

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).

We<sup>(1)</sup> HOECHST AKTIENGESELLSCHAFT,  
D-6230 Frankfurt am Main 80,  
Federal Republic of Germany.

(2) Here  
insert Title  
of Invention.

hereby apply for the grant of a Patent for an invention entitled:<sup>(2)</sup>  
PROCESS FOR THE PREPARATION OF A POLYOLEFIN

(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<sup>(3)</sup>  
P 40 15 254.5


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

for a patent or similar protection made in<sup>(4)</sup> Federal Republic of  
Germany on 12th May, 1990.

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

DATED this 26th day of April, 1991

(5) Signa-  
ture(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.

207-146

## 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 D-6230 Frankfurt am Main 80, Federal Republic of Germany

for a patent for an invention entitled:

## Process for the preparation of a polyolefin

1/We, Martin Fenske, Am Wiesenhof 10, D-6242 Kronberg im Taunus ) Fed.Rep.of Germany  
Franz Lapice, Sandweg 2, D-6233 Kelkheim (Taunus)

do solemnly and sincerely declare as follows:

1. We are authorized by HOECHST AKTIENGESELLSCHAFT  
the applicant/s for the patent to make this declaration on its/their behalf.
  2. The basic application/s as defined by Section 141 of the Act was/were made  
by HOECHST AKTIENGESELLSCHAFT
- Federal Republic of Germany P 40 15 254.5 of May 12, 1990

3.

- 1) Volker DOLLE, Hattersheimer Straße 15, D-6233 Kelkheim/Taunus
  - 2) Martin ANTBERG, Sachsenring 10, D-6238 Hofheim am Taunus
  - 3) Jürgen ROHRMANN, Die Ritterwiesen 10, D-6237 Liederbach
  - 4) Andreas WINTER, Gundelhardtstraße 2, D-6233 Kelkheim/Taunus
- 1)-4) Fed.Rep.of Germany

is/are the actual inventor/s of the invention and the facts upon which

HOECHST AKTIENGESELLSCHAFT

is/~~are~~ entitled to make the application are as follows:

The said HOECHST AKTIENGESellschaft

is/~~are~~ the assignee/s of the said inventor/s

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

Dated Frankfurt am Main, Fed.Rep.of Germany, April 5, 1991

HOECHST AKTIENGESELLSCHAFT

ppa Tunde i.v. Lazice

ppa. Fenske

i.V. Lapice

To the Commissioner of Patents

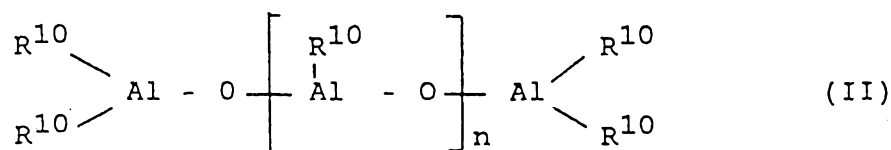


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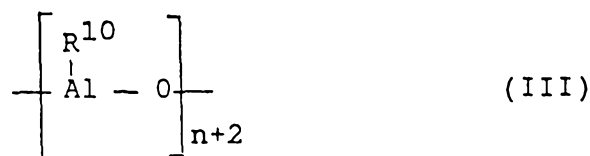
(12) PATENT ABRIDGMENT (11) Document No. AU-B-76223/91  
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 635419

- (54) Title  
PROCESS FOR THE PREPARATION OF A POLYOLEFIN
- International Patent Classification(s)  
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- (21) Application No. : 76223/91 (22) Application Date : 26.04.91
- (30) Priority Data
- (31) Number (32) Date (33) Country  
4015254 12.05.90 DE GERMANY
- (43) Publication Date : 14.11.91
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- (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  
AU 622826 61106/90 C08F 4/76  
AU 49398/90 C08F 4/76  
AU 49397/90 C08F 4/76
- (57) Claim

