(CONVENTION. By one or more persons and/or a Company.) 641639 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).

I/We(1) HOECHST AKTIENGESELLSCHAFT of 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:(2) A PROCESS FOR THE PREPARATION OF A SYNDIOTACTIC POLYOLEFIN

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

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

P 39 07 965.1

(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 11th March, 1989.

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

DATED this 8th day of March, 19 90

HOECHST AKTIENGESELLSCHAFT

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

09/03/90

(5)

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

for a patent for an invention entitled:

A process for the preparation of a syndiotactic polyolefin

I/We, Ulrich Tergau, Am Dornbusch 3, D-6239 Eppstein/Taunus
Franz Lapice, Sandweg 2, D-6233 Kelkheim (Taunus)) Fed.Rep.ofGermany

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 39 07 965.1 of March 11, 1989

3.

1) Andreas Winter, Gundelhardtstraße 2, D-6233 Kelkheim/Taunus
2) Jürgen Rohrmann, Die Ritterwiesen 10, D-6237 Liederbach
3) Martin Antberg, Sachsenring 10, D-6238 Hofheim am Taunus
4) Volker Dolle, Hattersheimer Straße 15, D-6233 Kelkheim/Taunus
5) Walter Spaleck, Sulzbacher Straße 63, D-6237 Liederbach
1)-5) 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 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, January 16, 1990

HOECHST AKTIENGESELLSCHAFT

ppa. Tergau i.V. Lapice

To the Commissioner of Patents

AU9051181

(12) PATENT ABRIDGMENT (11) Document No. AU-B-51181/90
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 641639

(54) Title
A PROCESS FOR THE PREPARATION OF A SYNDIOTACTIC POLYOLEFIN

International Patent Classification(s)
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(31) Number	(32) Date	(33) Country
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(71) Applicant(s)
HOECHST AKTIENGESELLSCHAFT

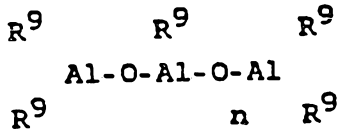
(72) Inventor(s)
ANDREAS WINTER; JURGEN ROHRMANN; MARTIN ANTBERG; VOLKER DOLLE; WALTER SPALECK

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

(56) Prior Art Documents
AU 31223/89 C08F 110/06
AU 31222/89 C08F 110/06

(57) Claim

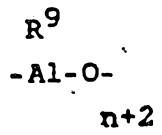
1. A process for the preparation of a syndiotactic polyolefin by polymerization or copolymerization of an olefin of the formula $R^aCH=CHR^b$, in which R^a and R^b are identical or different and denote a hydrogen atom or an alkyl radical having 1 to 28 carbon atoms, or R^a and R^b, with the atoms joining them, can form a ring, at a temperature of -60 to 200°C under a pressure of 0.5 to 100 bar in solution, suspension or the gas phase in the presence of a catalyst which consists of a metallocene as the transition metal component and an aluminoxane of the formula II



(II)

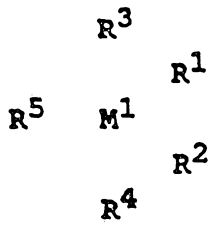
for the linear type and/or of the formula III

.../2



(III)

for the cyclic type, in which, in the formulae II and III, R^9 denotes a C_1-C_6-alkyl group or phenyl or benzyl and n is an integer from 2 to 50, which comprises carrying out the polymerization in the presence of a catalyst, the transition metal component of which is a compound of the formula I



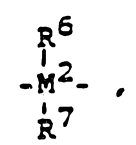
(I)

in which

M^1 is ~~titanium,~~ zirconium, ~~vanadium, niobium or tantalum,~~ R^1 and R^2 are identical or different and denote a hydrogen atom, a halogen 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 or a C_8-C_{40}-arylalkenyl group,

R^3 and R^4 are different and denote a mono- or polynuclear hydrocarbon radical which can form a sandwich structure with the central atom M^1,

R^5 is



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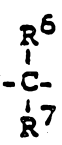

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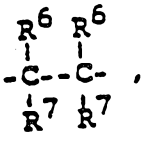


,

in which R^6 and R^7 are identical or different and denote 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}-fluoroaryl group, a C_6-C_{10}-aryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^6 and R^7 in each case with the atoms joining them, form a ring, and

M^2 is silicon.

641639

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-6230 Frankfurt am Main 80, Federal Republic of Germany

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

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

Complete Specification for the invention entitled:

A PROCESS FOR THE PREPARATIN OF A SYNDIOTACTIC POLYOLEFIN

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

HOECHST AKTIENGESELLSCHAFT HOE 89/F 083 Dr. DA/AP

Description

A process for the preparation of a syndiotactic polyolefin

The invention relates to a novel process, which can be employed on a large industrial scale, for the preparation of a syndiotactic polyolefin.

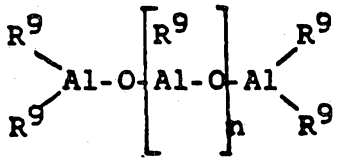
Syndiotactic polyolefins, in particular syndiotactic polypropylene, are known per se. However, it has not yet been possible to prepare such polymers in an adequate yield under polymerization conditions which are of industrial interest.

