(CONVENTION. By one more persons and/or a Company.) Form 4

COMMONWEALTH OF AUSTRALIA

612276

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 [XX] (1) HOECHST AKTIENGESELLSCHAFT

of 50 Bruningstrasse, D6230 Frankfurt/Main 80, Federal Republic of Germany

M

(2) Here insert Title of Invention.

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

1-OLEFIN ISOBLOCK POLYMER AND PROCESS FOR ITS MANUFACTURE

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

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

P38 26 075.1

(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 30th July 1988

My/Our address for service is ~~Messrs. Edwd. Waters & Sons, Patent Attorneys,~~ Watermark Patent & Trademark Attorneys 50 Queen Street, Melbourne, Victoria, Australia.

DATED this 27th day of July 19 89

(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.

Edwd. Waters & Sons, Melbourne.

Form 7

COMMONWEALTH OF AUSTRALIA

Patents Act 1952

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

In support of the Convention application made under Part XVI. of the Patents Act 1952 by HOECHST AKTIENGESELLSCHAFT of 45, Brüningstrasse, D-6230 Frankfurt/Main 80, Federal Republic of Germany for a patent for an invention entitled:

1-OLEFIN ISOBLOCK POLYMER AND PROCESS FOR ITS MANUFACTURE

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 38 26 075.1 on July 30, 1988
by HOECHST AKTIENGESELLSCHAFT

3. a) Volker Dolle, Hattersheimer Straße 15, D-6233 Kelkheim (Taunus)
b) Jürgen Rohrmann, Die Ritterwiesen 10, D-6237 Liederbach
c) Andreas Winter, Gundelhardtstraße 2, D-6233 Kelkheim (Taunus)
d) Martin Antberg, Sachsenring 10, D-6238 Hofheim am Taunus
e) Robert Klein, Im Neufeld 46, D-6000 Frankfurt am Main
a) - e) Federal Republic of Germany

is/are the actual inventor(s) of the invention and the facts upon which HOECHST AKTIENGESELLSCHAFT

is entitled to make the application are as follows:

The said HOECHST AKTIENGESELLSCHAFT

is the assignee of the said

Volker Dolle, Jürgen Rohrmann, Andreas Winter, Martin Antberg, Robert Klein

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 16th day of June 1989

To the Commissioner of Patents

HOECHST AKTIENGESELLSCHAFT

ppa. Tergau i.V. Lapice

Prokurist Authorized Signatory

PAT 510

(12) PATENT ABRIDGMENT (11) Document No. AU-B-39053/89
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 612276

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1-OLEFIN ISOBLOCK POLYMER AND PROCESS FOR ITS MANUFACTURE

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(56) Prior Art Documents
AU 27319/88 C08F 110/06
AU 39056/89 C08F 110/06
AU 27322/89 C08F 110/06

(57) Claim

1. An isoblock polymer of a 1-olefin of the formula $RCH=CH_2$, in which R is an alkyl radical having 1 to 28 C atoms, with molecular chains containing isotactic sequences which are separated from one another in each case by one monomer unit of opposite configuration, and with a sequence length of 8 to 50 monomer units.

Form 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952-69

COMPLETE SPECIFICATION

(ORIGINAL)

612276

Class Int. Class

Application Number:
Lodged:

Complete Specification Lodged:
Accepted:
Published:

Priority :

Related Art :

Name of Applicant : HOECHST AKTIENGESELLSCHAFT

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

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

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

Complete Specification for the invention entitled:

1-OLEFIN ISOBLOCK POLYMER AND PROCESS FOR ITS MANUFACTURE

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

HOECHST AKTIENGESELLSCHAFT Dr. DA/gm HOE 88/F 188

Description

1-Olefin isoblock polymer and process for its manufacture

The invention relates to a 1-olefin isoblock polymer with long isotactic sequences and to a process for its manufacture.

It is known that polypropylene exists in various structural isomers:

(a) highly isotactic polypropylene in whose molecular chains almost all tertiary C atoms have the same configuration,

(b) isotactic stereoblock PP in whose molecular chains isotactic blocks of opposite configuration alternate regularly with one another,

(c) syndiotactic polypropylene in whose molecular chains every other tertiary C atom has the same configuration,

(d) atactic polypropylene in whose molecular chains the tertiary C atoms have a random configuration,

and

(e) atactic-isotactic stereoblock PP in whose molecular chains isotactic and atactic blocks alternate with one another.

