OPIC
OFFICE DE LA PROPRIÉTÉ INTELLECTUELLE DU CANADA

CIPO
CANADIAN INTELLECTUAL PROPERTY OFFICE

(12) (19) (CA) **Demande-Application**

(21) (A1) **2,246,389**
(86) 1997/02/19
(87) 1997/08/28

(72) LYNCH, John, DE
(72) FISCHER, David, DE
(72) GÖRTZ, Hans-Helmut, DE
(72) SCHWEIER, Günther, DE
(71) BASF AKTIENGESELLSCHAFT, DE

(51) Int.Cl.^{6} C08F 10/00, C08F 4/62, C08F 4/02
(30) 1996/02/20 (19606166.0) DE

(54) **PROCEDE DE PRODUCTION DE POLYMERES D'ALCENES PAR POLYMERISATION EN SUSPENSION**

(54) **PROCESS FOR PRODUCING POLYMERS OF ALKENES BY SUSPENSION POLYMERISATION**

(57) Procédé de production de polymères d'alcènes par polymérisation en suspension, en présence de systèmes de catalyseurs, selon lequel on utilise des systèmes de catalyseurs à supports, pouvant être obtenus par A) réaction d'un matériau support inorganique avec un composé métallique de formule générale (I): $M^1(R^1)_r(R^2)_s(R^3)_t(R^4)_u$, dans laquelle M^1 représente un métal alcalin ou alcalinoterreux ou un métal du groupe principal III ou IV de la classification périodique des éléments; R^1 représente hydrogène, alkyle C_1-C_{10}, aryle C_6-C_{15}, alkylaryle ou arylalkyle comportant respectivement 1 à 10 atomes de carbone dans le radical alkyle et 6 à 20 atomes de carbone dans le radical aryle; R^2 à R^4 représentent hydrogène, halogène, alkyle C_1-C_{10}, aryle C_6-C_{15}, alkylaryle, arylalkyle, alcoxy ou dialkylamino comportant respectivement 1 à 10 atomes de carbone dans le radical alkyle et 6 à 20 atomes de carbone dans le radical aryle; r est un nombre entier compris entre 1 et 4; et s, t et u sont des nombres entiers compris entre 0 et 3, la somme r+s+t+u correspondant à la valence de M^1; B) par réaction du matériau obtenu

(57) A process for producing polymers of alkenes by suspension polymerisation in the presence of catalyst systems where use is made of supported catalyst systems obtainable by A) reacting an inorganic support material with a metal compound of the general formula (I): $M^1(R^1)_r(R^2)_s(R^3)_t(R^4)_u$, in which M^1 is an alkaline or alkaline earth metal or a metal from main group III or IV of the periodic system; R^1 is hydrogen, C_1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl or aryl alkyl with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; R^2 to R^4 are hydrogen, C_1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl or aryl alkyl, alkoxy or dialkylamino with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; r is a whole number from 1 to 4; and s, t and u are whole numbers from 0 to 3, where the sum r+s+t+u corresponds to the valency of M^1; B) reacting the material obtained from A) with a metallocene complex in its metal dihalogenide form and a metallocenium ion-forming compound; and C) subsequent reaction with a metal compound of the general formula (II): $M^2(R^5)_o(R^6)_p(R^7)_q$, in which M^2 is an alkaline or alkaline earth metal or a metal of

OPIC
Office de la propriété intellectuelle du Canada

CIPO
Canadian Intellectual Property Office

(21) (A1) **2,246,389**
(86) 1997/02/19
(87) 1997/08/28

selon A) avec un complexe métallocène sous sa forme dihalogénure métallique et un composé formant des ions métallocène; et C) réaction d'un composé métallique de formule générale (II): $M^2(R^5)_o(R^6)_p(R^7)_q$, dans laquelle M^2 représente un métal alcalin ou alcalinoterreux ou un métal du groupe principal III de la classification périodique des éléments; R^5 représente hydrogène, alkyle C_1-C_{10}, aryle C_6-C_{15}, alkylaryle ou arylalkyle comportant respectivement 1 à 10 atomes de carbone dans le radical alkyle et 6 à 20 atomes de carbone dans le radical aryle; R^6 et R^7 représentent hydrogène, halogène, alkyle C_1-C_{10}, aryle C_6-C_{15}, alkylaryle, arylalkyle, ou alcoxy comportant respectivement 1 à 10 atomes de carbone dans le radical alkyle et 6 à 20 atomes de carbone dans le radical aryle; o est un nombre entier compris entre 1 et 3; et p et q sont des nombres entiers compris entre 0 et 2, la somme o+p+q correspondant à la valence de M^2.

main group III of the periodic system; R^5 is hydrogen, C_1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl or aryl alkyl with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; R^6 and R^7 are hydrogen, halogen, C_1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl, aryl alkyl, or alkoxy with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical, o is a whole number from 1 to 3; and p and q are whole numbers from 0 to 2 where the sum o+p+q corresponds to the valency of M^2.