Thus, it is known that syndiotactic polypropylene can be prepared by polymerization of propylene at -78°C in the presence of a catalyst system consisting of VCl_4, anisole, heptane and diisobutylaluminum chloride (compare B. Lotz et al., Macromolecules 21 (1988), 2375). However, the syndiotactic index (= 76.9%) and the yield (= 0.16%) are too low.

It is furthermore known that a syndiotactic polypropylene having a narrow molecular weight distribution can be obtained in a significantly improved yield with the aid of a catalyst consisting of isopropylene(cyclopentadienyl)(9-fluorenyl)-zirconium dichloride or isopropylene(cyclopentadienyl)(9-fluorenyl)-hafnium dichloride and a methylaluminoxane at a temperature of 25 to 70°C (compare J. A. Ewen et al., J. Am. Chem. Soc., 110 (1988), 6255). Nevertheless, the molecular weight of the polymer which can be achieved with the zirconium compound is still too low and the yield which can be achieved by means of the hafnium compound is inadequate for an industrial process. Moreover, the syndiotactic characteristics which can be achieved are still in need of improvement.

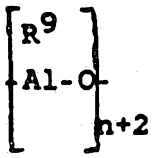
There was therefore the object of discovering a process which enables syndiotactic polyolefins of high molecular weight, narrow molecular weight distribution and a syndiotactic index of more than 90% to be obtained in a high yield.

The invention thus relates to a process for the preparation of a syndiotactic polyolefin by polymerization or copolymerization of an olefin of the formula $R^aCH=CHR^b$, in which R^a and R^b are identical or different and denote a hydrogen atom or an alkyl radical having 1 to 28 carbon atoms, or R^a and R^b, with the atoms joining them, can form a ring, at a temperature of -60 to 200°C under a pressure of 0.5 to 100 bar in solution, suspension or the gas phase in the presence of a catalyst which consists of a metallocene as the transition metal component and an aluminoxane of the formula II



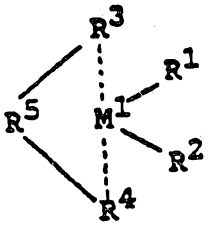
(II)

for the linear type and/or of the formula III



(III)

for the cyclic type, in which, in the formulae II and III, R^9 denotes a C_1-C_6-alkyl group or phenyl or benzyl and n is an integer from 2 to 50, which comprises carrying out the polymerization in the presence of a catalyst, the transition metal component of which is a compound of the formula I



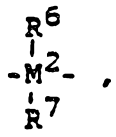
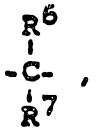
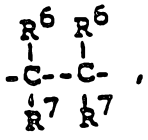
(I)

in which

M^1 is ~~titanium,~~ zirconium, ~~vanadium, niobium or tantalum,~~ R^1 and R^2 are identical or different and denote a hydrogen atom, a halogen 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 or a C_8-C_{40}-arylalkenyl group,

R^3 and R^4 are different and denote a mono- or polynuclear hydrocarbon radical which can form a sandwich structure with the central atom M^1,

R^5 is

 ,  ,  ,

in which R^6 and R^7 are identical or different and denote 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}-fluoroaryl group, a C_6-C_{10}-aryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^6 and R^7 in each case with the atoms joining them, form a ring, and

M^2 is silicon.

The catalyst to be used in the process according to the invention consists of an aluminoxane and a metallocene of the formula I.

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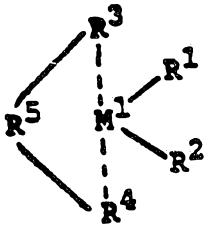


(I)

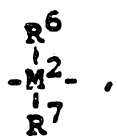
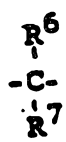
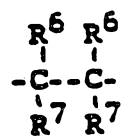
In formula I, M^1 is ~~a metal from the group comprising titanium, zirconium, vanadium, niobium and tantalum, preferably~~ zirconium.

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.

R^3 and R^4 are different and denote a mono- or polynuclear hydrocarbon radical which can form a sandwich structure with the central atom M^1.

R^3 and R^4 are preferably fluorenyl and cyclopentadienyl, it also being possible for the parent structure to carry additional substituents.

R^5 is a single- or multi-membered bridge which links the radicals R^3 and R^4 and denotes

