

- (72) FRITZE, Cornelia, DE
(72) BACHMANN, Bernd, DE
(72) KÜBER, Frank, DE
(71) TARGOR GMBH, DE
(71) EXXON CHEMICAL PATENTS INC., US
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(54) **SYSTEME DE CATALYSEUR SUPPORTE, SON PROCEDE DE PRODUCTION ET SON UTILISATION DANS LA POLYMERISATION D'OLEFINES**
(54) **SUPPORTED CATALYST SYSTEM, PROCESS FOR ITS PRODUCTION AND ITS USE IN POLYMERISING OLEFINES**

(57) L'invention concerne un système de catalyseur qui contient au moins un métallocène et au moins un support rendu inerte, ainsi que de préférence au moins un co-catalyseur. Le support inertisé est obtenu par traitement d'au moins un oxyde inorganique avec au moins un composé organo-métallique, de préférence dans un solvant inorganique. Cette invention concerne en outre un polymère dont le point de fusion ≥ 158 °C, l'activité triadique $> 98,0$ % et la part d'erreurs régiospécifiques $< 0,2$ %.

(57) The present invention relates to a catalyst system containing at least one metallocene and at least one inertised support and preferably at least one co-catalyst. To produce the inertised support, at least one inorganic oxide is treated with at least one metal-organic compound, preferably in an inorganic solvent. The present invention also relates to a polymer with a melting point ≥ 158 °C, a regio error proportion < 0.2 % and a triple activity > 98.0 %.



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(71) Anmelder (für alle Bestimmungsstaaten ausser US): HOECHST AKTIENGESELLSCHAFT [DE/DE]; Brüningstrasse 50, D-65929 Frankfurt am Main (DE). EXXON CHEMICAL PATENTS INC. [US/US]; 5200 Bayway Drive, Baytown, TX 77520 (US).	(88) Veröffentlichungsdatum des internationalen Recherchenberichts: 5. Juni 1997 (05.06.97)	
(72) Erfinder; und (75) Erfinder/Anmelder (nur für US): FRITZE, Cornelia [DE/DE]; Geisenheimer Strasse 97, D-60529 Frankfurt am Main (DE). BACHMANN, Bernd [DE/DE]; Kreuzheck 4, D-65817 Eppstein (DE). KÜBER, Frank [DE/DE]; Bleibiskopfstrasse 10, D-61440 Oberursel (DE).		
(54) Title: SUPPORTED CATALYST SYSTEM, PROCESS FOR ITS PRODUCTION AND ITS USE IN POLYMERISING OLEFINES		
(54) Bezeichnung: GETRÄGERTES KATALYSATORSYSTEM, VERFAHREN ZU SEINER HERSTELLUNG UND SEINE VERWENDUNG ZUR POLYMERISATION VON OLEFINEN		
(57) Abstract <p>The present invention relates to a catalyst system containing at least one metallocene and at least one inertised support and preferably at least one co-catalyst. To produce the inertised support, at least one inorganic oxide is treated with at least one metal-organic compound, preferably in an inorganic solvent. The present invention also relates to a polymer with a melting point ≥ 158 °C, a regio error proportion < 0.2 % and a triple activity > 98.0 %.</p>		
(57) Zusammenfassung <p>Die vorliegende Erfindung bezieht sich auf ein Katalysatorsystem, das mindestens ein Metallocen und mindestens einen inertisierten Träger und bevorzugt mindestens einen Cokatalysator enthält. Der inertisierte Träger wird hergestellt, indem mindestens ein anorganisches Oxid mit mindestens einer metallorganischen Verbindung, bevorzugt in einem anorganischen Lösungsmittel, behandelt wird. Die vorliegende Erfindung bezieht sich weiter auf ein Polymer mit einem Schmelzpunkt ≥ 158 °C und einem Anteil an Regiofehlern $< 0,2$ % und einer Triadentaktivität $> 98,0$ %.</p>		

Supported catalyst system, process for its preparation and its use for the polymerization of olefins

- 5 The present invention relates to a highly active, supported catalyst system which can advantageously be used in olefin polymerization and to a process for its preparation, and also to polymers which are prepared using the supported catalyst system.
- 10 Processes for preparing polyolefins with the aid of soluble, homogeneous catalyst systems comprising a transition metal component of the metallocene type and a cocatalyst component of the aluminoxane, Lewis acid or ionic type are known. These catalysts give polymers and copolymers having a narrow molar mass
- 15 distribution with high activity.

In polymerization processes using soluble, homogeneous catalyst systems, heavy deposits form on reactor walls and stirrer if the polymer is obtained as a solid. These deposits are always formed

20 by agglomeration of the polymer particles if metallocene and/or cocatalyst are present in dissolved form in the suspension. Such deposits in the reactor systems have to be removed regularly, since they quickly reach considerable thicknesses, have a high strength and prevent heat transfer to the cooling medium.

25 Furthermore, homogeneous catalyst systems cannot be used for preparing polyolefins in the gas phase.

To avoid deposit formation in the reactor, the use of supported catalyst systems in which the metallocene and/or the aluminum

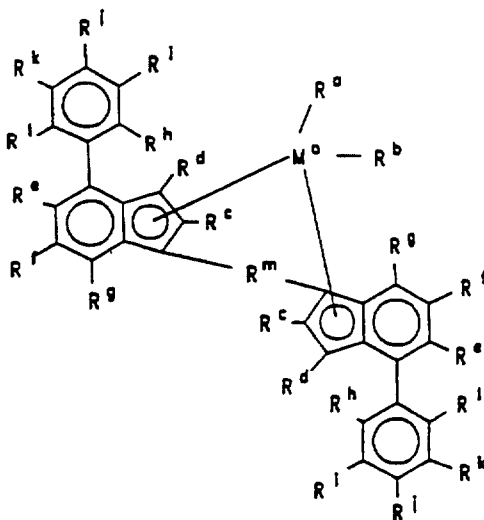
30 compound serving as cocatalyst are fixed on an inorganic support material have been proposed.

EP 576 970 A1 discloses a catalyst system comprising a metallocene of the formula

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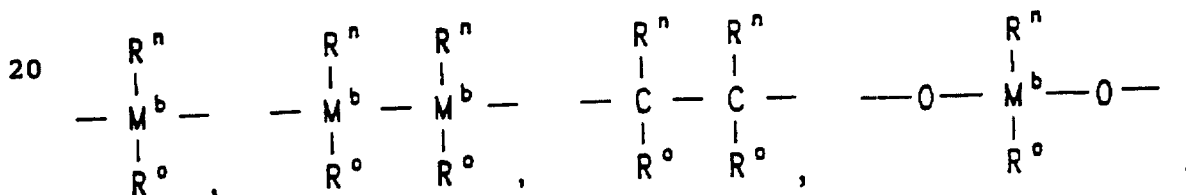


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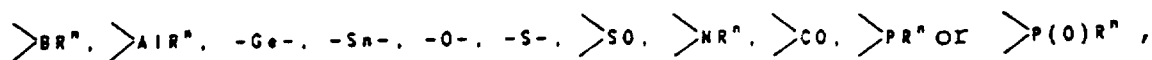
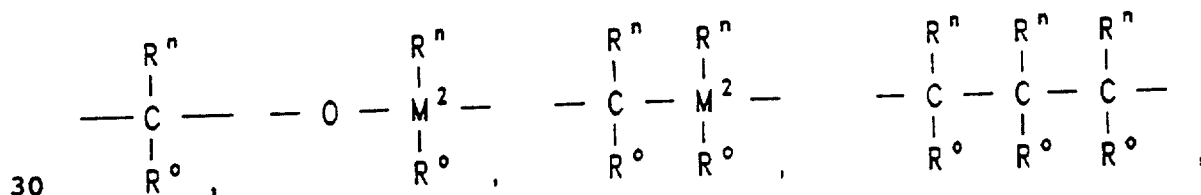
where

M^a is a metal of group IVb, Vb or VIb of the Periodic Table,
 R^a and R^b are identical or different and are each a hydrogen atom,
 a C₁-C₁₀-alkyl group, a C₁-C₁₀-alkoxy group, a C₆-C₁₀-aryl group, a
 5 C₆-C₁₀-aryloxy group, a C₂-C₁₀-alkenyl group, a C₇-C₄₀-arylalkyl
 group, a C₇-C₄₀-alkylaryl group, a C₈-C₄₀-arylalkenyl group, an OH
 group or a halogen atom,
 the radicals R^c are identical or different and are each a hydrogen
 atom, a halogen atom, a C₁-C₁₀-alkyl group which may be
 10 halogenated, a C₆-C₁₀-aryl group, an -NRP₂, -SRP, -OSiRP₃- or -PRP₂
 radical, where RP is a halogen atom, a C₁-C₁₀-alkyl group or a
 C₆-C₁₀-aryl group,
 R^d to R^l are identical or different and are as defined for R^c , or
 adjacent radicals R^d to R^l together with the atoms connecting them
 15 form one or more aromatic or aliphatic rings, or the radicals R^e
 and R^h or R^l together with the atoms connecting them form an
 aromatic or aliphatic ring,

R^m is



25



where R^n and R^o are identical or different and are each a hydrogen
 35 atom, a halogen atom, a C₁-C₁₀-alkyl group, a C₁-C₁₀-fluoroalkyl
 group, a C₁-C₁₀-alkoxy group, a C₆-C₁₀-aryl group, a
 C₆-C₁₀-fluoroaryl group, a C₆-C₁₀-aryloxy group, a C₂-C₁₀-alkenyl
 group, a C₇-C₄₀-arylalkyl group, a C₇-C₄₀-alkylaryl group or a
 C₈-C₄₀-arylalkenyl group, or R^n and R^o , in each case together with
 40 the atoms connecting them, form one or more rings and

M^b is silicon, germanium or tin,

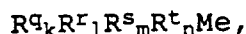
and a supported cocatalyst.

An isotactic polypropylene having a melting point below 157°C is
 obtained using this catalyst system.

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EP 287 666 B1 discloses a process for the polymerization of olefins in the presence of a catalyst comprising a compound of a transition metal, an inorganic support, an aluminoxane and an organoaluminum compound having a hydrocarbon group different from
 5 n-alkyl groups as solid catalyst component, wherein the transition metal compound has the formula



10 where R^q is a cycloalkadienyl group, R^r , R^s and R^t are identical or different and are each a cycloalkadienyl group, an aryl group, an alkyl group, an arylalkyl group, a halogen atom or a hydrogen atom, Me is zirconium, titanium or hafnium, k is 1, 2, 3 or 4, l, m and n are 0, 1, 2 or 3 and $k+l+m+n = 4$.
 15 This process gives polymers in good yields.

EP 336 593 B1 discloses a process for preparing a metallocene/aluminoxane catalyst provided with a support for olefin polymerization, in which trialkylaluminum and water are reacted
 20 in the presence of a water-absorbing solid material at a molar ratio of trialkylaluminum to water of from 10:1 to 1:1 and a metallocene of a transition metal is added to the reacted mixture, with the water being absorbed by the solid material in an amount of from 10 to 50% by weight prior to the reaction, the
 25 water-containing solid material being added to a solution of trialkylaluminum and the molar ratio of aluminum to metallocene transition metal being from 1000:1 to 1:1.

By this process, the cocatalyst is immobilized on the support. An
 30 advantageous molar ratio of aluminum to metallocene transition metal is obtained.

DE 4330667 A1 discloses a process for preparing catalyst systems using a pretreated support. In this process, the support material
 35 is reacted with a solution of triethylaluminum in heptane. Preference is given to using catalyst systems comprising a mixture of a plurality of metallocene complexes and/or a Ziegler-Natta catalyst system in the polymerization. When using metallocene complexes and Ziegler-Natta catalysts, polypropylenes
 40 having a melting point of $> 160^\circ\text{C}$ are obtained. Polypropylenes having melting points of $< 150^\circ\text{C}$ are prepared when only metallocenes are used as catalysts.

It is an object of the present invention to provide a highly
 45 active, supported catalyst system which gives polymers having a high regioregularity and stereoregularity and also an

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environmentally friendly and economical process for preparing the polymers.

We have found that this object is achieved by a catalyst system comprising at least one metallocene and at least one passivated support.