PCT

WELTORGANISATION FÜR GEISTIGES EIGENTUM
Internationales Büro

INTERNATIONALE ANMELDUNG VERÖFFENTLICHT NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES PATENTWESENS (PCT)

(51) Internationale Patentklassifikation 6 :
C08F 2/14, 10/00, 4/60

A1

(11) Internationale Veröffentlichungsnummer: WO 97/31029

(43) Internationales Veröffentlichungsdatum: 28. August 1997 (28.08.97)

(21) Internationales Aktenzeichen: PCT/EP97/00771

(22) Internationales Anmeldedatum: 19. Februar 1997 (19.02.97)

(30) Prioritätsdaten:
196 06 166.0 20. Februar 1996 (20.02.96) DE

(71) Anmelder *(für alle Bestimmungsstaaten ausser US)*: BASF AKTIENGESELLSCHAFT [DE/DE]; D-67056 Ludwigshafen (DE).

(72) Erfinder; und
(75) Erfinder/Anmelder *(nur für US)*: LYNCH, John [GB/DE]; Bachusstrasse 15, D-67590 Monsheim (DE). FISCHER, David [DE/DE]; Raiffeisenstrasse 12, D-67161 Gönnheim (DE). GÖRTZ, Hans-Helmut [DE/DE]; Am Wurmberg 11, D-67251 Freinsheim (DE). SCHWEIER, Günther [DE/DE]; Friedrich-Pietzsch-Strasse 14, D-67159 Friedelsheim (DE).

(74) Gemeinsamer Vertreter: BASF AKTIENGESELLSCHAFT; D-67056 Ludwigshafen (DE).

(81) Bestimmungsstaaten: AU, BG, BR, CA, CN, CZ, GE, HU, IL, JP, KR, LV, MX, NO, NZ, PL, RO, RU, SG, SI, SK, TR, UA, US, eurasisches Patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), europäisches Patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Veröffentlicht
Mit internationalem Recherchenbericht.

46596
040218

(54) Title: PROCESS FOR PRODUCING POLYMERS OF ALKENES BY SUSPENSION POLYMERISATION

(54) Bezeichnung: VERFAHREN ZUR HERSTELLUNG VON POLYMERISATEN VON ALKENEN DURCH SUSPENSIONSPOLYMERISATION

(57) Abstract

A process for producing polymers of alkenes by suspension polymerisation in the presence of catalyst systems where use is made of supported catalyst systems obtainable by A) reacting an inorganic support material with a metal compound of the general formula (I): $M^1(R^1)_r(R^2)_s(R^3)_t(R^4)_u$, in which M^1 is an alkaline or alkaline earth metal or a metal from main group III or IV of the periodic system; R^1 is hydrogen, C_1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl or aryl alkyl with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; R^2 to R^4 are hydrogen, C_1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl or aryl alkyl, alkoxy or dialkylamino with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; r is a whole number from 1 to 4; and s, t and u are whole numbers from 0 to 3, where the sum r+s+t+u corresponds to the valency of M^1; B) reacting the material obtained from A) with a metallocene complex in its metal dihalogenide form and a metallocenium ion-forming compound; and C) subsequent reaction with a metal compound of the general formula (II): $M^2(R^5)_o(R^6)_p(R^7)_q$, in which M^2 is an alkaline or alkaline earth metal or a metal of main group III of the periodic system; R^5 is hydrogen, C_1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl or aryl alkyl with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical; R^6 and R^7 are hydrogen, halogen, C_1-C_{10} alkyl, C_6-C_{15} aryl, alkyl aryl, aryl alkyl, or alkoxy with 1 to 10 C atoms in the alkyl radical and 6 to 20 C atoms in the aryl radical, o is a whole number from 1 to 3; and p and q are whole numbers from 0 to 2 where the sum o+p+q corresponds to the valency of M^2.

(57) Zusammenfassung

Verfahren zur Herstellung von Polymerisaten von Alkenen durch Suspensionspolymerisation in Gegenwart von Katalysatorsystemen, wobei als Katalysatorsysteme geträgerte Katalysatorsysteme, erhältlich durch A) Umsetzung eines anorganischen Trägermaterials mit einer Metallverbindung der allgemeinen Formel (I) $M^1(R^1)_r(R^2)_s(R^3)_t(R^4)_u$, in der M^1 ein Alkali-, ein Erdalkalimetall oder ein Metall der III. oder IV. Hautgruppe des Periodensystems bedeutet, R^1 Wasserstoff, C_1- bis C_{10}-Alkyl, C_6- bis C_{15}-Aryl, Alkylaryl oder Arylalkyl mit jeweils 1 bis 10 C-Atomen im Alkylrest und 6 bis 20 C-Atomen im Arylrest, R^2 bis R^4 Wasserstoff, Halogen, C_1- bis C_{10}-Alkyl, C_6- bis C_{15}-Aryl, Alkylaryl, Arylalkyl, Alkoxy oder Dialkylamino mit jeweils 1 bis 10 C-Atomen im Alkylrest und 6 bis 20 C-Atomen im Arylrest, r eine ganze Zahl von 1 bis 4, und s, t und u ganze Zahlen von 0 bis 3 bedeuten, wobei die Summe r+s+t+u der Wertigkeit von M^1 entspricht, B) Umsetzung des nach A) erhaltenen Materials mit einem Metallocenkomplex in seiner Metalldihalogenid-Form und einer metalloceniumionenbildenten Verbindung und C) anschließender Umsetzung mit einer Metallverbindung der allgemeinen Formel (II) $M^2(R^5)_o(R^6)_p(R^7)_q$, in der M^2 ein Alkali-, ein Erdalkalimetall oder ein Metall der III. Hauptgruppe des Periodensystems bedeutet, R^5 Wasserstoff, C_1- bis C_{10}-Alkyl, C_6- bis C_{15}-Aryl, Alkylaryl oder Arylalkyl mit jeweils 1 bis 10 C-Atomen im Alkylrest und 6 bis 20 C-Atomen im Arylrest, R^6 und R^7 Wasserstoff, Halogen, C_1- bis C_{10}-Alkyl, C_6- bis C_{15}-Aryl, Alkylaryl, Arylalkyl oder Alkoxy mit jeweils 1 bis 10 C-Atomen im Alkylrest und 6 bis 20 C-Atomen im Arylrest, o eine ganze Zahl von 1 bis 3 und p und q ganze Zahlen von 0 bis 2 bedeuten, wobei die Summe o+p+q der Wertigkeit von M^2 entspricht, eingesetzt werden.