 ,  ,  ,

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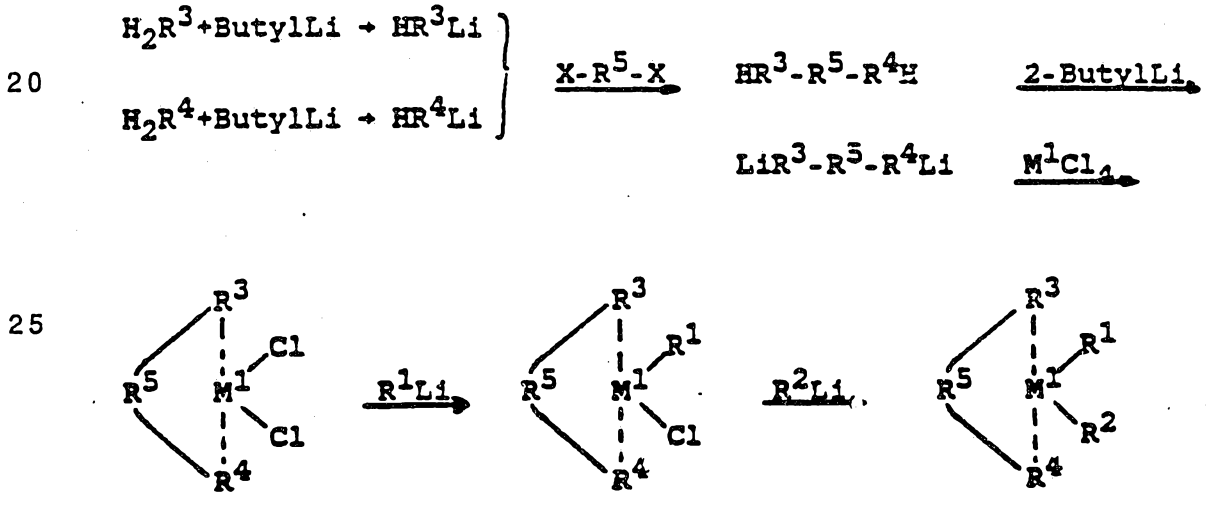
in which R^6 and R^7 are identical or different and denote a hydrogen atom, a halogen atom, preferably chlorine, a C_1-C_{10}, preferably C_1-C_3-alkyl group, in particular a methyl group, a C_1-C_{10}-fluoroalkyl group, preferably a CF_3 group, a C_1-C_{10}-fluoroalkyl group, preferably a CF_3 group, a C_6-C_{10}-fluoroaryl group, preferably a pentafluorophenyl group, a C_5-C_{10}-, preferably C_6-C_8-aryl group, a C_1-C_{10}-, preferably C_1-C_4-alkoxy group, in particular a methoxy group, a C_2-C_{10}-, preferably C_2-C_4-alkenyl group, a C_7-C_{40}- preferably C_7-C_{10}-arylalkyl group, a C_8-C_{40}-, preferably C_8-C_{12}-arylalkenyl group or a C_7-C_{40}-, preferably C_7-C_{12}-alkylaryl group, or R^6 and R^7 or R6 and R^8, in each case together with the atoms joining them, form a ring.

M^2 is silicon.

R^5 is preferably $=CR^6R^7$, $=SiR^6R^7$, $=GeR^6R^7$, -O-, -S-, =SO, $=PR^6$ or $=P(O)R^6$.

The metallocenes described above can be prepared in accordance with the following general reaction scheme:



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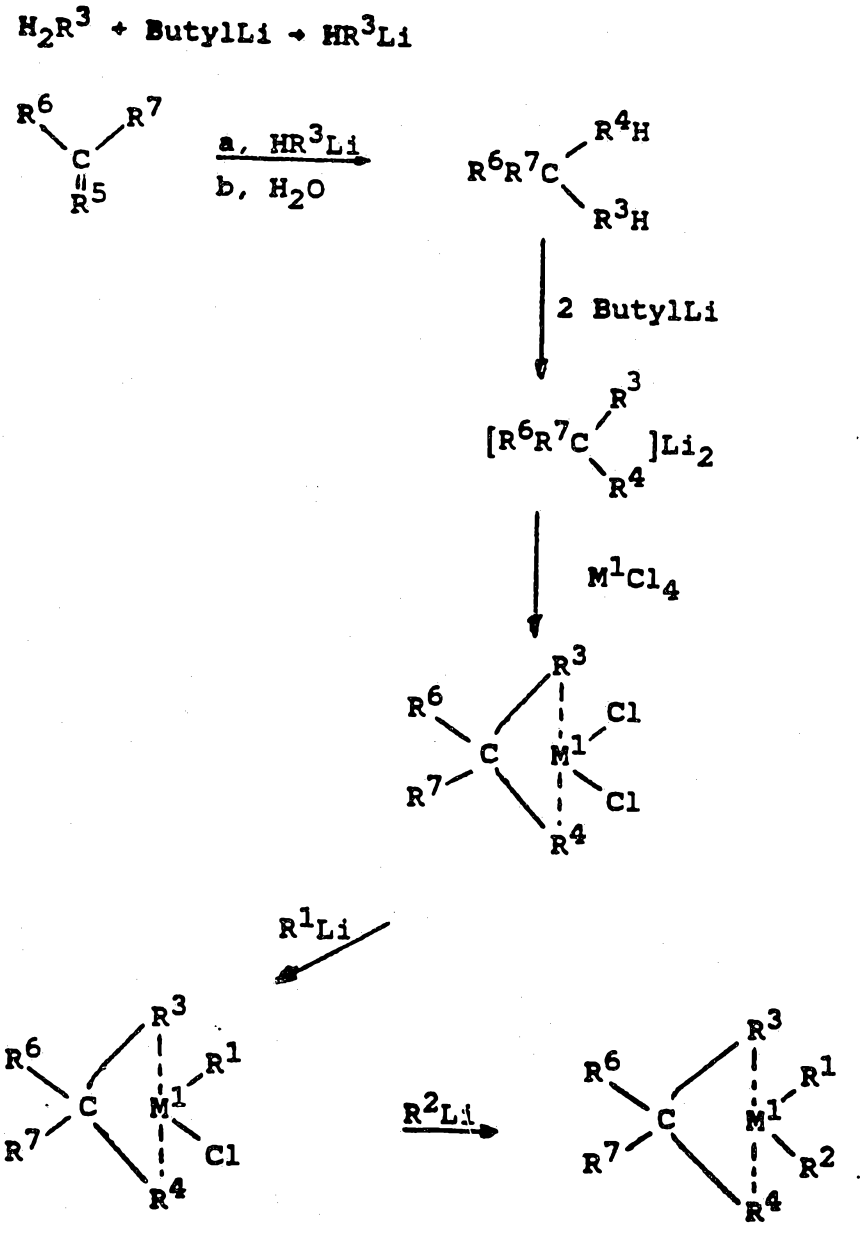

Metallocenes which are preferably employed are (arylalkylidene)(9-fluorenyl)(cyclopentadienyl)zirconium dichloride, (diarylmethylene)(9-fluorenyl)(cyclopentadienyl)zirconium dichloride and (dialkylmethylene)(9-fluorenyl)(cyclopentadienyl)zirconium dichloride.