According to the present invention, the catalyst system is prepared by mixing at least one metallocene and at least one passivated support.

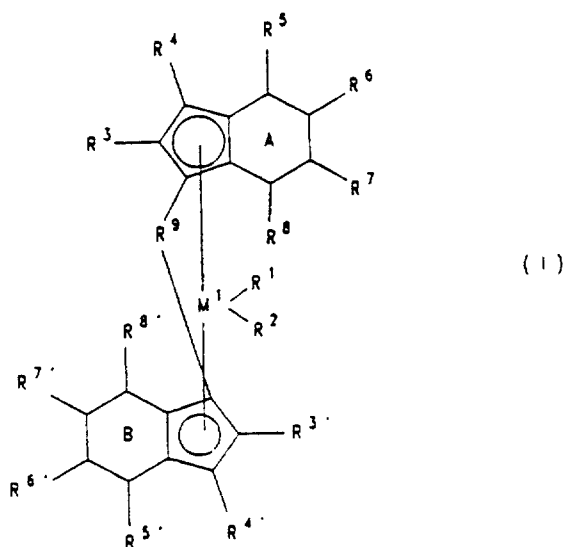
The metallocene component of the catalyst system of the present invention can be essentially any metallocene. The metallocene can be either bridged or unbridged and have identical or different ligands. Preference is given to metallocenes of group IVb of the Periodic Table of the Elements, viz. titanium, zirconium or hafnium, preferably zirconium.

The metallocenes preferably have the formula I

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35 where

M^1 is a metal of group IVb of the Periodic Table of the Elements,

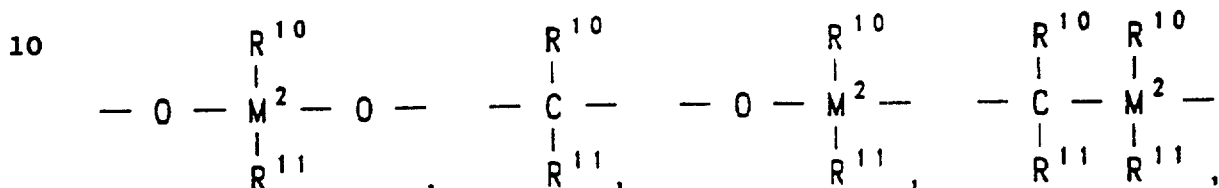
R^1 and R^2 are identical or different and are each a hydrogen atom, a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -alkoxy group, a C_6 - C_{20} -aryl group, a C_6 - C_{10} -aryloxy group, a C_2 - C_{10} -alkenyl group, an OH group, an NR^{12}_2 group, where R^{12} is a C_1 - C_2 -alkyl group or a C_6 - C_{14} -aryl group, or a halogen atom,

R^3 to R^8 and $R^{3'}$ to $R^{8'}$ are identical or different and are each a hydrogen atom, a C_1 - C_{40} -hydrocarbon group which may be linear, cyclic or branched, e.g. a C_1 - C_{10} -alkyl group, a C_2 - C_{10} -alkenyl group, a C_6 - C_{20} -aryl group, a C_7 - C_{40} -arylalkyl

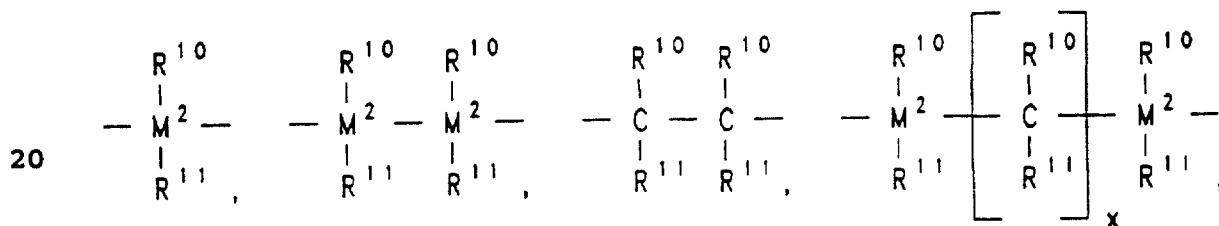
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group, a C₇-C₄₀-alkylaryl group or a C₈-C₄₀-arylalkenyl group, or adjacent radicals R⁴ to R⁸ and/or R^{4'} to R^{8'} together with the atoms connecting them form a ring system,

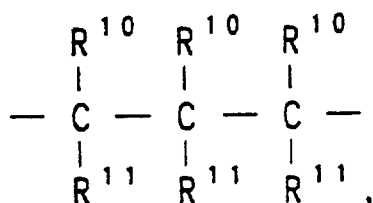
5 R⁹ is a bridge, preferably



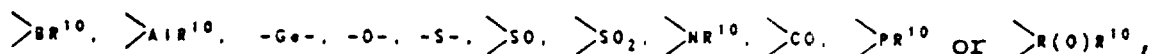
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where R¹⁰ and R¹¹ are identical or different and are each a hydrogen atom, a halogen atom or a C₁-C₄₀-group such as a C₁-C₂₀-alkyl group, a C₁-C₁₀-fluoroalkyl group, a C₁-C₁₀-alkoxy group, a C₆-C₁₄-aryl group, a C₆-C₁₀-fluoroaryl group, a

40 C₆-C₁₀-aryloxy group, a C₂-C₁₀-alkenyl group, a C₇-C₄₀-arylalkyl group, a C₇-C₄₀-alkylaryl group or a C₈-C₄₀-arylalkenyl group, or R¹⁰ and R¹¹, in each case together with the atoms connecting them, form one or more rings and x is an integer from zero to 18, M² is silicon, germanium or tin, and the rings A and B are

45 identical or different, saturated or unsaturated.

R⁹ can also link two units of the formula I to one another.

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The 4,5,6,7-tetrahydroindenyl analogs corresponding to the compounds I are likewise of importance.

In formula I, it is preferred that

- 5 M^1 is zirconium,
 R^1 and R^2 are identical and are methyl or chlorine, in particular chlorine, and $R^9 = M^2R^{10}R^{11}$, where M^2 is silicon or germanium and R^{10} and R^{11} are each a C_1 - C_{20} -hydrocarbon group such as C_1 - C_{10} -alkyl or C_6 - C_{14} -aryl,
 10 R^5 and $R^{5'}$ are preferably identical or different and are each a C_6 - C_{10} -aryl group, a C_7 - C_{10} -arylalkyl group, a C_7 - C_{40} -alkylaryl group or a C_8 - C_{40} -arylalkenyl group.

- The indenyl or tetrahydroindenyl ligands of the metallocenes of
 15 the formula I are preferably substituted in the 2 position, 2,4 positions, 4,7 positions, 2,6 positions, 2,4,6 positions, 2,5,6 positions, 2,4,5,6 positions or 2,4,5,6,7 positions, in particular in the 2,4 positions. Preferred substituents are a
 C_1 - C_4 -alkyl group such as methyl, ethyl or isopropyl or a
 20 C_6 - C_{10} -aryl group such as phenyl, naphthyl or mesityl. The 2 position is preferably substituted by a C_1 - C_4 -alkyl group such as methyl or ethyl.

- Particular preference is given to zirconocenes which bear
 25 tetrahydroindenyl derivatives and indenyl derivatives as ligands.

- Furthermore, particularly important metallocenes of the formula I are those in which the substituents in the 4 and 5 positions of the indenyl radicals (R^5 and R^6 or $R^{5'}$ and $R^{6'}$) together with the
 30 atoms connecting them form a ring system, preferably a 6-membered ring. This condensed ring system can likewise be substituted by radicals defined as for R^3 - R^8 . An example of such a compound I is dimethylsilanediylbis(2-methyl-4,5-benzindenyl)zirconium dichloride.

- 35 Very particular preference is given to those compounds of the formula I which bear a C_6 - C_{20} -aryl group in the 4 position and a C_1 - C_4 -alkyl group in the 2 position. An example of such a compound of the formula I is dimethylsilanediylbis(2-methyl-4-phenyl-
 40 indenyl)zirconium dichloride.

Examples of metallocene components of the catalyst system of the present invention are:

- dimethylsilanediylbis(indenyl)zirconium dichloride
 45 dimethylsilanediylbis(4-naphthylindenyl)zirconium dichloride
 dimethylsilanediylbis(2-methylbenzindenyl)zirconium dichloride
 dimethylsilanediylbis(2-methylindenyl)zirconium dichloride

- dimethylsilanediylbis(2-methyl-4-(1-naphthyl)indenyl)zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-(2-naphthyl)indenyl)zirconium dichloride
- 5 dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-t-butylindenyl)zirconium dichloride
- dimethylsilanediylbis(2-methyl-4-isopropylindenyl)zirconium
- 10 dichloride
- dimethylsilanediylbis(2-methyl-4-ethylindenyl)zirconium dichloride
- dimethylsilanediylbis(2-methyl-4- α -acenaphthindenyl)zirconium dichloride
- 15 dimethylsilanediylbis(2,4-dimethylindenyl)zirconium dichloride
- dimethylsilanediylbis(2-ethylindenyl)zirconium dichloride
- dimethylsilanediylbis(2-ethyl-4-ethylindenyl)zirconium dichloride
- dimethylsilanediylbis(2-ethyl-4-phenylindenyl)zirconium dichloride
- 20 dimethylsilanediylbis(2-methyl-4,5-benzindenyl)zirconium dichloride
- dimethylsilanediylbis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride
- dimethylsilanediylbis(2-methyl-4,5-diisopropylindenyl)zirconium
- 25 dichloride
- dimethylsilanediylbis(2,4,6-trimethylindenyl)zirconium dichloride
- dimethylsilanediylbis(2,5,6-trimethylindenyl)zirconium dichloride
- dimethylsilanediylbis(2,4,7-trimethylindenyl)zirconium dichloride
- dimethylsilanediylbis(2-methyl-5-isobutylindenyl)zirconium
- 30 dichloride
- dimethylsilanediylbis(2-methyl-5-t-butylindenyl)zirconium dichloride
- methyl(phenyl)silanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride
- 35 methyl(phenyl)silanediylbis(2-methyl-4,6-diisopropylindenyl)-zirconium dichloride
- methyl(phenyl)silanediylbis(2-methyl-4-isopropylindenyl)zirconium dichloride
- methyl(phenyl)silanediylbis(2-methyl-4,5-benzindenyl)zirconium
- 40 dichloride
- methyl(phenyl)silanediylbis(2-methyl-4,5-(methylbenzo)indenyl)-zirconium dichloride
- methyl(phenyl)silanediylbis(2-methyl-4,5-(tetramethylbenzo)-indenyl)zirconium dichloride
- 45 methyl(phenyl)silanediylbis(2-methyl-4- α -acenaphthindenyl)-zirconium dichloride
- methyl(phenyl)silanediylbis(2-methylindenyl)zirconium dichloride

- methyl(phenyl)silanediybis(2-methyl-5-isobutylindenyl)zirconium dichloride
- 1,2-ethanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride
- 1,4-butanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride
- 5 1,2-ethanediylbis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride
- 1,4-butanediylbis(2-methyl-4-isopropylindenyl)zirconium dichloride
- 1,4-butanediylbis(2-methyl-4,5-benzindenyl)zirconium dichloride
- 10 1,2-ethanediylbis(2-methyl-4,5-benzindenyl)zirconium dichloride
- 1,2-ethanediylbis(2,4,7-trimethylindenyl)zirconium dichloride
- 1,2-ethanediylbis(2-methylindenyl)zirconium dichloride
- 1,4-butanediylbis(2-methylindenyl)zirconium dichloride
- bis(butylcyclopentadienyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- 15 bis(methylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- dimethylsilanediybis(2-methyl-4,5-benzindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- 1,2-ethanediylbis(2-methylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- 1,4-butanediylbis(2-methylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- 20 dimethylsilanediybis(2-methyl-4,6-diisopropylindenyl)-Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- dimethylsilanediybis(2-ethyl-4-phenylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- dimethylsilanediybis(2-methyl-4-phenylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- 25 methyl(phenyl)silanediybis(2-methyl-4-phenylindenyl)-Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- dimethylsilanediybis(2-methylindenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- dimethylsilanediybis(indenyl)Zr⁺CH₂CHCHCH₂B⁻(C₆F₅)₃
- 30 dimethylsilanediyl(tert-butylamido)(tetramethylcyclopentadienyl)-zirconium dichloride
- [tris(pentafluorophenyl)(cyclopentadienylidene)borato](cyclopentadienyl)-1,2,3,4-tetraphenylbuta-1,3-dienylzirconium
- dimethylsilanediyl[tris(pentafluorophenyl)(2-methyl-4-phenylindenylidene)borato](2-methyl-4-phenylindenyl)-1,2,3,4-tetraphenylbuta-1,3-dienylzirconium
- 35 dimethylsilanediyl[tris(trifluoromethyl)(2-methylbenzindenylidene)borato](2-methylbenzindenyl)-1,2,3,4-tetraphenylbuta-1,3-dienylzirconium
- 40 dimethylsilanediyl[tris(pentafluorophenyl)(2-methylindenylidene)-borato](2-methylindenyl)-1,2,3,4-tetraphenylbuta-1,3-dienylzirconium
- dimethylsilanediylbis(indenyl)dimethylzirconium
- dimethylsilanediylbis(4-naphthylindenyl)dimethylzirconium
- 45 dimethylsilanediylbis(2-methylbenzindenyl)dimethylzirconium
- dimethylsilanediylbis(2-methylindenyl)dimethylzirconium
- dimethylsilanediylbis(2-methyl-4-(1-naphthyl)indenyl)dimethyl-

