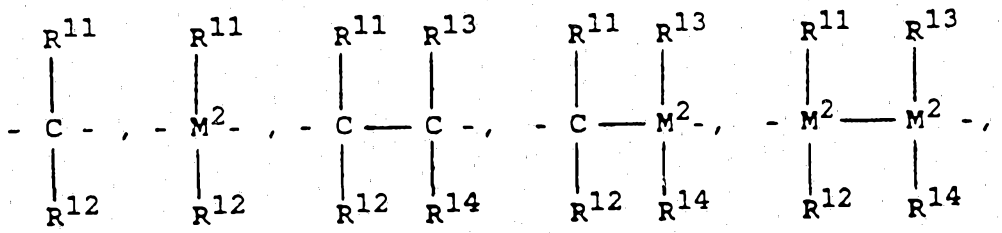
.../3

R^5 and R^6 are identical or different, and are substituents in the 3-position of R^3 and R^4 or are radicals of the formulae



in which M^2 is silicon, germanium or tin, R^8, R^9 and R^{10} are identical or different and are 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, a C_7-C_{40}-alkylaryl group, a trihalosilyl group, a C_1-C_{10}-trialkylsilyl group or a C_1-C_{10}-trialkoxysilyl group,

R^7 is

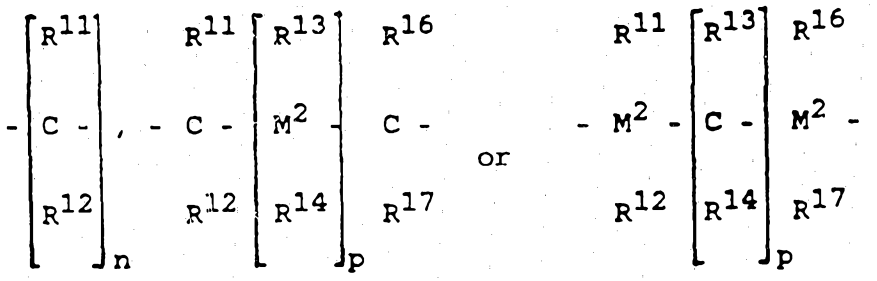


$=BR^{11}$, $=AlR^{11}$, -Ge-, -Sn-, -O-, -S-, =S=O, $=SO_2$, $=NR^{11}$, =CO, $=PR^{11}$ or $=P(O)R^{11}$,
where R^{11}, R^{12}, R^{13} and R^{14} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-aryl group, a 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

and R^7 together with the radicals R^3 and R^4 forms a ring, R^7 being linked to the radicals R^3 and R^4 in the 1-position of the radicals R^3 and R^4,

.../4

R^{15} is



in which R^{16} and R^{17} 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,

n is the number 3, 4 or 5 and p is 1, 2 or 3,
R^{15} together with the radicals R^3 and R^4 forms a ring, R^{15} being linked to the radicals R^3 and R^4 in the 1-position of the radicals R^3 and R^4,

Cp is a cyclopentadienyl radical and

R^{18} and R^{19} are identical or different substituents on the cyclopentadienyl radicals and are 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.

2. The process as claimed in claim 1, wherein the polymerization is carried out in the presence of a 1-olefin having 4 to 18 carbon atoms.

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION 615113

(ORIGINAL)

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

Name of Applicant : HOECHST AKTIENGESELLSCHAFT

Address of Applicant : 50 Bruningstrasse, D-6230 Frankfurt/Main 80, Federal Republic of Germany

Actual Inventor: MARTIN ANTBERG, WALTER SPALECK, JURGEN ROHRMANN, HARTMUT LUKER and ANDREAS WINTER

Address for Service : EDWD. WATERS & SONS, Watermark Patent & Trademark Attorneys
50 QUEEN STREET, MELBOURNE, AUSTRALIA, 3000.

Complete Specification for the invention entitled:

PROCESS FOR THE PREPARATION OF AN ETHYLENE/PROPYLENE COPOLYMER

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

HOECHST AKTIENGESELLSCHAFT Dr.DA/gm HOE 88/F 301

Description

Process for the preparation of an ethylene/propylene copolymer

The present invention relates to a process for the preparation of predominantly crystalline ethylene/propylene copolymers of various molecular weight ranges by means of metallocene/aluminoxane catalysts.

A process for the preparation of ethylene/1-olefin copolymers by means of metallocene/aluminoxane catalysts has already been described (cf. EP 69,951). In this process, a dispersant such as, for example, toluene, which is, in principle, inert towards the catalysts mentioned is used.

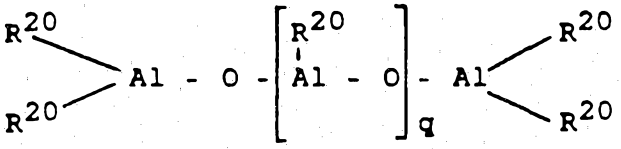
The use of metallocene/aluminoxane catalyst systems in liquid propylene as dispersant and monomer has also been proposed (cf. DE 3,726, 067). However, these metallocenes and the conditions used give highly isotactic polypropylene as the polymerization product. A preactivation method for the metallocenes, which leads to an increase in the activity of the catalysts and to an improvement in the particle morphology of the polymers, has also been proposed.

Industrial production plants which work with liquid propylene as dispersant (and monomer) are widely in use for the preparation of highly isotactic polypropylene and of random propylene/ethylene copolymers (containing < 15 mol% of ethylene). However, so far no process was known also to prepare predominantly crystalline ethylene/propylene copolymers (containing < 15 mol% of propylene) in these types of plants.

It has now been found that predominantly crystalline ethylene/propylene copolymers containing < 15 mol% of

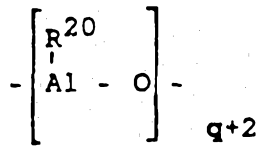
propylene units can be prepared in liquid propylene as dispersant, if metallocene catalyst components of a certain structure are used and the partial pressures of ethylene and propylene have a specific ratio.

