

5

(CONVENTION. By one or more persons and/or a Company.

622980

Form 4.

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).

~~xx~~(1) HOECHST AKTIENGESELLSCHAFT
We of 50 Bruningstrasse, D-6230 Frankfurt/Main 80, Federal Republic of Germany

(2) Here insert Title of Invention.

hereby apply for the grant of a Patent for an invention entitled: (2)
PROCESS FOR THE PREPARATION OF A RANDOM 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)
P39 04 469.6

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

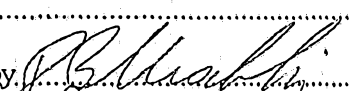
for a patent or similar protection made in (4) Federal Republic of Germany
on 15th February 1989

~~My~~ Our address for service is WATERMARK PATENT & TRADEMARK ATTORNEYS
290 Burwood Road, Hawthorn, Victoria, Australia.

FO14462

DATED this 14/02/90 13th day of February 1990

(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 Attorney

To: THE COMMISSIONER OF PATENTS.

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:

Process for the preparation of a random propylene copolymer

We, Ulrich Tergau, Am Dornbusch 3, D-6239 Eppstein/Taunus
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 39 04 469.6 on February 15, 1989
by HOECHST AKTIENGESELLSCHAFT
 3. a) Volker Dolle, Hattersheimer Straße 15, D-6233 Kelkheim (Taunus)
b) Martin Antberg, Sachsenring 10, D-6238 Hofheim am Taunus
c) Jürgen Rohrmann, Die Ritterwiesen 10, D-6237 Liederbach
d) Andreas Winter, Gundelhardtstraße 2, D-6233 Kelkheim (Taunus)
a) - d) 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
Volker Dolle, Martin Antberg, Jürgen Rohrmann, 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 January 16, 1990

To the Commissioner of Patents

HOECHST AKTIENGESELLSCHAFT

PAT 510

Prokurist

Authorized Signatory

ppa. Tergau

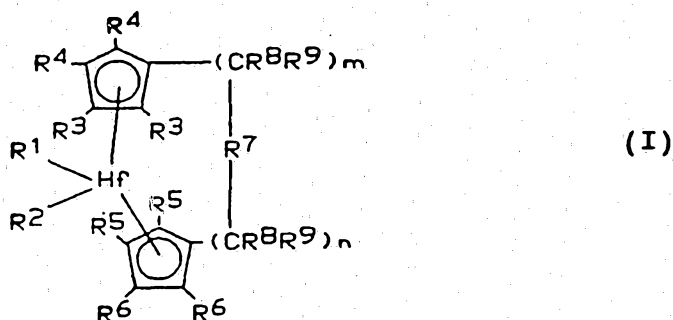
i.V. Lapice

(12) PATENT ABRIDGMENT (11) Document No. AU-B-49398/90
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 622980

- (54) Title
PROCESS FOR THE PREPARATION OF A RANDOM PROPYLENE COPOLYMER
- International Patent Classification(s)
(51)⁴ **C08F 210/06 C08F 004/76**
- (21) Application No. : **49398/90** (22) Application Date : **14.02.90**
- (30) Priority Data
- (31) Number (32) Date (33) Country
3904469 15.02.89 DE FEDERAL REPUBLIC OF GERMANY
- (43) Publication Date : **23.08.90**
- (44) Publication Date of Accepted Application : **30.04.92**
- (71) Applicant(s)
HOECHST AKTIENGESELLSCHAFT
- (72) Inventor(s)
VOLKER DOLLE; MARTIN ANTBERG; JURGEN ROHRMANN; ANDREAS WINTER
- (74) Attorney or Agent
WATERMARK PATENT & TRADEMARK ATTORNEYS , Locked Bag 5, HAWTHORN VIC 3122
- (56) Prior Art Documents
EP 284707
AU 76186/91 C08F 4/642
AU 68300/90 C08F 4/642 4/68 297/08
- (57) Claim

1. A process for the preparation of a propylene copolymer composed of 99.9 to 80.0 mol %, relative to the total polymer, of propylene units and 0.1 to 20.0 mol %, relative to the total polymer, of units which are derived from ethylene or from an olefin with at least 4 carbon atoms of the formula $R^{15}-CH=CH-R^{16}$, where R^{15} and R^{16} are identical or different and denote a hydrogen atom or an alkyl radical having 1 to 28 carbon atoms or R^{15} and R^{16} with the carbon atoms bonding them form a ring having 4 to 28 carbon atoms, by polymerizing 50 to 99.5 % by weight, relative to the total amount of monomers, of propylene and 0.5 to 50 % by weight, relative to the total amount of monomers, of at least one representative of the group consisting of ethylene and olefins having at least 4 carbon atoms of the formula $R^{15}-CH=CH-R^{16}$, where R^{15} and R^{16} have the meaning given above, at a temperature of 30°C to 150°C at a pressure of 0.5 to 100 bar in solution, in suspension or in the gas phase in the presence of a catalyst composed of a metallocene and an alumin-

oxane, wherein the metallocene is a compound of the formula I



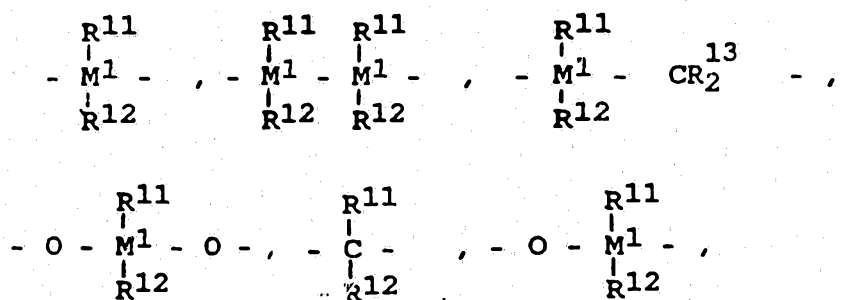
in which

R^1 and R^2 are identical or different and denote 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 , R^4 , R^5 and R^6 are identical or different and denote a hydrogen atom, a halogen atom, a C_1 - C_{10} -alkyl group, a radical $-NR_2^{10}$ -, $-SR^{10}$ -, $-OSiR_3^{10}$ -, $-SiR_3^{10}$ -, or $-PR_2^{10}$ - in which R^{10} is a C_1 - C_{10} -alkyl group, a C_6 - C_{10} -aryl group or if the radical contains Si or P may also be a halogen atom,

or each pair of adjacent radicals R^3 , R^4 , R^5 or R^6 forms a ring with the carbon atoms linking them,