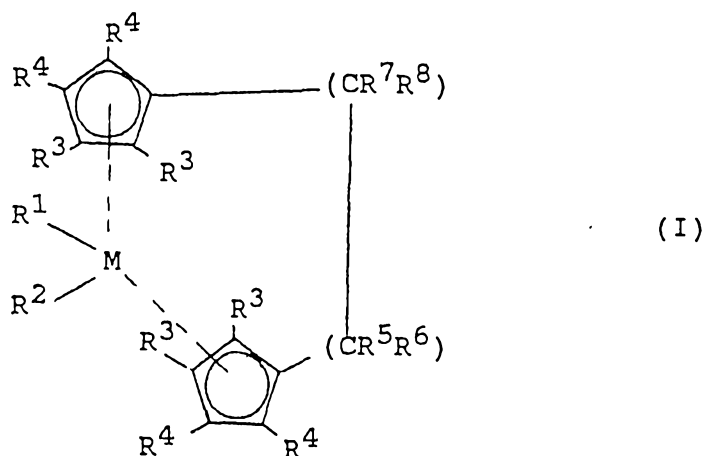
1. A process for the preparation of a polyolefin by polymerizing an olefin of the formula  $R^{11}-CH=CH-R^{12}$  in which  $R^{11}$  and  $R^{12}$  are identical or different and are a hydrogen atom or a  $C_1-C_{14}$ -alkyl radical or  $R^{11}$  and  $R^{12}$ , together with the carbon atom connecting them, form a ring having 4 to 28 carbon atoms, at a temperature of from  $0^\circ\text{C}$  to  $150^\circ\text{C}$ , at a pressure of from 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst which comprises a metallocene and an aluminoxane of the formula (II)



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



for the cyclic type, where, in the formulae (II) and (III), the radicals  $R^{10}$  are identical or different and are hydrogen, a  $C_1$ - $C_5$ -alkyl group, phenyl or benzyl, and  $n$  is an integer from 2 to 50, wherein the metallocene is a compound of the formula (I)



in which

$M$  is zirconium or hafnium,

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

$R^3$  and  $R^4$  are identical or different and are a hydrogen atom, a halogen atom or a  $C_1$ - $C_{10}$ -alkyl group, or any two adjacent radicals  $R^3$  and  $R^4$ , together with the carbon atoms connecting them, form a ring,

$R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  are identical or different and are 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

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(10) 635419

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C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>8</sub>-C<sub>40</sub>-arylalkenyl group, an -SiMe<sub>3</sub> group, an -OSiMe<sub>3</sub> group or a -CH<sub>2</sub>-SiMe<sub>3</sub> group, or R<sup>5</sup> and R<sup>6</sup> or R<sup>7</sup> and R<sup>8</sup>, in each case together with the atoms connecting them, form a ring, and the compound of the formula I is in the form of at least two of its stereoisomers originating from the metallocene preparation.

635419

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 : D-Frankfurt am 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 POLYOLEFIN

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 polyolefin

5 The invention relates to a process for the preparation of a 1-olefin polymer, specifically a bimodal propylene polymer of high isotacticity and molecular weight and of polydispersity, molecular weight distribution and separation between the molecular weight maximum which are substantially independent of the polymerization temperature.

10 Isotactic PP is prepared by suspension polymerization with the aid of ethylene bis(4,5,6,7)tetrahydro-1-indenyl)zirconium dichloride together with an aluminoxane (cf. US 4769510). The polymer has a narrow molecular weight distribution ( $M_w/M_n$  of from 1.6 to 2.6).

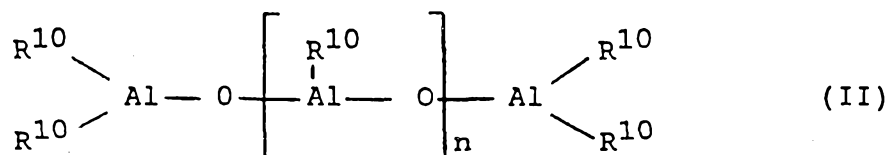
15 By means of a special preactivation method, it is has been possible to achieve a considerable increase in the activity of the catalyst system (cf. DE 3 726 067). The grain morphology of the polymer has likewise been improved by this preactivation method.

20 The molecular weights of the polymers obtained in accordance with these two applications are still too low for industrial use.

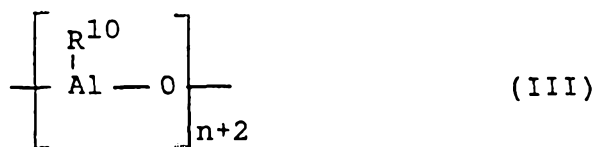
25 The object was thus to find a process for the preparation of a high-molecular-weight, isotactic, bimodal olefin polymer which can be carried out in an industrially useful temperature range with high catalyst activity.