The invention accordingly relates to a process for the preparation of an ethylene/propylene copolymer containing less than 15 mol% of propylene units, relative to the entire polymer, by polymerization of ethylene and propylene in a suspending agent, at a temperature of -60 to 90°C, at a pressure of 0.5 to 150 bar, in the presence of a catalyst which consists of a metallocene and an aluminoxane of the formula IV



(IV)

in the case of the linear type and/or of the formula V

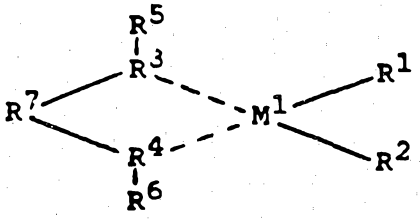


(V)

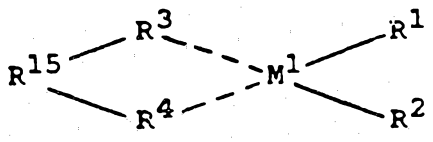
in the case of the cyclic type, in which in formulae IV and V R^{20} is a C_1-C_6-alkyl group and q is an integer from 2 to 50,
which comprises carrying out the polymerization in liquid propylene as suspending agent, in which the ratio of the partial pressure P_{C2} of ethylene in the gas phase to the partial pressure P_{C3} of propylene in the gas phase

$$\frac{P_{C2}}{P_{C3}}$$ is greater than 0.6

and the metallocene is a compound of the formulae I, II or III



(I),



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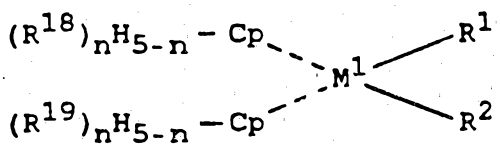


(III),

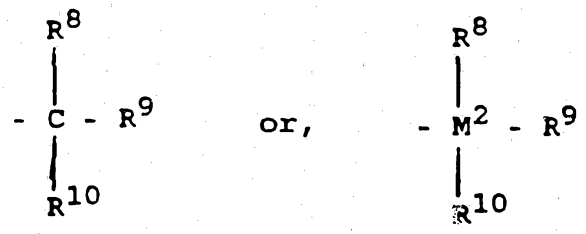
in which in formulae I, II and III

M^1 is a metal from 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 an indenyl or tetrahydroindenyl radical in which the five-membered rings of the radicals R^3 and R^4 form a sandwich structure with the central atom M^1,

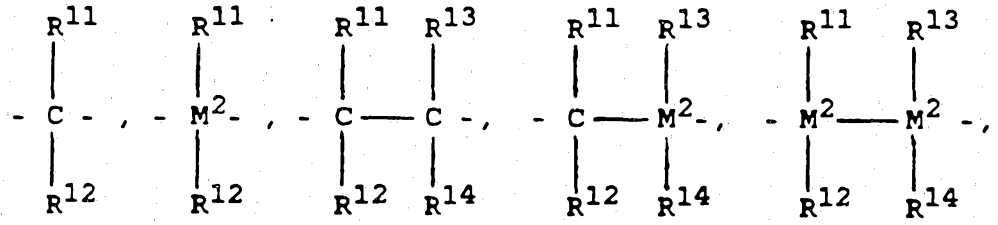
R^5 and R^6 are identical or different, and are substituents in the 3-position of R^3 and R^4 or are radicals of the formulae



in which M^2 is silicon, germanium or tin, R^8, R^9 and R^{10} are identical or different and are 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, a C_7-C_{40}-alkylaryl group, a trihalosilyl group, a C_1-C_{10}-trialkylsilyl group or a C_1-C_{10}-trialkoxysilyl group,

R^7 is

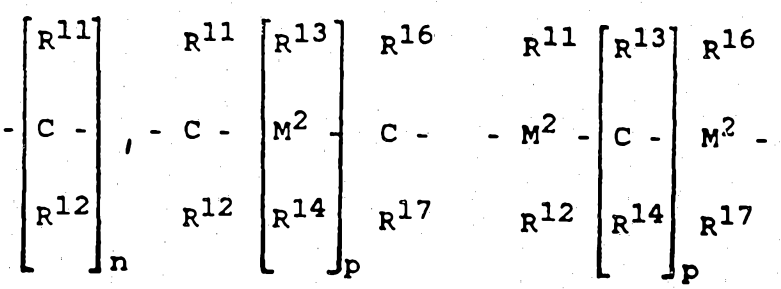


$=BR^{11}$, $=AlR^{11}$, -Ge-, -Sn-, -O-, -S-, =S=O, $=SO_2$, $=NR^{11}$, =CO, $=PR^{11}$ or $=P(O)R^{11}$,

where R^{11}, R^{12}, R^{13} and R^{14} 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

and R^7 together with the radicals R^3 and R^4 forms a ring, R^7 being linked to the radicals R^3 and R^4 in the 1-position of the radicals R^3 and R^4,

R^{15} is



in which R^{16} and R^{17} 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,

n is the number 3, 4 or 5 and p is 1, 2 or 3, and R^{15} together with the radicals R^3 and R^4 forms a ring, R^{15} being linked to the radicals R^3 and R^4 in the 1-position of the radicals R^3 and R^4,

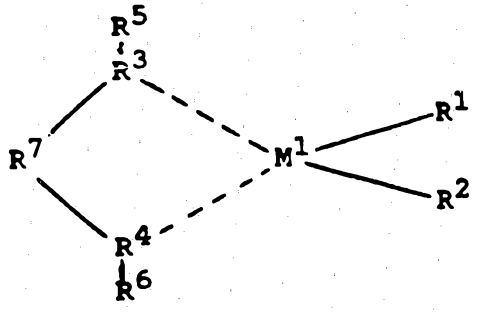
Cp is a cyclopentadienyl radical and

R^{18} and R^{19} are identical or different substituents on the cyclopentadienyl radicals and are 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.

The catalyst to be used for the process according to the invention consists of a metallocene compound of the structure types A, B or C according to formulae I, II or III and an aluminoxane.

These three structure types are distinguished by strong steric screening of the catalytically active transition metal central atom, which results in a particularly high selectivity of the polymerizing catalytic center towards the small monomer ethylene. Even in the presence of liquid propylene (= highest possible propylene concentration) and of ethylene, this leads mainly to incorporation of ethylene in the chain.

In formula I which represents structure type A



(I)

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

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

R^3 and R^4 are identical or different, preferably identical, and are an indenyl or tetrahydroindenyl radical in which the five-membered rings of the radicals R^3 and R^4 form a sandwich structure with the central atom M^1.