(Methyl(phenyl)methylene)(9-fluorenyl)(cyclopentadienyl-zirconium dichloride, (diphenylmethylene)(9-fluorenyl)-(cyclopentadienyl)zirconium dichloride and (di-

methylmethylene) (9-fluorenyl) (cyclopentadienyl) zirconium dichloride are particularly preferred here. Other metallocenes which may be mentioned are:-

(diphenylsilyl)(fluorenyl)(cyclopentadienyl) zirconium dichloride

(methyl(phenyl)silyl)(fluorenyl)(cyclopentadienyl) zirconium dichloride

(dimethylsilyl)(fluorenyl)(cyclopentadienyl) zirconium dichloride

(ethyiene)(fluorenyl)(cyclopentadienyl) zirconium dichloride

((methyl)ethylene)(fluorenyl)(cyclopentadienyl) zirconium dichloride

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- 20°C in an amount so that about 1 mol of $CuSO_4.5H_2O$ is available for every 4 Al atoms. After slow hydrolysis, alkane being split off, the reaction mixture is left at room temperature for 24 to 48 hours, during which it must be cooled if necessary, so that the temperature does not rise above 30°C. The aluminoxane dissolved in the toluene is then filtered off from the copper sulfate and the solution is concentrated in vacuo. It is assumed that the low molecular weight aluminoxanes undergo condensation to higher oligomers, aluminum trialkyl being split off, in these preparation processes.

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

Of the aluminum salts containing water of crystallization, those which have a high content of water of crystallization are used in particular. Aluminum sulfate hydrate is particularly preferred, above all the compounds $Al_2(SO_4)_3.16H_2O$ and $Al_2(SO_4)_3.18H_2O$, with the particularly high water of crystallization content of 16 and 18 mol of H_2O/mol of $Al_2(SO_4)_3$ respectively.

Another variant for the preparation of aluminoxanes comprises dissolving aluminum trialkyl, preferably aluminum trimethyl, in heptane or toluene in the suspending agent, preferably in liquid monomer, which has been initially introduced into the polymerization vessel, and then reacting the aluminum compound with water.

In addition to the processes described above for the preparation of aluminoxanes, there are others which can be used. Regardless of the nature of the preparation, all the aluminoxane solutions have the common feature of a varying content of unreacted aluminum trialkyl, which is present in free form or as an adduct. This content has an influence on the catalytic activity which has not yet been precisely clarified, and which varies according to the metallocene compound employed.

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

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

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

A significantly longer preactivation is possible, but this usually neither increases the activity nor reduces the activity, although it may be entirely appropriate for storage purposes.

The polymerization is carried out in a known manner in solution, in suspension or in the gas phase, continuously or discontinuously in one or more stages at a temperature of -60 to 200°C, preferably -30 to 100°C, in particular 0 to 80°C.

The total pressure in the polymerization system is 0.5 to 100 bar. Polymerization in the pressure range of 5 to 60 bar which is of particular industrial interest is preferred. Monomers of boiling point higher than the polymerization temperature are preferably polymerized under normal pressure.

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

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

A benzine or hydrogenated diesel oil fraction can furthermore be used. Toluene can also be used. The polymerization is preferably carried out in a liquid monomer.

Olefins of the formula $R^aCH=CHR^b$, in which R^a and R^b are identical or different and denote a hydrogen atom or an alkyl radical having 1 to 28 carbon atoms, or wherein R^a and R^b, with the atoms joining them, can form a ring, are polymerized or copolymerized. Examples of such olefins

are ethylene, propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, norbornene or norbornadiene. Propylene, 1-butene and 4-methyl-1-pentene are preferred.

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

Polymer powders which consist of compact spherical particles having a very narrow particle size distribution and a high bulk density can be prepared by means of the process according to the invention. The polymer powder is distinguished by very good free-flowing properties.

The polymer has a very high molecular weight, a very narrow molecular weight distribution (polydispersivity) and a very high syndiotactic index. Shaped articles produced from the polymers are distinguished by a high transparency, flexibility, tear strength and an excellent surface gloss.

Polymers of higher molecular weight are formed by using specifically bridged metallocenes according to the invention than by using metallocenes of the prior art. At the same time, the syndiotactic index is improved significantly.

The polymers prepared according to the invention are particularly suitable for the production of films and hollow bodies.

The following examples are intended to illustrate the invention.

In the examples:

VN = viscosity number in cm^3/g

M_w = weight-average molecular weight in g/mol

M_n = number-average molecular weight in g/mol

M_w/M_n = polydispersity

The molecular weights were determined by gel permeation chromatography.