A process for the manufacture of isotactic stereoblock polymers is known in which propylene is polymerized with the aid of a metallocene of a metal of group IVb, Vb or VIb of the periodic table (q.v. US patent 4,522,982). This metallocene is a mono-, di- or tri-cyclopentadienyl or substituted cyclopentadienyl compound of a metal, especially titanium. An aluminoxane is used as cocatalyst.

However, the titanocenes which are preferably used do not have sufficient heat stability in dilute solution to be

usable in an industrial process. Moreover, in this process, products with longer isotactic sequences (n greater than 6) are only obtained at very low temperature (-60°C). Finally, the cocatalysts must be used in comparatively high concentration in order to achieve an adequate catalytic yield, so the catalyst residues contained in the polymer product have to be removed in a separate purification step.

It is further known that stereoblock polymers of 1-olefins with long isotactic sequences can be obtained at industrially favorable polymerization temperatures by means of a catalyst consisting of a metallocene compound with cyclopentadienyl radicals substituted by chiral groups, and of an aluminoxane (q.v. European patent application A 269987).

It is further known that stereoblock polymers of 1-olefins with a broad monomodal or multimodal molecular weight distribution can be obtained when 1-olefins are polymerized using a catalyst consisting of a chiral metallocene containing bridges and of an aluminoxane (q.v. European patent application A 269986). The polymers are particularly suitable for the production of transparent sheets.

It is also known that when a catalyst based on bis-cyclopentadienyl compounds of zirconium and on an aluminoxane is used in the polymerization of propylene, only atactic polymer is obtained (q.v. European patent application A 69951).

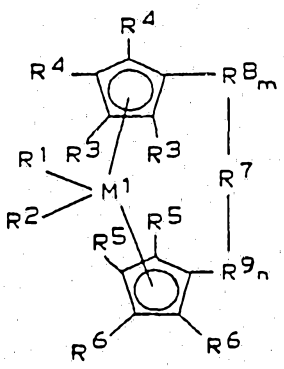
Finally, highly isotactic polypropylene can be manufactured by means of soluble stereorigid chiral zirconium compounds (q.v. European patent application A 185 918).

A polymerization process has been found in which a polymer of regular molecular structure and high molecular weight is obtained in high yield at industrially favo-

rable process temperatures.

The invention thus relates to an isoblock polymer of a 1-olefin of the formula $RCH=CH_2$, in which R is an alkyl radical having 1 to 28 C atoms, with molecular chains containing isotactic sequences which are separated from one another in each case by one monomer unit of opposite configuration, and with a sequence length of 3 to 50 monomer units.

The invention further relates to a process for the manufacture of the above-mentioned isoblock polymer by the polymerization of a 1-olefin of the formula $RCH=CH_2$, in which R is an alkyl radical having 1 to 28 C atoms, at a temperature of -60 to 100°C and a pressure of 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst consisting of a metallocene and an aluminoxane, wherein the metallocene is a compound of formula I:



(I),

in which

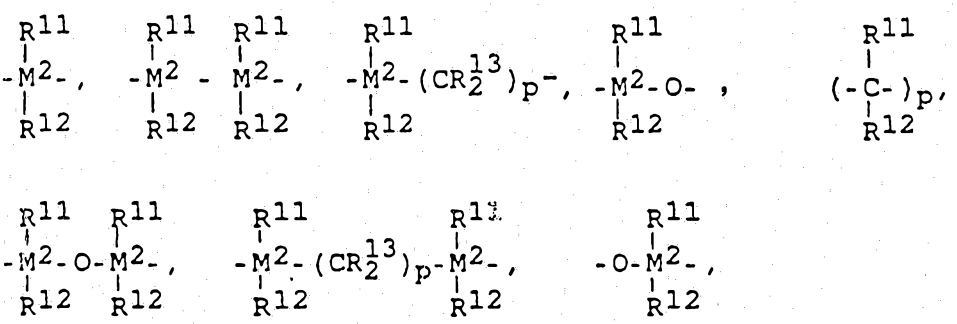
M^1 is a metal of group IVb, Vb or VIb of the periodic table,

