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(54) Titre : COPOLYMERES CYCLOOLEFINIQUES POSSEDANT UNE FAIBLE VISCOSITE A L'ETAT FONDU ET UNE FAIBLE ATTENUATION OPTIQUE

(54) Title: CYCLO-OLEFIN COPOLYMERS WITH LOW FUSION VISCOSITY AND LOW OPTICAL ATTENUATION

(57) Abrégé/Abstract:
A process for the preparation of a cycloolefin copolymer (COC) having low melt viscosity by copolymerization of from 0.1 to 99.9% by weight, based on the total amount of the monomers, of at least one monomer [lacuna] in which R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are identical or different and are a hydrogen atom or a C_1-C_8-alkyl radical or an aryl radical, where identical radicals in the various formulae can have different meanings, from 0 to 99.9% by weight, based on the total amount of the monomers, of a cycloolefin of the formula V in which n is a number from 2 to 10, and from 0.1 to 99.9% by weight, based on the total amount of the monomers, of at least one acyclic 1-olefin of the formula VI, in which R^9, R^{10}, R^{11} and R^{12} are identical or different and are a hydrogen atom or a C_1-C_8-alkyl radical, in solution, in suspension, in the liquid cycloolefin monomer or cycloolefin monomer mixture or in the gas phase, at a temperature of from -78 to 150°C, at a pressure of from 0.5 to 64 bar, in the presence of a catalyst comprising a metallocene as transition-metal component and an aluminoxane of the formula VII for the linear type and/or of the formula VIII for the cyclic type, where, in the formulae VII and VIII, R^{13} is a C_1-C_6-alkyl group or phenyl or benzyl, and n is an integer from 2 to 50, where the polymerization is carried out in the presence of a catalyst whose transition-metal component is at least one compound of the formula IX in which M^1 is titanium, zirconium, hafnium, vanadium, niobium or tantalum, R^{14} and R^{15} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group or a C_8-C_{40}-arylalkenyl group, and m may be one or two, depending on the valency of the central atom M^1, R^{18} is =BR^{19}, =AlR^{19}, -Ge-, -Sn-, -O-, -S-, =SO, =SO_2, =NR^{19}, =CO; = PR^{19} or =$P(O)R^{19}$, where R^{19}, R^{20} and R^{21} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-fluoroaryl group, a C_6-C_{10}-aryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_1-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^{19} and R^{20} or R^{19} and R^{21}, in each case with the atoms connecting them, form a ring, M^2 is silicon, germanium or tin, R^{16} and R^{17} are different and are a monocyclic or polycyclic hydrocarbon radical which can form a sandwich structure with the central atom M^1, wherein the metallocene of the formula IX has C_s-symmetry with respect to the ligands R^{16} and R^{17} and with respect to the central atom M^1 connecting them.

Abstract of the Disclosure

Cycloolefin copolymers having low melt viscosity and low optical attenuation

A process for the preparation of a cycloolefin copolymer (COC) having low melt viscosity by copolymerization of from 0.1 to 99.9% by weight, based on the total amount of the monomers, of at least one monomer [lacuna] in which R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are identical or different and are a hydrogen atom or a C_1-C_8-alkyl radical or an aryl radical, where identical radicals in the various formulae can have different meanings,
from 0 to 99.9% by weight, based on the total amount of the monomers, of a cycloolefin of the formula V in which n is a number from 2 to 10, and from 0.1 to 99.9% by weight, based on the total amount of the monomers, of at least one acyclic 1-olefin of the formula VI, in which R^9, R^{10}, R^{11} and R^{12} are identical or different and are a hydrogen atom or a C_1-C_8-alkyl radical, in solution, in suspension, in the liquid cycloolefin monomer or cycloolefin monomer mixture or in the gas phase, at a temperature of from -78 to 150°C, at a pressure of from 0.5 to 64 bar, in the presence of a catalyst comprising a metallocene as transition-metal component and an aluminoxane of the formula VII for the linear type and/or of the formula VIII for the cyclic type, where, in the formulae VII and VIII, R^{13} is a C_1-C_6-alkyl group or phenyl or benzyl, and n is an integer from 2 to 50, where the polymerization is carried out in the presence of a catalyst whose transition-metal component is at least one compound of the formula IX in which

M^1 is titanium, zirconium, hafnium, vanadium, niobium or tantalum,

R^{14} and R^{15} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group

or a C_8-C_{40}-arylalkenyl group, and

m may be one or two, depending on the valency of the central atom M^1,

R_{18} is

$=BR^{19}$, $=AlR^{19}$, -Ge-, -Sn-, -O-, -S-, =SO, $=SO_2$, $=NR^{19}$, =CO, $=PR^{19}$ or $=P(O)R^{19}$, where R^{19}, R^{20} and R^{21} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-fluoroaryl group, a C_6-C_{10}-aryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^{19} and R^{20} or R^{19} and R^{21}, in each case with the atoms connecting them, form a ring,

M^2 is silicon, germanium or tin,

R^{16} and R^{17} are different and are a monocyclic or polycyclic hydrocarbon radical which can form a sandwich structure with the central atom M^1,

wherein the metallocene of the formula IX has C_s-symmetry with respect to the ligands R^{16} and R^{17} and with respect to the central atom M^1 connecting them.

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Description

Cycloolefin copolymers having low melt viscosity and low optical attenuation

The invention relates to thermoplastic cycloolefin copolymers (COCs) having low melt viscosity and low optical attenuation, to a process for their preparation, and to their use as optical waveguides (optical fibers).

Optical waveguides are employed for the transport of light, for example for the purpose of illumination or signal transmission. They generally comprise a cylindrical, light-transmitting core surrounded by a cladding layer of a likewise transparent material with a lower refractive index. Thin-film optical waveguides comprise, for example, three transparent layers, where the two outer layers have a lower refractive index than the central layer. The conduction of light takes place by total reflection at the interface. Transparent materials which can be employed are glasses or (organic or inorganic) polymers.

The most widespread polymer for use as an optical waveguide, polymethyl methacrylate (PMMA), can only be employed at up to about 85°C due to its low glass transition temperature of about 106°C. Other known transparent thermoplastics having higher glass transition temperatures, such as, for example, polycarbonate or aromatic polyesters, contain aromatic units in the molecule. These result in increased light absorption in the short-wave spectral region. The use of such polymers for optical waveguides is described in illustrative terms in A. Tanaka et al., SPIE, Vol. 840 (1987).

The heat distortion resistance can be improved by reaction of polymethacrylates. An example which may be mentioned is the polymer-analogous conversion of polymethyl methacrylate into polymethacrylimide. The

copolymerization of poly(meth)acrylate with comonomers such as methacrylic anhydride or methacrylonitrile also gives polymers of higher heat resistance than unmodified PMMA. Another route to transparent polymers having increased glass transition temperatures is the use of (meth)acrylates of (per)halogenated or polycyclic aliphatic alcohols or of substituted phenols. The latter likewise have increased light absorption in the short-wave spectral region due to the aromatic units. Although the former compounds give transparent polymers having high glass transition temperatures, conversion, for example, into optical fibers is difficult or impossible due to their inherent brittleness.

All the classes of substances described are hygroscopic due to their polar nature. At elevated temperature, the water content in the polymer can cause undesired degradation reactions during conversion, reducing the practical use value.

However, lower water absorption is exhibited by thermoplastic COCs, which also have increased heat distortion resistance. The complete absence of chromophores, such as double bonds of all types, means that these polymers appear particularly suitable for optical applications. It should also be possible to employ these plastics in the area of light conduction (EP-A 0 355 682 and EP-A 0 485 893).

COCs can be prepared using specific Ziegler catalysts (EP-A 0 355 682), usually using alkylaluminum or alkylaluminum chlorides as cocatalysts. However, these compounds hydrolyze during the work-up process described to give extremely fine, gelatinous compounds which are difficult to filter. If alkylaluminum chlorides are employed, chlorine-containing compounds, such as hydrochloric acid or salts, which are likewise difficult to separate off, are formed during work-up. If hydrochloric acid is employed for the work-up

(EP-A 0 355 682 and EP-A 0 485 893), similar problems arise. In particular in the processing of COCs prepared in this way, a brown coloration occurs. In addition, a known problem in the preparation of ethylene-containing cycloolefin copolymers is the formation of partially crystalline ethylene polymers as a byproduct. EP-AU 447 072, for example, describes how cycloolefin copolymers prepared by vanadium catalysis (cf. EP-AO 156 464) can be freed from partially crystalline ethylene polymerization by a complex multistep filtration. The metallocene catalysts described in EP 404 870, with the exception of isopropylene (9-fluorenyl)cyclopentadienylzirconium dichloride and diphenylcarbyl(9-fluorenyl)cyclopentadienylzirconium dichloride, also produce partially crystalline ethylene polymers as a byproduct to the cycloolefin copolymer, as our own detailed investigations have shown. However, the higher the content of partially crystalline ethyl polymer, the higher the optical attenuation of the material.