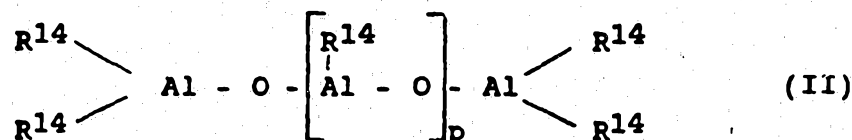
R^7 is



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

where

R^{11} , R^{12} and R^{13} are identical or different and denote a hydrogen atom, a halogen atom, a C_1 - C_{30} -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} -alkyl-aryl group or R^{11} and R^{12} or R^{11} and R^{13} in each case form a ring with the atoms bonding them, M^1 is silicon, germanium or tin, 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, m plus n being zero, 1 or 2, and the aluminoxane is one of the formula (II)



in the instance of the linear type and/or of the formula (III)



in the instance of the cyclic type, R^{14} in the formulae (II) and (III) denoting a C_1 - C_6 -alkyl group and p denoting an integer from 2 to 50.

4. A random propylene copolymer composed of 99.9 to 80.0 mol %, relative to the total polymer, of propylene units and 0.1 to 20.0 mol %, relative to the total polymer, of units which are derived from ethylene or from an olefin with at least 4 carbon atoms of the formula R^{15} -CH=CH- R^{16} where R^{15} and R^{16}

(11) AU-B-49398/90
(10) 622930

-4-

are identical or different and denote a hydrogen atom or an alkyl radical having 1 to 28 carbon atoms or R^{15} and R^{16} form a ring of 4 to 28 carbon atoms with the atoms bonding them, the said copolymer having an average molecular weight of more than 100000 g/mole, a polydispersity of 2.5 to 5.5 and a sequence length of below 1.25.

622980

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(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, D6230 Frankfurt/Main 80, Federal Republic of Germany

Actual Inventor : VOLKER DOLLE, MARTIN ANTBERG, JURGEN ROHRMANN and ANDREAS WINTER

Address for Service : WATERMARK PATENT & TRADEMARK ATTORNEYS.
LOCKED BAG NO. 5, HAWTHORN, VICTORIA 3122, AUSTRALIA

Complete Specification for the invention entitled:

PROCESS FOR THE PREPARATION OF A RANDOM PROPYLENE COPOLYMER

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

Description

Process for the preparation of a random propylene copolymer

5 The polymerization of olefins, depending on the process used, gives copolymers with different properties and different proportions of comonomers:

- 10 a) random copolymers with a low proportion of comonomers,
b) polymer blends containing a larger proportion of incorporated comonomers than the random copolymers and
c) copolymer rubbers containing the comonomers incorporated in similar proportions.

15 As a rule, random copolymers differ from the corresponding homopolymers in having a lower crystallinity and a lower hardness. It is desirable for the random copolymers to have as random a chain structure as possible. The prior art olefin copolymers which are prepared with the aid of heterogeneous catalysts can only fulfil this requirement to a very limited extent.

20 Random terpolymers of $C_2/C_3/C_n$ with $n > 3$ have been described and were obtained using heterogeneous catalysts (cf. EP 263,718). The proportion of C_3 is 97 to 86 mol %, the proportion of C_2 is 0.5 to 6 % and the proportion of C_n ($n > 3$) is 2 to 13 mol %. The material has good heat
25 sealing properties but is obtained in a two step process with a suspension polymerization step and a gas phase polymerization step. In order to obtain the desired anti-blocking properties, a terpolymer with a high proportion of the third monomer has to be prepared. However bipoly-
30 mers are however required since these are easier to manipulate and have a chemically homogeneous chain structure.

Furthermore, random C_2/C_3 copolymers are known, prepared by suspension polymerization (cf. EP 74,194). In order to

5 obtain the desired properties, the polymers obtained must be broken down. Moreover, the proportion of ethylene is greater than 6 %. This high proportion of C₂ is necessary in order to reduce the chemical inhomogeneity of a heterogeneous catalyst system, this inhomogeneity tending to produce a relatively high proportion of crystallizable sequences in the polymer.

10 Finally, an ethylene/propylene copolymer with a high proportion of ethylene and a process for its preparation has been described (cf. JP 62/121,707). The process is carried out using ethylenebisindenylzirconium dichloride at a temperature of less than -10°C and is consequently unsuitable for industrial production. Apart from that, the activity of the catalyst is very low.

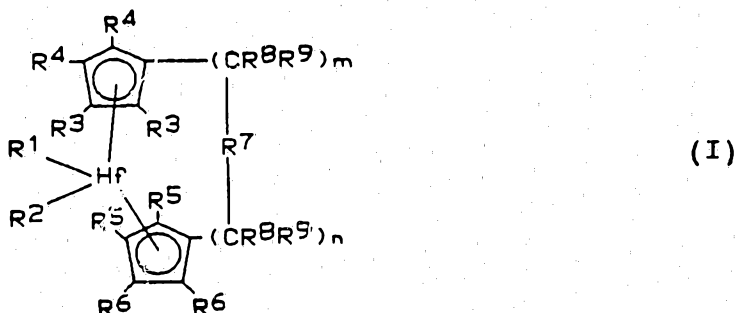
15 The object was therefore to provide a process for the preparation of a propylene copolymer, which can be carried out within an industrially relevant temperature range with adequate catalyst activity and provides a copolymer which is suitable for thermoforming and blow-molding.

20 It was found that this object can be achieved by copolymerization of propylene with other olefins in the presence of certain metallocene catalysts.