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

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

R^3, R^4, R^5 and R^6 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, $-NR^{10}_2$, $-SR^{10}$, $-OSi_rR^{10}_{3r+1}$, $-Si_rR^{10}_{3r+1}$ or $-PR^{10}_2$, in which R^{10} is a halogen atom or a C_1-C_{10}-alkyl group, or pairs of adjacent radicals R^3, R^4, R^5 and R^6 form a ring with the C atoms to which they are bonded, and

R^7 is



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

in which

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

M^2 is silicon, germanium or tin,

p is 1, 2 or 3,

R^8 and R^9 are identical or different and are a group =$CR^{11}R^{12}$, in which R^{11} and R^{12} are as defined above, and

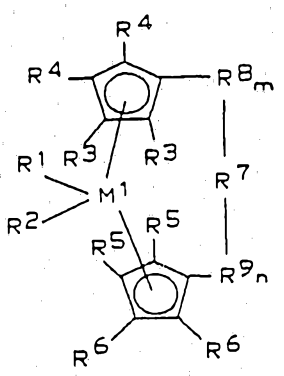
m and n are identical or different and are zero, 1 or 2, m + n being zero, 1 or 2.

The isoblock polymer according to the invention is a polymer of a 1-olefin of the formula $R-CH=CH_2$, in which R is an alkyl radical having 1 to 28 C atoms, preferably 1 to 10 C atoms, in particular one C atom, for example propylene, but-1-ene, hex-1-ene, 4-methylpent-1-ene or oct-1-ene. The polymer is especially a propylene polymer.

The molecular chains of this polymer contain isotactic sequences which are separated from one another in each case by one monomer unit of opposite configuration. The molecular chains preferably consist of isotactic sequences which are separated from one another in each case by one monomer unit of opposite configuration. The isotactic sequences have an average length of 3 to 50 monomer units.

As a consequence of this steric structure, the isoblock polymers according to the invention are amorphous or partly crystalline according to the molecular weight and the length of the isotactic sequences. Depending on the crystallinity, the polymers are obtained as granular powders or as compact masses. The partly crystalline isoblock polymers have a low melting point by comparison with isotactic polymers. Isoblock polymers possess rubber-like properties.

The catalyst to be used for the process according to the invention consists of a metallocene compound of formula I and an aluminoxane. In formula I:



(I),

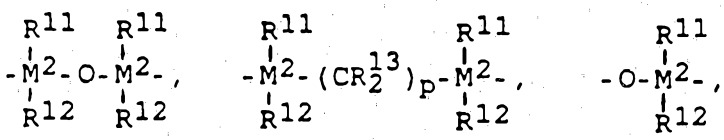
M^1 is a metal of group IVb, Vb or VIb of the periodic table, for example titanium, zirconium, hafnium, vanadium, nicbium, tantalum, chromium, molybdenum or tungsten, preferably zirconium or hafnium.

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

R^3, R^4, R^5 and R^6 are identical or different, preferably different, and are a hydrogen atom, a halogen atom, preferably a fluorine, chlorine or bromine atom, a C_1-C_{10}-, preferably C_1-C_3-alkyl group, $-NR^{10}_2$, $-SR^{10}$, $-OSi_rR^{10}_{3r+1}$, $-Si_rR^{10}_{3r+1}$ or $-PR^{10}_2$, in which R^{10} is a halogen atom, preferably a chlorine atom, or a C_1-C_{10}-, preferably C_1-C_3-alkyl group, or pairs of adjacent radicals R^3, R^4, R^5 and R^6 form a ring with the C atoms to which they are bonded.