Preparation of polymers of alkenes by suspension polymerization

The present invention relates to a process for the preparation of polymers of alkenes by suspension polymerization in the presence of catalyst systems.

The present invention furthermore relates to the resulting polymers of alkenes, the use of these polymers for the production of fibers, films and moldings and the fibers, films and moldings obtainable therefrom.

A preparation process for polymers of ethylene by suspension polymerization is described, for example, in WO 95/18160. Here, however, the dry catalyst is pyrophoric and already active with respect to polymerization.

WO 91/09882 discloses the preparation of a supported, cationic metallocene catalyst by applying the reaction mixture of a dialkylmetallocene with an ionic compound, which has a Brönsted acid as the cation and a noncoordinating opposite ion, such as tetrakis(pentafluorophenyl)borate as the anion to an inorganic carrier. Here too, an active catalyst is obtained.

Similar supported catalyst systems are also disclosed in WO 94/03506 and WO 95/14044.

EP-A 628 574 describes supported catalyst systems in which a metallocene dihalide is reacted with an alkylaluminum in the presence of a hydridoborate and this solution, which is active with respect to polymerization, is applied to a carrier.

Such already active catalysts readily give rise to problems in the metering of the catalyst into the reactor.

A catalyst which is still inactive and can be activated only subsequently, for example during metering or only in the reactor, is therefore advantageous.

EP-A 613 908 discloses supported metallocene catalyst systems, some of which are not activated until they are in the reactor. Here, however, the polymers formed have a broad molecular weight distribution M_w/M_n.

WO 95/15815 describes catalysts which are obtained by applying a metallocene dichloride and a borate to a crosslinked polymer as a carrier. The use of deactivated inorganic carriers gives cata-

lysts which, after activation in the polymerization reactor, have either only slight activity or no activity at all.

It is an object of the present invention to provide a process for the preparation of polymers of alkenes by suspension polymerization, which process does not have the stated disadvantages and in which in particular the catalyst system can be activated at any desired time, the catalyst system is air- and moisture-insensitive, can be stored for a long time and is not pyrophoric and the polymers formed have a narrow molecular weight distribution.

We have found that this object is achieved by a process for the preparation of polymers of alkenes by suspension polymerization in the presence of catalyst systems, wherein the catalyst systems used are supported catalyst systems obtainable by

A) reaction of an inorganic carrier with a metal compound of the general formula I

$$M^1(R^1)_r(R^2)_s(R^3)_t(R^4)_u \qquad I$$

where

M^1 is an alkali metal, an alkaline earth metal or a metal of main group III or IV of the Periodic Table,

R^1 is hydrogen, C_1-C_{10}-alkyl, C_6-C_{15}-aryl, alkylaryl or arylalkyl, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

R^2 to R^4 are each hydrogen, halogen, C_1-C_{10}-alkyl, C_6-C_{15}-aryl, alkylaryl, arylalkyl, alkoxy or dialkylamino, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

r is an integer from 1 to 4

and

s, t and u are integers from 0 to 3, the sum r+s+t+u corresponding to the valency of M^1,

B) reaction of the material obtained according to A) with a metallocene complex in its metal dihalide form and a compound forming metallocenium ions

and

C) subsequent reaction with a metal compound of the general formula II

$$M^2(R^5)_o(R^6)_p(R^7)_q \qquad II$$

in which

M^2 is an alkali metal, an alkaline earth metal or a metal of main group III of the Periodic Table,

R^5 is hydrogen, C_1-C_{10}-alkyl, C_6-C_{15}-aryl, alkylaryl or arylalkyl, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

R^6 and R^7 are each hydrogen, halogen, C_1-C_{10}-alkyl, C_6-C_{15}-aryl, alkylaryl, arylalkyl or alkoxy, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

o is an integer from 1 to 3

and

p and q are integers from 0 to 2, the sum o+p+q corresponding to the valency of M^2.