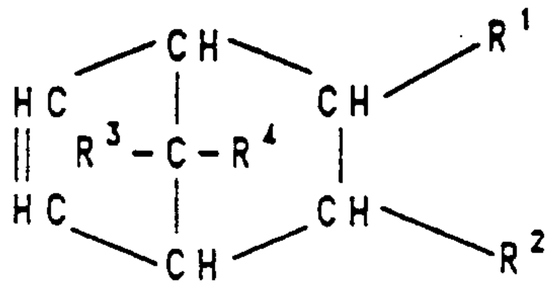
In addition to excellent transparency, a further important prerequisite for the use of a polymer for the production of a polymeric optical fiber or an optical waveguide is low melt viscosity in order to improve the processing conditions.

The invention provides a process for the preparation of COCs which are distinguished by improved melt viscosity, lower optical attenuation, increased glass transition temperature and low water absorption compared with the prior art. Further, the invention provides an optical waveguide whose core material comprises these COCs.

It has now been found that copolymerization of lower alpha-olefins, cyclic olefins and polycyclic olefins using a catalyst system comprising at least one metallocene catalyst and at least one cocatalyst allows the preparation of COCs having low melt viscosity if

metallocene catalysts of certain symmetries are employed. If the reaction mixture formed after the copolymerization is subjected to a specific work-up process, optical waveguides having a low optical attenuation of 0.1-5 dB/km, preferably 0.2-2 dB/km and particularly preferably 0.3-1.5 dB/km, can be prepared from the purified COC and a transparent polymer whose refractive index is lower than the refractive index of the COC.

The invention thus relates to a process for the preparation of COCs having low melt viscosity by polymerization of from 0.1 to 99.9% by weight, based on the total amount of the monomers, of at least one monomer of the formula I, II, III or IV



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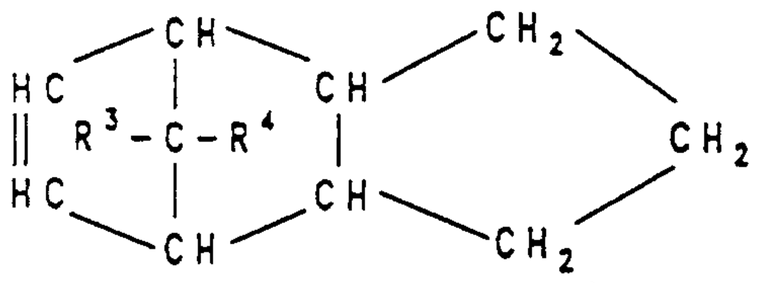

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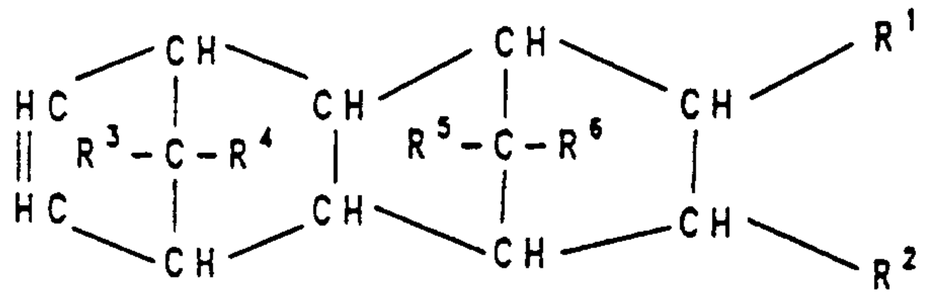

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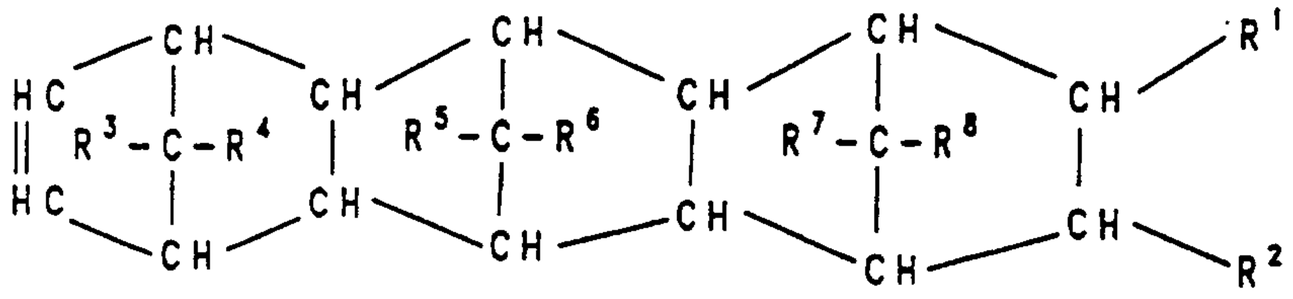
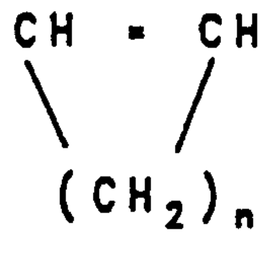


(IV),

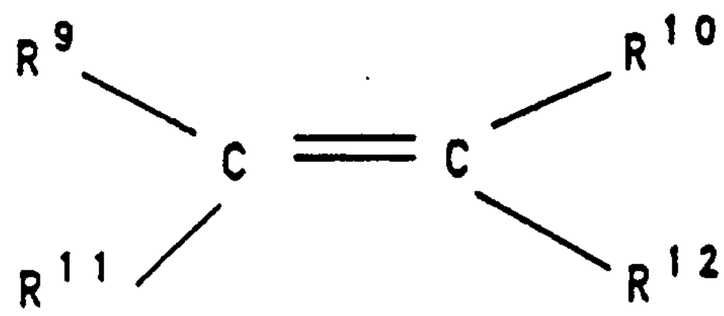
in which R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are identical or different and are a hydrogen atom or a C_1-C_8-alkyl

radical or a C_6-C_{16}-aryl radical, where identical radicals in the various formulae can have different meanings, from 0 to 99.9% by weight, based on the total amount of the monomers, of a cycloolefin of the formula V



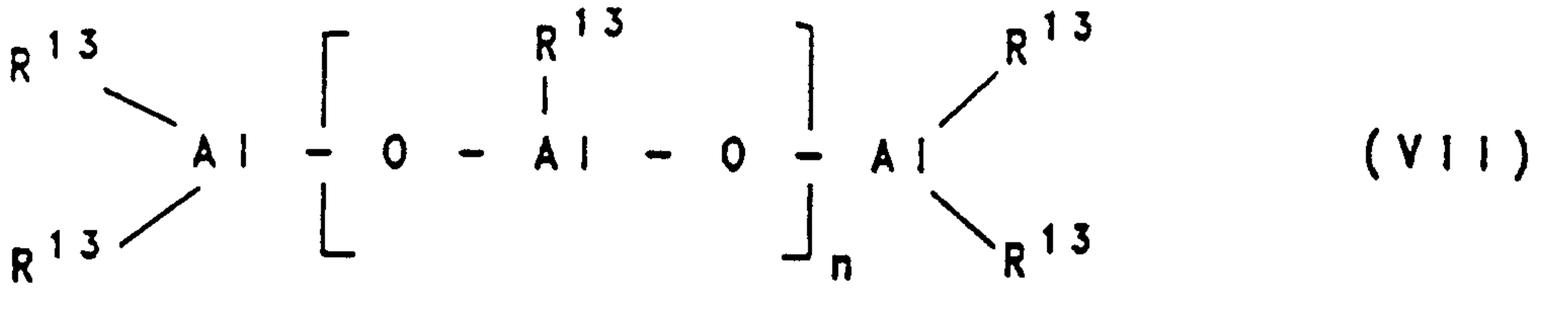
(V)

in which n is a number from 2 to 10, and from 0.1 to 99.9% by weight, based on the total amount of the monomers, of at least one acyclic 1-olefin of the formula VI



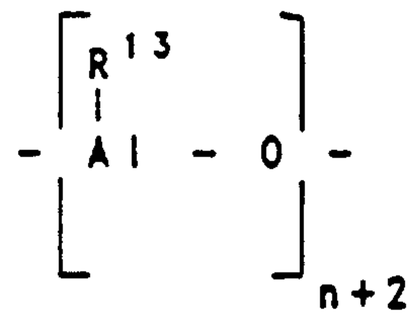
(VI),

in which R^9, R^{10}, R^{11} and R^{12} are identical or different and are a hydrogen atom or a C_1-C_8-alkyl radical or a C_6-C_{16}-aryl radical, in solution, in suspension, in the liquid cycloolefin monomer, or cycloolefin monomer mixture or in the gas phase, at a temperature of from -78 to 150°C, at a pressure of from 0.5 to 64 bar, in the presence of a catalyst comprising a metallocene as transition-metal component and an aluminoxane of the formula VII