25 The invention accordingly provides a process for the preparation of a propylene copolymer composed of 99.9 to 80.0 mol %, relative to the total polymer, of propylene units and 0.1 to 20.0 mol %, relative to the total polymer, of units which are derived from ethylene or from an olefin with at least 4 carbon atoms of the formula $R^{15}-CH=CH-R^{16}$, where R^{15} and R^{16} are identical or different and denote a hydrogen atom or an alkyl radical having 1 to 28 carbon atoms or R^{15} and R^{16} with the carbon atoms bonding them form a ring having 4 to 28 carbon atoms, by polymerizing 50 to 99.5 % by weight, relative to the total amount of monomers, of propylene and 0.5 to 50 % by

weight, relative to the total amount of monomers, of at least one representative of the group consisting of ethylene and olefins having at least 4 carbon atoms of the formula $R^{15}-CH=CH-R^{16}$, where R^{15} and R^{16} have the meaning given above, at a temperature of 30°C to 150°C at a pressure of 0.5 to 100 bar in solution, in suspension or in the gas phase in the presence of a catalyst composed of a metallocene and an aluminoxane, wherein the metallocene is a compound of the formula I

10



in which

R^1 and R^2 are identical or different and denote 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,

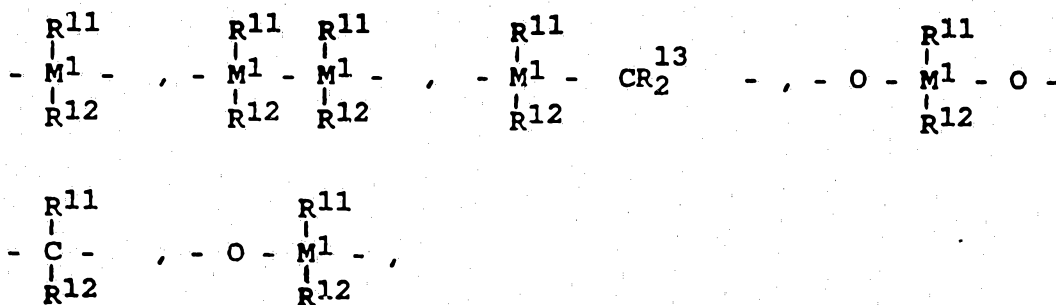
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R^3 , R^4 , R^5 and R^6 are identical or different and denote a hydrogen atom, a halogen atom, a C_1 - C_{10} -alkyl group, a radical $-NR_2^{10}-$, $-SR^{10}-$, $-OSiR_3^{10}-$, $-SiR_3^{10}-$ or $-PR_2^{10}-$ in which R^{10} is a C_1 - C_{10} -alkyl group, a C_6 - C_{10} -aryl group or if the radical contains Si or P may also be a halogen atom, or each pair of adjacent radicals R^3 , R^4 , R^5 or R^6 forms a ring with the carbon atoms linking them,

20

R^7 is

25



=BR¹¹, =AlR¹¹, -Ge-, -Sn-, -O-, -S-, =SO, =SO₂, =NR¹¹, =CO,
=PR¹¹ or =P(O)R¹¹

where

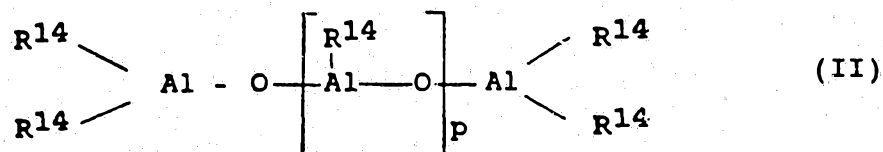
R¹¹, R¹² and R¹³ are identical or different and denote a
hydrogen atom, a halogen atom, a C₁-C₃₀-alkyl group,
a C₁-C₁₀-fluoroalkyl group, a C₆-C₁₀-aryl group, a
C₆-C₁₀-fluoroaryl group, a C₁-C₁₀-alkoxy group, a
C₂-C₁₀-alkenyl group, a C₇-C₄₀-arylalkyl group, a C₈-
C₄₀-arylalkenyl group, a C₇-C₄₀-alkylaryl group or R¹¹
and R¹² or R¹¹ and R¹³ in each case form a ring with
the atoms bonding them,

M¹ is silicon, germanium or tin,

R⁸ and R⁹ are identical or different and have the meaning
given for R¹¹,

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

and the aluminoxane is one of the formula (II)



in the instance of the linear type and/or of the formula
(III)

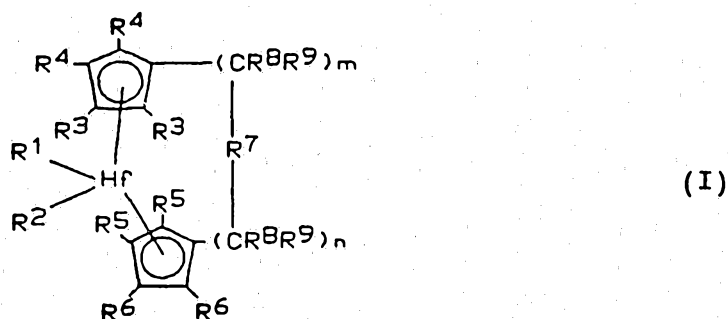


in the instance of the cyclic type, R¹⁴ in the formulae
(II) and (III) denoting a C₁-C₆-alkyl group and p denoting
an integer from 2 to 50.

The invention furthermore relates to the copolymer
prepared by the above process and to its use for the
preparation of thermoforming sheets and for the blow-

molding of hollow articles.

The catalyst which is to be used for the process according to the invention is composed of an aluminoxane and a metallocene of the formula I.



10

R^1 and R^2 are identical or different and denote 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.