30 It has been found that the object can be achieved by polymerizing olefins in the presence of certain metallocene catalysts.

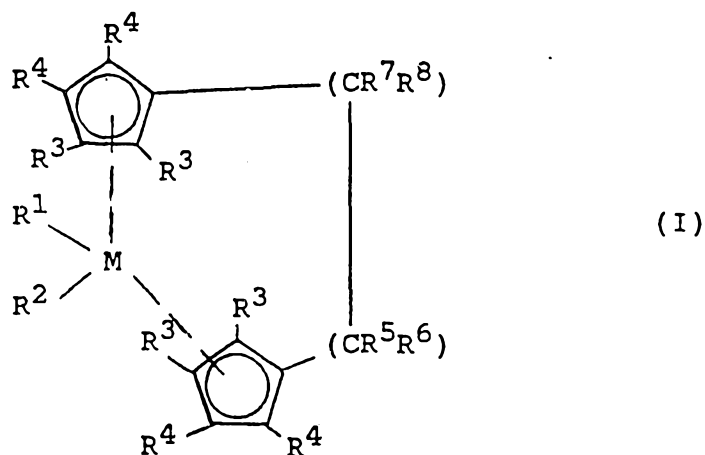
The invention thus relates to a process for the preparation of a polyolefin by polymerizing an olefin of the formula  $R^{11}-CH=CH-R^{12}$  in which  $R^{11}$  and  $R^{12}$  are identical or different and are a hydrogen atom or a  $C_1-C_{14}$ -alkyl radical or  $R^{11}$  and  $R^{12}$ , together with the carbon atom connecting them, form a ring having 4 to 28 carbon atoms, at a temperature of from  $0^\circ C$  to  $150^\circ C$ , at a pressure of from 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst which comprises a metallocene and an aluminoxane of the formula (II)



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



for the cyclic type, where, in the formulae (II) and (III), the radicals  $R^{10}$  are identical or different and are hydrogen, a  $C_1-C_6$ -alkyl group, phenyl or benzyl, and  $n$  is an integer from 2 to 50, wherein the metallocene is a compound of the formula (I)





in which

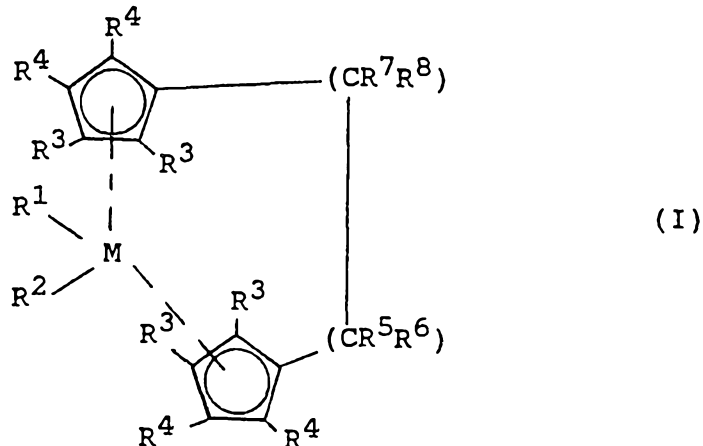
M is zirconium or hafnium,

R<sup>1</sup> and R<sup>2</sup> are identical or different and are a hydrogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>6</sub>-C<sub>10</sub>-aryloxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>7</sub>-C<sub>40</sub>-alkylaryl group, a C<sub>8</sub>-C<sub>40</sub>-arylalkenyl group or a halogen atom,

R<sup>3</sup> and R<sup>4</sup> are identical or different and are a hydrogen atom, a halogen atom or a C<sub>1</sub>-C<sub>10</sub>-alkyl group, or any two adjacent radicals R<sup>3</sup> and R<sup>4</sup>, together with the carbon atoms connecting them, form a ring,

R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>30</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-fluoroalkyl group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>6</sub>-C<sub>10</sub>-fluoroaryl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>8</sub>-C<sub>40</sub>-arylalkenyl group, an -SiMe<sub>3</sub> group, an -OSiMe<sub>3</sub> group or a -CH<sub>2</sub>-SiMe<sub>3</sub> group, or R<sup>5</sup> and R<sup>6</sup> or R<sup>7</sup> and R<sup>8</sup>, in each case together with the atoms connecting them, form a ring, and the compound of the formula I is in the form of at least two of its stereoisomers originating from the metallocene preparation.