R^7 is

$$-M^2(R^{11})(R^{12})-, \quad -M^2(R^{11})-M^2(R^{11})(R^{12})-, \quad -M^2(R^{11})(R^{12})-(CR^{13}_2)_p-, \quad -O-M^2(R^{11})(R^{12})-O-, \quad (-C(R^{11})(R^{12})-)_p,$$



=BR^{11}, =AlR^{11}, -Ge-, -Sn-, -O-, -S-, =S=O, =SO_2, =NR^{11}, =CO, =PR^{11} or =P(O)R^{11}, in which R^{11}, R^{12} and R^{13} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, preferably a C_1-C_4-alkyl group, especially a methyl group, a C_1-C_{10}-fluoroalkyl group, preferably a CF_3 group, a C_6-C_{10}-, preferably C_6-C_8-aryl group, a C_6-C_{10}-fluoroaryl group, preferably a hexafluorophenyl group, a C_1-C_{10}-, preferably C_1-C_4-alkoxy group, especially a methoxy group, a C_2-C_{10}-, preferably C_2-C_4-alkenyl group, a C_7-C_{40}-, preferably C_7-C_{10}-arylalkyl group, a C_8-C_{40}-, preferably C_8-C_{12}-arylalkenyl group or a C_7-C_{40}-, preferably C_7-C_{12}-alkylaryl group, or R^{11} and R^{12} or R^{11} and R^{13} form a ring together with the atoms to which they are bonded.

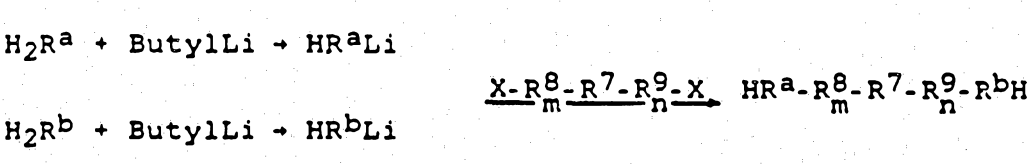
M^2 is Si, Ge or Sn and p is 1, 2 or 3.

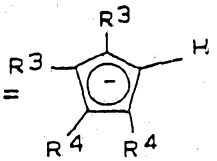
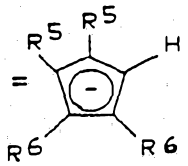
R^7 is preferably =$SiR^{11}R^{12}$, =$GeR^{11}R^{12}$, -S-, =S=O or =PR^{11}.

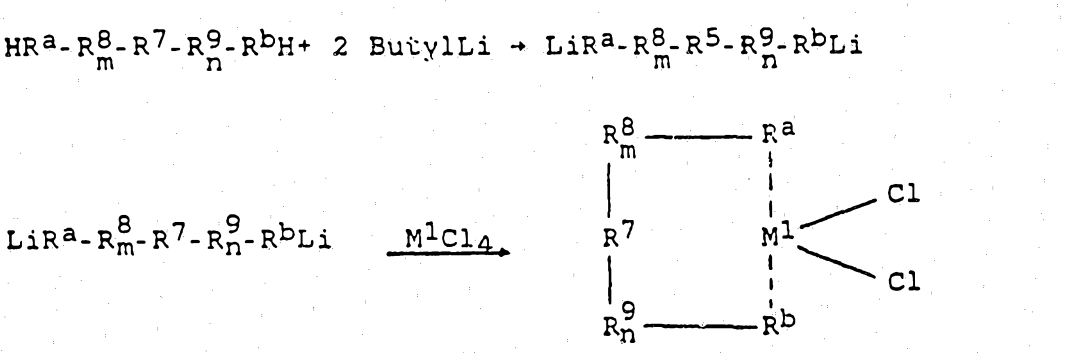
R^8 and R^9 are identical or different and are a group =$CR^{11}R^{12}$, in which R^{11} and R^{12} are as defined above.

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

The metallocenes described above can be prepared according to the following reaction scheme:

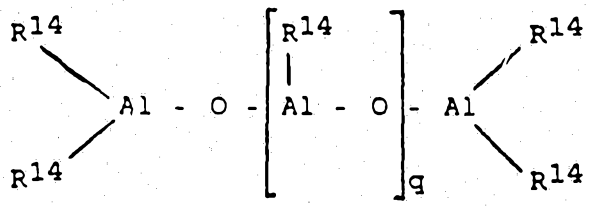


(X = Cl, Br, I, O-Tosyl, HR^a =  , HR^b = )



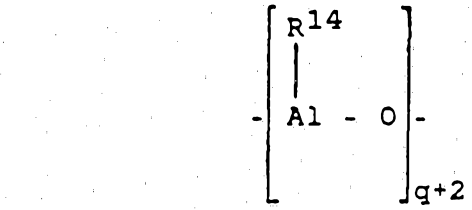
It is especially preferred to use indenyl(h5-cyclopentadienyl)(dimethylsilyl)hafnium dichloride (= 1) and indenyl(h5-cyclopentadienyl)(dimethylsilyl)zirconium dichloride (= 2) as the metallocene compounds.