- zirconium
 dimethylsilanediylbis(2-methyl-4-(2-naphthyl)indenyl)dimethyl-
 zirconium
 dimethylsilanediylbis(2-methyl-4-phenylindenyl)dimethylzirconium
 5 dimethylsilanediylbis(2-methyl-4-t-butylindenyl)dimethylzirconium
 dimethylsilanediylbis(2-methyl-4-isopropylindenyl)dimethyl-
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 dimethylsilanediylbis(2-methyl-4-ethylindenyl)dimethylzirconium
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 dimethylsilanediylbis(2-ethyl-4-ethylindenyl)dimethylzirconium
 dimethylsilanediylbis(2-ethyl-4-phenylindenyl)dimethylzirconium
 15 dimethylsilanediylbis(2-methyl-4,5-benzindenyl)dimethylzirconium
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 methyl(phenyl)silanediylbis(2-methyl-4,5-(methylbenzo)indenyl)-
 35 dimethylzirconium
 methyl(phenyl)silanediylbis(2-methyl-4,5-(tetramethylbenzo)-
 indenyl)dimethylzirconium
 methyl(phenyl)silanediylbis(2-methyl-4- α -acenaphthindenyl)-
 dimethylzirconium
 40 methyl(phenyl)silanediylbis(2-methylindenyl)dimethylzirconium
 methyl(phenyl)silanediylbis(2-methyl-5-isobutylindenyl)dimethyl-
 zirconium
 1,2-ethanediylbis(2-methyl-4-phenylindenyl)dimethylzirconium
 1,4-butanediylbis(2-methyl-4-phenylindenyl)dimethylzirconium
 45 1,2-ethanediylbis(2-methyl-4,6-diisopropylindenyl)dimethyl-
 zirconium
 1,4-butanediylbis(2-methyl-4-isopropylindenyl)dimethylzirconium

10

- 1,4-butanediylbis(2-methyl-4,5-benzindenyl)dimethylzirconium
 1,2-ethanediylbis(2-methyl-4,5-benzindenyl)dimethylzirconium
 1,2-ethanediylbis(2,4,7-trimethylindenyl)dimethylzirconium
 1,2-ethanediylbis(2-methylindenyl)dimethylzirconium
 5 1,4-butanediylbis(2-methylindenyl)dimethylzirconium

Particular preference is given to:

- dimethylsilanediylbis(2-methylindenyl)zirconium dichloride
 dimethylsilanediylbis(2-methyl-4-(1-naphthyl)indenyl)zirconium
 10 dichloride
 dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium
 dichloride
 dimethylsilanediylbis(2-methyl-4- α -acenaphthindenyl)zirconium
 dichloride
 15 dimethylsilanediylbis(2-ethyl-4-phenylindenyl)zirconium
 dichloride
 dimethylsilanediylbis(2-methyl-4,5-benzindenyl)zirconium
 dichloride
 dimethylsilanediylbis(2-methyl-4,6-diisopropylindenyl)zirconium
 20 dichloride.

Methods of preparing metallocenes of the formula I are described, for example, in Journal of Organometallic Chem. 288 (1985) 63 - 67 and the documents cited therein.

25

The catalyst system of the present invention preferably further comprises at least one cocatalyst.

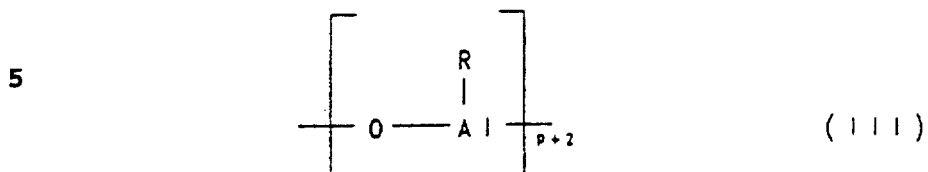
- The cocatalyst component which, according to the present
 30 invention, may be present in the catalyst system comprises at least one compound of the aluminoxane, Lewis acid or ionic type which reacts with a metallocene to convert the latter into a cationic compound.

- 35 As aluminoxane, preference is given to using a compound of the formula II

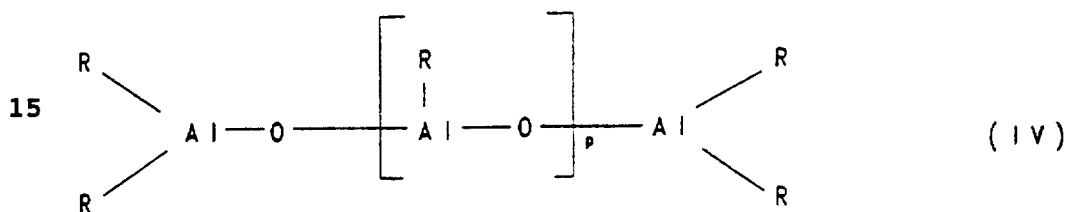


Aluminoxanes can be, for example, cyclic as in formula III

45



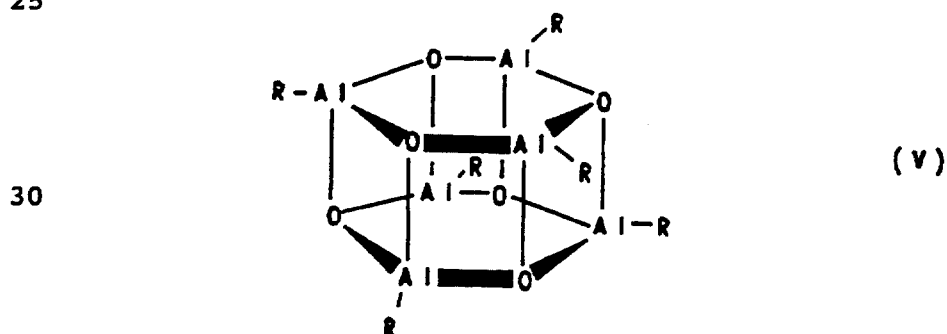
10 or linear as in formula IV



20

or of the cluster type as in formula V, as is described in recent literature; cf. JACS 117 (1995), 6465-74, Organometallics 13 (1994), 2957-2969.

25



35

The radicals R in the formulae (II), (III), (IV) and (V) can be identical or different and can each be a C₁-C₂₀-hydrocarbon group such as a C₁-C₆-alkyl group, a C₆-C₁₈-aryl group, benzyl or hydrogen, and p can be an integer from 2 to 50, preferably from 40 10 to 35.

Preferably, the radicals R are identical and are methyl, isobutyl, n-butyl, phenyl or benzyl, particularly preferably 45 methyl.

12

If the radicals R are different, they are preferably methyl and hydrogen, methyl and isobutyl or methyl and n-butyl, with hydrogen and isobutyl or n-butyl preferably being present in an amount of 0.01-40% (number of radicals R).

5

The aluminoxane can be prepared in various ways by known methods. One of the methods is, for example, reacting an aluminum-hydrocarbon compound and/or a hydridoaluminum-hydrocarbon compound with water (gaseous, solid, liquid or bound, for example
 10 as water of crystallization) in an inert solvent (such as toluene). To prepare an aluminoxane having different alkyl groups R, two different trialkylaluminums ($AlR_3 + AlR'_3$) corresponding to the desired composition and reactivity are reacted with water (cf. S. Pasykiewicz, Polyhedron 9 (1990) 429 and EP-A 302 424).

15

Regardless of the method of preparation, all aluminoxane solutions have in common a varying content of unreacted aluminum starting compound which is present in free form or as adduct.

20 As Lewis acid, preference is given to using at least one organoboron or organoaluminum compound comprising C_1-C_{20} - groups such as branched or unbranched alkyl or haloalkyl, e.g. methyl, propyl, isopropyl, isobutyl or trifluoromethyl, or unsaturated groups such as aryl or haloaryl, e.g. phenyl, tolyl, benzyl
 25 groups, p-fluorophenyl, 3,5-difluorophenyl, pentachlorophenyl, penta-fluorophenyl, 3,4,5-trifluorophenyl and 3,5-di(trifluoromethyl)- phenyl.

Particular preference is given to organoboron compounds. Examples
 30 of Lewis acids are trifluoroborane, triphenylborane, tris-(4-fluorophenyl)borane, tris(3,5-difluorophenyl)borane, tris(4-fluoromethylphenyl)borane, tris(pentafluorophenyl)borane, tris(tolyl)borane, tris(3,5-dimethylphenyl)borane, tris(3,5-difluorophenyl)borane and/or tris(3,4,5-trifluorophenyl)borane.
 35 Very particular preference is given to tris(pentafluorophenyl)-borane.

As ionic cocatalysts, preference is given to using compounds which contain a noncoordinating anion such as tetrakis(penta-
 40 fluorophenyl)borates, tetraphenylborates, SbF_6^\ominus , $CF_3SO_3^\ominus$ or ClO_4^\ominus . As cationic counterion, use is made of Lewis bases such as methylamine [sic], aniline, dimethylamine, diethylamine, N-methylaniline, diphenylamine, N,N-dimethylaniline, trimethylamine, triethylamine, tri-n-butylamine,
 45 methyldiphenylamine, pyridine, p-bromo-N,N-dimethylaniline, p-nitro-N,N-dimethylaniline, triethylphosphine,

triphenylphosphine, diphenylphosphine, tetrahydrothiophene and triphenylcarbenium.

Examples of such ionic compounds according to the present invention are

- 5 triethylammonium tetra(phenyl)borate,
- tributylammonium tetra(phenyl)borate,
- trimethylammonium tetra(tolyl)borate,
- tributylammonium tetra(tolyl)borate,
- 10 tributylammonium tetra(pentafluorophenyl)borate,
- tributylammonium tetra(pentafluorophenyl)aluminate,
- tripropylammonium tetra(dimethylphenyl)borate,
- tributylammonium tetra(trifluoromethylphenyl)borate,
- tributylammonium tetra(4-fluorophenyl)borate,
- 15 N,N-dimethylanilinium tetra(phenyl)borate,
- N,N-diethylanilinium tetra(phenyl)borate,
- N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate,
- N,N-dimethylanilinium tetrakis(pentafluorophenyl)aluminate,
- di(propyl)ammonium tetrakis(pentafluorophenyl)borate,
- 20 di(cyclohexyl)ammonium tetrakis(pentafluorophenyl)borate,
- triphenylphosphonium tetrakis(phenyl)borate,
- triethylphosphonium tetrakis(phenyl)borate,
- diphenylphosphonium tetrakis(phenyl)borate,
- tri(methylphenyl)phosphonium tetrakis(phenyl)borate,
- 25 tri(dimethylphenyl)phosphonium tetrakis(phenyl)borate,
- triphenylcarbenium tetrakis(pentafluorophenyl)borate,
- triphenylcarbenium tetrakis(pentafluorophenyl)aluminate,
- triphenylcarbenium tetrakis(phenyl)aluminate,
- ferrocenium tetrakis(pentafluorophenyl)borate and/or
- 30 ferrocenium tetrakis(pentafluorophenyl)aluminate.