We have also found the polymers of alkenes which are obtainable thereby, their use for the production of fibers, films and moldings and the fibers, films and moldings obtainable therefrom.

The novel process is used for the preparation of polymers of alkenes. The term polymers is understood as meaning both homopolymers and copolymers. Particularly suitable alkenes are alk-1-enes, preferably ethylene and propylene, in particular ethylene. Alk-1-enes are also suitable as comonomers, preferably straight-chain C_4-C_{10}-alk-1-enes, in particular but-1-ene, hex-1-ene and oct-1-ene. However, it is also possible to use other alkenes, for example cycloolefins or higher alkenes.

Supported catalyst systems which are obtainable by reacting an inorganic carrier with a metal compound of the general formula I in a first stage A) are used as supported catalyst systems.

The carriers used are preferably finely divided solids whose particle diameters are from 1 to 200 μm, in particular from 30 to 70 μm.

Examples of suitable carriers are silica gels, preferably those of the formula $SiO_2 \cdot a\ Al_2O_3$, where a is from 0 to 2, preferably from 0 to 0.5; these are therefore aluminosilicates or silica. Such products are commercially available, for example Silica Gel 332 from Grace.

Other inorganic compounds, such as Al_2O_3 or $MgCl_2$, or mixtures containing these compounds may also be used as carriers.

Preferred metal compounds of the general formula I are those in which M^1 is a metal of main group III of the Periodic Table, in particular aluminum, R^1 is C_1-C_{10}-alkyl and R^2 to R^4 are each C_1-C_{10}-alkyl. For the particularly preferred case where M^1 is aluminum, u is zero and R^1 to R^3 have in particular the same meaning, preferably methyl, ethyl, isobutyl or hexyl, preferably isobutyl.

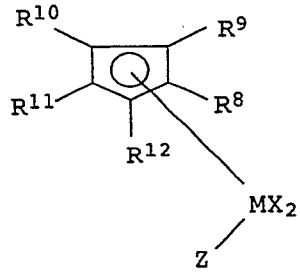
The metal compound of the general formula I is preferably added as a solution to a suspension of the carrier. Particularly suitable solvents or suspending agents are hydrocarbons, such as heptane. The amount of metal compound I can be varied within wide limits, the minimum amount depending on the number of hydroxyl groups of the carrier. The temperatures, reaction times and pressures are not critical per se, temperatures of from 0 to 80°C and reaction times of from 0.1 to 48 hours being preferred.

It has proven suitable to remove the excess metal compound I by thorough washing, for example with hydrocarbons, such as pentane or hexane, after the carrier pretreatment and to dry the carrier.

The material thus prepared can be stored for up to 6 months and is not pyrophoric.

This material is then reacted, in a further stage B), with a metallocene complex in its metal dihalide form and a compound forming metallocenium ions.

Examples of suitable metallocene complexes are compounds of the general formula III:



III

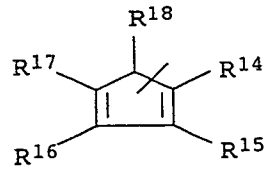
where

M is titanium, zirconium, hafnium, vanadium, niobium or tantalum,

X is fluorine, chlorine, bromine or iodine,

R^8 to R^{12} are each hydrogen, C_1-C_{10}-alkyl, 5- to 7-membered cycloalkyl which in turn may carry a C_1-C_{10}-alkyl as a substituent, C_6-C_{15}-aryl or arylalkyl, where two adjacent radicals together may furthermore form a cyclic group of 4 to 15 carbon atoms, or $Si(R^{13})_3$, where

R^{13} is C_1-C_{10}-alkyl, C_3-C_{10}-cycloalkyl or C_6-C_{15}-aryl,

Z is X or 

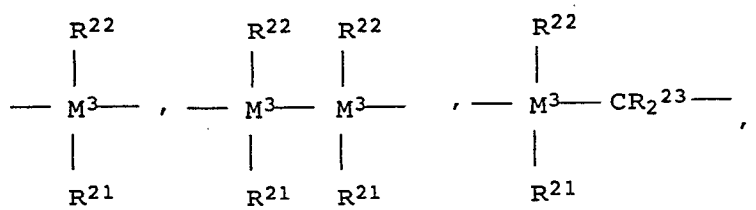
,] steht,

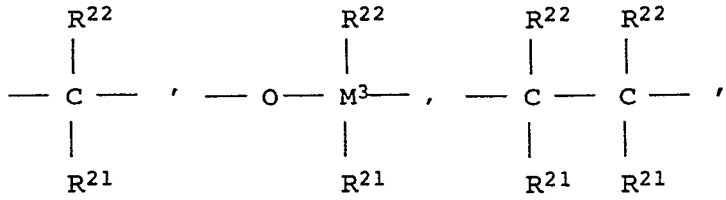
where

R^{14} to R^{18} are each hydrogen, C_1-C_{10}-alkyl, 5- to 7-membered cycloalkyl which in turn may carry a C_1-C_{10}-alkyl as a substituent, C_6-C_{15}-aryl or arylalkyl, where two adjacent radicals together may furthermore form a cyclic group of 4 to 15 carbon atoms, or $Si(R^{19})_3$, where