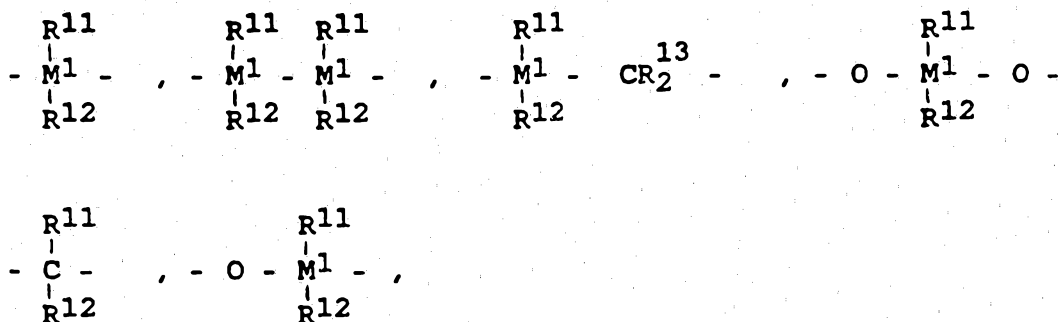
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R^3 , R^4 , R^5 and R^6 are identical or different and denote a hydrogen atom, a halogen atom, preferably a fluorine, chlorine or bromine atom, a C_1-C_{10} -, preferably C_1-C_3 -alkyl group, a radical $-NR_2^{10}$ -, $-SR^{10}$ -, $-OSiR_3^{10}$ -, $-SiR_3^{10}$ - or $-PR_2^{10}$ -, where R^{10} is a C_1-C_{10} -, preferably C_1-C_3 -alkyl group or C_6-C_{10} -, preferably C_6-C_8 -aryl group, or in the case of radicals containing Si or P may also be a halogen atom, preferably a chlorine atom, or each adjacent pair of radicals R^3 , R^4 , R^5 or R^6 forms a ring with the carbon atoms bonding them. Particular preference is given to indenyl, fluorenyl and cyclopentadienyl ligands.

25

R⁷ is



=BR¹¹, =AlR¹¹, -Ge-, -Sn-, -O-, -S-, =SO, =SO₂, =NR¹¹, =CO, =PR¹¹ or =P(O)R¹¹, where R¹¹, R¹² and R¹³ are identical or different and denote a hydrogen atom, a halogen atom, a C₁-C₃₀, preferably C₁-C₄-alkyl group, in particular a methyl group, a C₁-C₁₀-fluoroalkyl group, preferably a CF₃ group, a C₆-C₁₀-fluoroaryl group, preferably a pentafluorophenyl group, a C₆-C₁₉-, preferably C₆-C₈-aryl group, a C₁-C₁₀-, preferably C₁-C₄-alkoxy group, in particular a methoxy group, a C₂-C₁₀-, preferably C₂-C₄-alkenyl group, a C₇-C₄₀-, preferably C₇-C₁₀-arylalkyl group, a C₈-C₄₀-, preferably C₈-C₁₂-arylalkenyl group or a C₇-C₄₀-, preferably C₇-C₁₂-alkylaryl group, or R¹¹ and R¹² or R¹¹ and R¹³ in each case together form a ring with the atoms bonding them.

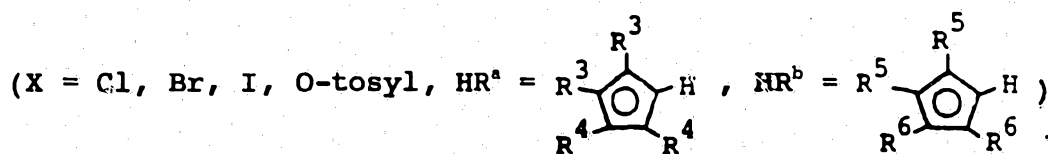
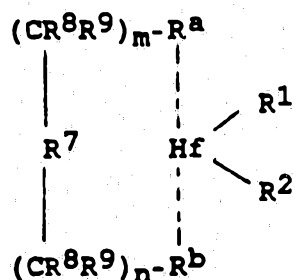
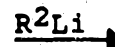
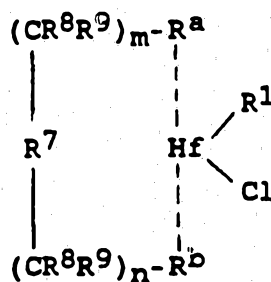
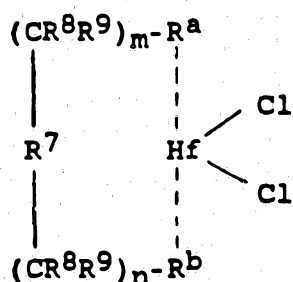
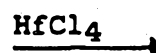
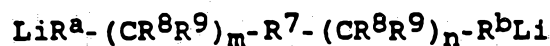
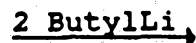
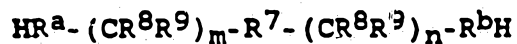
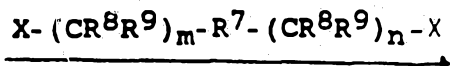
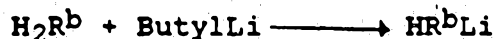
M¹ is silicon, germanium or tin, preferably silicon and germanium.

R⁷ is preferably =CR¹¹R¹², =SiR¹¹R¹², =GeR¹¹R¹², -O-, -S-, =SO, =PR¹¹ or =P(O)R¹¹.

R⁸ and R⁹ are identical or different and have the meaning given for R¹¹.

m and n are identical or different and denote zero, 1 or 2, preferably zero or 1, where m plus n is zero, 1 or 2, preferably zero or 1.

The metallocenes described above can be prepared by the following general reaction scheme:

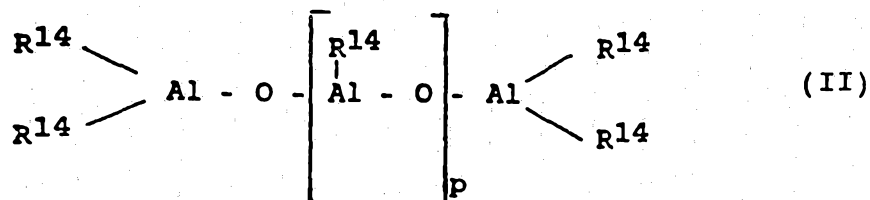


Preferred metallocenes are those of the formula I in which the radical $-(\text{CR}^8\text{R}^9)_m-\text{R}^7-(\text{CR}^8\text{R}^9)_n-$ denotes $-\text{CH}_2-\text{CH}_2-$, $-\text{Ge}(\text{CH}_3)_2-$, $-\text{Si}(\text{CH}_3)_2-$, $-\text{Si}(\text{C}_6\text{H}_5)_2-$ or $-\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)-$.

5 Particular preference is given to the use of the following metallocene compounds:

ethylenebisindenylhafnium dichloride (= 1) and
bisindenyl dimethylsilylhafnium dichloride (= 2).

The cocatalyst is an aluminoxane of the formula II



in the instance of the linear type and/or of the formula (III)



in the instance of the cyclic type. In these formulae, R^{14} denotes a C_1 - C_6 -alkyl group, preferably methyl, ethyl or isobutyl, in particular methyl, and p denotes an integer from 2 to 50, preferably 5 to 40. However, the exact structure of the aluminoxane is not known.