R^5 and R^6 are identical or different, preferably identical, and are substituents in the 3-position of the five-membered rings mentioned, which can have the following structure:

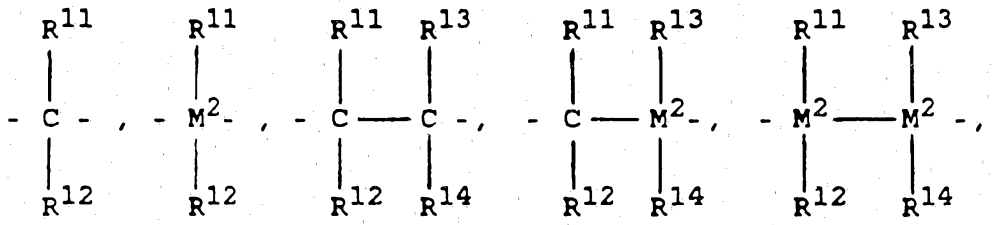


in which M^2 is silicon, germanium or tin, preferably silicon.

R^8, R^9 and R^{10} are identical or different, preferably identical, and are a halogen atom, a C_1-C_{10}-alkyl group, 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}-aryl group, preferably C_6-C_8-aryl group, a C_6-C_{10}-fluoroaryl group, preferably a pentafluorophenyl group, a C_1-C_{10}-alkoxy group, preferably C_1-C_4-alkoxy group, in

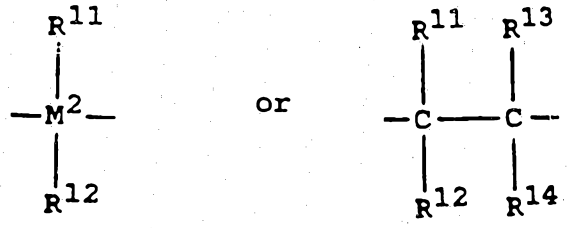
particular a methoxy group, a C_2-C_{10}-alkenyl group, preferably C_2-C_4-alkenyl group, a C_7-C_{40}-arylalkyl group, preferably C_7-C_{10}-arylalkyl group, a C_8-C_{40}-arylalkenyl group, preferably C_8-C_{12}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, preferably C_7-C_{12}-alkylaryl group, a trihalosilyl group, a C_1-C_{10}-trialkylsilyl group, preferably C_1-C_4-trialkylsilyl group, in particular a trimethylsilyl group or a C_1-C_{10}-trialkoxysilyl group, preferably C_1-C_4-trialkoxysilyl group.

R^7 is



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

preferably



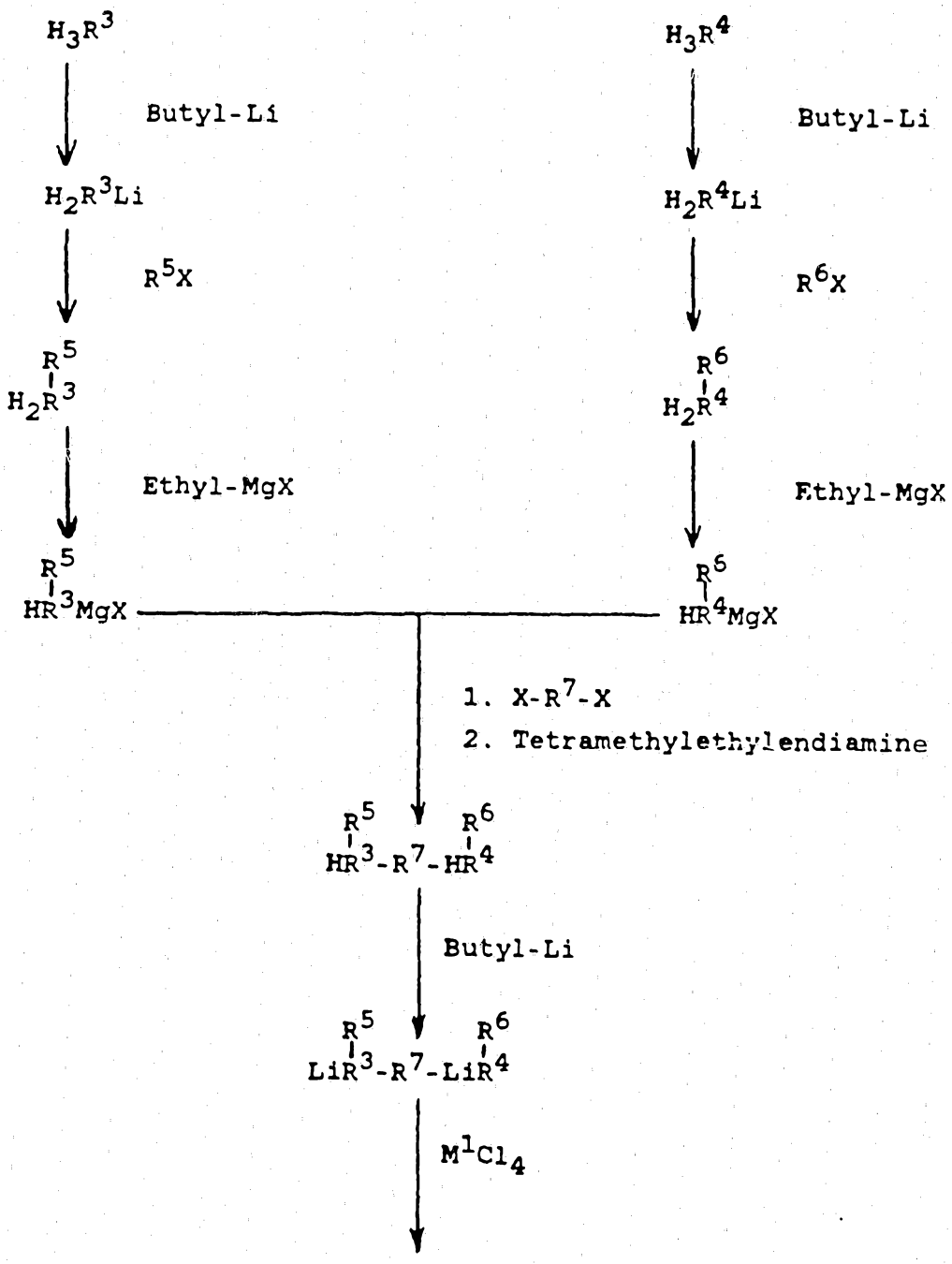
in which M^2 has the above meaning.