R^{19} is C_1-C_{10}-alkyl, C_6-C_{15}-aryl or C_3-C_{10}-cycloalkyl,

or R^{11} and Z together form a group $-R^{20}-A-$, in which

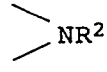
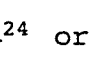
R^{20} is 



= BR^{22}, = AlR^{22}, -Ge-, -Sn-, -O-, -S-, = SO, = SO_2, = NR^{22}, = CO, = PR^{22} or = $P(O)R^{22}$,

where R^{21}, R^{22} and R^{23} are identical or different and are each hydrogen, halogen, C_1-C_{10}-alkyl, C_1-C_{10}-fluoroalkyl, C_6-C_{10}-fluoroaryl, C_6-C_{10}-aryl, C_1-C_{10}-alkoxy, C_2-C_{10}-alkenyl, C_7-C_{40}-arylalkyl, C_8-C_{40}-arylalkenyl or C_7-C_{40}-alkylaryl, or where two adjacent radicals, each with the atoms linking them, form a ring, and

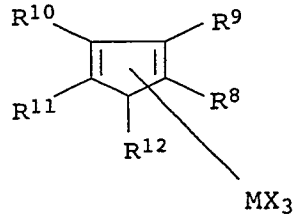
M^3 is silicon, germanium or tin,

A is —O—, —S—,  or  , where

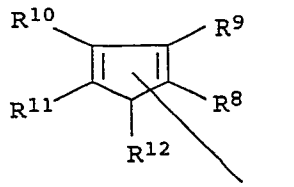
R^{24} is C_1-C_{10}-alkyl, C_6-C_{15}-aryl, C_3-C_{10}-cycloalkyl, alkylaryl or $Si(R^{25})_3$, and

R^{25} is hydrogen, C_1-C_{10}-alkyl, C_6-C_{15}-aryl, which in turn may be substituted by C_1-C_4-alkyl, or C_3-C_{10}-cycloalkyl, or where R^{11} and R^{17} together form a group $-R^{20}-$.

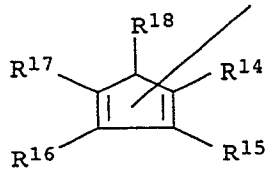
Among the metallocene complexes of the general formula III,

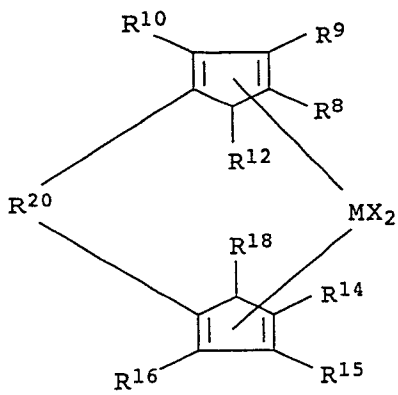


IIIa,

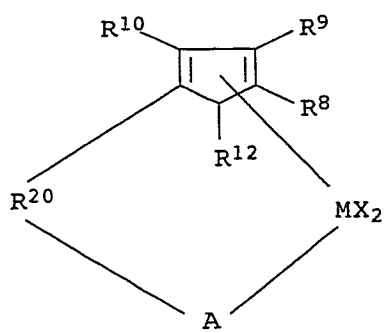


IIIb,





IIIc and



IIId

are preferred.

The radicals X may be identical or different but are preferably identical.

Among the compounds of the formula IIIa, those in which

M is titanium, zirconium or hafnium,

X	is chlorine and
R^8 to R^{12}	are each hydrogen or C_1-C_4-alkyl

are particularly preferred.

Among the compounds of the formula IIIb, those in which

M	is titanium, zirconium or hafnium,
X	is chlorine,
R^8 to R^{12}	are each hydrogen, C_1-C_4-alkyl or $Si(R^{13})_3$ and
R^{14} to R^{18}	are each hydrogen, C_1-C_4-alkyl or $Si(R^{19})_3$,

are preferred.

The compounds of the formula IIIb in which the cyclopentadienyl radicals are identical are particularly suitable.

Examples of particularly suitable compounds include
bis(cyclopentadienyl)zirconium dichloride,
bis(pentamethylcyclopentadienyl)zirconium dichloride,
bis(methylcyclopentadienyl)zirconium dichloride,
bis(ethylcyclopentadienyl)zirconium dichloride,
bis(n-butylcyclopentadienyl)zirconium dichloride and
bis(trimethylsilylcyclopentadienyl)zirconium dichloride.

Particularly suitable compounds of the formula IIIc are those in which

R^8 and R^{14}	are identical or different and are each hydrogen or C_1-C_{10}-alkyl,
R^{12} and R^{18}	are identical or different and are each hydrogen, methyl, ethyl, isopropyl or tert-butyl,
	R^{10} and R^{16} are each C_1-C_4-alkyl,
	R^9 and R^{15} are each hydrogen
	or two adjacent radicals R^9 and R^{10} on the one hand and R^{15} and R^{16} on the other hand together form a cyclic group of 4 to 12 carbon atoms,

R^{20} is $-M^3(R^{21})-$ or $-C(R^{21})-C(R^{21})-$,

M is titanium, zirconium or hafnium and
X is chlorine.