SI = syndiotactic index, determined by ^{13}C-NMR spectroscopy

n_{syn} = average syndiotactic block length $(1 + \frac{2rr}{m})$

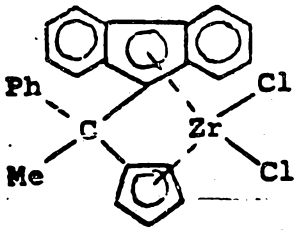
BIH = ball indentation hardness in Nmm^{-2} (measured on flat test specimens 4 mm thick in accordance with DIN 53456/1973)

MFI = melt flow index (230°C, 5 kg; DIN 53735)

All the following working operations of the metallocene synthesis are carried out under an inert gas using absolute solvents.

Example 1

(Phenyl(methyl)methylene)(9-fluorenyl)(cyclopentadienyl)-zirconium dichloride



A solution of 67.8 mmol of lithiumfluorene in 50 cm^3 of tetrahydrofuran is added to a solution of 11.4 g (67.8 mmol) of 6-methyl-6-phenyl-fulvene in 40 cm^3 of tetrahydrofuran at room temperature. After the mixture had been stirred at room temperature for 2 hours, 60 cm^3 of water were added. The substance which precipitated during this procedure was filtered off with suction, washed with diethyl ether and dried under an oil pump

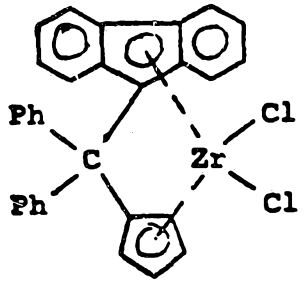
vacuum. 19.1 g (84.2%) of 2,2-cyclopentadienyl(9-fluorenyl)-ethylbenzene were obtained (correct elemental analyses; ^{1}H-NMR spectrum).

10.0 g (29.9 mmol) of the compound were dissolved in 60 cm^3 of tetrahydrofuran, and 26 cm^3 (65 mmol) of a 2.5 molar hexane solution of n-butyllithium were added at 0°C. After the mixture had been stirred for 15 minutes, the solvent was stripped off in vacuo. The dark red residue which remained was washed several times with hexane and dried under an oil pump vacuum. 15.6 g of the red dilithium salt were obtained as a tetrahydrofuran adduct; this contained about 30% of tetrahydrofuran.

14.9 mmol of the dilithium salt were added to a suspension of 3.48 g (14.9 mmol) of $ZrCl_4$ in 70 cm^3 of CH_2Cl_2 at -78°C. After the mixture had been slowly warmed to room temperature, it was stirred at room temperature for a further hour and filtered over a G4 frit; the residue was rinsed several times with CH_2Cl_2. The red filtrate was concentrated completely and the orange-red residue was recrystallized from CH_2Cl_2. 1.8 g (25%) of methylphenylmethylene-(cyclopentadienyl-9-fluorenyl)zirconium dichloride were obtained as a pink-colored crystalline powder. ^{1}H-NMR spectrum (100 MHz, $CDCl_3$): 7.1 - 8.25 (m, Flu-H, Ph-H), 6.90 (m, Ph-H), 6.10 - 6.50 (m, Ph-H, Cp-H), 5.90, 5.75 (2 x m, Cp-H), 2.55 (s, CH_3).

Example 2

Diphenylmethylene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride



12.3 cm^3 (30.7 mmol) of a 2.5 molar hexane solution of n-butyllithium were slowly added to a solution of 5.10 g (30.7 mmol) of fluorene in 60 cm^3 of tetrahydrofuran at room temperature. After 40 minutes, 7.07 g (30.7 mmol) of diphenylfulvene were added to the orange solution and the mixture was stirred overnight. 60 cm^3 of water were added to the dark red solution, whereupon the solution became yellow in color, and the solution was extracted with ether. The ether phase was dried over $MgSO_4$ and concentrated and the residue was left to crystallize at -35°C. 5.1 g (42%) of 1,1-cyclopentadienyl-(9-fluorenyl)-diphenylmethane were obtained as a beige powder.

2.0 g (5.0 mmol) of the compound were dissolved in 20 cm^3 of tetrahydrofuran, and 6.4 cm^3 (10 mmol) of a 1.6 molar solution of butyllithium in hexane were added at 0°C. After the mixture had been stirred at room temperature for 15 minutes, the solvent was stripped off and the red residue was dried under an oil pump vacuum and washed several times with hexane. After the product had been dried under an oil pump vacuum, the red powder was added to a suspension of 1.16 g (5.00 mmol) of $ZrCl_4$ at -78°C. After slowly warming up, the mixture was stirred at room temperature for a further 2 hours. The pink-colored suspension was filtered over a G3 frit. The pink-red residue was washed with 20 cm^3 of CH_2Cl_2, dried under an oil pump vacuum and extracted with 120 cm^3 of toluene. After the solvent had been stripped off and the residue had been dried under an oil pump vacuum, 0.55 g of the zirconium complex was obtained in the form of a pink-red crystalline powder.

The orange-red filtrate of the reaction mixture was concentrated and the residue was left to crystallize at -35°C. A further 0.45 g of the complex crystallized from CH_2Cl_2. Total yield 1.0 g (36%). Correct elemental analyses. The mass spectrum showed M^+ = 556. ^1H-NMR spectrum (100 MHz, $CDCl_3$): 6.90 - 8.25 (m, 16, Flu-H, Ph-H), 6.40 (m,2,Ph-H), 6.37 (t,z, Cp-H), 5.80 (t,z, Cp-H).