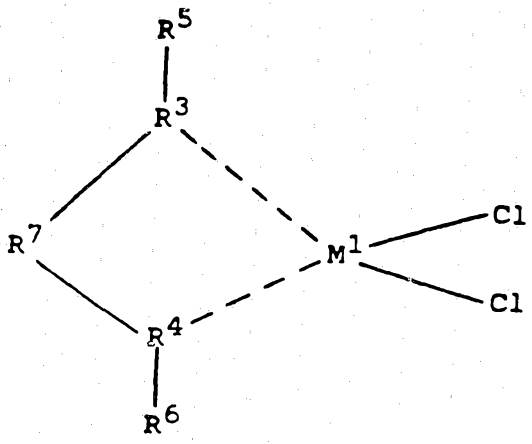
R^{11}, R^{12}, R^{13} and R^{14} are identical or different, and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, preferably C_1-C_4-alkyl group, in particular a methyl group, a C_1-C_{10}-fluoroalkyl group, preferably a CF_3 group, a C_6-C_{10}-aryl group, preferably C_6-C_8-aryl group, a C_6-C_{10}-fluoroaryl group, preferably a pentafluorophenyl group, a C_1-C_{10}-alkoxy group, preferably C_1-C_4-alkoxy group, in particular a methoxy group, a C_2-C_{10}-alkenyl group,

preferably C_2-C_4-alkenyl group, a C_7-C_{40}-arylalkyl group, preferably C_7-C_{10}-arylalkyl group, a C_8-C_{40}-arylalkenyl group, preferably C_8-C_{12}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, preferably C_7-C_{12}-alkylaryl group.

R^7 together with the radicals R^3 and R^4 forms a ring, R^7 being linked with the radicals R^3 and R^4 in the 1-position of the radicals R^3 and R^4.

The metallocenes of structure type A can be prepared according to the following reaction scheme:


H_3R^3
Butyl-Li
H_2R^3Li
R^5X
R^5
H_2R^3
Ethyl-MgX
R^5
HR^3MgX
H_3R^4
Butyl-Li
H_2R^4Li
R^6X
R^6
H_2R^4
Ethyl-MgX
R^6
HR^4MgX
1. $X-R^7-X$
2. Tetramethylethylendiamine
R^5 R^6
$HR^3-R^7-HR^4$
Butyl-Li
R^5 R^6
$LiR^3-R^7-LiR^4$
M^1Cl_4



(I)

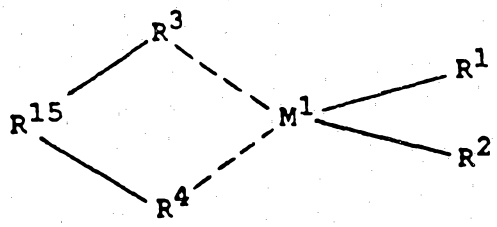
X is Cl, Br, I or O-tosyl.

Instead of the two chlorine atoms, it is also possible to introduce other R^1 and R^2 groups by known substitution reactions.

If R^3 and R^4 are indenyl radicals, they can be converted into tetrahydroindenyl radicals by hydrogenation of compound (I) by known methods.

A particularly preferred metallocene of structure type A is ethylenebis[1-(3-trimethylsilylindenyl)]zirconium dichloride.

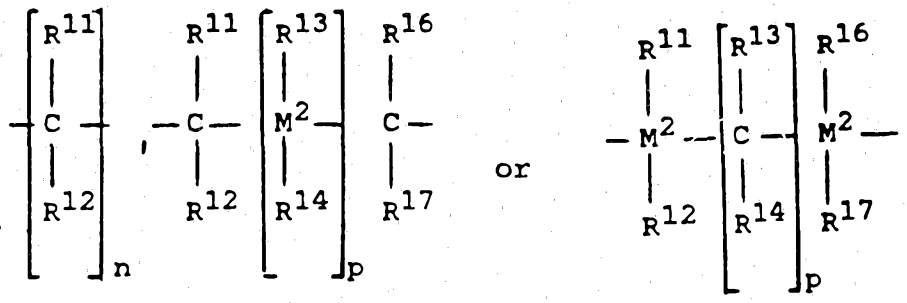
In formula II which represents structure type B



(II)

M^1, R^1, R^2, R^3 and R^4 have the abovementioned meanings.

R^{15} is

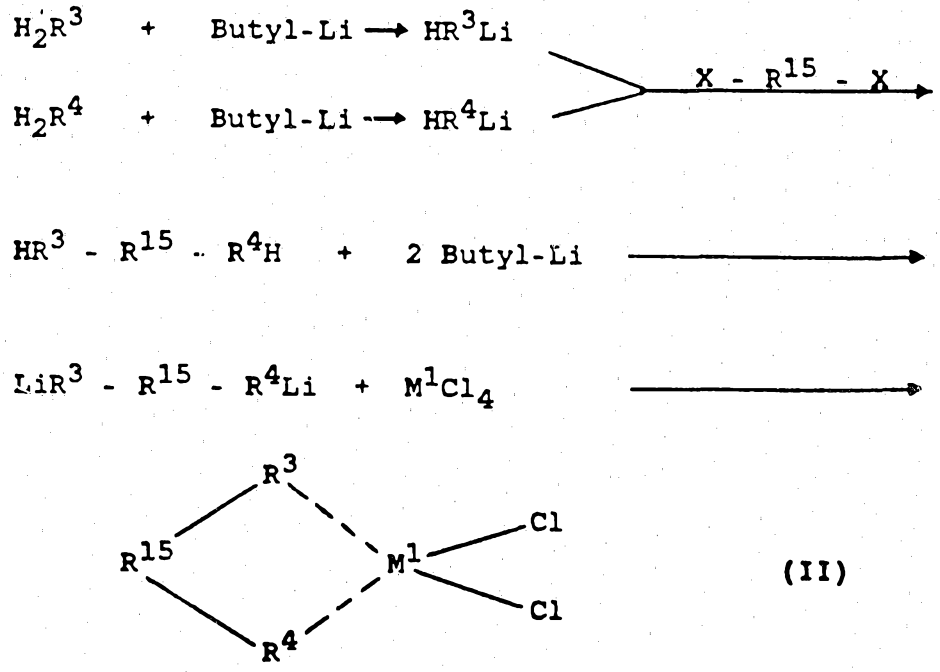


in which M^2, R^{11}, R^{12}, R^{13} and R^{14} have the abovementioned meaning and R^{16} and R^{17} have the meanings of R^{11}, R^{12}, R^{13} or R^{14}.

n is 3, 4 or 5 and p is 1, 2 or 3.