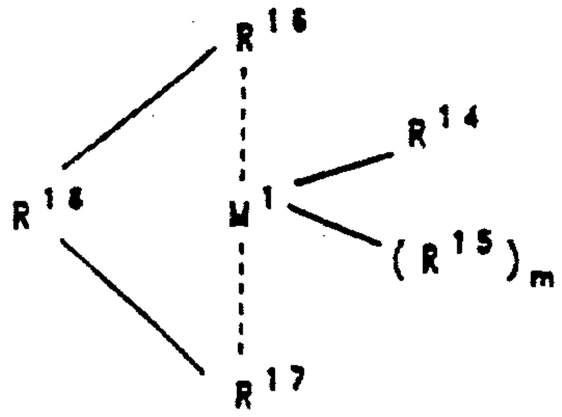
(VII)

for the linear type and/or of the formula VIII



(VIII)

for the cyclic type, where, in the formulae VII and VIII, R^{13} is a C_1-C_6-alkyl group or phenyl or benzyl, and n is an integer from 2 to 50, where the polymerization is carried out in the presence of a catalyst whose transition-metal component is at least one compound of the formula IX



(IX)

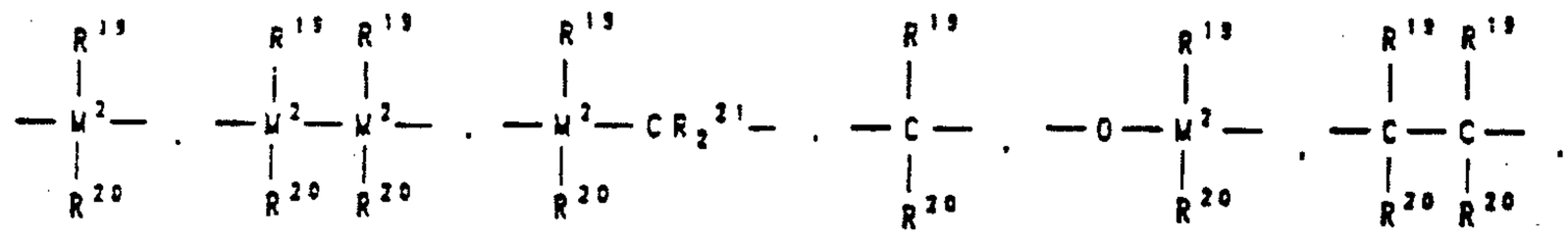
in which

M^1 is titanium, zirconium, hafnium, vanadium, niobium or tantalum,

R^{14} and R^{15} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group or a C_8-C_{40}-arylalkenyl group,

m may be one or two, depending on the valency of the central atom M^1,

R^{18} is



$=BR^{19}$, $=AlR^{19}$, -Ge-, -Sn-, -O-, -S-, =SO, $=SO_2$, $=NR^{19}$, =CO, $=PR^{19}$ or $=P(O)R^{19}$, where R^{19}, R^{20} and R^{21} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-fluoroaryl group, a C_6-C_{10}-aryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^{19} and R^{20} or R^{19} and R^{21}, in each case with the

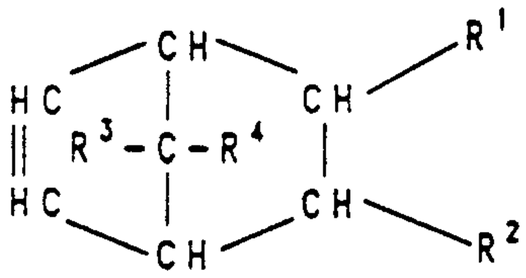
atoms connecting them, form a ring,

M^2 is silicon, germanium or tin,

R^{16} and R^{17} are different and are a monocyclic or polycyclic hydrocarbon radical which can form a sandwich structure with the central atom M^1,

wherein the metallocene of the formula IX has C_s-symmetry with respect to the ligands R^{16} and R^{17} and with respect to the central atom M^1 connecting them.

In the polymerization, at least one polycyclic olefin of the formula I, II, III or IV, preferably a cycloolefin of the formula I or III



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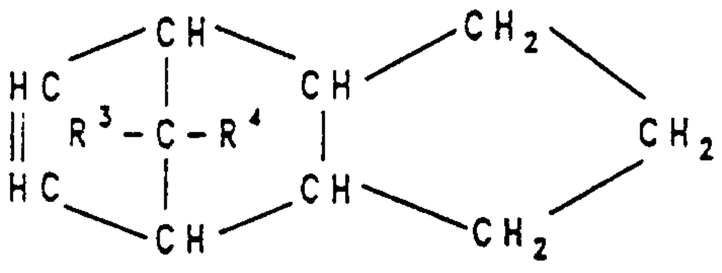

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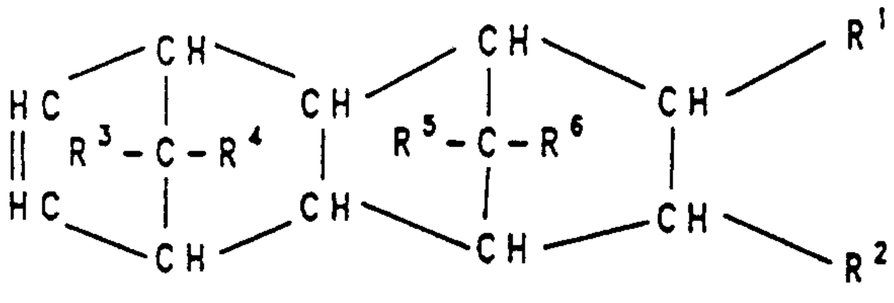

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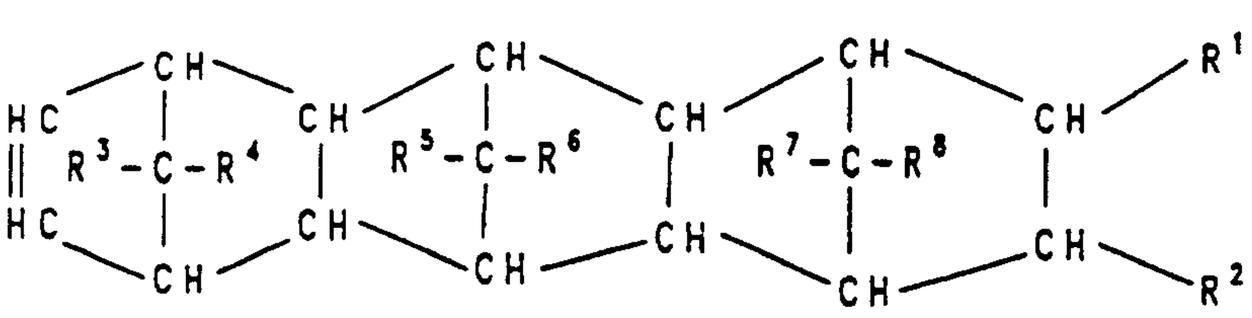
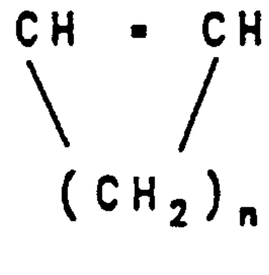


(IV),

in which R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are identical or different and are a hydrogen atom or a C_1-C_8-alkyl radical or a C_1-C_{16}-aryl radical, where identical radicals in the various formulae can have different meanings,

is polymerized.

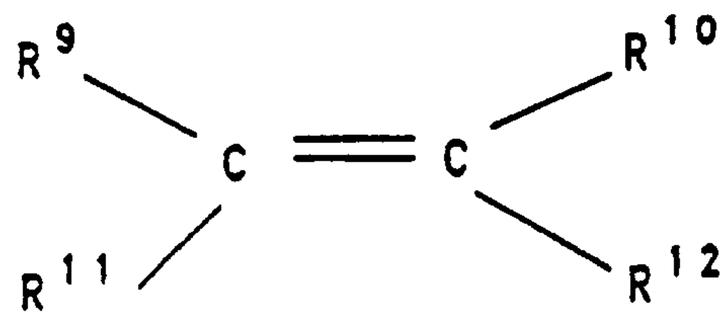
It is also possible to use a monocyclic olefin of the formula V



(V)

in which n is a number from 2 to 10.

Another comonomer is an acyclic 1-olefin of the formula VI



(VI),

in which R^9, R^{10}, R^{11} and R^{12} are identical or different and are a hydrogen atom or a C_1-C_8-alkyl radical, which may also contain a double bond, or a C_6-C_{16}-aryl radical. Preference is given to ethylene, propylene, butene, hexene, octene or styrene. Particular preference is given to ethene. In addition, it is also possible to employ dienes.

In particular, copolymers of polycyclic olefins of the formulae I and II are prepared.

The polycyclic olefin (I to IV) is employed in an amount of from 0.1 to 99.9% by weight, the monocyclic olefin (V) is employed in an amount of from 0.1 to 99.9% by weight and the acyclic 1-olefin (VI) is employed in an amount of from 0.1 to 99.9% by weight, in each case based on the total amount of the monomers.