Examples of particularly suitable complex compounds include dimethylsilanediylbis(cyclopentadienyl)zirconium dichloride, dimethylsilanediylbis(indenyl)zirconium dichloride, dimethylsilanediylbis(tetrahydroindenyl)zirconium dichloride, ethylenebis(cyclopentadienyl)zirconium dichloride, ethylenebis(indenyl)zirconium dichloride, ethylenebis(tetrahydroindenyl)zirconium dichloride, tetramethylethylene-9-fluoroenylcyclopentadienylzirconium dichloride, dimethylsilanediylbis(-3-tert-butyl-5-methylcyclopentadienyl)-zirconium [sic] dichloride, dimethylsilanediylbis(-3-tert-butyl-5-ethylcyclopentadienyl)-zirconium [sic] dichloride, dimethylsilanediylbis(-2-methylindenyl)zirconium [sic] dichloride, dimethylsilanediylbis(-2-isopropylindenyl)zirconium [sic] dichloride, diethylsilanediylbis(-2-tert-butylindenyl)zirconium [sic] dichloride, dimethylsilanediylbis(-2-methylindenyl)zirconium [sic] dibromide, dimethylsilanediylbis(-3-methyl-5-methylcyclopentadienyl)-zirconium [sic] dichloride, dimethylsilanediylbis(-3-ethyl-5-isopropylcyclopentadienyl)-zirkonium [sic] dichloride, dimethylsilanediylbis(-2-methylindenyl)zirconium [sic] dichloride, dimethylsilanediylbis(-2-methylbenzindenyl)zirconium [sic] dichloride and dimethylsilanediylbis(-2-methylindenyl)hafnium [sic] dichloride.

Particularly suitable compounds of the general formula IIId are those in which

M is titanium or zirconium,
X is chlorine,

R^{20} is $-M^3(R^{21})(R^{22})-$ or $-C(R^{21})(R^{22})-C(R^{21})(R^{22})-$,

A is $-O-$, $-S-$, $>NR^{24}$

and

R^8 to R^{10} and R^{12} are each hydrogen, C_1–C_{10}-alkyl, C_3–C_{10}-cycloalkyl, C_6–C_{15}-aryl or $Si(R^{14})_3$, or where two adjacent radicals form a cyclic group of 4 to 12 carbon atoms.

The synthesis of such complex compounds can be carried out by methods known per se, the reaction of the appropriately substituted, cyclic hydrocarbon anions with halides of titanium, zirconium, hafnium, vanadium, niobium or tantalum being preferred.

Examples of appropriate preparation processes are described, inter alia, in J. Organometal. Chem. 369 (1989), 359-370.

Mixtures of different metallocene complexes may also be used.

Particularly suitable compounds forming metallocenium ions are strong, neutral Lewis acids, ionic compounds having Lewis acid cations and ionic compounds having Brönsted acids as cations.

Preferred strong, neutral Lewis acids are compounds of the general formula IV

$$M^4X^1X^2X^3 \qquad IV$$

where

M^4 is an element of main group III of the Periodic Table, in particular B, Al or Ga, preferably B, and

X^1, X^2 and X^3 are each hydrogen, C_1–C_{10}-alkyl, C_6–C_{15}-aryl, alkylaryl, arylalkyl, haloalkyl or haloaryl, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical, or fluorine, chlorine, bromine or iodine, in particular haloaryl, preferably pentafluorophenyl.

Particularly preferred compounds of the general formula IV are those in which X^1, X^2 and X^3 are identical, preferably tris(pentafluorophenyl)borane.

Suitable ionic compounds having Lewis acid cations are compounds of the general formula V

$$[(Y^{a+})Q_1Q_2...Q_z]^{d+} \qquad V$$

where

Y	is an element of main groups I to VI or subgroups I to VIII of the Periodic Table,
Q_1 to Q_z	are each radicals having a single negative charge, such as C_1-C_{28}-alkyl, C_6-C_{15}-aryl, alkylaryl, arylalkyl, haloalkyl, haloaryl, each having 6 to 20 carbon atoms in the aryl radical and 1 to 28 carbon atoms in the alkyl radical, C_1-C_{10}-cycloalkyl, which may be substituted by C_1-C_{10}-alkyl, or halogen, C_1-C_{28}-alkoxy, C_6-C_{15}-aryloxy, silyl or mercaptyl,
a	is an integer from 1 to 6,
z	is an integer from 0 to 5 and
d	is the difference a-z, but d is greater than or equal to 1.

Carbonium cations, oxonium cations and sulfonium cations as well as cationic transition metal complexes are particularly suitable. Particular examples are the triphenylmethyl cation, the silver cation and the 1,1'-dimethylferrocenyl cation. They preferably have noncoordinating opposite ions, in particular boron compounds, as also mentioned in WO 91/09882, preferably tetrakis(pentafluorophenyl)borate.