The metallocene dimethylmethylene(fluorenyl)(cyclopentadienyl)zirconium dichloride was prepared in accordance with the literature reference J. Am. Chem. Soc. 110 (1988) 6255.

Example 3

A dry 16 dm^3 reactor was flushed with nitrogen and filled with 10 dm^3 of liquid propylene. 30 cm^3 of a toluene solution of methylaluminoxane (corresponding to 40 mmol of Al, average degree of oligomerization of the methylaluminoxane n = 20) were then added and the mixture was stirred for 15 minutes. In parallel with this, 12.4 mg (0.223 mmol) of diphenylmethylene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride were dissolved in 15 cm^3 of a toluene solution of methylaluminoxane (20 mmol of Al). After 15 minutes, the solution was introduced into the reactor and the polymerization temperature was brought to 70°C. The polymerization had ended after a polymerization time of 1 hour. 2.19 kg of polypropylene, corresponding to a metallocene activity of 176.6 kg of polypropylene/g of metallocene x hour, were obtained.
VN = 385 cm^3/g; M_w = 519,000, M_n = 173,000, M_w/M_n = 3.0; SI = 95.9%, n_{syn} = 36.7; MFI 230/5 = 0.2 dg/minute.

Example 4

The procedure was analogous to Example 3, but 11.9 mg (0.021 mmol) of diphenylmethylene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride was employed. The polymerization temperature was 60°C and the polymerization time was 1 hour. 0.95 kg of polypropylene, corresponding to a metallocene activity of 79.8 kg of polypropylene/g of metallocene x hour, were obtained.
VN = 459 cm^3/g; M_w = 547,000, M_n = 188,000, M_w/M_n = 2.9; SI = 96.5%, n_{syn} = 38.4; MFI 230/5 = < 0.1 dg/minute.

Example 5

The procedure was analogous to Example 3, but 18.5 mg (0.033 mmol) of diphenylmethylene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride were employed. The

polymerization temperature was 50°C and the polymerization time was 80 minutes.
0.69 kg of polypropylene, corresponding to a metallocene activity of 28.0 kg of polypropylene/g of metallocene x hour, were obtained.
VN = 565 cm^3/g; M_w = 584,000, M_n = 241,500, M_w/M_n = 2.4; SI = 95.9%, n_{syn} = 36.4; MFI 230/5 = < 0.1 dg/minute.

Example 6

The procedure was analogous to Example 3, but 30.1 mg (0.054 mmol) of diphenylmethylene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride were employed. The polymerization temperature was 40°C and the polymerization lasted 1 hour.
0.35 kg of polypropylene, corresponding to a metallocene activity of 11.6 kg of polypropylene/g of metallocene x hour, was obtained.
VN = 664 cm^3/g; M_w = 925,000, M_n = 329,000, M_w/M_n = 2.8; SI = 96.7%, n_{syn} = 40.1; MFI 230/5 = < 0.1 dg/minute.

Example 7

The procedure was analogous to Example 3, but 40.0 mg (0.072 mmol) of diphenylmethylene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride were employed. The polymerization temperature was 30°C and the polymerization time was 2 hours.
0.50 kg of polypropylene, corresponding to a metallocene activity of 6.3 kg of polypropylene/g of metallocene x hour, was obtained.
VN = 788 cm^3/g; $M_w = 1.05 \cdot 10^6$, M_n = 367,000, M_w/M_n = 2.8; SI = 97.1%, n_{syn} = 46.0; MFI 230/5 = < 0.1 dg/minute.

Example 8

The procedure was analogous to Example 3, but 10.9 mg (0.022 mmol) of phenyl(methyl)methylene(9-fluorenyl)-(cyclopentadienyl)zirconium dichloride were employed. 2.05 kg of polypropylene were obtained, corresponding to a metallocene activity of 188.1 kg of polypropylene/g of metallocene x hour.

VN = 305 cm^3/g; M_w = 435,000, M_n = 181,000, M_w/M_n = 2.4; SI = 96.1%, n_{syn} = 37.4; MFI 230/5 = 0.5 dg/minute.

Example 9

The procedure was analogous to Example 4, but 13.5 mg (0.027 mmol) of phenyl(methyl)methylene(9-fluorenyl)-(cyclopentadienyl)zirconium dichloride were employed. 0.94 kg of polypropylene, corresponding to a metallocene activity of 69.5 kg of polypropylene/g of metallocene x hour, was obtained.

VN = 364 cm^3/g; M_w = 490,000, M_n = 188,500, M_w/M_n = 2.6; SI = 97.0%, n_{syn} = 40.2; MFI 230/5 = 0.25 dg/minute.

Example 10

The procedure was analogous to Example 6, but 35.0 mg (0.071 mmol) of phenyl(methyl)methylene(9-fluorenyl)-(cyclopentadienyl)zirconium dichloride were employed and the polymerization lasted 5 hours.

1.77 kg of polypropylene were obtained, corresponding to a metallocene activity of 10.1 kg of polypropylene/g of metallocene x hour.

VN = 545 cm^3/g; M_w = 554,000, M_n = 205,000, M_w/M_n = 2.7; SI = 96.9%, n_{syn} = 39.4; MFI 230/5 = < 0.1 dg/minute.