R^{15} together with the radicals R^3 and R^4 form a ring, R^{15} being linked to R^3 and R^4 in the 1-position of the radicals R^3 and R^4.

The metallocenes of structure type B can be prepared by the following reaction scheme:



X is Cl, Br, I or O-tosyl.

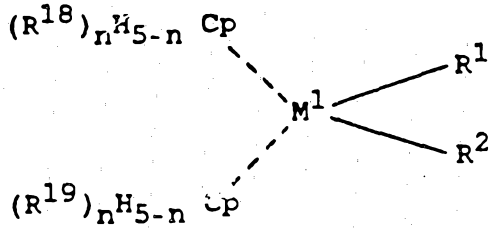
Instead of the two chlorine atoms, it is also possible to

introduce other R^1 and R^2 groups by known substitution reactions.

If R^3 and R^4 are indenyl radicals, they can be converted into tetrahydroindenyl radicals by hydrogenation of the compound (II) by known methods.

A particularly preferred metallocene of structure type B is propylenebis(1-indenyl)zirconium dichloride.

In formula III which represents structure type C,



(III),

M^1, R^1 and R^2 have the already mentioned meanings.

Cp is a cyclopentadienyl radical and
n is the number 3, 4 or 5.

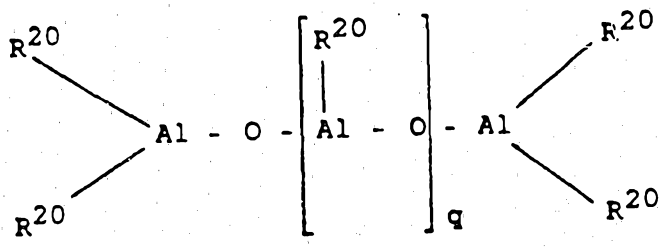
R^{18} and R^{19} are identical or different, preferably identical, radicals on the cyclopentadienyl rings and are a halogen atom, a C_1-C_{10}-alkyl group, preferably C_1-C_4-alkyl group, in particular a methyl group, a C_1-C_{10}-fluoroalkyl group, preferably a CF_3 group, a C_6-C_{10}-aryl group, preferably C_6-C_8-aryl group, a C_6-C_{10}-fluoroaryl group, preferably a pentafluorophenyl group, a C_1-C_{10}-alkoxy group, preferably C_1-C_4-alkoxy group, in particular a methoxy group, a C_2-C_{10}-alkenyl group, preferably C_2-C_4-alkenyl group, a C_7-C_{40}-arylalkyl group, preferably C_7-C_{10}-arylalkyl group, a C_8-C_{40}-arylalkenyl group, preferably C_8-C_{12}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, preferably C_7-C_{12}-alkylaryl group.

The synthesis of metallocenes of structure type C can be carried out by methods described in the literature, for

example in: J.M. Manriquez, D.R. McAlister, E. Rosenberg, A.M. Shiller, K.L. Williamson, S.I. Chan, J.E. Bercaw J. Amer. Chem. Soc. 100, 3078 (1978).

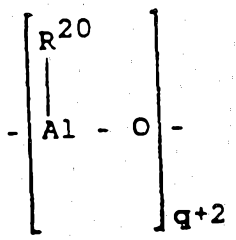
A particularly preferred metallocene of structure type C is bis(pentamethylcyclopentadienyl)zirconium dichloride.

In addition to the metallocene, the catalyst system to be used according to the invention additionally contains an alkyl aluminum compound as activator. This activator is an aluminoxane of the formula IV



(IV)

in the case of the linear type and/or of the formula V



(V)

in the case of the cyclic type. In these formula, R^{20} is a C_1-C_6-alkyl group, preferably methyl, ethyl or isobutyl, in particular methyl and q is an integer from 2 to 50, preferably 10 to 40. However, the exact structure of the aluminoxane is not secured.

The aluminoxane can be prepared by different methods.

One possibility is the careful addition of water to a dilute solution of a trialkyl aluminum by stirring the solution of trialkyl aluminum and the water each in small portions into an initially introduced very large amount of an inert solvent and waiting after each addition until

the evolution of gas has ceased.

In a different method, finely powdered copper sulfate pentahydrate is suspended in toluene, and at about -20°C trialkyl aluminum is added in a glass flask under inert gas in such an amount that 1 mol of $CuSO_4 \cdot 5H_2O$ is available for every 4 Al atoms . After slow hydrolysis with the elimination of alkane, the reaction mixture is left to stand at room temperature for 24 to 48 hours, during which cooling may be necessary to prevent the temperature from rising above 30°C. The aluminoxane dissolved in toluene is then filtered from copper sulfate, and the solution is concentrated in vacuo. It is assumed that in this preparation method the low-molecular-weight aluminoxanes undergo condensation with the elimination of trialkyl aluminum to give higher oligomers.

Aluminoxanes are further obtained by reacting trialkyl aluminum, preferably trimethyl aluminum, which is dissolved in an inert aliphatic or aromatic solvent, preferably heptane or toluene, at a temperature of -20 to 100°C with hydrated aluminum salts, preferably aluminum sulfate. In this reaction, the volume ratio between solvent and the alkyl aluminum used is 1:1 to 50:1 - preferably 5:1 - and the reaction time which can be controlled by the elimination of the alkane is 1 to 200 hours - preferably 10 to 40 hours.

Of the hydrated aluminum salts, in particular those are used which have a high content of water of crystallization. Particular preference is given to aluminum sulfate hydrate, in particular the compounds $Al_2(SO_4)_3 \cdot 16H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$ which have a particularly high content of water of crystallization of 16 and 18 mol of H_2O/mol of $Al_2(SO_4)_3$.

A further variation for the preparation of aluminoxanes consists in dissolving trialkyl aluminum, preferably trimethyl aluminum, in the suspending agent initially

introduced into the polymerization boiler, preferably in the liquid monomer, in heptane or toluene and then reacting the aluminum compound with water.

In addition to the process for the preparation of aluminoxanes described above, other methods are suitable.

It is possible to preactivate the metallocene by means of an aluminoxane of the formula IV and/or V before using it in the polymerization reaction. This considerably increases the polymerization activity.