Preference is given to triphenylcarbenium tetrakis(pentafluorophenyl)borate and/or N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate.

It is also possible to use mixtures of at least one Lewis acid and at least one ionic compound.

- Cocatalyst components which are likewise of importance are borane or carborane compounds such as 7,8-dicarbaundecaborane(13), undecahydrido-7,8-dimethyl-7,8-dicarbaundecaborane,
- 40 dodecahydrido-1-phenyl-1,3-dicarbaborane,
 - tri(butyl)ammonium undecahydrido-8-ethyl-7,9-dicarbaundecaborate,
 - 4-carbaborane(14)bis(tri(butyl)ammonium) nonaborate,
 - bis(tri(butyl)ammonium) undecaborate,
 - bis(tri(butyl)ammonium) dodecaborate,
 - 45 bis(tri(butyl)ammonium) decachlorodecaborate,
 - tri(butyl)ammonium 1-carbadecaborates,
 - tri(butyl)ammonium 1-carbadodecaborates,

tri(butyl)ammonium 1-trimethylsilyl-1-carbadecaborates,
 tri(butyl)ammonium bis(nonahydrido-1,3-dicarbanonaborato)-
 cobaltates(III),
 tri(butyl)ammonium bis(undecahydrido-7,8-dicarbaundecaborato)-
 5 ferrate(III).

The support components of the catalyst system of the present invention is a passivated support, preferably at least one inorganic oxide such as silicon oxide, aluminum oxide, zeolites,
 10 MgO, ZrO₂, TiO₂, B₂O₃, CaO, ZnO, ThO₂, Na₂CO₃, K₂CO₃, CaCO₃, MgCO₃, Na₂SO₄, Al₂(SO₄)₃, BaSO₄, KNO₃, Mg(NO₃)₂, Al(NO₃)₃, Na₂O, K₂O, Li₂O in particular silicon oxide and/or aluminum oxide. The support thus has a specific surface area in the range from 10 to 1000 m²/g, preferably from 150 to 500 m²/g, particularly
 15 preferably from 200 to 400 m²/g. The mean particle size of the support is from 1 to 500 μm, preferably from 5 to 350 μm, particularly preferably from 10 to 200 μm. The pore volume of the support is from 0.5 to 4.0 ml/g, preferably from 1.0 to 3.5 ml/g, very particularly preferably from 1.2 to 3 ml/g. This support
 20 component is passivated using at least one organometallic, preferably organoaluminum, compound. The porous structure of the support results in a proportion of voids (pore volume) in the support particle, the support material or the shaped support body.

25

The shape of the pores is irregular, frequently spherical. Some of the pores are connected to one another by means of small pore openings. The pore diameter is from about 2 to 50 nm.

30 The particle shape of the porous support is dependent on the aftertreatment and can be irregular or spherical. The support particle sizes can be set to any desired value by, for example, cryogenic milling and/or sieving.

35 The passivated support of the present invention comprises a product derived from one or more inorganic oxides, preferably silicon oxide and/or aluminum oxide, and an organometallic, preferably organoaluminum, compound.

40 The present invention also provides for the support material to be heated to < 800°C or for its surface to be silanized or esterified. The support of the present invention is dried at from 100°C to 800°C at from 0.01 bar to 0.001 bar or at from 100°C to 800°C in an inert gas stream for 5-15 hours in order to remove
 45 physisorbed water. The dried support material contains < 1.5% by weight of water and from 0.1 to 6% by weight of silanol groups. The water content is determined by the weight loss after drying

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at 200°C for 4 hours. The proportion of silanol groups on the surface can be determined by DTA (differential thermal analysis) or according to the following formula: % by weight = $[(\text{SiO}_2 \text{ dried at } 200^\circ\text{C, } 4 \text{ h}) - (\text{SiO}_2 \text{ dried at } 1000^\circ\text{C, } 20 \text{ h})] / (\text{SiO}_2 \text{ dried at } 200^\circ\text{C, } 4 \text{ h}) \cdot 100$.

The support material dried in this way is reacted with at least one organometallic compound. The organometallic compound is preferably an organoaluminum compound. Particular preference is given to organoaluminum compounds containing linear, cyclic or branched, saturated or unsaturated C₁-C₉ carbon-containing groups, e.g. trimethylaluminum, triethylaluminum, triisobutylaluminum, methylaluminoxane, tripropylaluminum, tri-n-butylaluminum, tri-sec-butylaluminum, isobutylaluminoxane, trihexylaluminum, tridodecylaluminum, triphenylaluminum, butylaluminoxane, tri(cyclohexyl)aluminum, dimethylaluminum methoxide, diethylaluminum ethoxide, diisobutylaluminum methoxide, diethylaluminum trimethylsilyloxy, lithium butyldiisobutylaluminum, lithium tri-tert-butoxyaluminum, lithium tert-butyl-diisobutylaluminum and/or diisobutylaluminum trimethylsilyloxy. Also suitable are organomagnesium or organoboron compounds such as diethylmagnesium, diisopropylmagnesium, dipropylmagnesium, dibutylmagnesium, dioctylmagnesium, dihexylmagnesium, didodecylmagnesium, dicyclohexylmagnesium, dibenzylmagnesium, ditolylmagnesium, dixylylmagnesium, ethylmagnesium ethoxide, octylmagnesium ethoxide, octylmagnesium octoxide, ethylpropylmagnesium, ethylbutylmagnesium, amylhexylmagnesium, n-butyl-sec-butylmagnesium, butyloctylmagnesium, triethylborane, triisobutylborane, tripropylborane, tri-n-butylborane, tri-sec-butylborane, trihexylborane, triphenylborane, tri(cyclohexyl)borane, dimethylmethoxyborane, diisobutylmethoxyborane, diethyltrimethylsilyloxyborane, lithium butyldiisobutylborane, lithium tri-tert-butoxyborane, lithium tert-butyl-diisobutylborane, 2-biphenylboronic acid, tris(trimethylsilylmethyl)borane and/or phenylboronic acid.

Very particular preference is given to using trimethylaluminum, tributylaluminum, triethylborane and/or tributylborane, but not triethylaluminum.

The passivation of the support is carried out by suspending the support material in a suitable solvent such as pentane, hexane, heptane, toluene or dichloromethane and slowly adding a solution of the organoaluminum compound, e.g. an aluminum alkyl solution, dropwise to this suspension and stirring to react the components, or slowly adding a solution of the organoaluminum compound, e.g.

an aluminum alkyl solution, dropwise to the dry support material while stirring and only then preparing a suspension using a suitable solvent.

The reaction temperature is preferably from -20 to +150°C, in particular 15-40°C. The reaction time is from 1 to 120 minutes, preferably 10-30 minutes. An aluminum concentration of greater than 0.01 mol/liter, in particular greater than 0.5 mol/liter, is preferably employed. Preference is given to using from 0.01 to 0.1 mol of aluminum compound per g of support material. The reaction is carried out under inert conditions.

The support is then separated from the solvent. The residue is washed twice with a suitable solvent such as pentane, hexane, heptane, toluene or dichloromethane and, if desired, dried in an oil pump vacuum at from 20 to 40°C and 0.01 to 0.001 bar. This gives a passivated support according to the present invention whose proportion of hydroxyl groups on the support surface has been reduced by the above-described treatment. The proportion of silanol groups on a passivated silica surface has dropped, for example, to < 2% by weight, preferably < 1.5% by weight.

For the purposes of the present invention, the expression "passivated support" means a support which has been treated as described above.

25

To prepare the catalyst system of the present invention, the passivated support component is reacted with at least one metallocene component and preferably with at least one cocatalyst component. The order in which the components are reacted is of no consequence. The reaction is carried out in a suitable solvent such as pentane, heptane, toluene, dichloromethane or dichlorobenzene in which the passivated support component is suspended and a solution of the metallocene and cocatalyst components is added dropwise, preferably by adding a solution of the metallocene and cocatalyst components in such an amount that the total solution volume is from 110 to 370% of the pore volume of the support component. The preparation of the catalyst system of the present invention is carried out at from -20 to 150°C, preferably from 20 to 50°C, and a contact time of from 15 minutes to 25 hours, preferably from 15 minutes to 5 hours.

The resulting catalyst system of the present invention has a metallocene content, preferably zirconium content, of from 0.001 to 2 mmol of Zr/g_{support}, preferably from 0.01 to 0.5 mmol of Zr/g_{support}, particularly preferably from 0.01 to 0.1 mmol of Zr/g_{support}, and an aluminum content of from 0.001 to 0.1 mol of Al/g_{support}, preferably from 1 to 50 mmol of Al/g_{support}. The

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aluminum/zirconium ratio is from 50:1 to 1000:1 (Al:Zr), preferably from 400:1 to 700:1 (Al:Zr).

The catalyst system of the present invention gives polymers such as polypropylene having extraordinarily high stereospecificity and regiospecificity.

Particularly characteristic for the stereospecificity and regiospecificity of polymers, in particular polypropylene, is, for example, the triad tacticity (TT) and the proportion of 2-1-inserted propene units (RI), which can be determined from the ¹³C-NMR spectra.

The ¹³C-NMR spectra are measured in a mixture of hexachlorobutadiene and d₂-tetrachloroethane at elevated temperature (365 K). All ¹³C-NMR spectra of the polypropylene samples measured are calibrated to the resonance signal of d₂-tetrachloroethane (δ = 73.81 ppm).

The triad tacticity of the polypropylene is determined from the methyl resonance signals in the ¹³C-NMR spectrum between 23 and 16 ppm; cf. J. C. Randall, *Polymer Sequence Determination: Carbon-13 NMR Method*, Academic Press New York 1978; A. Zambelli, P. Locatelli, G. Bajo, F. A. Bovey, *Macromolecules* 8 (1975), 687-689; H. N. Cheng, J. A. Ewen, *Makromol. Chem.* 190(1989), 1931-1943. Three successive 1-2-inserted propene units whose methyl groups are arranged on the same side in the "Fischer projection" are referred to as mm triads (δ = 21.0 ppm to 22.0 ppm). If only the second methyl group of the three successive propene units points to the other side, the sequence is referred to as an rr triad (δ = 19.5 ppm to 20.3 ppm) and if only the third methyl group of the three successive propene units points to the other side, the sequence is referred to as an mr triad (δ = 20.3 ppm to 21.0 ppm). The triad tacticity is calculated according to the following formula:

$$TT (\%) = mm / (mm + mr + rr) \cdot 100$$

If a propene unit is inserted in reverse into the growing polymer chain, this is referred to as a 2-1 insertion; cf. T. Tsutsui, N. Ishimaru, A. Mizuno, A. Toyota, N. Kashiwa, *Polymer* 30, (1989), 1350-56. The following different structural arrangements are possible:

19

Preference is given to polymerizing olefins of the formula $R^u-CH=CH-R^v$, where R^u and R^v are identical or different and are each a hydrogen atom or a carbon-containing radical having from 1 to 20 carbon atoms, in particular from 1 to 10 carbon atoms, and 5 R^u and R^v together with the atoms connecting them can form one or more rings. Examples of such olefins are 1-olefins having from 2 to 40, preferably from 2 to 10, carbon atoms, e.g. ethylene, propene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene or 1-octene, styrene, dienes such as 1,3-butadiene, 1,4-hexadiene, 10 vinylnorbornene or norbornadiene and cyclic olefins such as norbornene, tetracyclododecene or methylnorbornene. In the process of the present invention, preference is given to homopolymerizing ethene or propene or copolymerizing ethene with one or more 1-olefins having from 3 to 20 carbon atoms, e.g. 15 propene, and/or one or more dienes having from 4 to 20 carbon atoms, e.g. 1,4-butadiene or norbornadiene. Examples of such copolymers are ethene-propene copolymers and ethene-propene-1,4-hexadiene copolymers.

20 The polymerization is preferably carried out at from -60 to 250°C , particularly preferably from 50 to 200°C . The pressure is preferably from 0.5 to 2000 bar, particularly preferably from 5 to 64 bar.