The monomers are preferably incorporated in the following ratios:

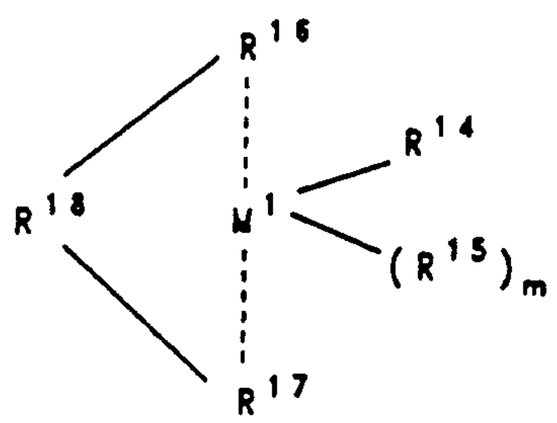
a) the molar polycyclic olefin (I to IV):1-olefin (VI) monomer ratio in the corresponding polymers is from 1:99 to 99:1, preferably from 20:80 to 80:20;

b) in polymers comprising polycyclic olefins (I to IV) and monocyclic olefins (V), the molar polycyclic olefin:monocyclic olefin ratio is from 10:90 to 90:10;

c) in polymers comprising polycyclic olefins (I to IV), monocyclic olefins (V) and 1-olefins (VI), the molar polycyclic olefin:monocyclic olefin:1-olefin monomer ratio is from 93:5:2 to 5:93:2 to 5:5:90, i.e. the molar ratio is within a mixture triangle whose corners are determined by the molar ratios 93:5:2, 5:93:2 and 5:5:90;

d) in a), b) and c), polycyclic olefins, monocyclic olefins and 1-olefins are also taken to mean mixtures of two or more olefins of the particular type.

The catalyst used in the polymerization comprises an aluminoxane and at least one metallocene of the formula IX



(IX)

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

R^{14} and R^{15} are identical or different and are a hydrogen atom, a C_1-C_{10}-, preferably C_1-C_3-alkyl group, a C_1-C_{10}-,

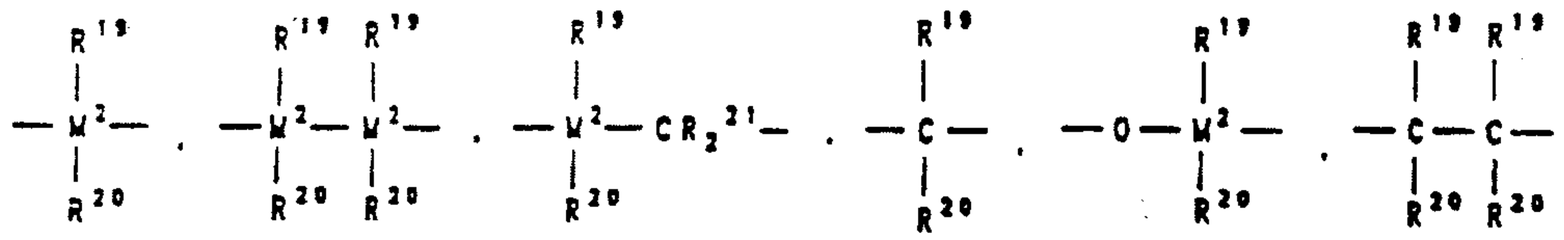
preferably C_1-C_3-alkoxy group, a C_6-C_{10}, preferably C_6-C_8-aryl group, a C_6-C_{10}-, preferably C_6-C_8-aryloxy group, a C_2-C_{10}-, preferably C_2-C_4-alkenyl group, a C_7-C_{40}, preferably C_7-C_{10}-arylalkyl group, a C_7-C_{40}-, preferably C_7-C_{12}-alkylaryl group, a C_8-C_{40}-, preferably C_8-C_{12}-arylalkenyl group, or a halogen atom, preferably chlorine.

R^{16} and R^{17} are different and are a monocyclic or polycyclic hydrocarbon radical which can form a sandwich structure with the central atom M^1.

The metallocene of the formula IX has C_s-symmetry with respect to the ligands R^{16} and R^{17} and with respect to the central atom M^1 connecting them.

R^{16} is preferably fluorenyl and R^{17} is preferably cyclopentadienyl.

R^{18} is a single- or multimembered bridge which links the radicals R^{16} and R^{17} and is



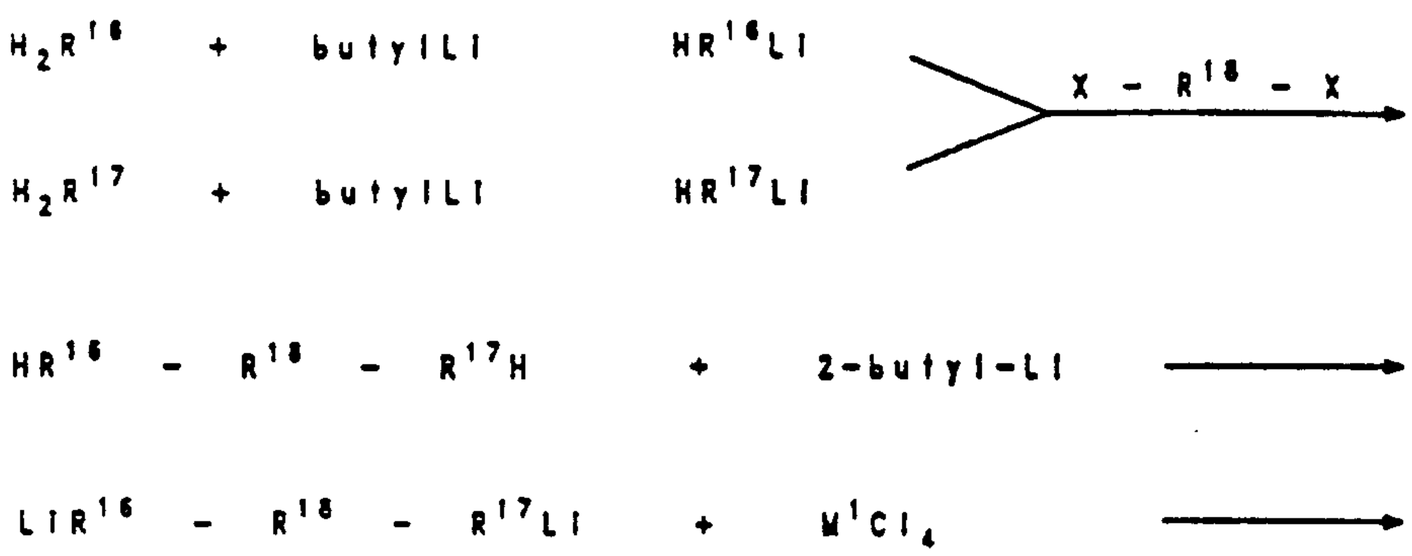
$=BR^{19}$, $=AlR^{19}$, -Ge-, -Sn-, -O-, -S-, =SO, $=SO_2$, $=NR^{19}$, =CO, $=PR^{19}$ or $=P(O)R^{19}$, where R^{19}, R^{20} and R^{21} are identical or different and are a hydrogen atom, a halogen atom, preferably chlorine, a C_1-C_{10}-, preferably C_1-C_3-alkyl group, in particular a methyl group, a C_1-C_{10}-fluoroalkyl group, preferably a CF_3 group, a C_6-C_{10}-fluoroaryl group, preferably a pentafluorophenyl group, a C_6-C_{10}, preferably C_6-C_8-aryl group, a C_1-C_{10}, preferably C_1-C_4-alkoxy group, in particular a methoxy group, a C_2-C_{10}, preferably C_2-C_4-alkenyl group, a C_7-C_{40}, preferably C_7-C_{10}-arylalkyl group, a C_8-C_{40}, preferably C_8-C_{12}-arylalkenyl group, or a C_7-C_{40}, preferably C_7-C_{12}-alkylaryl group, or R^{19} and R^{20} or R^{19} and R^{21}, in each

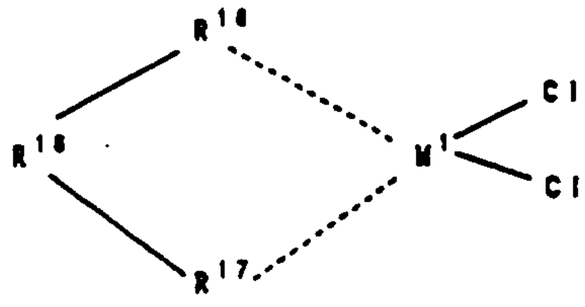
case together with the atoms connecting them, form a ring.

M^2 is silicon, germanium or tin, preferably silicon or germanium.

R^{18} is preferably $=CR^{19}R^{20}$, $=SiR^{19}R^{20}$, $=GeR^{19}R^{20}$, -O-, -S-, =SO, $=PR^{19}$ or $=P(O)R^{19}$.