The preactivation of the transition metal compound is carried out in solution. This is preferably done by dissolving the metallocene in a solution of the aluminoxane in an inert hydrocarbon. A suitable inert hydrocarbon is an aliphatic or aromatic hydrocarbon. Preferably, toluene is used. The concentration of the aluminoxane in the solution is in the range from about 1% by weight up to the saturation limit, preferably 5 to 30% by weight, each relative to the entire solution. The metallocene can be used in the same concentration, but preferably it is used in an amount of 10^{-4} to 1 mol per mol of aluminoxane. The preactivation time is 5 minutes to 60 hours, preferably 5 to 60 minutes. The temperature in this process is from -78°C to 100°C, preferably 0 to 70°C.

The catalyst system to be used according to the invention is used for the copolymerization of ethylene with propylene and, if desired, a further 1-olefin which had 4 to 18 carbon atoms, for example 1-butene, 1-hexene, 4-methyl-1-pentene, or 1-octene.

The polymerization is carried out continuously or batchwise in liquid propylene, in one or many steps at a temperature from -60°C to 90°C, preferably 20°C to 70°C. Ethylene is added to the polymerization mixture in such an amount that a partial pressure ratio of $P_{C2}/P_{C3} > 0.6$, preferably > 0.9 (P_{C2} = partial pressure of ethylene in

the gas phase above the suspension; P_{C3} = partial pressure of propylene in the gas phase above the suspension) is established above the liquid phase. The total pressure is 0.5 to 150, preferably 14.5 to 120 bar.

The metallocene compound is preferably employed in a concentration, relative to the transition metal, of 10^{-3} to 10^{-8}, more preferably 10^{-4} to 10^{-7}, mol of transition metal per dm^3 of liquid propylene. The aluminoxane is preferably used in a concentration of 10^{-4} to 10^{-1} mol, more preferably 10^{-3} to 10^{-2} mol per dm^3 of liquid propylene. However, in principle higher concentrations are also possible.

The molecular weight of the polymer can be regulated in a known manner; preferably, hydrogen is used for this.

The process according to the invention increases the versality of the use of plants in which polymerization can be carried out in liquid propylene. Depending on the propylene content in the polymer and the density of the product affected thereby, the predominantly crystalline ethylene/propylene copolymers are obtained as "HDPE" ("High Density Polyethylene"), "MDPE" ("Medium Density Polyethylene") and "LLDPE" ("Linear Low Density Polyethylene"). By using molecular weight regulators, low-molecular weight ethylene/propylene copolymers, which can be designated as polyethylene waxes ("HDPE", "MDPE" and "LLDPE" waxes), can also be obtained in the process according to the invention. Even the preparation of ethylene/propylene/1-olefin terpolymers is possible by means of the process according to the invention.

The examples which follow are intended to illustrate the invention.

VN is the viscosity number in cm^3/g,
M_w is the average molecular weight in g/mol,
M_w/M_n is the molecular weight distribution determined by gel permeation chromatography (GPC)

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The pressures in the examples are given in bar above atmospheric pressure.

The propylene contents of the polymers were determined by ^{13}C-NMR spectroscopy and the crystallinity as relative crystallinity by IR spectroscopy.

The melt index MFI 190/2.16 was determined by DIN 53,735 and the density by DIN 53,479, process A.

The melting points were determined by DSC measurement.

Example 1

In this Example, ethylenebis[1-(3-trimethylsilylindenyl)] zirconium dichloride was used as the metallocene. This compound can be present as a chiral isomer (in the form of a racemic mixture of two optically active enantiomers) or as an achiral meso isomer. The compound used had a racemate to meso form ratio of 3.5:1.

A dry 70 dm^3 boiler was first flushed with nitrogen and then with ethylene, and 40 dm^3 of liquid propylene were then added. 80 cm^3 of a methylaluminoxane solution in toluene (which corresponds to 114 mmol of Al and an average oligomerization degree n of 17) were then added, and the mixture was stirred at 30°C for 15 minutes. The temperature was then raised to 55°C, which led to a pressure of 21.9 bar in the gas phase above the liquid. The addition of ethylene resulted in a total pressure of 45 bar. The partial pressure ratio P_{C2}/P_{C3} was thus 1.05. Parallel to this, 8.0 mg of metallocene were dissolved in 30 cm^3 of a methylaluminoxane solution in toluene (43 mmol of Al) and preactivated by letting the mixture stand for 15 minutes. The solution was then poured into the boiler, thus initiating the polymerization. The mixture was polymerized at 55°C for 90 minutes, while maintaining the total pressure in the boiler constant at 45 bar by continuously feeding in ethylene.

The polymerization was then stopped by the addition of isopropanol. This gave 6.2 kg of polymer. The resulting product was in the form of a coarse-ground powder which had a bulk density of 0.35 g/cm^3 and the following particle size distribution determined by sifting:

Particle size (μm)	Content (% by weight)	Sum (% by weight)
< 100	2.1	2.1
100 - 200	7.5	9.6
200 - 300	17.5	27.1
300 - 400	14.8	41.9
400 - 500	11.4	53.3
500 - 630	13.2	66.5
630 - 800	12.4	78.9
800 - 1000	11.4	90.3
> 1000	9.7	100.0

Furthermore, the following properties of the ethylene/propylene copolymer were determined:

VN = 166 cm^3/g
M_w = 79,000 g/mol, M_w/M_n = 35.8
MFI 190/2.16 = 8.03 g/10 min
Propylene content: 7.7 mol%
Crystallinity: 53%
Density: 0.921 g/cm^3
Melting point: 109.1°C

Example 2

In this Example, the same metallocene as in Example 1 was employed.

A dry 70 dm^3 boiler was first flushed with nitrogen and then with ethylene, and 40 dm^3 of liquid propylene were then added. 60 cm^3 of a methylaluminoxane solution in toluene (which corresponds to 86 mmol of Al and an

average oligomerization degree n of 17) were then added, and the mixture was stirred at 30°C for 15 minutes. The temperature was then raised to 51°C, which led to a pressure of 20.1 bar in the gas phase above the liquid. The addition of hydrogen resulted in a total pressure of 22.1 bar, and then in a total pressure of 50 bar by adding ethylene. The partial pressure ratio P_{C2}/P_{C3} was thus 1.39.