The aluminoxane can be prepared by various methods.

One possibility is the careful addition of water to a dilute solution of a trialkylaluminum by adding the solution of the trialkylaluminum, preferably trimethylaluminum, and the water each in small portions to a previously introduced relatively large amount of an inert solvent and at each stage waiting until gas evolution has ended.

In another process, a slurry of finely powdered copper sulfate pentahydrate is prepared in toluene and admixed in a glass flask, under inert gas at about -20°C , with an amount of trialkylaluminum such that for every 4 gram

atoms of Al there is available about 1 mole of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. After slow hydrolysis with alkane elimination the reaction mixture is left for 24 to 48 hours at room temperature, which may require cooling so that the temperature does not exceed 30°C . The aluminoxane dissolved in toluene is then separated from the copper sulfate by filtration and the solution is concentrated in vacuo. It is assumed that during this preparation the low molecular weight aluminoxanes condense with elimination of trialkylaluminum to form higher oligomers.

Furthermore, aluminoxanes are obtained if trialkylaluminum, preferably trimethylaluminum, dissolved in an inert aliphatic or aromatic solvent, preferably heptane or toluene, is brought into reaction at a temperature of -20 to 100°C with aluminum salts containing water of crystallization, preferably aluminum sulfate. In this process, the ratio by volume between the solvent and the alkylaluminum used is 1:1 to 50:1, preferably 5:1, and the reaction time, which can be monitored from the elimination of the alkane, is 1 to 200 hours, preferably 10 to 40 hours.

Particular preference is given to aluminum salts containing a high proportion of water of crystallization. Hydrated aluminum sulfate is especially preferred, particularly the compounds $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ with the particularly high proportion of water of crystallization of 16 and 18 moles of H_2O /mole of $\text{Al}_2(\text{SO}_4)_3$.

Another alternative for the preparation of aluminoxanes is to dissolve trialkylaluminum, preferably trimethylaluminum, in a suspension medium which has been previously introduced into the polymerization vessel, preferably in liquid monomer in heptane or toluene and then to react the aluminum compound with water.

In addition to the processes which have been described

above for the preparation of aluminoxanes, there are other usable processes.

5 Whatever the method of preparation, all solutions of aluminoxane contain a variable amount of unconverted trialkylaluminum which is present in the free state or as an adduct.

10 The metallocene can be preactivated before use in the polymerization reaction with an aluminoxane of the formula (II) and/or (III). This significantly increases the polymerization activity and improves the particle morphology.

15 The preactivation of the transition metal compound is carried out in solution. Here, it is preferable to dissolve the metallocene in a solution of the aluminoxane in an inert hydrocarbon. Suitable hydrocarbons are aliphatic or aromatic hydrocarbons. Toluene is preferably used.

20 The concentration of the aluminoxane in the solution is in the range of from about 1 % by weight up to the saturation limit, preferably of 5 to 30 % by weight, relative in each case to the total solution. The metallocene can be used in the same concentration, but is preferably used in an amount of 10^{-4} - 1 mole per mole of aluminoxane. The preactivation time is 5 minutes to 25 60 hours, preferably 5 to 60 minutes. Preactivation is carried out at a temperature of -78°C to 100°C , preferably 0 to 70°C .

30 The polymerization is carried out in a known manner in solution, suspension or in the gas phase, continuously or batchwise, in one or more steps at a temperature of 30 to 150°C , preferably 30 to 80°C . Propylene is copolymerized with at least one representative of the group consisting of ethylene and olefins having at least 4 carbon atoms of the formula $\text{R}^{15}\text{-CH=CH-R}^{16}$. In this formula, R^{15} and R^{16} are 35 identical or different and denote a hydrogen atom or an

alkyl radical having 1 to 28 carbon atoms. However, R^{15} and R^{16} may also form a ring with the carbon atoms bonding them which contains 4 to 28 carbon atoms. Examples of olefins of this type are 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, norbornene, norbornadiene, cyclopentene, cyclohexene and cyclooctene. The amount of propylene used is 50 to 99.5, preferably 60 to 99 % by weight, relative to the total amount of monomers, and the amount of comonomer, there being at least one, is 0.5 to 50, preferably 1 to 40 % by weight relative to the total amount of monomers.

If necessary, hydrogen is added as a molecular weight regulator. The total pressure in the polymerization system is 0.5 to 100 bar. Preference is given to polymerization in the industrially particularly relevant pressure range of 5 to 64 bar.

In polymerization, the metallocene compound is used in a concentration, relative to the transition metal, of 10^{-3} to 10^{-7} , preferably 10^{-4} to 10^{-6} moles, 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} moles, preferably 10^{-4} to 10^{-2} moles per dm^3 of solvent or per dm^3 of reactor volume. However, in principle higher concentrations can also be used.

If the polymerization is a suspension or solution polymerization, an inert solvent customary for the Ziegler process is used. The polymerization may be carried out for example in an aliphatic or cycloaliphatic hydrocarbon; examples of these are butane, pentane, hexane, heptane, isooctane, cyclohexane, and methylcyclohexane.

A naphtha fraction or hydrogenated diesel oil fraction may also be used. It is also possible to use toluene. Preference is given to polymerization in liquid monomer. If inert solvents are used, the monomers are metered in in the gaseous or liquid form. If only one monomer is

used as the suspending medium, the comonomer(s) is/are metered in in the gaseous or liquid form. Furthermore, it is possible to carry out the polymerization in a mixture of different monomers as the suspending medium; a further monomer can then be metered in liquid or gaseous form. It is advantageous when using ethylene to charge part of the ethylene initially and then to meter in the remainder during the polymerization.

The duration of the polymerization is optional, since the catalyst system which is to be used according to the invention has only a slight loss of polymerization activity over time.