25 The polymerization time is from 10 minutes to 10 hours, preferably from 30 minutes to 120 minutes.

The polymerization can be carried out in solution, in bulk, in suspension or in the gas phase, continuously or batchwise, in one 30 or more stages.

The catalyst system used in the process of the present invention preferably comprises one transition metal compound of the metallocene component. It is also possible to use mixtures of two 35 or more transition metal compounds of the metallocene component, e.g. for preparing polyolefins having a broad or multimodal molar mass distribution and reactor blends.

A prepolymerization can be carried out by means of the catalyst 40 system of the present invention. The prepolymerization is preferably carried out using the (or one of the) olefin(s) used in the polymerization.

20

The supported catalyst system can be resuspended in an inert suspension medium either as powder or while still moist with solvent. The suspension can be introduced into the polymerization system.

5

Before addition of the supported catalyst system of the present invention to the polymerization system, it is advantageous to purify the olefin using an aluminum alkyl compound such as trimethylaluminum, triethylaluminum, triisobutylaluminum, 10 trioctylaluminum, isoprenylaluminum or aluminoxanes to make the polymerization system inert (for example to remove catalyst poisons present in the olefin). This purification can be carried out either in the polymerization system itself or the olefin is brought into contact with the Al compound and subsequently 15 separated off again before addition to the polymerization system. If this purification is carried out in the polymerization system itself, the aluminum alkyl compound is added to the polymerization system in a concentration of from 0.01 to 100 mmol of Al per kg of reactor contents. Preference is given to using 20 triisobutylaluminum and triethylaluminum in a concentration of from 0.1 to 10 mmol of Al per kg of reactor contents.

If necessary, hydrogen is added as molar mass regulator and/or to increase the activity. The total pressure in the polymerization 25 system is from 0.5 to 2500 bar, preferably from 2 to 1500 bar.

The catalyst system is employed in a concentration, based on the transition metal, of preferably from 10^{-3} to 10^{-8} mol, particularly preferably from 10^{-4} to 10^{-7} mol, of transition metal 30 per dm^3 of solvent or per dm^3 of reactor volume.

If the polymerization is carried out as a suspension or solution polymerization, an inert solvent customary for the Ziegler low-pressure process is used. For example, the polymerization is 35 carried out in an aliphatic or cycloaliphatic hydrocarbon, for example propane, butane, hexane, heptane, isooctane, cyclohexane or methylcyclohexane. It is also possible to use a petroleum or hydrogenated diesel oil fraction. Toluene can also be used. Preference is given to carrying out the polymerization in the 40 liquid monomer.

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

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The duration of the polymerization can be as desired, since the catalyst system to be used according to the present invention displays only a slight time-dependent drop in the polymerization activity.

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The polymers prepared by the process of the present invention are particularly suitable for producing shaped bodies such as films, sheets or large hollow bodies (e.g. pipes).

- 10 When using the catalyst system of the present invention, a catalyst activity of from 170 to 250 kg of PP/g of metallocene x h is achieved. The polymers of the present invention have melting points of from 158 to 165°C. The polymers of the present invention have triad tacticities of from 98.0 to 99.5% and reverse
15 insertions of from 0.05 to 0.12%.

The invention is illustrated by a drawing and examples.

The drawing consists of Figure 1 and Figure 2.

20

Fig. 1 shows extracts from a ^{13}C -NMR spectrum (from 23 to 13 ppm and from 47 to 27 ppm) of a polypropylene which has been prepared using the novel, supported catalyst as described in Example 12.

- 25 Fig. 2 shows extracts from a ^{13}C -NMR spectrum (from 23 to 13 ppm and from 47 to 27 ppm) of a polypropylene which has been prepared using the supported catalyst "MAO on SiO_2 " similar to that in EP 576 970 A1 as described in Comparative Example 4.

30

The measurement of the ^{13}C -NMR spectra was carried out in a mixture of C_4Cl_6 and $\text{C}_2\text{D}_2\text{Cl}_4$ at 365 K and 100.6 MHz on a Bruker AM 400.

- 35 Table 1 shows the evaluation of relevant resonance signals of the ^{13}C -NMR spectra.

40

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Table 1

		Peaks									
Sample 1 (Fig. 1)	ppm	16.89	17.12	19.10	20.7	21.47	29.91	35.35	41.62	45.88	
	Integral	0.215	0.215	0.05	1.00	68.61	0.05	0.04	0.03	68.83	
		Peaks									
Sample 2 (Fig. 2)	ppm	16.89	17.13	19.10	20.70	21.48	29.91	35.37	41.3	45.88	
	Integral	0.395	0.395	1.00	2.66	64.80	0.30	0.31	0.43	70.33	

Comparison of the NMR spectra of Samples 1 and 2 shows that Sample 1 has a significantly lower proportion of 2-1-inserted propene units (RI = 0.06%) than Sample 2 (RI = 0.43%). This is
5 evidence of the lower proportion of reverse insertions in Sample 1 compared to Sample 2.

Examples

General procedures: The preparation and handling of the
10 organometallic compounds was carried out with exclusion of air and moisture under argon (Schlenk technique). All solvents required were dried before use by boiling for a number of hours over a suitable desiccant and subsequent distillation under argon. The spherical, porous support materials used were silicas
15 such as MS grades from PQ Corporation, ES or EP grades from Crosfield, or silica grades 948, 952, 955 from Grace Davison or the like.

The compounds were characterized using ^1H -NMR [sic], ^{13}C -NMR and
20 IR spectroscopy.

Example 1:

Passivation of the support material:

25 40 ml of 20% strength trimethylaluminum solution in Varsol were slowly added dropwise while stirring to 10 g of SiO_2 (ES 70, Crosfield Catalysts, dried at 140°C and 10 mbar). Sufficient toluene to form a readily stirrable suspension was then added. The mixture was stirred for another 10 minutes and the solid was
30 then filtered off from the solvent. The filtration residue was washed twice with 10 ml of toluene. The support material which had been pretreated in this way was dried at 40°C in an oil pump vacuum.

Preparation of the supported catalyst system:

35 In parallel thereto, 4.5 mg ($7.2 \mu\text{mol}$) of dimethylsilanediyl-bis(2-methyl-4-phenylindenyl)zirconium dichloride were mixed with 10 cm^3 of 30% strength (48.1 mmol) methylaluminoxane solution in toluene and an additional 1.5 cm^3 of toluene and the mixture was stirred for 15 minutes.
40 1 g of the passivated support material was resuspended in toluene and added dropwise to the above metallocene/methylaluminoxane solution. The reaction mixture was stirred for 30 minutes at room temperature. The mixture was subsequently filtered and the solid was washed 3 times with 10 cm^3 of hexane. The hexane-moist
45 filtration residue which remained was resuspended in 20 cm^3 of hexane for the polymerization.

Polymerization:

In parallel thereto, a dry 16 dm³ reactor was flushed first with nitrogen and subsequently with propylene and charged with 10 dm³ of liquid propylene. 3 cm³ of triisobutylaluminum (pure, 12 mmol) 5 diluted with 30 cm³ of hexane were then introduced into the reactor and the mixture was stirred at 30°C for 15 minutes. The catalyst suspension was subsequently introduced into the reactor. The reaction mixture was heated to the polymerization temperature of 50°C (4°C/min) and the polymerization system was held at 50°C 10 for 1 hour by cooling. The polymerization was stopped by addition of 20 cm³ of isopropanol. The excess monomer was vented, the polymer was dried under reduced pressure.

This gave 1.01 kg of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity 15 was 242 kg of PP/g of metallocene × h.

VN = 793 cm³/g; m.p. = 160°C; M_w = 1,155,000; M_w/M_n = 3.2;

BD = 356 d/dm³ [sic].

Example 2:

20 The synthesis of the supported catalyst system of Example 1 was repeated, except that 5 cm³ of 30% strength (24 mmol) methylaluminumoxane solution in toluene, 1.8 mg of dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride (2.9 μmol of Zr) and 3 g of passivated support material were used.

25 The polymerization was carried out using a method similar to Example 1 at 70°C. This gave 480 g of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity was 267 kg of PP/g of metallocene × h.

VN = 811 cm³/g; m.p. = 161°C; M_w = 1,182,000 g/mol; M_w/M_n = 3.2;

30 BD = 343 g/dm³.

Example 3:

The synthesis of the supported catalyst system of Example 1 was repeated, except that 70 cm³ of 30% strength (337 mmol) 35 methylaluminumoxane solution in toluene, 2.5 g of passivated support material and 44.2 mg of dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride (70.3 μmol of Zr) were used and the reaction mixture was stirred for 60 minutes at room temperature. The solid was subsequently filtered off and washed 3 40 times with 50 cm³ of hexane.

The hexane-moist filtration residue which remained was dried under reduced pressure to give a free-flowing, pale pink powder. This gave 5.36 g of supported, dry catalyst.

For the polymerization, 2 g of this dry catalyst (16.5 mg = 45 26.2 μmol of Zr) were resuspended in 20 cm³ of hexane.

The polymerization was carried out using a method similar to Example 1 at 70°C.

25

This gave 3.93 kg of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity was 238 kg of PP/g of metallocene \times h. $VN = 824 \text{ cm}^3/\text{g}$; m.p. = 160°C ; $M_w = 1,194,000 \text{ g/mol}$; $M_w/M_n = 3.0$; $BD = 377 \text{ g/dm}^3$.

5

Example 4:

Passivation of the support material:

40 ml of 20% strength triisobutylaluminum solution in Varsol were slowly added dropwise while stirring to 10 g of SiO_2 (ES 70, 10 Crosfield Catalysts, dried at 140°C and 10 mbar). Sufficient toluene to form a readily stirrable suspension was then added. The mixture was stirred for another 10 minutes and the solid was then filtered off from the solvent. The filtration residue was washed twice with 10 ml of toluene. The support material which 15 had been pretreated in this way was dried in an oil pump vacuum.

Preparation of the supported catalyst system:

In parallel thereto, 4.5 mg of dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride ($7.2 \mu\text{mol}$) were mixed with 1 cm^3 of 30% strength (4.81 mmol) methylaluminoxane solution in 20 toluene and an additional 2 cm^3 of toluene and the mixture was stirred for 15 minutes. This metallocene/methylaluminoxane solution in toluene was then added dropwise to 1 g of passivated support material resuspended in toluene. The reaction mixture was stirred for 30 minutes at room temperature. The mixture was 25 subsequently filtered and the solid was washed 3 times with 10 cm^3 of hexane. The hexane-moist filtration residue which remained was resuspended in 20 cm^3 of hexane for the polymerization.

Polymerization:

In parallel thereto, a dry 16 dm^3 reactor was flushed first with 30 nitrogen and subsequently with propylene and charged with 10 dm^3 of liquid propylene. 3 cm^3 of triisobutylaluminum (pure, 12 mmol) were then diluted with 30 cm^3 of hexane, introduced into the reactor and the mixture was stirred at 30°C for 15 minutes. The catalyst suspension was subsequently introduced into the reactor, 35 the mixture was heated to the polymerization temperature of 50°C ($4^\circ\text{C}/\text{min}$) and the polymerization system was held at 50°C for 1 hour by cooling. The polymerization was stopped by addition of 20 cm^3 of isopropanol. The excess monomer was vented, the polymer was dried under reduced pressure.

40 This gave 895 g of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity was 199 kg of PP/g of metallocene \times h.

$VN = 812 \text{ cm}^3/\text{g}$; m.p. = 161°C ; $M_w = 1,188,000 \text{ g/mol}$; $M_w/M_n = 3.3$; $BD = 380 \text{ g/dm}^3$.

45

Example 5:

The synthesis of the supported catalyst system of Example 4 was repeated, except that 10 cm³ of 30% strength methylaluminoxane solution in toluene (48.1 mmol), 44.2 mg of dimethylsilane-
5 diylbis(2-methyl-4-phenylindenyl)zirconium dichloride (70.3 g [sic] μmol of Zr) and 5 g of passivated support material were used and the reaction mixture was stirred for 60 minutes at room temperature. The solid was subsequently filtered off and washed 3 times with 50 cm³ of hexane. The hexane-moist filtration residue
10 which remained was dried under reduced pressure to give a free-flowing, pale pink powder. This gave 5.4 g of supported, dry catalyst.