The catalyst to be used for the process according to the invention comprises an aluminoxane and a metallocene of the formula I



in which

M is hafnium or zirconium, preferably zirconium,

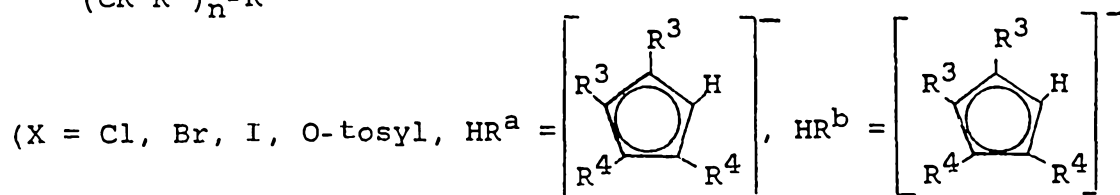
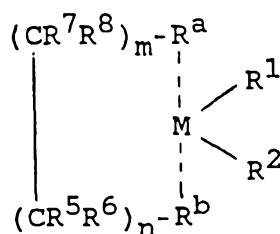
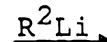
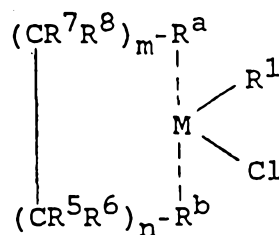
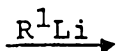
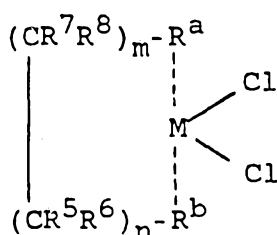
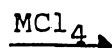
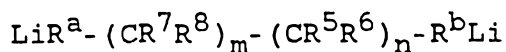
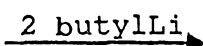
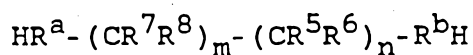
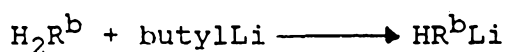
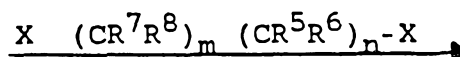
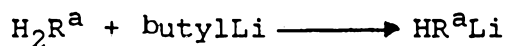
5 R<sup>1</sup> and R<sup>2</sup> are identical or different and are a hydrogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, preferably a C<sub>1</sub>-C<sub>3</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, preferably a C<sub>1</sub>-C<sub>3</sub>-alkoxy group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, preferably a C<sub>6</sub>-C<sub>8</sub>-aryl group, a C<sub>6</sub>-C<sub>10</sub>-aryloxy group, preferably a C<sub>6</sub>-C<sub>8</sub>-aryloxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, preferably a C<sub>2</sub>-C<sub>4</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, preferably a C<sub>7</sub>-C<sub>10</sub>-arylalkyl group, a C<sub>7</sub>-C<sub>40</sub>-alkylaryl group, preferably a C<sub>7</sub>-C<sub>12</sub>-alkylaryl group, a C<sub>8</sub>-C<sub>40</sub>-arylalkenyl group, preferably a C<sub>8</sub>-C<sub>12</sub>-arylalkenyl group, or a halogen atom, preferably chlorine.

15 R<sup>3</sup> and R<sup>4</sup> are identical or different and are a hydrogen atom, a halogen atom, preferably a fluorine, chlorine or bromine atom, or a C<sub>1</sub>-C<sub>10</sub>-alkyl group, preferably a C<sub>1</sub>-C<sub>3</sub>-alkyl group, or any two adjacent radicals R<sup>3</sup> and R<sup>4</sup>, together with the carbon atoms connecting them, form a ring. Particularly preferred ligands are indenyl, fluorenyl and cyclopentadienyl.