Ionic compounds having Brönsted acids as cations and preferably likewise noncoordinating opposite ions are mentioned in WO 91/09882; a preferred cation is N,N-dimethylanilinium.

The amount of compounds forming metallocenium ions is preferably from 0.1 to 10 equivalents, based on the metallocene complex III.

The conditions for the reaction of the metallocene complex with the compound forming metallocenium ions are not critical per se, but the reaction is preferably carried out in solution, particularly suitable solvents being hydrocarbons, preferably aromatic hydrocarbons, such as toluene.

The material prepared according to A) is then added to this. An amount of from 0.1 to 10% by weight, based on the inorganic carrier, of metallocene complex is particularly suitable. The conditions for this reaction are likewise not critical; temperatures of from 20 to 80°C and reaction times of from 0.1 to 20 hours have proven particularly suitable.

The material obtained according to B) can then be isolated and can be stored for up to at least 6 months.

In a further stage C), the activation stage, the material obtained according to B) is reacted with a metal compound of the general formula II. This activation can be carried out at any desired time, i.e. before, during or after the metering of the material obtained according to B) into the reactor. The activation is preferably affected after the material obtained according to B) has been metered into the reactor.

Among the metal compounds of the general formula II

$$M^2(R^5)_o(R^6)_p(R^7)_q \qquad II$$

where

M^2 is an alkali metal, an alkaline earth metal or a metal of main group III of the Periodic Table, ie. boron, aluminum, gallium, indium or thallium,

R^5 is hydrogen, C_1–C_{10}-alkyl, C_6–C_{15}-aryl, alkylaryl or arylalkyl, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

R^6 and R^7 are each hydrogen, halogen, C_1–C_{10}-alkyl, C_6–C_{15}-aryl, alkylaryl, arylalkyl or alkoxy, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

o is an integer from 1 to 3

and

p and q are integers from 0 to 2, the sum o+p+q corresponding to the valency of M^2,

preferred compounds are those in which

M^2 is lithium, magnesium or aluminum and

R^5 to R^7 are each C_1–C_{10}-alkyl.

Particularly preferred metal compounds of the general formula II are n-butyllithium, n-butyl-n-octylmagnesium, n-butyl-n-heptylmagnesium and tri-n-hexylaluminum.

The conditions for the reaction in stage C) are not critical per se. Temperatures, reaction times and pressures depend on the time when the reaction, ie. activation, is carried out.

The suspension polymerization is known per se. In a conventional procedure, polymerization is carried out in a suspending agent, preferably in an alkane. The polymerization temperatures are in general from -20 to 115°C and the pressure is generally from 1 to 100 bar. The solids content of the suspension is in general from 10 to 80%. The reaction may be carried out either batchwise, for example in a stirred autoclave, or continuously, for example in a tubular reactor, preferably in a loop reactor. In particular, the reaction can be carried out by the Phillips PF process, as described in US-A 3 242 150 and US-A 3 248 179.

In the novel processes, there are no problems at all with wall coatings and the formation of lumps. The catalyst systems used can be activated at any desired time, can be stored for a long time and are not pyrophoric. Furthermore, polymers which have a narrow molecular weight distribution and are suitable for the production of fibers, films and moldings are formed.

Examples

Examples 1 and 2: Reaction of SiO_2 with triisobutylaluminum (stage A))

Example 1

100 g of SiO_2 (SG 332 from Grace; dried for 12 hours at 200°C) were suspended in 1 l of dry heptane. At room temperature, 140 ml of a 2 molar solution of triisobutylaluminum in heptane were added dropwise in the course of 30 minutes, the temperature increasing to 35°C. Thereafter, stirring was carried out overnight and the solid was filtered off and washed twice with pentane. It was then dried under a reduced pressure from an oil pump until the weight remained constant (carrier 1).

Example 2

50 g of SiO_2 (ES 70F from Crosfield; dried for 7 hours at 110°C under reduced pressure) were suspended in 500 ml of dry heptane. At room temperature, 70 ml of a 2 molar solution of triisobutyl-

aluminum in heptane were added dropwise in the course of 30 minutes, the temperature increasing to 35°C. Thereafter, stirring was carried out overnight and the solid was filtered off and washed with heptane. It was then dried under a reduced pressure from an oil pump until the weight remained constant (carrier 2).

Example 3 Reaction of metallocene complex and N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate (stage B))

0.5 mmol of the respective metallocene complex and in each case 0.5 mmol of N,N-dimethylanilinium tetrakis(pentafluorophenyl)borate were dissolved in 50 ml of absolute toluene at 80°C. In each case 5 g of the material obtained according to Example 1 or 2 were added to this and the dispersion thus obtained was stirred for 30 minutes at 80°C. Thereafter, the solvent was dripped off at 10 mbar and the solid residue was dried under reduced pressure from an oil pump until a free-flowing powder remained.