For the polymerization, 2 g of this dry catalyst (16.5 mg = 26.2 μmol of Zr) were resuspended in 20 cm³ of hexane.
15 The polymerization was carried out using a method similar to Example 1 at 70°C.

This gave 3.2 kg of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity was 194 kg of PP/g of metallocene \times h. VN = 907 cm³/g;
20 m.p. = 162°C; M_w = 1,329,000 g/mol; M_w/M_n = 3.3; BD = 397 g/dm³.

Example 6:

Passivation of the support material:
40 ml of 20% strength trimethylaluminum solution in Varsol were
25 slowly added dropwise while stirring to 10 g of SiO₂ (PQ MS 3030, PQ Corporation, dried at 140°C and 10 mbar). Sufficient toluene to form a readily stirrable suspension was then added. The mixture was stirred for another 10 minutes and the solid was then filtered off from the solvent. The filtration residue was washed
30 twice with 10 ml of toluene. The support material which had been pretreated in this way was dried at room temperature in an oil pump vacuum. This gave 18 g of passivated support material.

In parallel thereto, 4.5 mg (7.2 μmol of Zr) of dimethylsilane-diylbis(2-methyl-4-phenylindenyl)zirconium dichloride were mixed
35 with 1 cm³ of 30% strength (4.81 mmol) methylaluminoxane solution in toluene and the mixture was stirred for 15 minutes.

1 g of the passivated support material was resuspended in toluene and the above metallocene/methylaluminoxane solution was added dropwise. The reaction mixture was stirred for 30 minutes at room
40 temperature. The mixture was subsequently filtered and the solid was washed 3 times with 10 cm³ of hexane. The hexane-moist filtration residue which remained was resuspended in 20 cm³ of hexane for the polymerization.

Polymerization:

45 In parallel thereto, a dry 16 dm³ reactor was flushed first with nitrogen and subsequently with propylene and charged with 10 dm³ of liquid propylene. 3 cm³ of triisobutylaluminum (pure, 12 mmol)

were then diluted with 30 cm³ of hexane, introduced into the reactor and the mixture was stirred at 30°C for 15 minutes. The catalyst suspension was subsequently introduced into the reactor, the mixture was heated to the polymerization temperature of 50°C
 5 (4°C/min) and the polymerization system was held at 50°C for 1 hour by cooling. The polymerization was stopped by addition of 20 cm³ of isopropanol. The excess monomer was vented, the polymer was dried under reduced pressure.

This gave 990 g of polypropylene powder. The reactor displayed no
 10 deposits on the inner wall or stirrer. The catalyst activity was 220 kg of PP/g of metallocene × h. VN = 868 cm³/g; m.p. = 160°C; M_w = 1,275,000 g/mol; M_w/M_n = 3.4; BD = 386 g/dm³.

Example 7:

15 The synthesis of the supported catalyst system of Example 1 was repeated, except that 5 cm³ of 30% strength (24 mmol) methylaluminumoxane solution in toluene, 1.8 mg of dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride (2.9 μmol of Zr) and 3 g of passivated support material were used.

20 The polymerization was carried out using a method similar to Example 1 at 70°C. This gave 369 g of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity was 205 kg of PP/g of metallocene × h. VN = 842 cm³/g; m.p. = 160°C; M_w = 1,229,000 g/mol; M_w/M_n = 3.2;
 25 BD = 373 g/dm³.

Example 8:

40 ml of 20% strength triisobutylaluminum solution in Varsol were slowly added dropwise while stirring to 10 g of SiO₂ (PQ MS 3030,
 30 PQ Corporation, dried at 140°C and 10 mbar). Sufficient toluene to form a readily stirrable suspension was then added. The mixture was stirred for another 10 minutes and the solid was then filtered off from the solvent. The filtration residue was washed twice with 10 ml of toluene. The support material which had been
 35 pretreated in this way was dried in an oil pump vacuum.

Preparation of the supported catalyst system:

In parallel thereto, 20 mg (32 μmol) of dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride were mixed with
 3 cm³ of 30% strength (14.43 mmol) methylaluminumoxane solution and
 40 a further 20 ml of toluene. The mixture was stirred for another 30 minutes.

This metallocene/methylaluminumoxane solution was then added dropwise while stirring vigorously to 5 g of the passivated support material and the mixture was stirred for another 15
 45 minutes. The mixture was filtered and the solid was washed three times with 10 cm³ of hexane and dried in an oil pump vacuum. 20 ml

of toluene were subsequently added and the catalyst system was resuspended.

Polymerization:

In parallel thereto, a dry 16 dm³ reactor was flushed first with
5 nitrogen and subsequently with propylene and charged with 10 dm³
of liquid propylene. 3 cm³ of triisobutylaluminum (pure, 12 mmol)
were then diluted with 30 cm³ of hexane, introduced into the
reactor and the mixture was stirred at 30°C for 15 minutes. The
catalyst suspension was subsequently introduced into the reactor,
10 the mixture was heated to the polymerization temperature of 70°C
(4°C/min) and the polymerization system was held at 70°C for 1
hour by cooling. The polymerization was stopped by addition of
20 cm³ of isopropanol. The excess monomer was vented, the polymer
was dried under reduced pressure.

15 This gave 2.86 kg of polypropylene powder. The reactor displayed
no deposits on the inner wall or stirrer. The catalyst activity
was 143 kg of PP/g of metallocene × h. VN = 946 cm³/g; m.p. =
162°C; M_w = 1,374,000 g/mol; M_w/M_n = 3.0; BD = 360 g/dm³.

20 Example 9

40 ml of 20% strength trimethylaluminum solution in Varsol were
slowly added dropwise while stirring to 10 g of SiO₂ (PQ MS 3030,
PQ Corporation, dried at 140°C and 10 mbar). Sufficient toluene to
form a readily stirrable suspension was then added. The mixture
25 was stirred for another 10 minutes and the solid was then
filtered off from the solvent. The filtration residue was washed
twice with 10 ml of toluene. The support material which had been
pretreated in this way was dried in an oil pump vacuum.

In parallel thereto, a dry 16 dm³ reactor was flushed first with
30 nitrogen and subsequently with propylene and charged with 10 dm³
of liquid propylene. 3 cm³ of triisobutylaluminum (pure, 12 mmol)
were then diluted with 30 cm³ of hexane, introduced into the
reactor and the mixture was stirred at 30°C for 15 minutes.

35 Preparation of the supported catalyst system:

20 mg (32 μmol) of dimethylsilanediybis(2-methyl-4-phenyl-
indenyl)zirconium dichloride were mixed with 3 ml of 30% strength
(14.43 mmol) methylaluminumoxane solution in toluene and a further
20 ml of toluene. The mixture was stirred for another 30 minutes
40 at room temperature.

This solution was then added dropwise to 5 g of passivated
support material. The mixture was stirred for a further 15
minutes. under. [sic]

The mixture was subsequently filtered and the solid was washed
45 three times with 10 cm³ of hexane. The hexane-moist filtration
residue which remained was resuspended in 20 cm³ of toluene for

the polymerization.

The catalyst suspension was subsequently introduced into the reactor, the mixture was heated to the polymerization temperature 5 of 20°C (4°C/min) and the polymerization system was heated [sic] at 70°C for 1 hour by cooling. The polymerization was stopped by addition of 20 cm³ of isopropanol. The excess monomer was vented, the polymer was dried under reduced pressure.

10 This gave 2.94 kg of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity was 147 kg of PP/Kg [sic] of metallocene × h. VN = 842 cm³/g; m.p. = 160°C, M_w = 1,217,000 g/mol; M_w/M_n = 2.9; BD = 356 g/dm³.

15 Example 10:

40 ml of 20% strength triisobutylaluminum solution in Varsol were slowly added dropwise while stirring to 10 g of SiO₂ (PMQS 3030, PQ Corporation, dried at 140°C and 10 mbar). Sufficient toluene to form a readily stirrable suspension was then added. The mixture

20 was stirred for another 10 minutes and the solid was then filtered off from the solvent. The filtration residue was washed twice with 10 ml of toluene. The support material which had been pretreated in this way was dried in an oil pump vacuum.

In parallel thereto, a dry 16 dm³ reactor was flushed first with 25 nitrogen and subsequently with propylene and charged with 10 dm³ of liquid propylene. 3 cm³ of triisobutylaluminum (pure, 12 mmol) were then diluted with 30 cm³ of hexane, introduced into the reactor and the mixture was stirred at 30°C for 15 minutes.

30 Preparation of the supported catalyst system:

20 mg (32 μmol) of dimethylsilanediylbis(2-methyl-4-phenyl-indenyl)zirconium dichloride were mixed with 3 ml of 30% strength (14.43 mmol) methylaluminoxane solution in toluene and a further 20 ml of toluene. The mixture was stirred for another 60 minutes

35 at room temperature. This solution was then added dropwise to 2 g of passivated support material. The mixture was stirred for a further 15 minutes.

The mixture was subsequently filtered and the solid was washed once with 10 cm³ of hexane. The hexane-moist residue which

40 remained was dried in an oil pump vacuum and then resuspended in 20 cm³ of toluene.

The catalyst suspension was subsequently introduced into the reactor, the mixture was heated to the polymerization temperature 45 of 20°C (4°C/min) and the polymerization system was heated [sic] at 70°C for 1 hour by cooling. The polymerization was stopped by addition of 20 cm³ of isopropanol. The excess monomer was vented,

30

the polymer was dried under reduced pressure.

This gave 3.26 kg of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity
5 was 163 kg of PP/g. VN = 910 cm³/g; m.p. = 162°C;
M_w = 1,323,000 g/mol; M_w/M_n = 3.0; BD = 340 g/dm³.

Example 11:

40 ml of 20% strength trimethylaluminum solution in Varsol were
10 slowly added dropwise while stirring to 10 g of SiO₂ (PMQS 3030,
PQ Corporation, dried at 140°C and 10 mbar). Sufficient toluene to
form a readily stirrable suspension was then added. The mixture
was stirred for another 10 minutes and the solid was then
filtered off from the solvent. The filtration residue was washed
15 twice with 10 ml of toluene. The support material which had been
pretreated in this way was dried in an oil pump vacuum.
In parallel thereto, a dry 16 dm³ reactor was flushed first with
nitrogen and subsequently with propylene and charged with 10 dm³
of liquid propylene. 3 cm³ of triisobutylaluminum (pure, 12 mmol)
20 were then diluted with 30 cm³ of hexane, introduced into the
reactor and the mixture was stirred at 30°C for 15 minutes.

Preparation of the supported catalyst system:

20 mg (32 μmol) of dimethylsilanediybis(2-methyl-4-phenyl-
25 indenyl)zirconium dichloride were mixed with 3 ml of 30% strength
(14.43 mmol) methylaluminumoxane solution in toluene and a further
20 ml of toluene. The mixture was stirred for another 30 minutes
at room temperature.

This solution was then added dropwise to 2 g of passivated
30 support material. The mixture was stirred for a further
15 minutes.

The mixture was subsequently filtered and the solid was washed
once with 10 cm³ of hexane. The hexane-moist residue which
remained was dried in an oil pump vacuum and then resuspended in
35 20 cm³ of hexane.

The catalyst suspension was subsequently introduced into the
reactor, the mixture was heated to the polymerization temperature
of 20°C (4°C/min) and the polymerization system was heated [sic]
40 at 70°C for 1 hour by cooling. The polymerization was stopped by
addition of 20 cm³ of isopropanol. The excess monomer was vented,
the polymer was dried under reduced pressure.

This gave 3.3 kg of polypropylene powder. The reactor displayed
45 no deposits on the inner wall or stirrer. The catalyst activity
was 165 kg of PP/g. VN = 874 cm³/g; m.p. = 160°C;

$M_w = 1,254,000$ g/mol; $M_w/M_n = 2.9$; $BD = 375$ g/dm³.