Example 11

The procedure was analogous to Example 3, but 30 mg (0.061 mmol) of phenyl(methyl)methylene(9-fluorenyl)-(cyclopentadienyl)zirconium dichloride were employed, the polymerization temperature was 22°C and the polymerization time was 5 hours.

0.83 kg of polypropylene, corresponding to a metallocene activity of 5.5 kg of polypropylene/g of metallocene x hour, was obtained.

VN = 750 cm^3/g; M_w = 925,000, M_n = 330,500, M_w/M_n = 2.8; SI = 98.1%, n_{syn} = 54.7; MFI 230/5 = < 0.1 dg/minute.

Examples 3 to 11 demonstrate that molecular weights of the polymers which are greater than those achieved with the best hafnocenes known from the literature can be

achieved with zirconocenes, coupled with excellent metallocene activities.

Example 12

A dry 16 dm^3 reactor was flushed with nitrogen and filled with 1.6 Ndm^3 (corresponding to 0.1 bar) of hydrogen and with 10 dm^3 of liquid propylene. 30 cm^3 of a toluene solution of methylaluminoxane (corresponding to 40 mmol of Al, average degree of oligomerization of the methylaluminoxane n = 20) were then added and the mixture was stirred for 15 minutes. In parallel with this, 20.2 mg (0.047 mmol) of dimethylmethylene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride were dissolved in 15 cm^3 of a toluene solution of methylaluminoxane (20 mmol of Al). After 15 minutes, the solution was metered into the reactor and the polymerization temperature was brought to 50°C. The polymerization lasted 2 hours. 1.38 kg of syndiotactic polypropylene, corresponding to a metallocene activity of 34.2 kg of polypropylene/g of metallocene x hour, were obtained.

VN = 117 cm^3/g; M_w = 101,000, M_n = 45,150, M_w/M_n = 2.2; SI = 95.0%, BIH = 35 Nmm^{-2}; MFI 230/5 = 44 dg/minute.

Example 13

The procedure was as in Example 12, but 8 Ndm^3 (corresponding to 0.5 bar) of hydrogen and 11.9 mg (0.028 mmol) of the metallocene were employed. The polymerization temperature was 60°C and the polymerization lasted 2 hours.

1.19 kg of syndiotactic propylene, corresponding to a metallocene activity of 50.0 kg of polypropylene/g of metallocene x hour, were obtained.

VN = 85.0 cm^3/g; M_w = 74,100, M_n = 35,000, M_w/M_n = 2.1; SI = 96.1%, BIH = 40 Nmm^{-2}; MFI 230/5 = 123 dg/minute.

Example 14

The procedure was as in Example 12, but 40 Ndm^3 (corresponding to 2.5 bar) of hydrogen and 12.0 mg (0.028 mmol) of the metallocene were employed. The poly-

merization temperature was 60°C and the polymerization lasted 3 hours.

2.34 kg of syndiotactic propylene, corresponding to a metallocene activity of 65.0 kg of polypropylene/g of metallocene x hour, were obtained.

VN = 68 cm^3/g; M_w = 57,100, M_n = 22,850, M_w/M_n = 2.5; SI = 97.2%, BIH = 40 Nmm^{-2}; MFI 230/5 = 0.25 dg/minute.

Example 15

The procedure was analogous to Example 12, but 10.3 mg (0.019 mmol) of diphenylmethylene(fluorenyl)(cyclopentadienyl)zirconium dichloride were employed. The polymerization lasted 4 hours.

1.78 kg of polypropylene, corresponding to a metallocene activity of 43.2 kg of polypropylene/g of metallocene x hour, were obtained.

VN = 430cm^3/g; M_w = 434,000, M_n = 179,500, M_w/M_n = 2.4; SI = 96.7%, n_{syn} = 38.5.

According to the ^{13}C-NMR, the polymer chains contained no unsaturated chain ends.

Example 16

The procedure was analogous to Example 12, but 40 Ndm^3 (corresponding to 2.5 bar) of hydrogen and 10.7 mg (0.019 mmol) of diphenylmethylene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride were employed. The polymerization lasted 1 hour.

1.06 kg of polypropylene were obtained, corresponding to a metallocene activity of 99.1 kg of polypropylene/g of metallocene x hour.

VN = 137 cm^3/g; M_w = 88,700, M_n = 39,400, M_w/M_n = 2.3; SI = 96.9%, n_{syn} = 39.1; MFI 230/5 = 36 dg/min, BIH = 39 Nmm^{-2}.

Examples 12 - 16 show that the molecular weight can be regulated using hydrogen.

Example 17

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

In parallel with this, 10.3 mg (0.024 mmol) of dimethylmethylene(9-fluoenyl)(cyclopentadienyl)zirconium dichloride were dissolved in 15 cm^3 of a toluene solution of methylaluminoxane (20 mmol of Al). After 15 minutes, the solution was introduced into the reactor and the polymerization temperature was brought to 70°C. The polymerization had ended after 1 hour.

1.33 kg of syndiotactic polypropylene, corresponding to a metallocene activity of 129.1 kg of polypropylene/g of metallocene x hour, were obtained.

VN = 105 cm^3/g; M_w = 84,300, M_n = 39,900, M_w/M_n = 2.1; SI = 94.6%, BIH = 33 Nmm^{-2}; MFI 230/5 = 97 dg/minute.

Example 18

The procedure was analogous to Example 17, but 13.9 mg (0.032 mmol) of the metallocene were used, the polymerization temperature was 60°C and the polymerization lasted 2.5 hours.