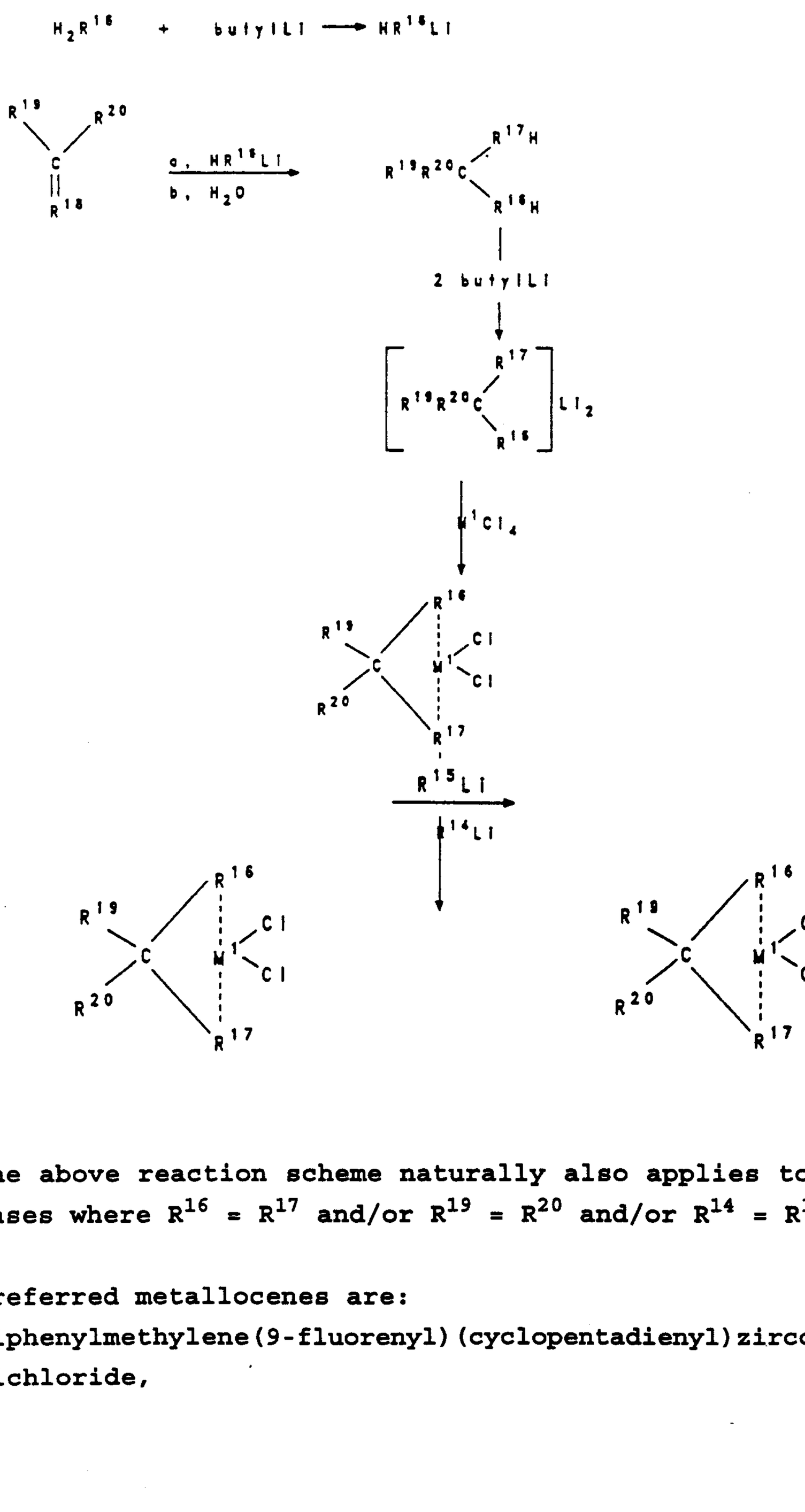
The metallocenes can be prepared in accordance with the following reaction scheme:





(IX)

or



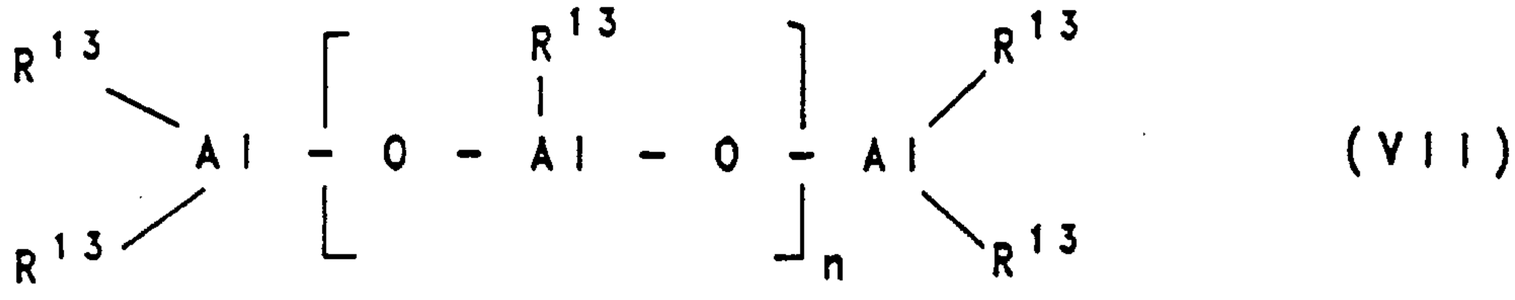
The above reaction scheme naturally also applies to the cases where $R^{16} = R^{17}$ and/or $R^{19} = R^{20}$ and/or $R^{14} = R^{15}$.

Preferred metallocenes are:
diphenylmethylene(9-fluorenyl)(cyclopentadienyl)zirconium dichloride,

isopropylene(9-fluorenyl)cyclopentadienylzirconium dichloride,
methylphenylcarbyl(9-fluorenyl)(cyclopentadienyl)-zirconium dichloride,
or mixtures thereof.

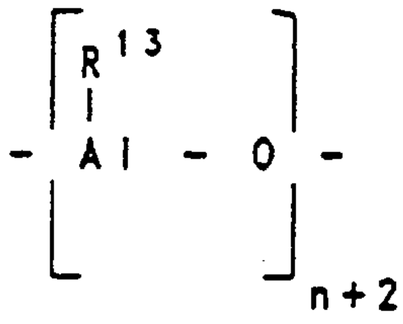
Particular preference is given to isopropylene(9-fluorenyl)cylcopentadienylzirconium dichloride or mixtures thereof.

The cocatalyst is an aluminoxane of the formula VII



(VII)

for the linear type and/or of the formula VIII



(VIII)

for the cyclic type. In these formulae, R^{13} is a C_1-C_6-alkyl group, preferably methyl, ethyl, isobutyl, butyl or neopentyl, or phenyl or benzyl. Particular preference is given to methyl. n is an integer from 2 to 50, preferably 5 to 40. However, the precise structure of the aluminoxane is unknown.

The aluminoxane can be prepared in various ways.

In one of the processes, finely powdered copper sulfate pentahydrate is slurried in toluene, and sufficient trialkylaluminum is added in a glass flask under inert gas at about -20°C so that about 1 mol of $CuSO_4 \cdot 5H_2O$ is available per 4 Al atoms. After slow hydrolysis with elimination of alkane, the reaction mixture is left at

room temperature for from 24 to 48 hours, during which cooling may be necessary so that the temperature does not exceed 30°C. The aluminoxane dissolved in toluene is subsequently separated from the copper sulfate by filtration, and the solution is evaporated in vacuo. It is assumed that this preparation process involves condensation of low-molecular-weight aluminoxanes to give higher oligomers with elimination of trialkylaluminum.

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

The aluminum salts containing water of crystallization are in particular those which have a high content of water of crystallization. Particular preference is given to aluminum sulfate hydrate, in particular the compounds $Al_2(SO_4)_3 \cdot 16H_2O$ and $Al_2(SO_4)_3 \cdot 18H_2O$ having the particularly high water of crystallization contents of 16 and 18 mol of H_2O/mol of $Al_2(SO_4)_3$ respectively.

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

In addition to the processes outlined above for the preparation of aluminoxanes, there are others which can be used. Irrespective of the preparation method, all

aluminoxane solutions have in common a varying content of unreacted trialkylaluminum, in free form or as an adduct. This content has an effect on the catalytic activity which has not yet been explained precisely and varies depending on the metallocene compound employed.

It is possible to preactivate the metallocene by means of an aluminoxane of the formula II and/or III before use in the polymerization reaction. This significantly increases the polymerization activity.

The preactivation of the transition-metal compound is carried out in solution. It is preferred here to dissolve the metallocene in a solution of the aluminoxane in an inert hydrocarbon. Suitable inert hydrocarbons are aliphatic or aromatic hydrocarbons. Preference is given to toluene.

The concentration of the aluminoxane in the solution is in the range from 1% by weight to the saturation limit, preferably from 5 to 30% by weight, in each case based on the entire solution. The metallocene can be employed in the same concentration, but is preferably employed in an amount of from 10^{-4} to 1 mol per mol of aluminoxane. The preactivation time is from 5 minutes to 60 hours, preferably from 5 to 60 minutes. The reaction temperature is from -78°C to 150°C, preferably from 20 to 100°C.

Significantly longer preactivation is possible, but normally neither increases nor reduces the activity, but may be appropriate for storage purposes.

The polymerization is carried out in an inert solvent customary for the Ziegler low-pressure process, for example in an aliphatic or cycloaliphatic hydrocarbon; examples of these which may be mentioned are butane, pentane, hexane, heptane, isooctane, cyclohexane and methylcyclohexane. It is furthermore possible to use a gasoline or hydrogenated diesel oil fraction which has

been carefully freed from oxygen, sulfur compounds and moisture. It is also possible to use toluene, decalin and xylene.

Finally, the monomer to be polymerized can also be employed as solvent or suspending medium. In the case of norbornene, bulk polymerizations of this type are carried out at a temperature above 45°C. The molecular weight of the polymer can be regulated in a known manner; hydrogen is preferably used for this purpose.