Example 12:

40 ml of 20% strength trimethylaluminum solution in Varsol were
5 slowly added dropwise while stirring to 10 g of SiO₂ (PMQS 3030,
PQ Corporation, dried at 140°C and 10 mbar). Sufficient toluene to
form a readily stirrable suspension was then added. The mixture
was stirred for another 10 minutes and the solid was then
filtered off from the solvent. The filtration residue was washed
10 twice with 10 ml of toluene. The support material which had been
pretreated in this way was dried in an oil pump vacuum.
In parallel thereto, a dry 16 dm³ reactor was flushed first with
nitrogen and subsequently with propylene and charged with 10 dm³
of liquid propylene. 3 cm³ of triisobutylaluminum (pure, 12 mmol)
15 were then diluted with 30 cm³ of hexane, introduced into the
reactor and the mixture was stirred at 30°C for 15 minutes.

Preparation of the supported catalyst system:

- 20 20 mg (32 μmol) of dimethylsilanediylbis(2-methyl-4-phenyl-
indenyl)zirconium dichloride were mixed with 3 ml of 30% strength
(14.43 mmol) methylaluminumoxane solution in toluene and a further
6 ml of toluene. The mixture was stirred for another 30 minutes
at room temperature.
- 25 This solution was then added dropwise to 2 g of passivated
support material. The mixture was stirred for a further
15 minutes and the catalyst system was resuspended in 20 ml of
toluene.
- 30 The catalyst suspension was subsequently introduced into the
reactor, the mixture was heated to the polymerization temperature
of 20°C (4°C/min) and the polymerization system was heated [sic]
at 70°C for 1 hour by cooling. The polymerization was stopped by
addition of 20 cm³ of isopropanol. The excess monomer was vented,
35 the polymer was dried under reduced pressure.

This gave 3.42 kg of polypropylene powder. The reactor displayed
no deposits on the inner wall or stirrer. The catalyst activity
was 171 kg of PP/g. $VN = 868$ cm³/g; m.p. = 161°C;

40 $M_w = 1,254,000$ g/mol; $M_w/M_n = 3.2$; $BD = 360$ g/dm³.

As Comparative Examples 1 to 3, the Examples 3, 4 and 5 from the
Patent Application EP 576 970 A1 have been incorporated into the
present description.

Comparative Example 1:

22 cm³ of the suspension of the "MAO on SiO₂" (49 mmol of Al) were introduced under argon into a G3 Schlenk frit and admixed with a solution of 4.5 mg of dimethylsilanediylbis(2-methyl-4-phenyl-
5 indenyl)zirconium dichloride in 10 cm³ of toluene (7.2 μmol of Zr).

The reaction mixture was stirred at room temperature for 30 minutes, with a spontaneous color change to red gradually becoming paler. The mixture was subsequently filtered and the
10 solid was washed 3 times with 10 cm³ of hexane. The hexane-moist filtration residue which remained was resuspended in 20 cm³ of hexane for the polymerization.

In parallel thereto, a dry 16 dm³ reactor was flushed first with nitrogen and subsequently with propylene and charged with 10 dm³
15 of liquid propylene. 3 cm³ of triisobutylaluminum (pure, 12 mmol) were then diluted with 30 cm³ of hexane, introduced into the reactor and the mixture was stirred at 30°C for 15 minutes. The catalyst suspension was subsequently introduced into the reactor, the mixture was heated to the polymerization temperature of 50°C
20 (4°C/min) and the polymerization system was held at 50°C for 1 hour by cooling. The polymerization was stopped by addition of 20 cm³ of isopropanol. The excess monomer was vented, the polymer was dried under reduced pressure.

This gave 300 g of polypropylene powder. The reactor displayed no
25 deposits on the inner wall or stirrer. The catalyst activity was 67 kg of PP/g of metallocene × h. VN = 1380 cm³/g; m.p. = 156°C.

Comparative Example 2:

The synthesis of the supported catalyst system of Comparative
30 Example 1 was repeated, except that 13 cm³ (29 mmol of Al) of the suspension of "MAO on SiO₂" and 1.8 mg of rac-5 (2.9 μmol of Zr) were used.

The polymerization was carried out using a method similar to Comparative Example 1 at 70°C. This gave 420 g of polypropylene
35 powder. The reactor showed no deposits on the inner wall or stirrer. The catalyst activity was 233 kg of PP/g of metallocene × h. VN = 787 cm³/g; m.p. = 149.5°C.

Comparative Example 3:

40 The synthesis of the supported catalyst system of Comparative Example 1 was repeated, except that 150 cm³ (335 mmol of Al) of the suspension of "MAO on SiO₂" and 44.2 mg (70.3 μmol of Zr) were used and the reaction mixture was stirred for 60 minutes at room temperature.

45 The solid was subsequently filtered off and washed 3 times with 50 cm³ of hexane. The hexane-moist filtration residue which

33

remained was dried under reduced pressure to give a free-flowing, pale pink powder. This gave 33.3 g of supported, dry catalyst. For the polymerization, 2.98 g (4 mg = 6.3 μmol of Zr) of this dry catalyst were resuspended in 20 cm^3 of hexane.

5 The polymerization was carried out using a method similar to Comparative Example 1 at 70°C.

This gave 1.05 kg of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity was 263 kg of PP/g of metallocene \times h. VN = 944 cm^3/g ;

10 m.p. = 156°C.

Comparative Example 4:

Preparation of the supported catalyst system:

6.5 cm^3 of the suspension of "MAO on SiO_2 " (14.4 mmol of Al) were
15 introduced into a G3 Schlenk frit and mixed with a solution of 20 mg (32 μmol) of dimethylsilanediylbis(2-methyl-4-phenyl-indenyl)zirconium dichloride in 10 cm^3 of toluene and a further 20 ml of toluene. The mixture was stirred for another 30 minutes at room temperature.

20 The mixture was subsequently filtered and the solid was washed three times with 10 cm^3 of hexane. The hexane-moist filtration residue which remained was resuspended in 20 cm^3 of hexane for the polymerization.

25 In parallel thereto, a dry 16 dm^3 reactor was flushed first with nitrogen and subsequently with propylene and charged with 10 dm^3 of liquid propylene. 3 cm^3 of triisobutylaluminum (pure, 12 mmol) diluted with 30 cm^3 of hexane were then introduced into the reactor and the mixture was stirred at 30°C for 15 minutes.

30

The catalyst suspension was subsequently introduced into the reactor, the mixture was heated to the polymerization temperature of 20°C (4°C/min) and the polymerization system was heated [sic] at 70°C for 1 hour by cooling. The polymerization was stopped by
35 addition of 20 cm^3 of isopropanol. The excess monomer was vented, the polymer was dried under reduced pressure.

This gave 3.45 kg of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity
40 was 172 kg of PP/g of metallocene \times h. M.p. = 149°C; VN = 872 cm^3/g ; $M_w = 1,290,000$ g/mol; $M_w/M_n = 2.9$; BD = 410 g/dm^3 .

Comparative Example 5:

Preparation of the supported catalyst system:

45 5 g of SiO_2 (PQMS 3030, PQ Corporation, dried at 140°C and 10 mbar) were suspended in 30 ml of toluene and admixed with the above metallocene/MAO/toluene solution.

34

20 mg (32 μmol) of dimethylsilanediylbis(2-methyl-4-phenyl-indenyl)zirconium dichloride were mixed with 3 ml of 30% strength (14.43 mmol) methylaluminoxane solution in toluene and a further 10 ml of toluene. The mixture was stirred for another 30 minutes at room temperature.

In parallel thereto, a dry 16 dm^3 reactor was flushed first with nitrogen and subsequently with propylene and charged with 10 dm^3 of liquid propylene. 13 cm^3 instead of 3 cm^3 of 20% strength triisobutylaluminum solution in Vargol [sic] were then introduced into the reactor and the mixture was stirred at 30°C for 15 minutes.

The catalyst suspension was subsequently introduced into the reactor, the mixture was heated to the polymerization temperature of 20°C (4°C/min) and the polymerization system was heated [sic] at 70°C for 1 hour by cooling. The polymerization was stopped by addition of 20 cm^3 of isopropanol. The excess monomer was vented, the polymer was dried under reduced pressure.

This gave 3.58 kg of polypropylene powder. The reactor displayed no deposits on the inner wall or stirrer. The catalyst activity was 179 kg of PP/g. VN = 910 cm^3/g ; m.p. = 149°C; $M_w = 1,328,0000$ [sic] g/mol; $M_w/M_n = 3.3$; BD = 95 g/dm^3 .

Table 2 below indicates which examples are compared with which comparative examples.

Table 2

Examples	Comparative Example
1, 4, 6	1
2,7	2
3,5	3
8,9,10,11,12	4, 5

Table 3 below shows the characteristic data of the catalyst system and the polymers obtained.

Table 3

	Examples (E)/ Comparative Examples (C)	Cat. activity ¹⁾	VN ²⁾	m.p. ³⁾	M _w ³⁾	M _w /M _n ⁵⁾	BD ⁶⁾	TT ⁷⁾	RI ⁸⁾
5	E1	242	793	160	1155000	3.2	356	98.2	0.09
10	E2	267	811	161	1182000	3.2	343	98.7	0.09
	E3	238	824	160	1194000	3.0	377	98.2	0.11
15	E4	199	812	161	1188000	3.3	380	99.3	0.10
	E5	194	907	162	1329000	3.3	397	99.5	0.07
	E6	220	868	160	1275000	3.4	386	98.5	0.08
20	E7	205	842	160	1229000	3.2	373	98.2	0.09
	E8	143	946	162	1374000	3.0	360	99.5	0.06
	E9	147	842	160	1217000	2.9	356	98.9	0.10
25	E10	163	910	162	1323000	3.0	340	99.1	0.09
	E11	165	874	160	1254000	2.9	375	99.2	0.11
	E12	171	868	161	125000	3.2	360	98.5	0.06
30	C1	67	1380	156	-	-	-	-	-
	C2	223	787	149.5	-	-	-	-	-
	C3	263	944	156	-	-	-	-	-
35	C4	172	872	149	1290000	2.9	410	94.7	0.43
	C5	179	910	149	1328000	3.3	395	95.4	0.49

40 1) Catalyst activity in kg of PP/g of metallocene × h

2) Viscosity number in cm³/g

3) Melting point in °C; determined using DSC, 20°C/min
45 heating/cooling rate; second heating

36

4) Weight average molar mass in g/mol; determined by gel permeation chromatography

5) Polydispersity

5

6) Polymer bulk density in g/dm³

7) Triad tacticity $TT = mm/(mm+mr+rr) \cdot 100$ in %; determined by ¹³C-NMR spectroscopy

10

8) Reverse insertions in %; determined by ¹³C-NMR spectroscopy

Comparison of the Examples E1 to E12 carried out according to the present invention with the Examples C1 to C4 carried out according to the prior art shows the following advantages of the invention.

15

1. Polymers of the invention having melting points of from 160°C to 162°C compared to 149°C to 156°C were obtained.

20

2. The proportion of 2-1-inserted propene units (RI) was significantly lower in the polymers of the present invention.

Comparison of Examples E1 to E12 with Comparative Example C5 showed that polymers having high melting points ($\geq 160^\circ\text{C}$) were obtained only when using passivated support material.