Parallel to this, 5.3 mg of metallocene were dissolved in 20 cm^3 of a methylaluminoxane solution in toluene (28 mmol of Al) and preactivated by letting the mixture stand for 15 minutes. The solution was then poured into the boiler, thus initiating the polymerization. The mixture was polymerized at 51°C for 60 minutes, while maintaining the total pressure in the boiler constant at 50 bar by continuously feeding in ethylene. The polymerization was then stopped by the addition of isopropanol. This gave 2.1 kg of polymer. The resulting product was in the form of a coarse-ground powder consisting of spherical particles which had a bulk density of 0.47 g/cm^3 and the following particle size distribution determined by sifting:

Particle size (µm)	Content (% by weight)	Sum (% by weight)
< 100	0.8	0.8
100 - 200	3.1	3.9
200 - 300	7.7	11.6
300 - 400	5.5	17.1
400 - 500	9.5	26.6
500 - 630	16.4	43.0
630 - 800	20.5	63.5
800 - 1000	22.0	85.5
> 1000	14.5	100.0

Furthermore, the following properties of the copolymer wax obtained above were determined:

VN = 63 cm^3/g
M_w = 10,090 g/mol, M_w/M_n = 20.1
Propylene content: 7.0 mol%
Crystallinity: 52%
Density: 0.903 g/cm^3

The product did not have a uniform melting point; the DSC curve showed peaks at 88°C, 101°C and 114°C.

Example 3

In this Example, the same metallocene as in Example 1 was employed.

A dry 70 dm^3 boiler was first flushed with nitrogen and then with ethylene, and 40 dm^3 of liquid propylene were then added. 50 cm^3 of a methylaluminoxane solution in toluene (which corresponds to 72 mmol of Al and an average oligomerization degree n of 17) were then added, and the mixture was stirred at 30°C for 15 minutes. The temperature was then raised to 65°C, which led to a pressure of 26.8 bar in the gas phase above the liquid. The addition of hydrogen resulted in a total pressure of 28.3 bar, and then in a total pressure of 46 bar by adding ethylene. The partial pressure ratio P_{C2}/P_{C3} was thus 0.66.

Parallel to this, 10.3 mg of metallocene were dissolved in 20 cm^3 of a methylaluminoxane solution in toluene (29 mmol of Al) and preactivated by letting the mixture stand for 15 minutes. The solution was then poured into the boiler, thus initiating the polymerization. The mixture was polymerized at 65°C for 60 minutes, while maintaining the total pressure in the boiler constant at 46 bar by continuously feeding in ethylene. The polymerization was then stopped by the addition of isopropanol. This gave 1.9 kg of ethylene/propylene copolymer wax. The resulting product was in the form of a coarse-ground slightly tacky powder which had a bulk density of 0.45 g/cm^3.

Furthermore, the following properties of the polymer were determined:

VN = 30 cm^3/g
Propylene content: 12.2 mol%
Crystallinity: 51%

Example 4

In this Example, propylenebis(1-indenyl)zirconium dichloride was employed as the metallocene.

A dry 15 dm^3 boiler was first flushed with nitrogen, then with ethylene, and 10 dm^3 of liquid propylene were added. 30 cm^3 of a methylaluminoxane solution in toluene (which corresponds to 46 mmol of Al and an average oligomerization degree n of 22) were added, and the mixture was stirred at 30°C for 15 minutes. This resulted in a pressure in the gas phase above the liquid of 12.2 bar. A total pressure of 33 bar was then established by the addition of ethylene and the partial pressure ratio P_{C2}/P_{C3} was thus 1.7.

Parallel to this, 1.6 mg of metallocene was dissolved in 20 cm^3 of a methylaluminoxane solution in toluene (31 mmol of Al) and preactivated by letting the mixture stand for 15 minutes. The solution was poured into the boiler, thus initiating the polymerization. The mixture was polymerized for 70 minutes at 30°C, while maintaining the total pressure in the boiler constant at 33 bar by continuously feeding in ethylene. The polymerization was then stopped by releasing the pressure from the reactor. This gave 0.8 kg of polymer as a flocculent powder.

The following properties of the polymer were determined:

Propylene content: 8.5 mol%
Crystallinity: 54%
VN = 380 cm^3/g

M_w = 277,000 g/mol
M_w/M_n = 10.2
MFI - 190/5 = 16.5 g/10 min.

Example 5

In this Example, 1,1,4,4-tetramethyl-1,4-disilabutylene-bis(1'-indenyl)zirconium dichloride was employed as the metallocene. 95% of the compound was present in the form of the racemic mixture of the chiral enantiomers.

The procedure analogous to Example 4 was repeated except that 2.2 mg of metallocene were employed.
This gave 0.07 kg of polymer as a flocculent powder.

The following properties of the polymer were determined:

VN = 310 cm^3/g
Propylene content: 10.3 mol%
Crystallinity: 52%

Example 6

In this Example, 2,2-dimethyl-2-silapropylenebis(1'-indenyl)hafnium dichloride was employed as the metallocene.

The procedure analogous to Example 4 was repeated, except that 5.1 mg of metallocene were employed.
This gave 0.10 kg of polymer as a flocculent powder.

The following properties of the polymer were determined:

VN = 350 cm^3/g
Propylene content: 9.8 mol%
Crystallinity: 54%

Example 7

In this Example, bis(pentamethylcyclopentadienyl)zirconium dichloride was employed as the metallocene.

A dry 70 dm^3 boiler was first flushed with nitrogen and then with ethylene, and 40 dm^3 of liquid propylene were then added. 60 cm^3 of a methylaluminoxane solution in toluene (which corresponds to 89 mmol of Al and an average oligomerization degree n of 19) were then added, and the mixture was stirred at 30°C for 15 minutes. The temperature was then raised to 45°C, which led to a pressure of 17.6 bar in the gas phase above the liquid. The addition of ethylene resulted in a total pressure of 50 bar. The partial pressure ratio P_{C2}/P_{C3} was thus 1.84.

Parallel to this, 5.0 mg of metallocene were dissolved in 60 cm^3 of a methylaluminoxane solution in toluene (89 mmol of Al) and preactivated by letting the mixture stand for 15 minutes. The solution was then poured into the boiler, thus initiating the polymerization. The mixture was polymerized at 45°C for 80 minutes, while maintaining the total pressure in the boiler constant at 40 bar by continuously feeding in ethylene. The polymerization was then stopped by the addition of isopropanol. This gave 1.9 kg of ethylene/propylene copolymer. The resulting product was in the form of powder which had a bulk density of 0.2 g/cm^3.