2.56 kg of syndiotactic polypropylene, corresponding to a metallocene activity of 73.7 kg of polypropylene/g of metallocene x hour, were obtained.

VN = 125 cm^3/g; M_w = 95,250, M_n = 45,950, M_w/M_n = 2.1; SI = 94.6%, MFI 230/5 = 55 dg/minute.

Example 19

The procedure was analogous to Example 17, but 26.4 mg (0.061 mmol) of the metallocene were employed and the polymerization temperature was 50°C.

1.25 kg of syndiotactic polypropylene were obtained, corresponding to a metallocene activity of 47.3 kg of

polypropylene/g of metallocene x hour.
VN = 135 cm^3/g; M_w = 114,500, M_n = 55,750, M_w/M_n = 2.1; SI = 95.0%, MFI 230/5 = 27.5 dg/minute.

Example 20

The procedure was analogous to Example 17, but 36.6 mg (0.085 mmol) of the metallocene were used and the polymerization temperature was 40°C.
0.5 kg of syndiotactic polypropylene, corresponding to a metallocene activity of 13.7 kg of polypropylene/g of metallocene x hour, was obtained.
VN = 155 cm^3/g; M_w = 129,000, M_n = 56,000, M_w/M_n = 2.3; SI = 96.0%; MFI 230/5 = 17.3 dg/minute.

Example 21

The procedure was analogous to Example 17, but 51.5 mg (0.119 mmol) of the metallocene were employed, the polymerization temperature was 25°C and the polymerization lasted 4 hours.
0.98 kg of syndiotactic polypropylene, corresponding to a metallocene activity of 4.8 kg of polypropylene/g of metallocene x hour, was obtained.
VN = 200 cm^3/g; M_w = 175,500, M_n = 66,550, M_w/M_n = 2.6; SI = 95.7%, MFI 230/5 = 6.3 dg/minute.

Using the metallocene dimethylmethylene(9-fluorenyl)-(cyclopentadienyl)zirconium dichloride, which is known from the literature, Examples 17 - 21 show that, by the polymerization process according to the invention, in each case polymers having significantly higher molecular weights can be prepared than has been found in the literature (J. Am. Chem. Soc. 110 (1988), 6255) at the particular polymerization temperature.

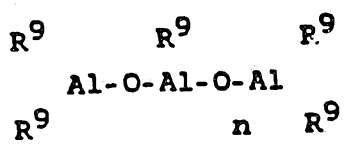
Polymerization temperature [°C]	M_w [g/mol] Process according to the invention	Literature
70	84 300	55 000
60	95 250	52 000
50	114 500	69 000
25	175 500	133 000

In particular, the significant decrease in the molecular weight at a polymerization temperature above 25°C and a reduction to a constant molecular weight value at a polymerization temperature below 50°c does not occur in the polymerization process according to the invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

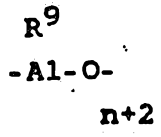
Patent claims

1. A process for the preparation of a syndiotactic polyolefin by polymerization or copolymerization of an olefin of the formula $R^aCH=CHR^b$, in which R^a and R^b are identical or different and denote a hydrogen atom or an alkyl radical having 1 to 28 carbon atoms, or R^a and R^b, with the atoms joining them, can form a ring, at a temperature of -60 to 200°C under a pressure of 0.5 to 100 bar in solution, suspension or the gas phase in the presence of a catalyst which consists of a metallocene as the transition metal component and an aluminoxane of the formula II



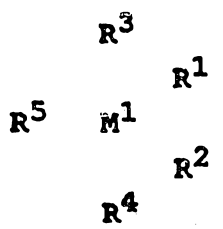
(II)

for the linear type and/or of the formula III



(III)

for the cyclic type, in which, in the formulae II and III, R^9 denotes a C_1-C_6-alkyl group or phenyl or benzyl and n is an integer from 2 to 50, which comprises carrying out the polymerization in the presence of a catalyst, the transition metal component of which is a compound of the formula I



(I)

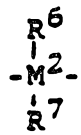
in which

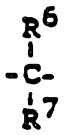
M^1 is ~~titanium,~~ zirconium, ~~vanadium, niobium or tantalum,~~ R^1 and R^2 are identical or different and denote a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group or a C_8-C_{40}-arylalkenyl group,

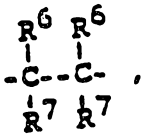
R^3 and R^4 are different and denote a mono- or polynuclear hydrocarbon radical which can form a sandwich structure with the central atom M^1,

R^5 is

$$\begin{array}{c} R^6 \\ | \\ -M^2- \\ | \\ R^7 \end{array}, \qquad \begin{array}{c} R^6 \\ | \\ -C- \\ | \\ R^7 \end{array}, \qquad \begin{array}{cc} R^6 & R^6 \\ | & | \\ -C- & -C- \\ | & | \\ R^7 & R^7 \end{array},$$







in which R^6 and R^7 are identical or different and denote 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}-fluoroaryl group, a C_6-C_{10}-aryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^6 and R^7 in each case with the atoms joining them, form a ring, and

M^2 is silicon.

2. The use of the syndiotactic polyolefin prepared as claimed in claim 1 for the production of films and shaped articles by extrusion, injection molding, blow molding or compression sintering.

DATED this 6th day of March 1992.

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