The activator is an aluminoxane of formula (II):



(II)

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



(III)

for the cyclic type. In these formulae, R^{14} is a C_1-C_6-alkyl group, preferably methyl, ethyl or isobutyl, in particular methyl, and q is an integer from 2 to 50, preferably 10 to 40. However, the exact structure of the aluminoxane is not certain.

The aluminoxane can be prepared in a variety of ways.

One possibility is carefully to add water to a dilute solution of an aluminum trialkyl, the aluminum trialkyl solution and the water each being introduced in small portions into a larger amount of an inert solvent and the evolution of gas being allowed to finish between successive additions.

In another process, finely powdered copper sulfate pentahydrate is suspended in toluene and, in a glass flask, aluminum trialkyl is added, under inert gas at about -20°C, in an amount such that about 1 mol of $CuSO_4 \cdot 5H_2O$ is available for every 4 Al atoms. After slow hydrolysis with the elimination of alkane, the reaction mixture is left for 24 to 48 hours at room temperature, during which time it must be cooled, if necessary, to prevent the temperature from rising above 30°C. The aluminoxane dissolved in the toluene is then isolated from the copper sulfate by filtration and the solution is concentrated under vacuum. It is assumed that, in this preparative process, the low-molecular aluminoxanes condense to form higher-molecular oligomers with the elimination of aluminum trialkyl.

Furthermore, aluminoxanes are obtained when aluminum trialkyl, preferably aluminum trimethyl, dissolved in an inert aliphatic or aromatic solvent, preferably heptane or toluene, is reacted, at a temperature of -20 to 100°C, with aluminum salts containing water of crystallization, preferably aluminum sulfate. The volume ratio of solvent to aluminum alkyl used is 1:1 to 50:1 - preferably 5:1 - and the reaction time, which can be monitored by means of the alkane eliminated, is 1 to 200 hours - preferably 10 to 40 hours.

Aluminum salts containing water of crystallization which are used in particular are those with a high content of water of crystallization. Aluminum sulfate hydrates are especially preferred, in particular the compounds $Al_2(SO_4)_3 \cdot 16H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$ with the especially high contents of water of crystallization of 16 and 18 mol of H_2O/mol of $Al_2(SO_4)_3$ respectively.

Another variant for the preparation of aluminoxanes consists in dissolving aluminum trialkyl, preferably aluminum trimethyl, in the suspending agent, preferably in the liquid monomer or in heptane or toluene, previously placed in the polymerization kettle, and then reacting the aluminum compound with water.

There are other processes for the preparation of aluminoxanes which can be used in addition to those described above.

Before it is used in the polymerization reaction, the metallocene can be preactivated with an aluminoxane of formula (II) and/or (III), which markedly increases the polymerization activity.

The preactivation of the transition metal compound is carried out in solution, the metallocene preferably being dissolved in a solution of the aluminoxane in an inert hydrocarbon. An aliphatic or aromatic hydrocarbon is

suitable for this purpose. Toluene is preferably used. The concentration of the aluminoxane in the solution is in the range from approx. 1% by weight to the saturation limit, preferably from 5 to 30% by weight, based in each case on the total solution. The metallocene can be used in the same concentration, although it is preferably used 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 temperature is -78°C to 100°C, preferably 0 to 70°C.

The catalyst to be used according to the invention is employed for the polymerization of 1-olefins of the formula $R-CH=CH_2$, in which R is an alkyl radical having 1 to 28 C atoms, preferably 1 to 10 C atoms, in particular one C atom, for example propylene, but-1-ene, hex-1-ene, 4-methylpent-1-ene or oct-1-ene. Propylene is especially preferred.