Furthermore, the following properties of the polymer were determined:

VN = 142 cm^3/g

M_w = 200,000 g/mol, M_w/M_n = 6.5

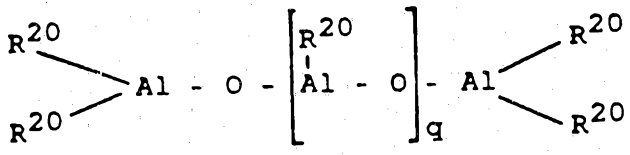
Propylene content: 3.5 mol%

Crystallinity: 57%

Density: 0.940 g/cm^3

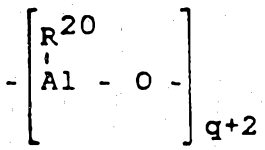
~~Patent claims:~~
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the preparation of an ethylene/propylene copolymer containing less than 15 mol% of propylene units, relative to the entire polymer, by polymerization of ethylene and propylene in ~~a suspending agent~~ liquid propylene, at a temperature of -60 to 90°C, at a pressure of 0.5 to 150 bar, in the presence of a catalyst which consists of a metallocene and an aluminoxane of the formula IV



(IV)

in the case of the linear type and/or of the formula V

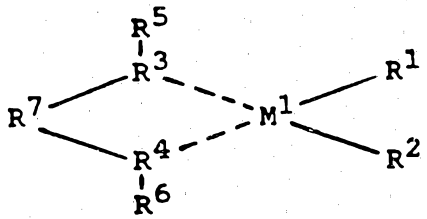


(V)

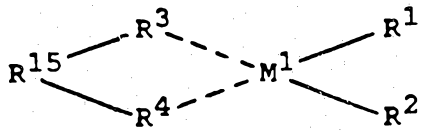
in the case of the cyclic type, in which in formulae IV and V R^{20} is a C_1-C_6-alkyl group and q is an integer from 2 to 50,
which comprises carrying out the polymerization in liquid propylene as suspending agent, in which the ratio of the partial pressure P_{C2} of ethylene in the gas phase to the partial pressure P_{C3} of propylene in the gas phase

$$\frac{P_{C2}}{P_{C3}} \text{ is greater than } 0.6$$

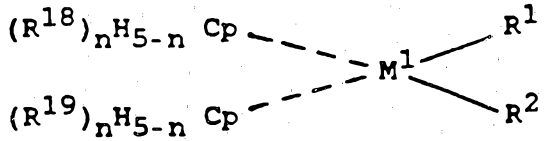
and the metallocene is a compound of the formulae I, II or III



(I),



(II),



(III),

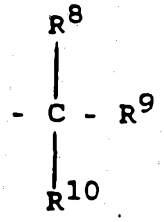
in which in formulae I, II and III

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

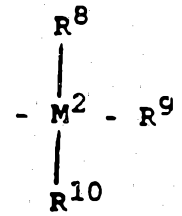
R^1 and R^2 are identical or different and are a hydrogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group, a C_8-C_{40}-arylalkenyl group or a halogen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

R^3 and R^4 are identical or different and are an indenyl or tetrahydroindenyl radical in which the five-membered rings of the radicals R^3 and R^4 form a sandwich structure with the central atom M^1,

R^5 and R^6 are identical or different, and are substituents in the 3-position of R^3 and R^4 or are radicals of the formulae

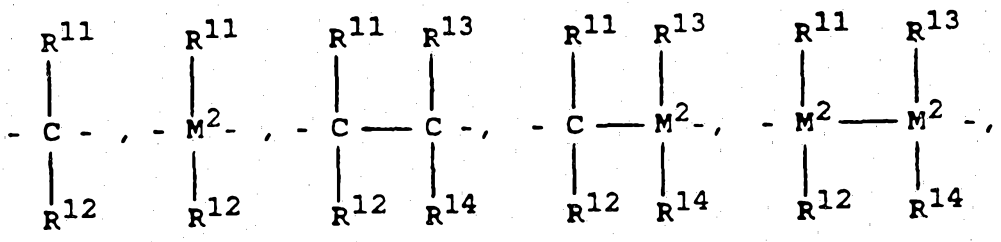


or,



in which M^2 is silicon, germanium or tin, R^8, R^9 and R^{10} are identical or different and are 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, a C_7-C_{40}-alkylaryl group, a trihalosilyl group, a C_1-C_{10}-trialkylsilyl group or a C_1-C_{10}-trialkoxysilyl group,

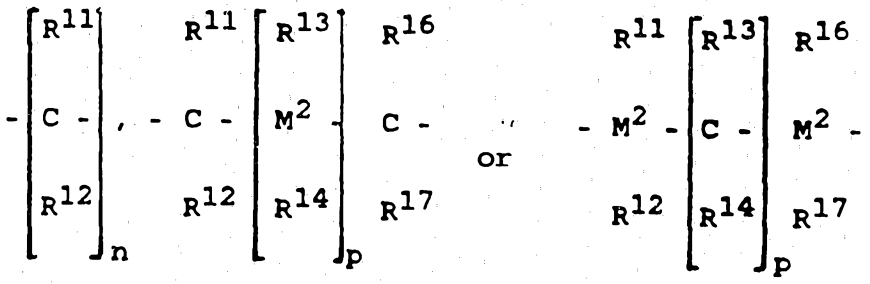
R^7 is



$=BR^{11}$, $=AlR^{11}$, -Ge-, -Sn-, -O-, -S-, =S=O, $=SO_2$, $=NR^{11}$, =CO, $=PR^{11}$ or $=P(O)R^{11}$,
where R^{11}, R^{12}, R^{13} and R^{14} 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

and R^7 together with the radicals R^3 and R^4 forms a ring, R^7 being linked to the radicals R^3 and R^4 in the 1-position of the radicals R^3 and R^4,

R^{15} is



in which R^{16} and R^{17} 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,

n is the number 3, 4 or 5 and p is 1, 2 or 3,
R^{15} together with the radicals R^3 and R^4 forms a ring, R^{15} being linked to the radicals R^3 and R^4 in the 1-position of the radicals R^3 and R^4,

Cp is a cyclopentadienyl radical and

R^{18} and R^{19} are identical or different substituents on the cyclopentadienyl radicals and are 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.

2. The process as claimed in claim 1, wherein the polymerization is carried out in the presence of a 1-olefin having 4 to 18 carbon atoms.

3. The process as claimed in claim 1, wherein the metallocene is ethylenebis[1-(3-trimethylsilylindenyl)]-zirconium dichloride.

4. The process as claimed in claim 1, wherein the metallocene is propylenebis(1-indenyl)zirconium dichloride.

5. The process as claimed in claim 1, wherein the metallocene is bis(pentamethylcyclopentadienyl)zirconium dichloride.

DATED this 19th day of October 1989.
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