A feature of the process according to the invention is that the hafnium compounds used are very heat stable so that they can also be used with high activity at temperatures up to 90°C. Moreover, the aluminoxanes used as cocatalysts can be added in lower concentrations than hitherto. Finally, it has now become possible to prepare random copolymers at industrially relevant temperatures.

which may be

The copolymer (or terpolymer) prepared according to the invention is a copolymer (terpolymer) composed of 99.9 to 80.0 mol %, relative to the total polymer, of propylene units and 0.1 to 20.0 mol %, relative to the total polymer, of units which are derived from the above comonomers in which the comonomers are incorporated in blocks with an average sequence length $n < 1.25$. The copolymers have a uniform composition i.e. no distribution of composition is observed. The polydispersity M_w/M_n is in the range of 2.5 to 5.5 and the molecular weight is in the range of about 100,000 to 360,000 g/mole. Due to these molecular properties, the copolymers have, in addition to low crystallinity, a high transparency, are not tacky and have an enormous tensile strength.

The sequence length of the comonomer blocks in the copolymers according to the invention are preferably



below 1.25, particularly below 1.2 and especially below 1.1.

The invention is described in more detail in the following examples.

5 The following symbols are used:

VZ = viscosity number in cm^3/g

M_w = weight average molecular weight

M_n = number average molecular weight

M_w/M_n = polydispersity

determined by gel permeation chromatography (data in units of g/mole)

average block length

n_{C2} = polyethylene

(the block lengths were determined by ^{13}C -NMR spectroscopy)

Example 1

20 A dry 16 dm^3 vessel was purged with nitrogen and charged with 10 dm^3 of liquid propylene. Then 35 cm^3 of methylaluminumoxane solution in toluene (= MAO, corresponding to 50.7 mmols of Al, having an average degree of oligomerization $n = 30$) were added and the batch was stirred at 30°C for 15 minutes. 12 g of ethylene were then added.

25 Meanwhile, 52.5 mg (= 0.103 mmols) of bisindenylethylene-hafnium dichloride were dissolved in 16 cm^3 of MAO (= 23.2 mmols of Al) and preactivated by being left to stand for 15 minutes.

30 The solution was then added to the vessel. The polymerization system was brought to a temperature of 60°C and the polymerization begun. During the following 120 minutes, 38 g of ethylene were added in small portions and the temperature maintained.

1.33 kg of random ethylene-propylene copolymer were obtained. The activity was thus 12.7 kg of PP/g of metallocene/h or 6.5 PP/mmoles of Hf/h.

5 The following analytical data were determined from the polymer:

VZ = 168 cm³/g, M_w = 196000 g/mole, M_n = 44550 g/mole, M_w/M_n = 4.4, n_{C_2} = 1.0, 3.5 % by weight of incorporated ethylene, T_m = 126.5°C, ΔH_m = 65 J/g.

Example 2

10 The procedure of Example 1 was followed. 23 g of ethylene were charged. During the polymerization, 68 g of ethylene were metered in.

15 The polymerization time was likewise 2 hours. 40.0 mg (0.078 mmols) of metallocene compound were used. 1.42 kg of random ethylene-propylene copolymer were obtained. The activity of the metallocene was thus 17.8 kg of PP/g of metallocene/h or 9.0 kg of PP/mmol of Hf/h.

20 VZ = 182 cm³/g, M_w = 207000 g/mole, M_n = 46000 g/mole, M_w/M_n = 4.5, n_{C_2} = 1.0, 6.4 % by weight of incorporated ethylene, T_m = 127°C, ΔH_m = 67 J/g.

Example 3

The procedure of Example 1 was followed. 1.5 g of ethylene were charged. During the polymerization, 4.5 g of ethylene were metered in.

25 The polymerization time was likewise 2 hours. 49.0 mg (0.096 mmols) of metallocene compound were used. 2.43 kg of random ethylene-propylene copolymer were obtained. The activity of the metallocene was thus 22.8 kg of PP/g of metallocene/h or 11.6 kg of PP/mmol of Hf/h.

VZ = 137 cm³/g, M_w = 151000 g/mole, M_n = 30200 g/mole, M_w/M_n = 5.0, n_{C_2} = 1.0, 2.4 % of incorporated ethylene, T_m = 126°C, ΔH_m = 69 J/g.

Example 4

- 5 The procedure of Example 1 was followed, but 13.5 g of ethylene were charged. During the polymerization, 40 g of ethylene were metered in.

The polymerization time was likewise 2 hours. 53.4 mg (0.105 mmol) of metallocene compound were used. 2.53 kg of random ethylene-propylene copolymer were obtained. The activity of the metallocene was therefore 23.7 kg of PP/g of metallocene/h or 12.0 kg of PP/mmol of Hf/h.

- 15 VZ = 154 cm³/g, M_w = 168000 g/mole, M_n = 303500 g/mole, M_w/M_n = 5.8, n_{C_2} = 1.0, 2.1 % by weight of incorporated ethylene, T_m = 126.8°C, ΔH_m = 70 J/g.

Example 5

The procedure of Example 1 was followed, but 30.5 g of ethylene were charged. During the polymerization, 92 g of ethylene were metered in.

- 20 The polymerization time was likewise 2 hours. 56.5 mg (0.111 mmol) of metallocene compound were used. 1.45 kg of random ethylene-propylene copolymer were obtained. The activity of the metallocene was thus 15.5 kg of PP/g of metallocene/h or 7.9 kg of PP/mmol of Hf/h.

- 25 VZ = 190 cm³/g, M_w = 217000 g/mole, M_n = 41750 g/mole, M_w/M_n = 5.2, n_{C_2} = 1.0, 8.4 % of incorporated ethylene, T_m = 127°C, ΔH_m = 61 J/g.

Example 6

The procedure of Example 1 was followed. 13 g of ethylene

were charged and then 120 g of 1-butene. During the polymerization, 40 g of ethylene were metered in.

The polymerization time was likewise 2 hours. 64.5 mg (0.127 mmol) of metallocene compound were used.

- 5 2.05 kg of random ethylene-propylene-butene terpolymer were obtained. The activity of the metallocene was thus 15.9 kg of PP/g of metallocene/h or 8.1 kg of PP/mmol of Hf/h.

VZ = 160 cm³/g, M_w = 179000 g/mole, M_n = 40000 g/mole, M_w/M_n = 4.5, n_{C_2} = 1.0, 2.6 % of incorporated ethylene, T_m = 126.5°C, ΔH_m = 65 J/g.

Example 7

15 The procedure of Example 1 was followed. 35 g of ethylene were charged and then 70 g of 1-butene. During the polymerization, 105 g of ethylene were metered in.