25

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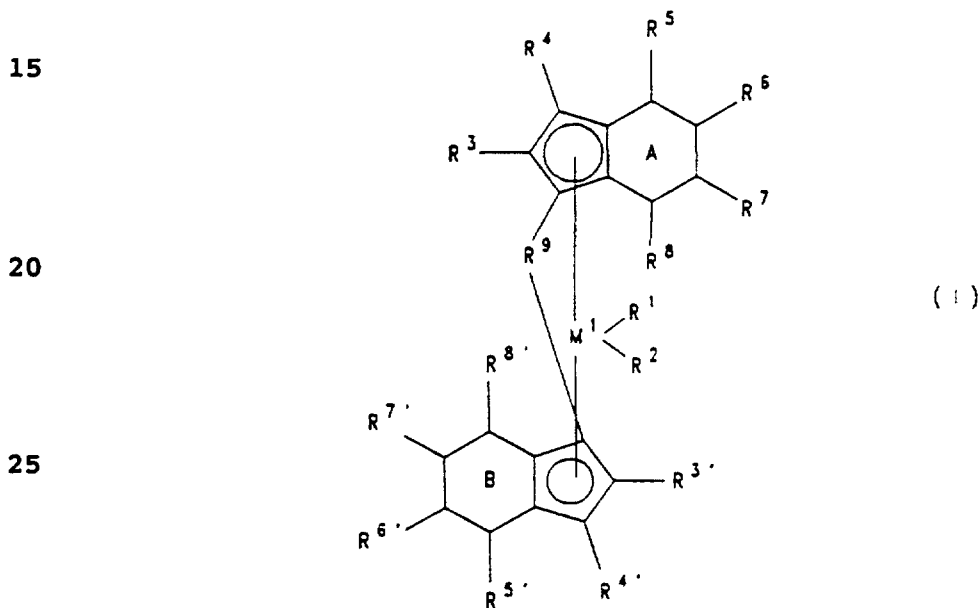
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We claim:-

1. A catalyst system comprising at least one metallocene and at
5 least one passivated support.
2. A catalyst system as claimed in claim 1 which can be prepared
by passivating at least one support and combining this with
at least one metallocene.
- 10 3. A catalyst system as claimed in claim 1 or 2 comprising at
least one metallocene having the formula I



30 where

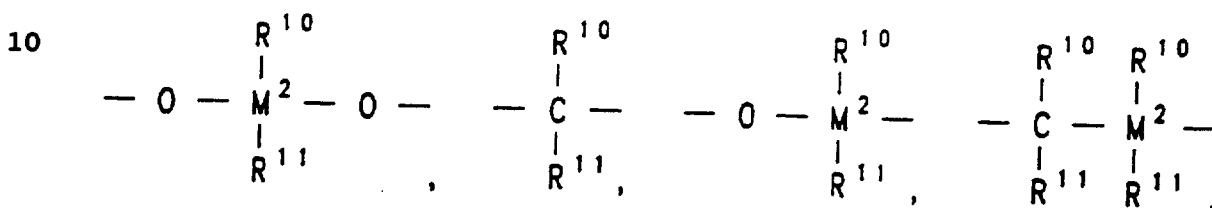
- M^1 is a metal of group IVb of the Periodic Table of the
Elements,
- R^1 and R^2 are identical or different and are each a hydrogen
35 atom, a C_1 - C_{10} -alkyl group, a C_1 - C_{10} -alkoxy group, a
 C_6 - C_{20} -aryl group, a C_6 - C_{10} -aryloxy group, a C_2 - C_{10} -alkenyl
group, an OH group, an NR^{12}_2 group, where R^{12} is a
 C_1 - C_2 -alkyl group or a C_6 - C_{14} -aryl group, or a halogen
atom,
- 40 R^3 to R^8 and $R^{3'}$ to $R^{8'}$ are identical or different and are
each a hydrogen atom, a C_1 - C_{40} -hydrocarbon group which
may be linear, cyclic or branched, e.g. a C_1 - C_{10} -alkyl
group, a C_2 - C_{10} -alkenyl group, a C_6 - C_{20} -aryl group, a
 C_7 - C_{40} -arylalkyl group, a C_7 - C_{40} -alkylaryl group or a
45 C_8 - C_{40} -arylalkenyl group, or adjacent radicals R^4 to R^8

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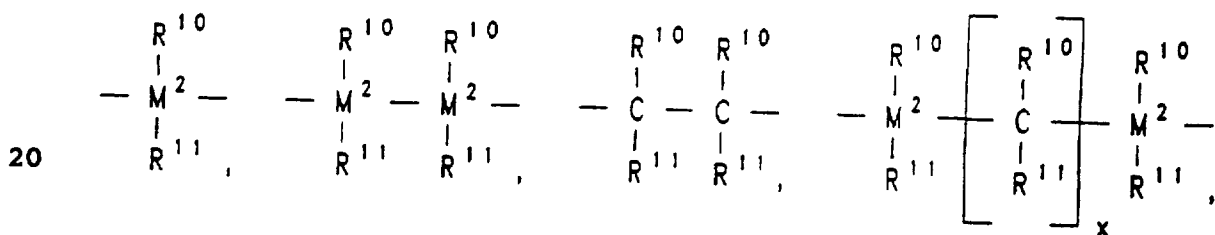
and/or R^{4'} to R^{8'} together with the atoms connecting them form a ring system,

R⁹ is a bridge, preferably

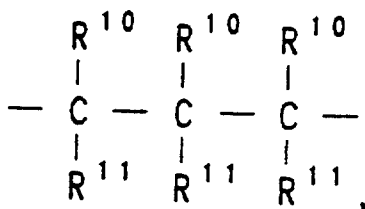
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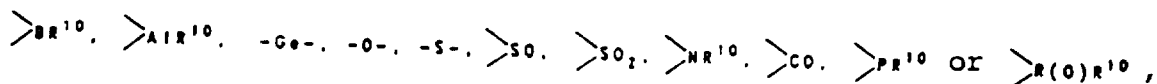
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where R¹⁰ and R¹¹ are identical

or different and are each a hydrogen atom, a halogen atom or a C₁-C₄₀-group such as a C₁-C₂₀-alkyl group, a

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C₁-C₁₀-fluoroalkyl group, a C₁-C₁₀-alkoxy group, a C₆-C₁₄-aryl group, a C₆-C₁₀-fluoroaryl group, a C₆-C₁₀-aryloxy group, a C₂-C₁₀-alkenyl group, a C₇-C₄₀-arylalkyl group, a

C₇-C₄₀-alkylaryl group or a C₈-C₄₀-arylalkenyl group, or R¹⁰ and R¹¹, in each case together with the atoms connecting them, form one or more rings and x is an integer from zero to 18,

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M² is silicon, germanium or tin, and the rings A and B are identical or different, saturated or unsaturated.

R⁹ can also link two units of the formula I to one another.

4. A catalyst system as claimed in any of claims 1 to 3 comprising at least one metallocene selected from among
5 dimethylsilanediylbis(2-methylindenyl)zirconium dichloride, dimethylsilanediylbis(2-methyl-4-(1-naphthyl)indenyl)-zirconium dichloride, dimethylsilanediylbis(2-methyl-4-phenylindenyl)zirconium dichloride, dimethylsilanediylbis(2-methyl-4- α -acenaphthindenyl)zirconium dichloride,
10 dimethylsilanediylbis(2-ethyl-4-phenylindenyl)zirconium dichloride, dimethylsianediylbis(2-methyl-4,5-benzindenyl)-zirconium [sic] dichloride, dimethylsilanediylbis(2-methyl-4,6-diisopropylindenyl)zirconium dichloride.
- 15 5. A catalyst system as claimed in any of claims 1 to 4 comprising at least one cocatalyst.
6. A catalyst system as claimed in any of claims 1 to 5 comprising at least one passivated, inorganic oxide.
20
7. A process for preparing a catalyst system as claimed in any of claims 1 to 6, which comprises passivating at least one support and combining this with at least one metallocene.
- 25 8. A process for preparing a catalyst system as claimed in any of claims 1 to 6, which comprises passivating at least one inorganic oxide and mixing this with at least one metallocene and at least one cocatalyst.
- 30 9. A passivated support comprising a product derived from one or more inorganic oxides, preferably silicon oxide and/or aluminum oxide and an organometallic, preferably organoaluminum, compound.
- 35 10. A passivated support which can be prepared by passivating at least one inorganic oxide, preferably silicon oxide and/or aluminum oxide, using at least one organometallic, preferably organoaluminum, compound, preferably in an organic solvent.
- 40 11. A process for preparing a passivated support as claimed in claim 9 or 10, which comprises passivating at least one inorganic oxide, preferably silicon oxide and/or aluminum oxide, using at least one organometallic, preferably organoaluminum, compound, preferably in an organic solvent.
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12. A polymer comprising polymerized monomer units of C₃-C₂₀-olefins and having a proportion of reverse insertions of < 0.2% and a triad tacticity of > 98.0%.
- 5 13. A polymer as claimed in claim 12 having a melting point of \geq 158°C.
14. A polymer which can be prepared by polymerization in the presence of a catalyst system.
- 10 15. A process for preparing a polymer in the presence of a catalyst system.
16. An extruded or injection-molded article or a polymer blend
15 comprising at least one polymer.
17. The use of a catalyst system for preparing polymers having a low proportion of reverse insertions and/or a high melting point.
- 20 18. The use of a passivated support for preparing a catalyst system.
19. The use of a polymer having a low proportion of reverse
25 insertions and/or a high melting point for producing extruded and injection-molded articles and also polymer blends.

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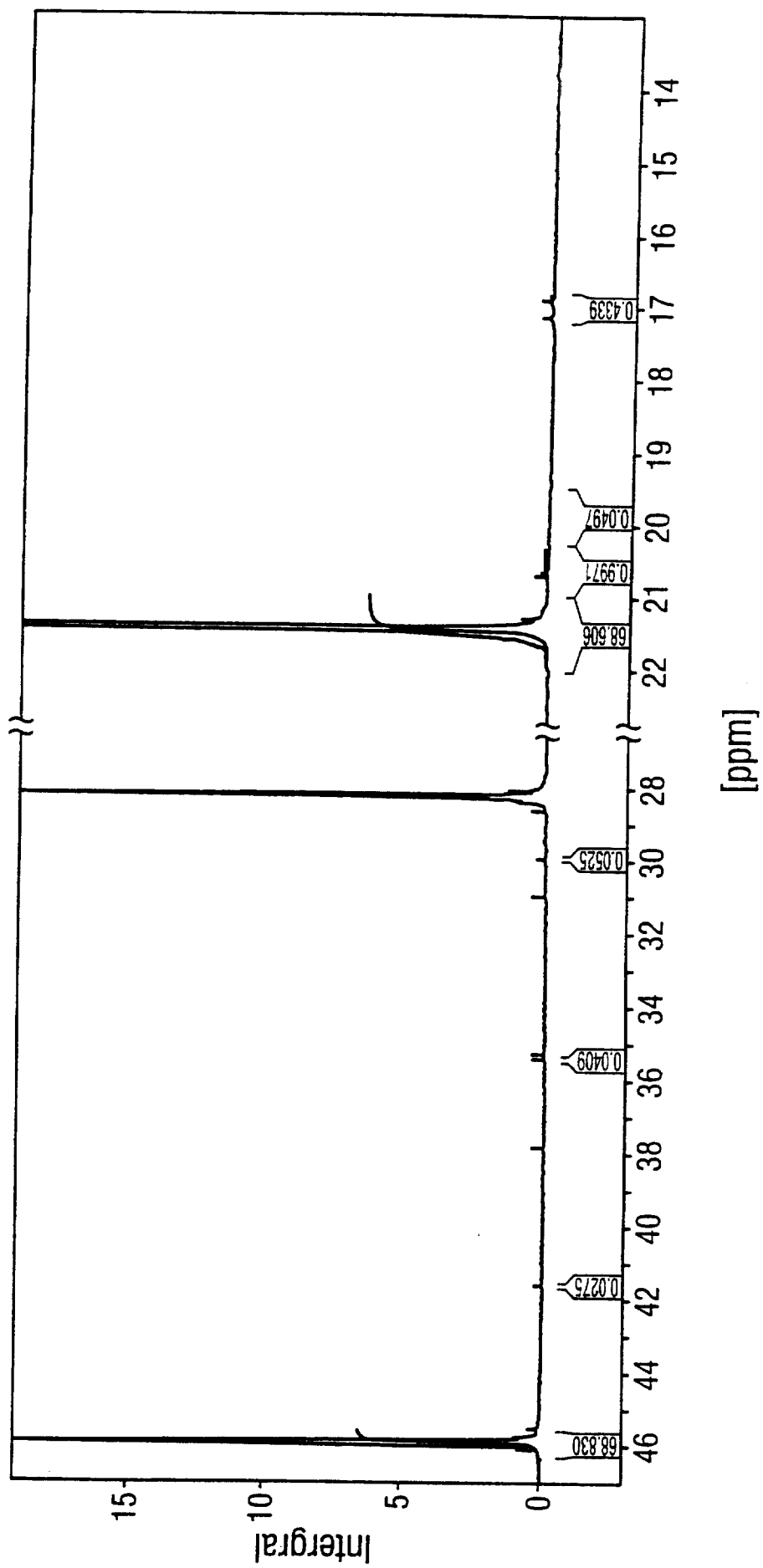
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Fig. 1: Extracts from a ^{13}C -NMR spectrum of a polypropylene described in Example 12



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Fig. 2: Extracts from a ^{13}C -NMR spectrum of a polypropylene described in Example 4