The polymerization is carried out in known manner in solution, in suspension or in the gas phase, continuously or batchwise, in one or more steps, at a temperature of -60 to 100°C, preferably 0 to 80°C. The pressure is 0.5 to 100 bar. Polymerization preferably takes place in the pressure range from 5 to 60 bar, which is of particular interest to industry.

The metallocene compound is used in a concentration 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^{-4} to 10^{-1} mol, preferably 10^{-3} to 10^{-2} mol per dm^3 of solvent or per dm^3 of reactor volume. In principle, however, higher concentrations are also possible.

In a preferred embodiment of this invention two different metallocenes may be used for the manufacture of polypropylene blends. Accordingly, a further aspect of

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this invention provides a method of manufacture of polypropylene blends comprising following the process of manufacture of an isoblock polymer as described hereinabove but substituting the catalyst used therein for a catalyst consisting of 2 different metallocenes.

If the polymerization is carried out in suspension or solution, the reaction is performed in an inert solvent conventionally used for the Ziegler low-pressure process, for example in an aliphatic or cycloaliphatic hydro-

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carbon; examples of such hydrocarbons which may be mentioned are butane, pentane, hexane, heptane, isooctane, cyclohexane and methylcyclohexane. It is also possible to use a naphtha or hydrogenated diesel oil fraction from which oxygen, sulfur compounds and moisture have been carefully removed. Toluene can also be used. Preferably, the monomer to be polymerized is used as the solvent or suspending agent. The molecular weight of the polymer can be regulated in known manner, hydrogen preferably being used for this purpose. The polymerization time is arbitrary since the time-dependent loss of polymerization activity shown by the catalyst system to be used according to the invention is only slight.

The process according to the invention is distinguished by the fact that the zirconium and hafnium compounds which are preferably used are very temperature-resistant, so they can also be used at temperatures up to about 90°C. Moreover, the aluminoxanes used as cocatalysts can be added in a smaller concentration than hitherto. Finally, it is now possible to manufacture isoblock polymers at temperatures which are of interest to industry.

The following Examples will serve to illustrate the invention. The abbreviations used have the meanings given below:

VN = viscosity number in cm^3/g,
M_w = weight-average molecular weight in g/mol,
M_w/M_n = molecular weight distribution determined by gel permeation chromatography (GPC),
II = isotacticity index determined by ^{13}C NMR spectroscopy, and
n_{iso} = average length of the isotactic sequences.

Isoblock polymers can be detected and distinguished from other 1-olefin polymers by NMR spectroscopy with the aid of triple resonance analysis (q.v. A. Zambelli et al., Macromolecules 8, 687-689 (1975)). Markoff statistics

are valid for isoblock polymers if the following equation is satisfied:

$$2(rr)/(mr) = 1$$

The experimental results are collated in the Table.

Example 1

A dry 16 dm^3 kettle was flushed with nitrogen and filled with 10 dm^3 of liquid propylene. 96 cm^3 of a toluene solution of methylaluminoxane (= MAO, corresponding to 68 mmol of Al, average degree of oligomerization n = 30) were then added and the reaction mixture was stirred at 30°C for 15 minutes.

In a parallel procedure, 43 mg (0.088 mmol) of indenyl-(cyclopentadienyl)(dimethylsilyl)hafnium dichloride were dissolved in 46 cm^3 of MAO (= 33 mmol of Al) and pre-activated by standing for 15 minutes. The solution was then introduced into the kettle. The polymerization system was brought to a temperature of 70°C and then kept for 5 hours at this temperature.

0.69 kg of isoblock polymer was obtained. The activity of the metallocene was therefore 1.57 kg of PP/mmol of Hf/h or 3.2 kg of PP/g of metallocene/h.

The following analytical data were determined on the polymer:
VN = 19 cm^3/g, M_w = 16,100, M_n = 5800, M_w/M_n = 2.8, II = 72.8%, n_{iso} = 5.3.

Example 2

The procedure was analogous to that in Example 1 except that 60°C was selected as the polymerization temperature. The polymerization time was 5 hours. 32.7 mg (= 0.067 mmol) of metallocene compound were used. 0.15 kg of

isoblock polymer was obtained. The activity of the metallocene was therefore 0.45 kg of PP/mmol of Hf/h or 0.92 kg of PP/g of metallocene/h. The following analytical data were determined on the polymer:
VN = 35 cm^3/g, M_w = 16,200, M_n = 9300, M_w/M_n = 1.7, II = 72.6%, n_{iso} = 5.0.