20 The polymerization time was likewise 2 hours. 64.5 mg (0.127 mmol) of metallocene compound were used. 2.70 kg of random ethylene-propylene-butene terpolymer were obtained. The activity of the metallocene was thus 21.0 kg of PP/g of metallocene/h or 10.6 kg of PP/mmol of Hf/h.

VZ = 130 cm³/g, M_w = 142000 g/mole, M_n = 26320 g/mol, M_w/M_n = 5.4, n_{C_2} = 1.0, 5.2 % of incorporated ethylene, T_m = 126°C, ΔH_m = 67 J/g.

25 Example 8

The procedure of Example 1 was followed, but 50°C was selected as the polymerization temperature. 30 g of ethylene were charged. During the polymerization, 95 g of ethylene were metered in.

5 The polymerization time was likewise 2 hours. 55.7 mg (0.110 mmol) of metallocene compound were used. 2.15 kg of random ethylene/propylene copolymer were obtained. The activity of the metallocene was thus 19.3 kg of PP/g of metallocene/h or 9.8 kg of PP/mmol of Hf/h.

VZ = 134 cm³/g, M_w = 115000 g/mole, M_n = 20900 g/mole, M_w/M_n = 5.5, n_{C_2} = 1.0, 5.7 % of incorporated ethylene, T_m = 127°C, ΔH_m = 69 J/g.

Example 9

10 The procedure of Example 1 was followed, but 70°C was selected as the polymerization temperature. 11 g of ethylene were charged. During the polymerization, 35 g of ethylene were metered in.

15 The polymerization time was likewise 2 hours. 45.5 mg (0.089 mmol) of metallocene compound were used. 1.74 kg of random ethylene/propylene copolymer were obtained. The activity of the metallocene was thus 19.1 kg of PP/g of metallocene/h or 9.7 kg of PP/mmol of Hf/h.

20 VZ = 158 cm³/g, M_w = 158000 g/mole, M_n = 32400 g/mole, M_w/M_n = 4.9, n_{C_2} = 1.0, 2.6 % by weight of incorporated ethylene, T_m = 128°C, ΔH_m = 68.5 J/g.

Example 10

25 The procedure of Example 1 was followed, but the catalyst used was bisindenyl dimethylsilylhafnium dichloride. 10 g of ethylene were charged. During the polymerization, 35 g of ethylene were metered in. Polymerization was carried out for two hours at 60°C. 53 mg (0.099 mmol) of metallocene compound were used. 0.88 kg of random ethylene-propylene copolymer were obtained. The activity of the metallocene was thus 8.3 kg of PP/g of metallocene/h or 4.4 kg of PP/mmol of Hf/h.

30

VZ = 285 cm³/g, M_w = 336000 g/mole, M_n = 65900 g/mole, M_w/M_n = 5.1, n_{C_2} = 1.0, 4.9 % of incorporated ethylene, T_m = 127.5°C, ΔH_m = 62 J/g.

Example 11

5 The procedure of Example 10 was followed. 1 g of ethylene was charged. During the polymerization, 5 g of ethylene were metered in. Polymerization was carried out for two hours at 60°C. 47.2 mg (0.088 mmol) of metallocene compound were used. 2.4 kg of random ethylene-propylene copolymer were obtained. The activity of the metallocene was thus 25.4 kg of PP/g of metallocene/h or 13.6 kg of PP/mmol of Hf/h.

10
VZ = 272 cm³/g, M_w = 310000 g/mole, M_n = 68000 g/mole, M_w/M_n = 4.7, n_{C_2} = 1.0, 0.2 % of incorporated ethylene, T_m = 126.5°C, ΔH_m = 65 J/g.

Example 12

15
The procedure of Example 10 was followed. 7.5 g of ethylene were charged. During the polymerization, 25 g of ethylene were metered in. Polymerization was carried out for two hours at 60°C. 53.3 mg (0.103 mmol) of metallocene compound were used. 2.3 kg of random ethylene-propylene copolymer were obtained. The activity of the metallocene was thus 20.8 kg of PP/g of metallocene/h or 11.2 kg of PP/mmol of Hf/h.

20
VZ = 295 cm³/g, M_w = 349000 g/mole, M_n = 79000 g/mole, M_w/M_n = 4.4, n_{C_2} = 1.0, 1.3 % of incorporated ethylene, T_m = 128°C, ΔH_m = 67 J/g.

Example 13

25
The procedure of Example 10 was followed. 11 g of ethylene were charged. During the polymerization, 36 g of ethylene were metered in. Polymerization was carried out

30

for two hours at 60°C. 57.8 mg (0.108 mmol) of metallocene compound were used. 1.7 kg of random ethylene-propylene copolymer were obtained. The activity of the metallocene was thus 14.7 kg of PP/g of metallocene/h or 7.8 kg of PP/mmol of Hf/h.

VZ = 277 cm³/g, M_w = 320000 g/mole, M_n = 77600 g/mole, M_w/M_n = 4.2, n_{C_2} = 1.0, 2.7 % of incorporated ethylene, T_m = 127°C, ΔH_m = 63 J/g.

Example 14

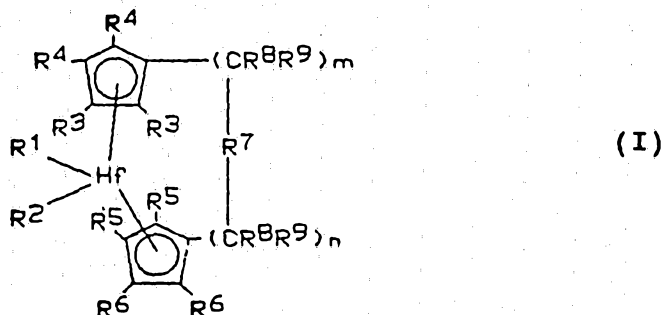
The procedure of Example 1 was followed. 37 g of ethylene were charged. During the polymerization, 112 g of ethylene were metered in. Polymerization was carried out for two hours at 60°C. 53.6 mg (0.100 mmol) of metallocene compound were used. 2.0 kg of random ethylene-propylene copolymer were obtained. The activity of the metallocene was thus 18.7 kg of PP/g of metallocene/h or 10.0 kg of PP/mmol of Hf/h.