The polymerization is carried out in a known manner in solution, in suspension, in the liquid cycloolefin monomer or cycloolefin monomer mixture or in the gas phase, continuously or batchwise, in one or more steps, at a temperature of from -78 to 150°C, preferably from 20 to 100°C. The pressure is from 0.5 to 64 bar and is established either by means of the gaseous olefins or with the aid of inert gas.

Particularly advantageous are continuous and multistep processes since they allow efficient use of the polycyclic olefin, which is fed as residual monomer together with the reaction mixture.

The metallocene compound is used here in a concentration, based on the transition metal, of from 10^{-3} to 10^{-7} mol, preferably from 10^{-5} to 10^{-6} mol, of transition metal per dm^3 of reactor volume. The aluminoxane is used in a concentration of from 10^{-4} to 10^{-1} mol, preferably from 10^{-4} to $2 \cdot 10^{-2}$ mol, per dm^3 of reactor volume, based on the aluminum content. In principle, however, higher concentrations are also possible in order to employ the polymerization properties of various metallocenes.

In the preparation of copolymers, the molar ratios between the polycyclic olefin and the 1-olefin employed can be varied within a broad range. The choice of polymerization temperature, the concentration of the

catalyst components and the molar ratio employed allow the incorporation rate of comonomer to be controlled virtually as desired. In the case of norbornene, an incorporation rate of greater than 40 mol% is achieved.

The mean molecular weight of the copolymer formed can be varied in a known manner by varying the catalyst concentration or the temperature.

The polydispersity M_w/M_n of the copolymers is extremely narrow, with values between 1.9 and 3.5. This results in a property profile of the polymers which makes them particularly suitable for extrusion.

The copolymerization of polycyclic olefins with acyclic olefins, in particular with propylene, gives polymers having a viscosity index of greater than 20 cm^3/g. Copolymers of norbornene with acyclic olefins, in particular ethylene, have a glass transition temperature of above 100°C.

In order to prepare COCs having a low optical attenuation of 0.1-5 dB/m, the reaction mixture is subjected to purification. Purification is preferably carried out by a process wherein, in a first step, the reaction mixture is suspended with a filtration aid and with a substance which precipitates the organometallic compounds in the reaction mixture, the heterogeneous components are filtered off in a second step, and, in a third step, the purified COC is precipitated from the COC filtrate with the aid of a precipitant or the solvent of the COC filtrate is evaporated off.

In step three, it is possible to employ evaporation methods such as, for example, evaporation with the aid of a flash chamber, a thin-film evaporator, a ®List compounder (List, England), a vented extruder or a ®Diskpack (Farrel, USA).

Substances which precipitate the organometallic compound in the reaction mixture are preferably polar compounds, such as water, ethylene glycol, glycerol and acetic acid. The suspending medium is preferably a hydrocarbon. Particularly suitable filtration aids are kieselguhr, for example ®Celite 545 (LuV, Hamburg), Perlite, for example ®Celite Perlite J-100 (LuV), modified cellulose, for example ®Diacel (LuV); porous carbon and absorptive asbestos fibers are also suitable.

The use of filtration aids enables good depth filtration to be achieved. Continuous or batch filtration techniques can be employed. Filtration can be carried out as a pressure filtration or a centrifugation. The filtration is preferably carried out by means of pressure filters, for example by filtration through a nonwoven material, or by skimmer centrifugation. It is also possible to use other conventional filtration techniques. The filtered COC solution can be fed continuously or batchwise a number of times through the same filter so that the filtration action is further intensified. A suitable precipitant is acetone, isopropanol or methanol.

In order to produce optical waveguides, the resultant polymers, which have been subjected to the above-described purification step and have been dried, are melted using a ram or screw extruder and forced through a die. A cladding layer of a second polymer is applied to the resultant filament, by coextrusion or by coating from a solution, the refractive index of the second polymer being lower than that of the core material. Suitable cladding materials are polymers and copolymers of 4-methylpentene, inter alia olefins, copolymers of ethylene and vinylidene fluoride, with or without addition of other comonomers, such as, for example, hexafluoropropene, tetrafluoroethylene, terpolymers of tetrafluoroethylene, hexafluoropropene and vinylidene fluoride, if desired also ethylene, copolymers of methyl methacrylate and methacrylates of (partially) fluorinated

alcohols, for example tetrafluoro-n-propyl methacrylate.

In order to produce flat-film optical waveguides, the polymers purified by the above-described process are melted in an extruder and forced through a flat-film die. The reflection layer on the surface can be applied by coextrusion or by coating from solution with a second polymer whose refractive index is lower than that of the core material.

The cladding layer of the optical waveguide may comprise a thermoplastic polymer having a refractive index of from 1.34 to 1.47 (at 589 nm).

The cycloolefin copolymers of the invention may have less than 0.1% by weight of a partially crystalline ethylene polymer, based on the total weight of the polymer, formed during the polymerization.

The invention is described by the examples below.

Examples

Example 1

A clean and dry 75 dm^3 polymerization reactor fitted with stirrer was flushed with nitrogen and then with ethylene and charged with 22,000 g of norbornene melt (Nb) and 6 liters of toluene. The reactor was then heated to a temperature of 70°C with stirring, and 3.4 bar of ethylene were injected. 500 cm^3 of a toluene solution of methylaluminoxane (10.1% by weight of methylaluminoxane having a molecular weight of 1300 g/mol, according to cryoscopic determination) were then metered into the reactor, and the mixture was stirred at 70°C for 15 minutes, during which the ethylene pressure was kept topped up at 3.4 bar. In parallel, 350 mg of

diphenylcarbyl(cyclopentadienyl)(9-fluorenyl)zirconium dichloride were dissolved in 500 cm^3 of a toluene solution of methylaluminoxane (concentration and quality see above) and preactivated by standing for 15 minutes. The solution of the complex (cat. solution) was then metered into the reactor. For molecular weight regulation, 0.7 liter of hydrogen was introduced at the outset. During the polymerization, 780 ml/h of hydrogen were metered in continuously. The mixture was then polymerized at 70°C for 1.5 hours with stirring (750 revolutions per minute), during which the ethylene pressure was kept topped up at

3.4 bar.

The reaction solution was discharged into a 150 liter stirred reactor containing 500 g of kieselguhr (®Celite 545, LuV, Hamburg) or alternatively cellulose filtration aid (®Diacel, LuV, Hamburg), 200 ml of water, 0.5 g of peroxide decomposer (®Hostanox 3, Hoechst) and 0.5 g of antioxidant (®Hostanox 03, Hoechst) in 50 liters of a hydrogenated diesel oil fraction (®Exsol, boiling range 100-120°C, Exxon). The mixture was stirred at 60°C for 30 minutes.

A filter cake of 500 g of ®Celite (or alternatively 500 g of cellulose), suspended in 10 liters of ®Exsol, was built up on the filter fabric of a 120 liter pressure filter. The polymer solution was filtered through the pressure filter in such a manner that the filtrate was first returned to the filter for 15 minutes. A pressure of up to 2.8 bar of nitrogen was built up above the solution.

The filtrate was then filtered through 7 filter cartridges (Fluid Dynamics, Dynalloy XS64, 5 μm, 0.1 m^2/cartridge) mounted in a steel housing. The polymer solution was stirred into 500 liters of acetone by means of a disperser (®Ultraturax) and precipitated. During this, the acetone suspension was circulated through a 680 liter stirred pressure filter with opened base valve. The base valve was closed, and the product was washed three times with 200 l of acetone. 50 g of stabilizer (®Irganox 1010, Ciba) were added to the final wash. After the final filtration, the product was predried at 100°C in a stream of nitrogen and then dried for 24 hours at 0.2 bar in a drying cabinet. 4160 g of product were obtained. A viscosity index (VI) of 62 cm^3/g (DIN 53728) and a glass transition temperature (T_g) of 181°C were measured on the product. Its melt viscosity was 400 PaS.

Example 2 (comparative example to Example 1, EP 407 870)

A clean and dry 75 dm^3 polymerization reactor fitted with stirrer was flushed with nitrogen and then with ethylene and charged with 22,000 g of norbornene melt (Nb) and 6 liters of toluene. The reactor was then heated to a temperature of 70°C with stirring, and 3.4 bar of ethylene were injected. 500 cm^3 of a toluene solution of methylaluminumoxane (10.1% by weight of methylaluminoxane having a molecular weight of 1300 g/mol, according to cryoscopic determination) were then metered into the reactor, and the mixture was stirred at 70°C for 15 minutes, during which the ethylene pressure was kept topped up at 3.4 bar. In parallel, 350 mg of diphenylcarbyl(cyclopentadienyl)(9-fluorenyl)zirconium dichloride were dissolved in 500 cm^3 of a toluene solution of methylaluminoxane (concentration and quality see above) and preactivated by standing for 15 minutes. The solution of the complex (cat. solution) was then metered into the reactor. For molecular weight regulation, 0.7 liter of hydrogen was introduced at the outset. During the polymerization, 780 ml/h of hydrogen were metered in continuously. The mixture was then polymerized at 70°C for 1.5 hours with stirring (750 revolutions per minute), during which the ethylene pressure was kept topped up at 3.4 bar.