Example 3

The procedure was analogous to that in Example 1 except that 50°C was selected as the polymerization temperature. The polymerization time was 25 hours. 30.0 mg (= 0.062 mmol) of metallocene compound were used in the appropriate amount of MAO. 0.43 kg of isoblock polymer was obtained. The activity of the metallocene was therefore 0.28 kg of PP/mmol of Hf/h or 0.57 kg of PP/g of metallocene/h. The following analytical data were determined on the polymer:
VN = 43 cm^3/g, M_w = 31,000, M_n = 14,300, M_w/M_n = 2.2, II = 74.0%, n_{iso} = 5.7.

Example 4

The procedure was analogous to that in Example 1 except that 40°C was selected as the polymerization temperature. The polymerization time was 35 hours. 34.4 mg (= 0.071 mmol) of metallocene compound were used. 0.28 kg of isoblock polymer was obtained. The activity of the metallocene was therefore 0.11 kg of PP/mmol of Hf/h or 0.23 kg of PP/g of metallocene/h. The following analytical data were determined on the polymer:
VN = 70 cm^3/g, M_w = 56,100, M_n = 24,100, M_w/M_n = 2.3, II = 75.5%, n_{iso} = 6.0.

Example 5

The procedure was analogous to that in Example 1 except that 10°C was selected as the polymerization temperature. The polymerization time was 12 hours. 207.7 mg (= 0.426

mmol) of metallocene compound were used. 0.07 kg of isoblock polymer was obtained. The activity of the metallocene was 13.7 g of PP/mmol of Hf/h or 0.03 kg of PP/g of metallocene/h. The following analytical data were determined on the polymer:
VN = 62 cm^3/g, M_w = 59,900, M_n = 29,800, M_w/M_n = 2.0, II = 75.7%, n_{iso} = 6.9.

Example 6

The procedure was analogous to that in Example 1 except that indenyl(cyclopentadienyl)(dimethylsilyl)zirconium dichloride, in an amount of 5.0 mg (= 0.013 mmol), was selected as the metallocene compound (the metallocene was dissolved in 20 cm^3 of MAO (= 13.4 mmol of Al), and 40 cm^3 of MAO (= 26.8 mmol of Al) were added to the liquid propylene).

The polymerization system was brought to a temperature of 60°C and then kept for 15 hours at this temperature. 1.2 kg of isoblock polymer were obtained. The activity of the metallocene was therefore 6.15 kg of PP/mmol of Zr/h or 16.0 kg of PP/g of metallocene/h. The following analytical data were determined on the polymer:
VN = 30 cm^3/g, M_w = 17,000, M_n = 5800, M_w/M_n = 2.9, II = 69.0%, n_{iso} = 4.6.

Example 7

The procedure was analogous to that in Example 6 except that 50°C was selected as the polymerization temperature. The polymerization time was 5 hours. 15.0 mg (= 0.038 mmol) of metallocene compound were used and 1.1 kg of isoblock polymer were obtained. The activity of the metallocene was 5.8 kg of PP/mmol of Zr/h or 14.7 kg of PP/g of metallocene/h. The following analytical data were determined on the polymer:
VN = 28 cm^3/g, M_w = 25,200, M_n = 7900, M_w/M_n = 3.2, II = 71.5%, n_{iso} = 4.9.

Example 8

The procedure was analogous to that in Example 6 except that 40°C was selected as the polymerization temperature. The polymerization time was 15 hours. 13.5 mg (= 0.034 mmol) of metallocene compound were used and 0.60 kg of isoblock polymer was obtained. The activity of the metallocene was therefore 1.18 kg of PP/mmol of Zr/h or 3.0 kg of PP/g of metallocene/h.