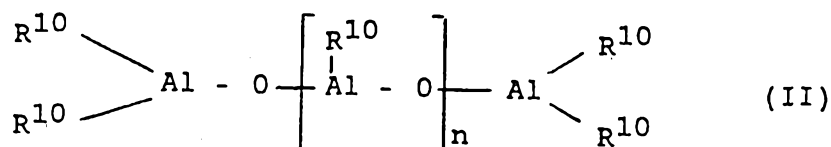
20 R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>30</sub>-alkyl group, preferably a C<sub>1</sub>-C<sub>4</sub>-alkyl group, in particular a methyl or ethyl group, a C<sub>1</sub>-C<sub>10</sub>-fluoroalkyl group, preferably a CF<sub>3</sub> group, a C<sub>6</sub>-C<sub>10</sub>-fluoroaryl group, preferably a pentafluorophenyl group, a C<sub>6</sub>-C<sub>19</sub>-aryl group, preferably a C<sub>6</sub>-C<sub>8</sub>-aryl group, in particular -CH<sub>2</sub>-C<sub>6</sub>H<sub>5</sub> or -C<sub>6</sub>H<sub>5</sub>, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, preferably a C<sub>1</sub>-C<sub>4</sub>-alkoxy group, in particular a methoxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, preferably a C<sub>2</sub>-C<sub>4</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, preferably a C<sub>7</sub>-C<sub>10</sub>-arylalkyl group, a C<sub>8</sub>-C<sub>40</sub>-arylalkenyl group, preferably a C<sub>8</sub>-C<sub>12</sub>-arylalkenyl group, an -SiMe<sub>3</sub> group, an -OSiMe<sub>3</sub> group or a -CH<sub>2</sub>-SiMe<sub>3</sub> group, preferably a -CH<sub>2</sub>-SiMe<sub>3</sub> group, or R<sup>5</sup> and R<sup>6</sup> or R<sup>7</sup> and R<sup>8</sup>, in each case together with the atoms connecting them, form a ring. The metallocene of the formula I is in the form of its stereoisomers.

It is very particularly preferred for one of the radicals  $R^5$ ,  $R^6$ ,  $R^7$  and  $R^8$  to be the  $-\text{CH}_2\text{-SiMe}_3$  group, each of the other three radicals being a hydrogen atom.

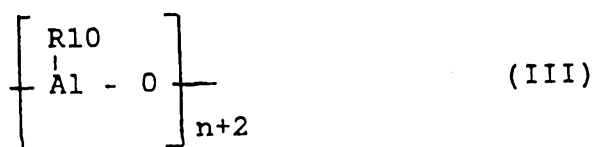
5 The above-described metallocenes can be prepared in accordance with the general reaction scheme below:



The cocatalyst is an aluminoxane of the formula II



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



for the cyclic type. In these formulae,  $\text{R}^{10}$  is preferably a  $\text{C}_1$ - $\text{C}_6$ -alkyl group, preferably methyl, ethyl or isobutyl, in particular methyl, and  $n$  is an integer from 2 to 50, preferably from 5 to 40. However, the exact structure of the aluminoxane is not known.

The aluminoxane can be prepared in various ways. Examples are given below, in particular, for the preparation of aluminoxanes where  $\text{R}^{10} = \text{alkyl}$ . Compounds where  $\text{R}^{10} \neq \text{alkyl}$  can be prepared analogously from corresponding starting compounds.

One possibility is the careful addition of water to a dilute solution of a trialkylaluminum by introducing the solution of the trialkylaluminum, preferably trimethylaluminum, and the water, in each case in small portions, into a relatively large amount of an inert solvent, awaiting the cessation of gas evolution between the addition of each portion.

In another process, finely powdered copper sulfate pentahydrate is slurried in toluene, and sufficient trialkylaluminum to provide about 1 mol of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  for every 4 Al atoms is added at about  $-20^\circ\text{C}$  under an inert

gas in a glass flask. After slow hydrolysis with elimination of alkane, the reaction mixture is left at room temperature for from 24 to 48 hours, during which it may be necessary to cool the mixture so that the temperature does not exceed 30°C. The copper sulfate is subsequently filtered off from the aluminoxane dissolved in the toluene, and the solution is evaporated in vacuo. It is assumed that, in this preparation process, the low-molecular-weight aluminoxanes condense with elimination of trialkylaluminum to form higher oligomers.

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

The aluminum salts containing water of crystallization are in particular those which have a high content of water of crystallization. Particular preference is given to aluminum sulfate hydrate, in particular the compounds  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  and  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  having the particularly high water of crystallization content of 16 and 18 mol of  $\text{H}_2\text{O}$ /mol of  $\text{Al}_2(\text{SO}_4)_3$  respectively.