VZ = 284 cm³/g, M_w = 334000 g/mole, M_n = 67000 g/mole, M_w/M_n = 5.0, n_{C_2} = 1.0, 7.4 % of incorporated ethylene, T_m = 126.5°C, ΔH_m = 64.5 J/g.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:
~~XXXXXXXXXXXX~~
Claims:

HOE 89/F 053

1. A process for the preparation of a propylene copolymer composed of 99.9 to 80.0 mol %, relative to the total polymer, of propylene units and 0.1 to 20.0 mol %, relative to the total polymer, of units which are derived from ethylene or from an olefin with at least 4 carbon atoms of the formula $R^{15}-CH=CH-R^{16}$, where R^{15} and R^{16} are identical or different and denote a hydrogen atom or an alkyl radical having 1 to 28 carbon atoms or R^{15} and R^{16} with the carbon atoms bonding them form a ring having 4 to 28 carbon atoms, by polymerizing 50 to 99.5 % by weight, relative to the total amount of monomers, of propylene and 0.5 to 50 % by weight, relative to the total amount of monomers, of at least one representative of the group consisting of ethylene and olefins having at least 4 carbon atoms of the formula $R^{15}-CH=CH-R^{16}$, where R^{15} and R^{16} have the meaning given above, at a temperature of 30°C to 150°C at a pressure of 0.5 to 100 bar in solution, in suspension or in the gas phase in the presence of a catalyst composed of a metallocene and an alumin-oxane, wherein the metallocene is a compound of the formula I

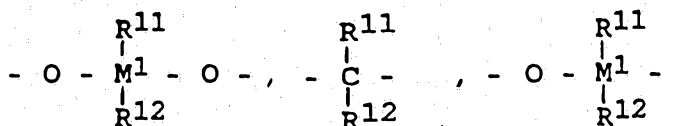
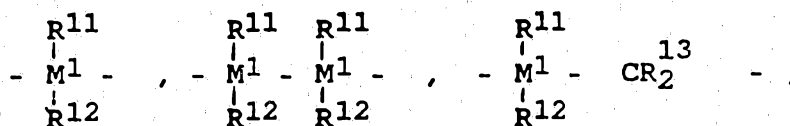


in which

R^1 and R^2 are identical or different and denote 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 C₈-C₄₀-arylalkenyl group or a halogen atom,

R³, R⁴, R⁵ and R⁶ are identical or different and denote a hydrogen atom, a halogen atom, a C₁-C₁₀-alkyl group, a radical -NR¹⁰₂-, -SR¹⁰-, -OSiR¹⁰₃-, -SiR¹⁰₃-, or -PR¹⁰₂- in which R¹⁰ is a C₁-C₁₀-alkyl group, a C₆-C₁₀-aryl group or if the radical contains Si or P may also be a halogen atom, or each pair of adjacent radicals R³, R⁴, R⁵ or R⁶ forms a ring with the carbon atoms linking them, R⁷ is



=BR¹¹, =AlR¹¹, -Ge-, -Sn-, -O-, -S-, =SO, =SO₂, =NR¹¹, =CO, =PR¹¹ or =P(O)R¹¹

where

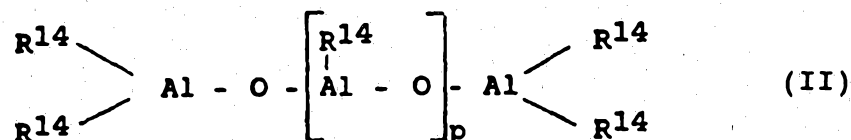
R¹¹, R¹² and R¹³ are identical or different and denote a hydrogen atom, a halogen atom, a C₁-C₃₀-alkyl group, a C₁-C₁₀-fluoroalkyl group, a C₆-C₁₀-aryl group, a C₆-C₁₀-fluoroaryl group, a C₁-C₁₀-alkoxy group, a C₂-C₁₀-alkenyl group, a C₇-C₄₀-arylalkyl group, a C₈-C₄₀-arylalkenyl group, a C₇-C₄₀-alkyl-aryl group or R¹¹ and R¹² or R¹¹ and R¹³ in each case form a ring with the atoms bonding them,

M¹ is silicon, germanium or tin,

R⁸ and R⁹ are identical or different and have the meaning given for R¹¹,

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

and the aluminoxane is one of the formula (II)



in the instance of the linear type and/or of the formula (III)



in the instance of the cyclic type, R^{14} in the formulae (II) and (III) denoting a C_1 - C_6 -alkyl group and p denoting an integer from 2 to 50.

2. The process as claimed in claim 1, wherein the metallocene is a compound of the formula I in which the radical $-(\text{CR}^8\text{R}^9)_m-\text{R}^7-(\text{CR}^8\text{R}^9)_n-$ denotes $-\text{CH}_2-\text{CH}_2-$, $-\text{Ge}(\text{CH}_3)_2-$, $-\text{Si}(\text{CH}_3)_2-$, $-\text{Si}(\text{C}_6\text{H}_5)_2-$ or $-\text{Si}(\text{CH}_3)(\text{C}_6\text{H}_5)-$.
3. The process as claimed in claim 1, wherein the metallocene is ethylenebisindenylhafnium dichloride or bisindenyldimethylsilylhafnium dichloride.
4. A random propylene copolymer composed of 99.9 to 80.0 mol %, relative to the total polymer, of propylene units and 0.1 to 20.0 mol %, relative to the total polymer, of units which are derived from ethylene or from an olefin with at least 4 carbon atoms of the formula $\text{R}^{15}-\text{CH}=\text{CH}-\text{R}^{16}$ where R^{15} and R^{16} are identical or different and denote a hydrogen atom or an alkyl radical having 1 to 28 carbon atoms or R^{15} and R^{16} form a ring of 4 to 28 carbon atoms with the atoms bonding them, the said copolymer having an average molecular weight of more than

100000 g/mole, a polydispersity of 2.5 to 5.5 and a sequence length of below 1.25.

5. The use of the propylene copolymer prepared as claimed in claim 1 for the preparation of sheets for thermoforming, and for the blowmolding of hollow articles.

DATED this 13th day of February 1990.

HOECHST AKTIENGESELLSCHAFT

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"THE ATRIUM"
290 BURWOOD ROAD
HAWTHORN. VIC. 3122.