The reactor contents were then quickly discharged into a 150 l stirred vessel containing 200 cm^3 of isopropanol in 10 l of Exsol. The mixture was precipitated in 500 l of acetone and stirred for 10 minutes, and the suspended polymer solid was then filtered off. The filtered-off polymer was then added to 200 l of a mixture of two parts of 3 normal hydrochloric acid and one part of ethanol, and this suspension was stirred for 2 hours. The polymer was then re-filtered, washed with water until neutral and dried at 80°C and 0.2 bar for 15 hours. 4320 g of product were obtained. A viscosity index VI of 60 cm^3 (DIN 53728) and a glass transition temperature (T_g) of 182°C were

measured on the product. No melt endotherm was found in the DSC.

Example 3 (comparative example to Example 1, EP 407 870)

The process was analogous to Example 1. However, the catalyst used was 1200 mg of rac-dimethylsilylbis(1-indenyl)zirconium dichloride. After a reaction time of 150 minutes, at an ethylene pressure of 3.2 bar and using the work-up process described in Example 1, 5070 g of polymer were obtained, on which a VI of 61 cm^3/g (DIN 53728) and a T_g of 179°C were measured.

Table 1

	COC (Example 1)	COC (Example 3)
Melt viscosity (Pa*S)	400	2000

(measured as the zero shear viscosity, i.e. as the approximate viscosity at a shear rate of 0.1 s^{-1}, measurement by capillary viscometer, measurement at T = Tg + 120°C)

Example 4

The polymer from Example 1 is melted in a ram extruder at a barrel temperature of from 210 to 260°C and forced at a flow rate of 610 cm^3/h through a die having an internal diameter of 2 mm. A terpolymer of tetrafluoroethylene, vinylidene fluoride and hexafluoropropene having a melt flow index of 32 g/10 min at 265°C and a load of 11 kg is melted in a ram extruder and conveyed at a flow rate of 39 cm^3/h to an annular slit arranged concentrically around the core die. The core/cladding fiber produced is cooled in a spinning bath and taken up at a rate of 35 m/min. In order to improve the mechanical properties, the fiber is subsequently stretched at 190°C in a hot-air oven at a ratio of 1:2.5 and then wound up. A

core/cladding fiber having a core diameter of 970 µm and a cladding diameter of 1 mm is obtained.

Tear strength	4.5 cN/tex (DIN [lacuna])
Elongation at break	27% (DIN [lacuna])
Optical attenuation	1.2 dB/m (at 650 nm)

Example 5

The polymer from Example 2 is melted in a ram extruder at a barrel temperature of from 210 to 260°C and forced at a flow rate of 610 cm^3/h through a die having an internal diameter of 2 mm. A terpolymer of tetrafluoroethylene, vinylidene fluoride and hexafluoropropene having a melt flow index of 32 g/10 min at 265°C and a load of 11 kg is melted in a ram extruder and likewise conveyed at a flow rate of 39 cm^3/h to an annular slit arranged concentrically around the core die. The core/cladding fiber produced is cooled in a spinning bath and taken up at a rate of 5.5 m/min. In order to improve the mechanical properties, the fiber is subsequently stretched at 190°C in a hot-air oven at a ratio of 1:2.5 and then wound up. A core/cladding fiber having a core diameter of 970 µm and a cladding diameter of 1 mm is obtained.

Tear strength	5.2 cN/tex (DIN [lacuna])
Elongation at break	28% (DIN [lacuna])
Optical attenuation	12.2 dB/m (at 650 nm)

Example 6

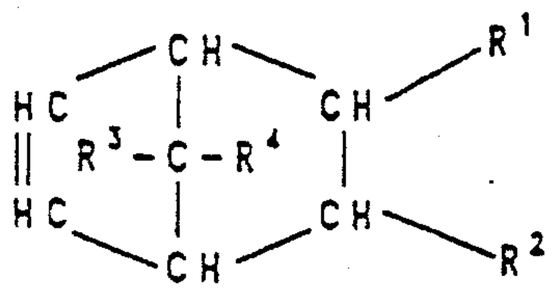
A polymerization solution was prepared analogously to Example 3, but the solution was worked up analogously to Example 2, i.e. the polymer solution was not filtered.

The DSC showed, in addition to the glass transition temperature (T_g = 178°C), a melt endotherm at 127°C with a melt enthalpie of 1 J/g, attributable to a partially

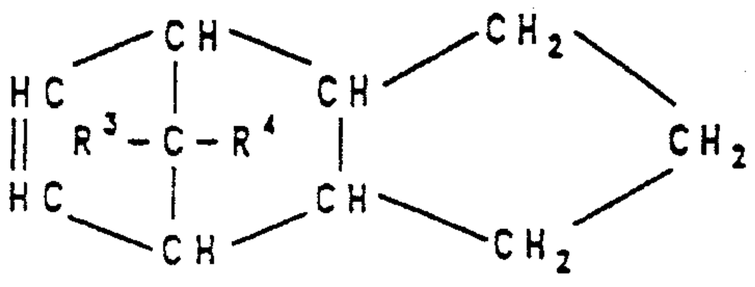
crystalline ethylene-rich polymer. This value corresponds to the polyethylene content of from 0.5 to 1% by weight in the dried and purified product. A pressed sheet with a thickness of 1 mm was cloudy (pressing conditions: 240°C, 10 minutes, 50 bar pressure).

CLAIMS:

1. A process for the preparation of a cycloolefin copolymer (COC) having low melt viscosity by copolymerization of from 0.1 to 99.9% by weight, based on the total amount of the monomers, of at least one monomer of the formula I, II, III or IV



(I),



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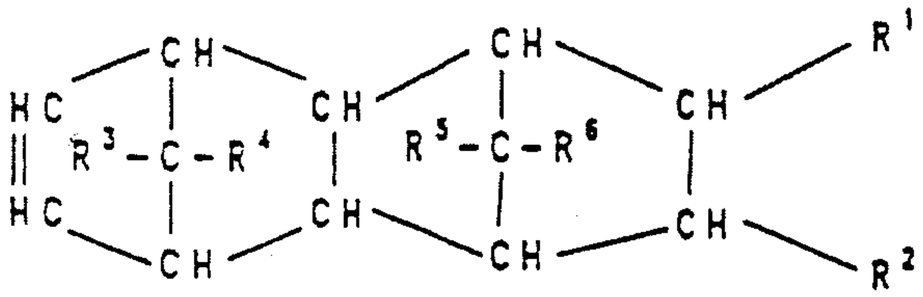

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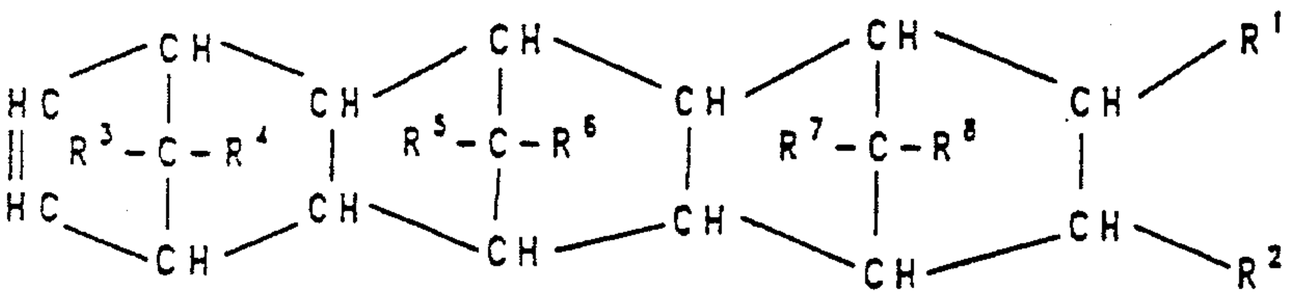
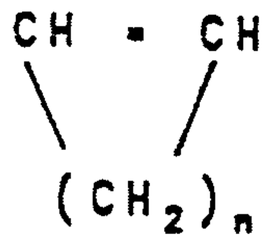


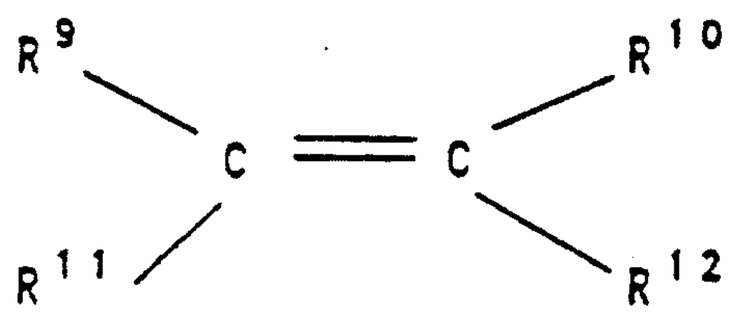
(IV),

in which R^1, R^2, R^3, R^4, R^5, R^6, R^7 and R^8 are identical or different and are a hydrogen atom or a C_1-C_8-alkyl radical or a C_6-C_{16}-aryl radical, where identical radicals in the various formulae can have different meanings,
from 0 to 99.9% by weight, based on the total amount of the monomers, of a cycloolefin of the formula V