Metallocene complexes used:

III 1: bis(cyclopentadienyl)zirconium dichloride
III 2: bis(n-butylcyclopentadienyl)zirconium dichloride
III 3: bis(trimethylsilylcyclopentadienyl)zirconium dichloride
III 4: dimethylsilanediylbis(indenyl)zirconium dichloride
III 5: dimethylsilanediylbis(-2-methylbenzindenyl)zirconium [sic] dichloride
III 6: dimethylsilanediyl(N-tert-butylamido)($\bullet^5$-2,3,4,5-tetramethylcyclopentadienyl)titanium dichloride

Examples 4 to 17: Preparation of polyethylene in suspension

A 1 l steel autoclave was heated to 70°C, after which the corresponding metal compound II was injected through a lock with 20 ml of isobutane. Thereafter, ethylene was passed in until the pressure in the autoclave reached 40 bar, and a corresponding amount of the material prepared in Example 3 was blown in with ethylene. The polymerization was carried out at 70°C until 200 g of ethylene had been absorbed, and was stopped by letting down the pressure.

Metal compounds II used:

II 1: tri-n-hexylaluminum
II 2: n-butyl-n-heptylmagnesium
II 3: n-butyllithium

Table 1 below provides information about the compounds used in each case and the properties of the polyethylenes.

The limiting viscosity η was determined according to ISO 1628/3.

Table 1:

Ex.	Carrier	Metallocene complex	Amount used of the material prepared according to Ex. 3 [mg]	Metal compound	Productivity [g of polymer/g of catalyst]*)	η [dl/g]
4	1	III 1	107	180 mg II 1	1495	3.75
5	2	III 1	68	168 mg II 1	3970	4.04
6	2	III 1	88	80 mg II 2	3460	4.06
7	1	III 2	66	40 mg II 3	2560	3.97
8	2	III 2	98	80 mg II 2	3010	4.24
9	2	III 2	54	40 mg II 3	4900	4.05
10	1	III 3	83	80 mg II 3	228	6.34
11	1	III 4	116	20 mg II 3	1422	2.43
12	2	III 4	41	60 mg II 2	4580	2.89
13	2	III 5	94	80 mg II 2	2660	2.11
14	1	III 6	140	60 mg II 2	2210	24.8
15	1	III 6	81	20 mg II 3	2690	22.89
16	1	III 6	250	40 mg II 3	506	21.2
17	1	III 6	197	80 mg II 2	535	20.22

*) Catalyst means the product obtained in stage B)

We claim:

1. A process for the preparation of polymers of alkenes by suspension polymerization in the presence of catalyst systems, wherein the catalyst systems used are supported catalyst systems obtainable by

A) reaction of an inorganic carrier with a metal compound of the formula I

$$M^1(R^1)_r(R^2)_s(R^3)_t(R^4)_u \qquad I$$

where

M^1 is an alkali metal, an alkaline earth metal or a metal of main group III or IV of the Periodic Table,

R^1 is hydrogen, C_1-C_{10}-alkyl, C_6-C_{15}-aryl, alkylaryl or arylalkyl, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

R^2 to R^4 are each hydrogen, halogen, C_1-C_{10}-alkyl, C_6-C_{15}-aryl, alkylaryl, arylalkyl, alkoxy or dialkylamino, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

r is an integer from 1 to 4

and

s, t and u are integers from 0 to 3, the sum r+s+t+u corresponding to the valency of M^1,

B) reaction of the material obtained according to A) with a metallocene complex in its metal dihalide form and a compound forming metallocenium ions

C) subsequent reaction with a metal compound of the formula II

$$M^2(R^5)_o(R^6)_p(R^7)_q \qquad II$$

in which

M^2 is an alkali metal, an alkaline earth metal or a metal of main group III of the Periodic Table,

R^5 is hydrogen, C_1-C_{10}-alkyl, C_6-C_{15}-aryl, alkylaryl or arylalkyl, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

R^6 and R^7 are each hydrogen, halogen, C_1-C_{10}-alkyl, C_6-C_{15}-aryl, alkylaryl, arylalkyl or alkoxy, each having 1 to 10 carbon atoms in the alkyl radical and 6 to 20 carbon atoms in the aryl radical,

o is an integer from 1 to 3

and

p and q are integers from 0 to 2, the sum o+p+q corresponding to the valency of M^2.

2. A process as claimed in claim 1, wherein the material obtained according to A) is isolated and dried.

3. A supported catalyst system as claimed in claims 1 and 2, wherein, in the formula I, M^1 is aluminum, R^1 to R^3 are each C_1-C_{10}-alkyl and u is zero.

4. A process as claimed in any of claims 1 to 3, wherein a coordination complex compound selected from the group consisting of the strong, neutral Lewis acids, the ionic compounds having Lewis acid cations and the ionic compounds having Brönsted acids as cations is used as the compound forming metallocenium ions.

5. A process as claimed in any of claims 1 to 4, wherein, in the formula II, R^5 to R^7 are each C_1-C_{10}-alkyl.

6. A process as claimed in any of claims 1 to 5 for the preparation of polymers of ethylene.

7. A polymer of alkenes, obtainable by a process as claimed in any of claims 1 to 6.

8. The use of polymers of alkenes as claimed in claim 7 for the production of fibers, films and moldings.

9. A fiber, film or molding containing polymers of alkenes as claimed in claim 7 as essential components.