A further variant of the preparation of aluminoxanes comprises dissolving trialkylaluminum, preferably trimethylaluminum, in the suspending agent, preferably in the liquid monomer, heptane or toluene, in the polymerization reactor and then reacting the aluminum compound with water.

In addition to the above-outlined process for the

preparation of aluminoxanes, it is possible to use other processes.

Irrespective of the preparation method, all the alumin-  
oxane solutions have a varying content of unreacted  
5 trialkylaluminum, in free form or as an adduct.

It is possible to preactivate the metallocene, before use  
in the polymerization reaction, using an aluminoxane of  
the formula (II) and/or (III). This considerably  
increases the polymerization activity and improves the  
grain morphology.

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The preactivation of the transition-metal compound is  
carried out in solution. The metallocene is preferably  
dissolved in a solution of the aluminoxane in an inert  
hydrocarbon. Suitable inert hydrocarbons are aliphatic or  
aromatic hydrocarbon. Toluene is preferred. The con-  
centration of the aluminoxane solution is in the range  
from about 1% by weight to the saturation limit, prefer-  
ably from 5 to 30% by weight, in each case based on the  
overall solution. The metallocene can be employed in the  
same concentration, but is preferably employed in an  
amount of from  $10^{-4}$  -1 mol per mol of aluminoxane. The  
preactivation time is from 5 minutes to 60 hours, prefer-  
ably from 5 to 60 minutes. A temperature of from  $-78^{\circ}\text{C}$  to  
 $100^{\circ}\text{C}$ , preferably from 0 to  $70^{\circ}\text{C}$ , is used.

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The polymerization is carried out in a known manner in  
solution, in suspension or in the gas phase, continuously  
or batchwise, in one or more steps, at a temperature of  
from 0 to  $150^{\circ}\text{C}$ , preferably from 30 to  $80^{\circ}\text{C}$ . Olefins of  
the formula  $\text{R}^{11}\text{-CH=CH-R}^{12}$  are polymerized. In this formula,  
 $\text{R}^{11}$  and  $\text{R}^{12}$  are identical or different and are a hydrogen  
atom or an alkyl radical having 1 to 28 carbon atoms.  
However,  $\text{R}^{11}$  and  $\text{R}^{12}$  may also, together with the carbon  
atoms connecting them, form a ring having 4 to 28 carbon  
atoms. Examples of such olefins are ethylene, propylene,  
1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene,

norbornene or norbornadiene. In particular, propylene is polymerized.

5 The molecular weight regulator added, if necessary, is hydrogen. The total pressure in the polymerization system is from 0.5 to 100 bar. The polymerization is preferably carried out in the industrially particularly useful pressure range of from 5 to 64 bar.

10  
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The metallocene is used in a concentration, based on the transition metal, of from  $10^{-3}$  to  $10^{-7}$  mol, preferably from  $10^{-4}$  to  $10^{-6}$  mol, of transition metal per  $\text{dm}^3$  of solvent or per  $\text{dm}^3$  of reactor volume. The aluminoxane is used in a concentration of from  $10^{-5}$  to  $10^{-1}$  mol, preferably from  $10^{-4}$  to  $10^{-2}$  mol, per  $\text{dm}^3$  of solvent or per  $\text{dm}^3$  of reactor volume. In principle, however, higher concentrations are also possible.

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The metallocene employed is a compound of the formula I, in the form of at least two of its stereoisomers originating from the metallocene preparation.

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

30

In addition, a petroleum or hydrogenated diesel oil fraction can be used. It is also possible to use toluene. The polymerization is preferably carried out in liquid monomer.

30 If inert solvents are used, the monomers are metered in in gas or liquid form.

The polymerization can be carried out for as long as

desired since the catalyst system to be used according to the invention exhibits only a slight time-dependent drop in polymerization activity.

5 The process according to the invention is distinguished by the fact that the metallocenes used are very temperature-stable, so that they can be used with high activity even at temperatures up to 90°C. In addition, the alumin-oxanes serving as cocatalysts can be added in lower concentrations than hitherto.

10

The metallocene mixture to be used according to the invention has the advantage over the prior art of being produced together in one synthesis operation, which saves time, space, equipment and solvent. It contains compounds which are able to polymerize 1-olefins, particularly propylene, to give polymers having a molecular weight  $M_w$  of greater than 70,000 g/mol. This is confirmed by the molecular weight distribution, which has a high  $M_w/M_n$  ratio ( $> 2$ ). The molecular weight distribution is bimodal.