Comparative Example A

In an experiment analogous to Example 1, a polymer with a VN of 43.5 cm^3/g, an M_w of 35,200 and an M_w/M_n of 2.5 was obtained with rac-bis(indenyl)(dimethylsilyl)zirconium dichloride. The isotacticity index was 96.6% and the length of the isotactic sequences was found to be 51.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

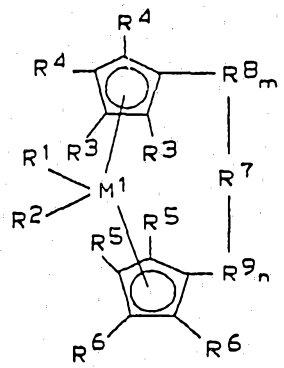
1. An isoblock polymer of a 1-olefin of the formula $RCH=CH_2$, in which R is an alkyl radical having 1 to 28 C atoms, with molecular chains containing isotactic sequences which are separated from one another in each case by one monomer unit of opposite configuration, and with a sequence length of 3 to 50 monomer units.

2. The isoblock polymer according to claim 1 with molecular chains consisting of isotactic sequences which are separated from one another in each case by one monomer unit of opposite configuration.

3. Isoblock polypropylene with molecular chains containing isotactic sequences which are separated from one another in each case by one propylene unit of opposite configuration, and with a sequence length of 3 to 50 propylene units.

4. Isoblock polypropylene with molecular chains consisting of isotactic sequences which are separated from one another in each case by one propylene unit of opposite configuration, and with a sequence length of 3 to 50 propylene units.

5. A process for the manufacture of the isoblock polymer according to claim 1 by the polymerization of a 1-olefin of the formula $RCH=CH_2$, in which R is an alkyl radical having 1 to 28 C atoms, at a temperature of -60 to 100°C and a pressure of 0.5 to 100 bar, in solution, in suspension or in the gas phase, in the presence of a catalyst consisting of a metallocene and an aluminoxane, wherein the metallocene is a compound of formula I:



(I),

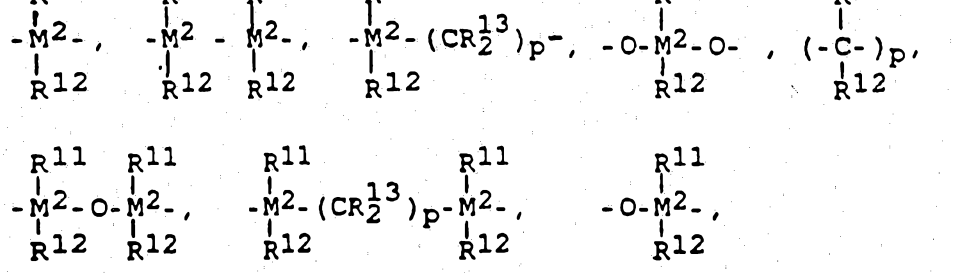
in which

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

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

R^3, R^4, R^5 and R^6 are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, $-NR^{10}_2$, $-SR^{10}$, $-OSi_rR^{10}_{3r+1}$, $-Si_rR^{10}_{3r+1}$ or $-PR^{10}_2$, in which R^{10} is a halogen atom or a C_1-C_{10}-alkyl group, or pairs of adjacent radicals R^3, R^4, R^5 and R^6 form a ring with the C atoms to which they are bonded, and

R^7 is



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

in which

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

M^2 is silicon, germanium or tin,

p is 1, 2 or 3,

R^8 and R^9 are identical or different and are a group $=CR^{11}R^{12}$, in which R^{11} and R^{12} are as defined above, and

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

6. The process according to claim 5, wherein the 1-olefin is propylene.

7. The process according to claim 5, wherein the metallocene is indenyl(dimethylsilyl)(h5-cyclopentadienyl)-hafnium dichloride or indenyl(dimethylsilyl)(h5-cyclopentadienyl)zirconium dichloride.

8. The process according to claim 5, wherein two different metallocenes are used for the manufacture of polypropylene blends.

~~9. Use of the isoblock polymer according to claim 1 for the manufacture of polymer mixtures.~~

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9. A method of manufacture of polymer mixtures comprising using an isoblock polymer according to claim 1.

10. A method of manufacture of polypropylene blends comprising carrying out the process as claimed in claim 5 but substituting the catalyst used therein for a catalyst consisting of two different metallocenes.

DATED this 25th day of March, 1991.

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