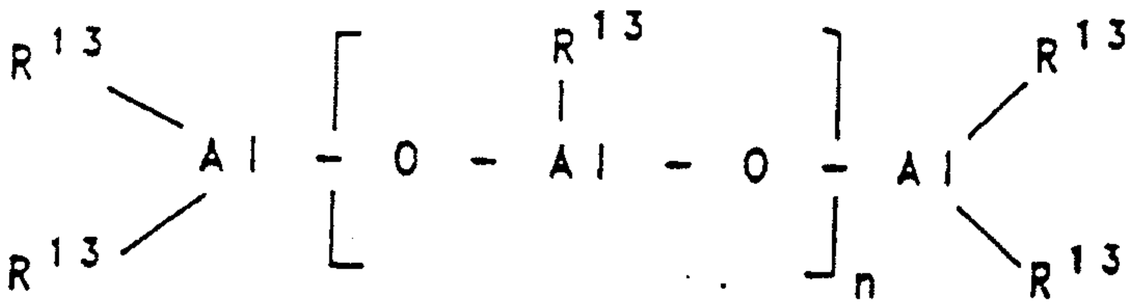
(V)

in which n is a number from 2 to 10, and from 0.1 to 99.9% by weight, based on the total amount of the monomers, of at least one acyclic 1-olefin of the formula VI



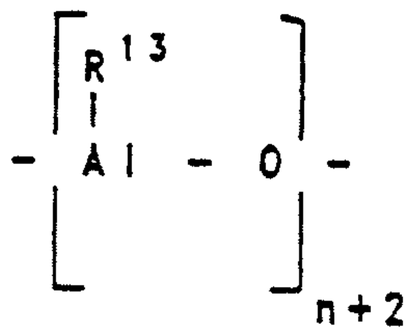
(VI),

in which R^9, R^{10}, R^{11} and R^{12} are identical or different and are a hydrogen atom or a C_1-C_8-alkyl radical, in solution, in suspension, in the liquid cycloolefin monomer or cycloolefin monomer mixture or in the gas phase, at a temperature of from -78 to 150°C, at a pressure of from 0.5 to 64 bar, in the presence of a catalyst comprising a metallocene as transition-metal component and an aluminoxane of the formula VII



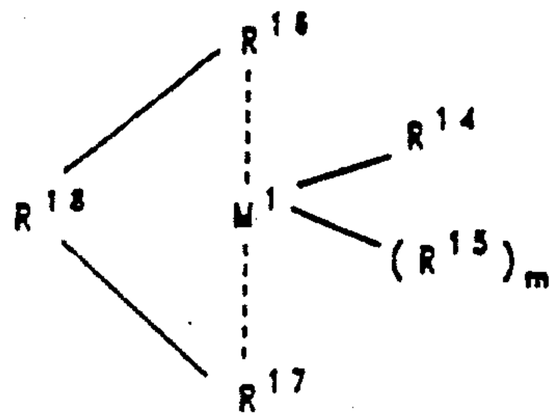
(VII)

for the linear type and/or of the formula VIII



(VIII)

for the cyclic type, where, in the formulae VII and VIII, R^{13} is a C_1-C_6-alkyl group or phenyl or benzyl, and n is an integer from 2 to 50, where the polymerization is carried out in the presence of a catalyst whose transition-metal component is at least one compound of the formula IX



(IX)

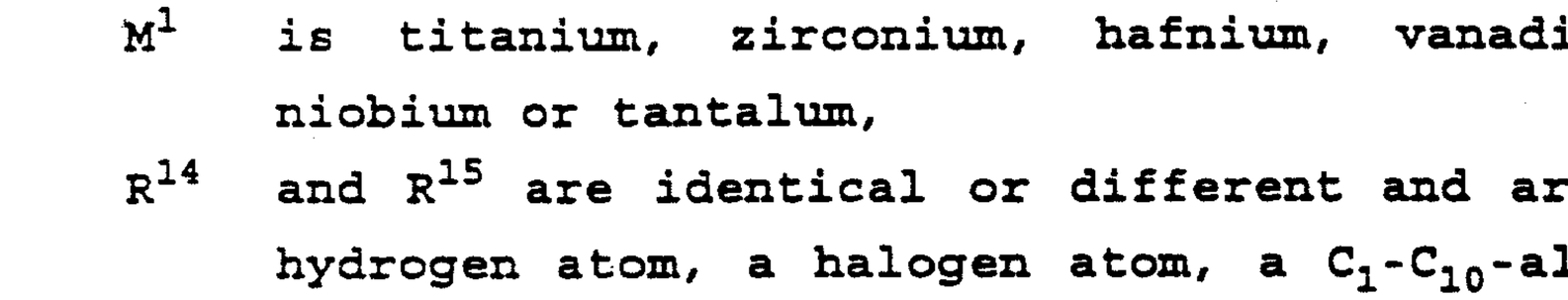
in which

M^1 is titanium, zirconium, hafnium, vanadium, niobium or tantalum,

R^{14} and R^{15} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-alkoxy group, a C_6-C_{10}-aryl group, a C_6-C_{10}-aryloxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_7-C_{40}-alkylaryl group or a C_8-C_{40}-arylalkenyl group, and

m may be one or two, depending on the valency of the central atom M^1,

R^{18} is



$=BR^{19}$, $=AlR^{19}$, -Ge-, -Sn-, -O-, -S-, =SO, $=SO_2$,

$=NR^{19}$, $=CO$, $=PR^{19}$ or $=P(O)R^{19}$, where R^{19}, R^{20} and R^{21} are identical or different and are a hydrogen atom, a halogen atom, a C_1-C_{10}-alkyl group, a C_1-C_{10}-fluoroalkyl group, a C_6-C_{10}-fluoroaryl group, a C_6-C_{10}-aryl group, a C_1-C_{10}-alkoxy group, a C_2-C_{10}-alkenyl group, a C_7-C_{40}-arylalkyl group, a C_8-C_{40}-arylalkenyl group or a C_7-C_{40}-alkylaryl group, or R^{19} and R^{20} or R^{19} and R^{21}, in each case with the atoms connecting them, form a ring,

M^2 is silicon, germanium or tin,

R^{16} and R^{17} are different and are a monocyclic or polycyclic hydrocarbon radical which can form a sandwich structure with the central atom M^1,

wherein the metallocene of the formula IX has C_s-symmetry with respect to the ligands R^{16} and R^{17} and with respect to the central atom M^1 connecting them, the copolymer being subjected, when the copolymerization is complete, to work-up which results in an optical attenuation of the material of from 0.1 to 5 dB/m;

wherein prior to the work-up, in a first step of a purification process, the reaction mixture is suspended with a filtration aid and with a substance which precipitates the organometallic compounds in the reaction mixture, the heterogeneous components are filtered off in a second step, and, in a third step, the purified COC is precipitated from the COC filtrate with the aid of a precipitant or the solvent of the COC filtrate is evaporated off.

2. The process as claimed in claim 1, wherein the catalyst used is a metallocene of the formula IX in which R^{16} is fluorenyl and R^{17} is cyclopentadienyl.

3. The process as claimed in claim 2, wherein the metallocene used is diphenylmethylene(9-fluorenyl)-cyclopentadienylzirconium dichloride.

4. The process as claimed in claim 2, wherein the metallocene used is isopropylene(9-fluorenyl)-cyclopentadienylzirconium dichloride.

5. The process as claimed in any one of claims 1 to 4, wherein the 1-olefin employed is ethylene.

6. The process as claimed in claim 5, wherein the polycyclic olefin employed is norbornene.

7. A cycloolefin copolymer (COC) prepared by the process claimed in any one of claims 1 to 6.

8. A cycloolefin copolymer as claimed in claim 7, wherein its glass temperature is above 100°C.

9. Use of a COC as claimed in claim 8 for flat-film and cylindrical optical waveguides.

10. An optical waveguide comprising a light-transmitting core or a light-transmitting layer and a cladding layer of a transparent polymer whose refractive index is lower than the refractive index of the light-transmitting medium, wherein the light-transmitting core or the light-transmitting and/or cladding layer comprises a COC as claimed in claim 8.

11. An optical waveguide as claimed in claim 10, wherein the cladding layer comprises a thermoplastic polymer having a refractive index of from 1.34 to 1.47 (at 589 nm).

12. An optical waveguide as claimed in claim 10, wherein the cladding layer comprises polymers or copolymers

of 4-methylpentene and other olefins, copolymers of ethylene and vinylidene fluoride, with or without addition of other comonomers, copolymers of tetrafluoroethylene, hexafluoropropene and vinylidene fluoride, if desired also ethylene, copolymers of methyl methacrylate and methacrylates of fluorinated or partially fluorinated alcohols.

13. An optical waveguide as claimed in claim 12, wherein the other comonomers are hexafluoropropene, tetrafluoroethylene or a mixture thereof, and the fluorinated or partially fluorinated alcohol is tetrafluoro-n-propyl alcohol.

14. A cycloolefin copolymer prepared by the process claimed in any one of claims 1 to 6, wherein less than 0.1% by weight of a partially crystalline ethylene polymer, based on the total weight of the polymer, is formed during the polymerization.

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