15

20 Example 1

$[(\eta^5\text{-1-Indenyl-CH}_2\text{*CH(CH}_2\text{SiMe}_3)(\eta^5\text{-1-indenyl)]ZrCl}_2$

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14 cm<sup>3</sup> of a 1.6 N (22.4 mmol) butyllithium/hexane solution were added dropwise over the course of 1 hour at room temperature to 12.2 g (42.6 mmol) of the ligand (diastereomer mixture) in 50 cm<sup>3</sup> of THF, and the batch was stirred at 60°C until 0.5 hour after cessation of the evolution of butane.

30

The dilithio salt solution obtained was added dropwise, simultaneously with a solution of 4.21 g (11.16 mmol) of  $ZrCl_4(\text{thf})_2$  in 80 cm<sup>3</sup> of THF, at ambient temperature over the course of 1 hour to 30 cm<sup>3</sup> of THF. The batch was then stirred at room temperature for 8 hours and evaporated. The salts deposited initially during the evaporation were filtered off, and the batch was finally evaporated to



dryness. The residue was suspended in n-pentane and separated off. The solid was subsequently taken up in ether, the ether-soluble components were separated off by filtration, and the ether was stripped off, leaving 38 g (5.94 mmol, 53%) of a yellow powder, whose NMR spectrum showed the presence of a complex mixture of at least three compounds. The elemental analysis had the following result:

C 55.8 (calc. 57.12), H 5.4 (calc. 5.19) and Cl 14.1 (calc. 14.05), all in %.

#### Examples 2 to 5

A dry 16 dm<sup>3</sup> reactor was flushed with nitrogen and charged with 10 dm<sup>3</sup> of liquid propylene. Two-thirds of the amount of methylaluminoxane (MAO) indicated in the table for each experiment were then added as a toluene solution, and the batch was stirred at 30°C for 15 minutes.

In parallel, a solution of the metallocene was prepared in one third of the amount of MAO in the table, and was preactivated by being left to stand for 15 minutes.

This solution was then introduced into the reactor. The polymerization system was heated to the appropriate polymerization temperature, and the polymerization was initiated. The polymerization was terminated after 60 minutes by cooling the reactor and decompressing the contents. The polymer yield obtained and the analytical data determined are shown in the table.

The following abbreviations have been used in the table:

VN = viscosity number in cm<sup>3</sup>/g,

M<sub>w</sub> = weight average molecular weight in g/mol,

M<sub>w</sub>/M<sub>n</sub> = polydispersity, determined by gel permeation chromatography (GPC)

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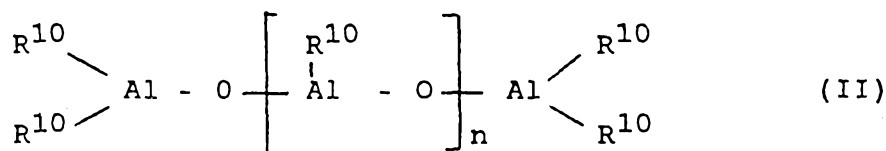
Polymerization experiments using [(IND)-CH\*CH<sub>2</sub>SiMe<sub>3</sub>-CH<sub>2</sub>-(IND)]ZrCl<sub>2</sub>

Tempera- ture [°C]	Amount of cata- lyst [mg]	Cata- lyst molecu- lar weight [g/mol]	Amount of activa- tor [cm <sup>3</sup> ]	MAO [%]	[mmol]	Yield [kg]	Activity [kg of PP/g of catalyst/h]	Bulk density [g/dm <sup>3</sup> ]	VZ [cm <sup>3</sup> /g]	M <sub>w</sub> [g/mol]	M <sub>w</sub> /M <sub>n</sub>
40	19.9	504.5	40.2	10.0	60	0.140	7.0	101	89	70700	7.3
50	13.9	504.5	40.2	10.0	60	0.880	63.1	183	81	59300	8.5
60	19.8	504.5	40.2	10.0	60	1.280	129.1	264	77	58200	5.9
70	6.0	504.5	40.2	10.0	60	1.040	172.2	246	55	43300	6.9

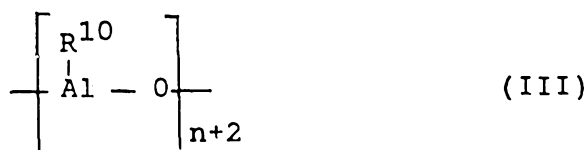
~~PATENT CLAIMS~~

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

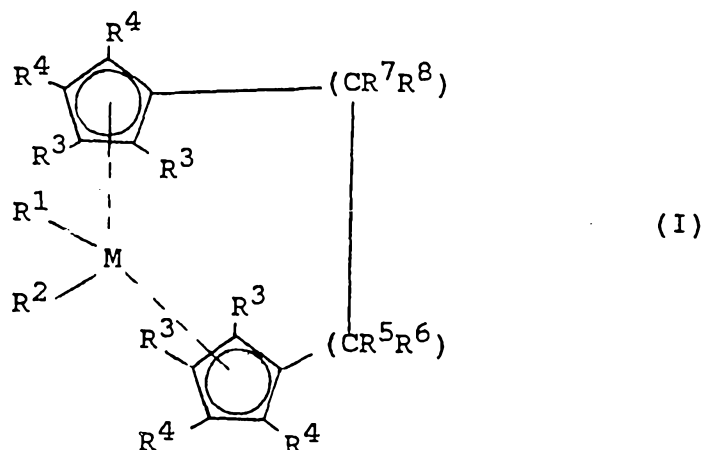
1. A process for the preparation of a polyolefin by polymerizing an olefin of the formula  $R^{11}-CH=CH-R^{12}$  in which  $R^{11}$  and  $R^{12}$  are identical or different and are a hydrogen atom or a  $C_1-C_{14}$ -alkyl radical or  $R^{11}$  and  $R^{12}$ , together with the carbon atom connecting them, form a ring having 4 to 28 carbon atoms, at a temperature of from  $0^\circ C$  to  $150^\circ C$ , at a pressure of from 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst which comprises a metallocene and an aluminoxane of the formula (II)



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



for the cyclic type, where, in the formulae (II) and (III), the radicals  $R^{10}$  are identical or different and are hydrogen, a  $C_1-C_6$ -alkyl group, phenyl or benzyl, and  $n$  is an integer from 2 to 50, wherein the metallocene is a compound of the formula (I)



in which

M is zirconium or hafnium,

R<sup>1</sup> and R<sup>2</sup> are identical or different and are a hydrogen atom, a C<sub>1</sub>-C<sub>10</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>6</sub>-C<sub>10</sub>-aryloxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>7</sub>-C<sub>40</sub>-alkylaryl group, a C<sub>8</sub>-C<sub>40</sub>-arylalkenyl group or a halogen atom,

R<sup>3</sup> and R<sup>4</sup> are identical or different and are a hydrogen atom, a halogen atom or a C<sub>1</sub>-C<sub>10</sub>-alkyl group, or any two adjacent radicals R<sup>3</sup> and R<sup>4</sup>, together with the carbon atoms connecting them, form a ring,

R<sup>5</sup>, R<sup>6</sup>, R<sup>7</sup> and R<sup>8</sup> are identical or different and are a hydrogen atom, a halogen atom, a C<sub>1</sub>-C<sub>30</sub>-alkyl group, a C<sub>1</sub>-C<sub>10</sub>-fluoroalkyl group, a C<sub>6</sub>-C<sub>10</sub>-aryl group, a C<sub>6</sub>-C<sub>10</sub>-fluoroaryl group, a C<sub>1</sub>-C<sub>10</sub>-alkoxy group, a C<sub>2</sub>-C<sub>10</sub>-alkenyl group, a C<sub>7</sub>-C<sub>40</sub>-arylalkyl group, a C<sub>8</sub>-C<sub>40</sub>-arylalkenyl group, an -SiMe<sub>3</sub> group, an -OSiMe<sub>3</sub> group or a -CH<sub>2</sub>-SiMe<sub>3</sub> group, or R<sup>5</sup> and R<sup>6</sup> or R<sup>7</sup> and R<sup>8</sup>, in each case together with the atoms connecting them, form a ring, and the compound of the formula I is in the form of at least two of its stereoisomers originating from the metallocene preparation.

2. The process as claimed in claim 1, wherein propylene is polymerized.
3. Polypropylene having a molecular weight of greater than 70,000 g/mol, prepared by the process as claimed in claim 1.

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