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(54) Title: PROCESS FOR PRODUCING A POLYPROPYLENE HOMO- OR COPOLYMER

(57) Abstract: Process for the production of a polypropylene homo- or copolymer, the process comprising the steps of a) prepolymerising propylene in a first reactor in the presence of hydrogen and a metallocene catalyst yielding a first polypropylene homo- or copolymer fraction, wherein a ratio of the feed of hydrogen to the feed of propylene is in the range of 0.01 to 0.08 mol/kmol, and wherein the temperature in the first reactor is from 15 to 29°C, b) transferring the first polypropylene homo- or copolymer fraction to a second reactor, c) polymerising in the second reactor propylene in the presence of the first polypropylene homo- or copolymer fraction, yielding a second polypropylene homo- or copolymer fraction, wherein a residence time in the second reactor is from 10 to 40 min, d) withdrawing the first and the second polypropylene homo- or copolymer fraction from the second reactor or transferring the first and the second polypropylene homo- or copolymer fraction to a third reactor.

Process for Producing a Polypropylene homo- or copolymer

The present invention is concerned with a process for producing a polypropylene homo- or copolymer, using a defined temperature and hydrogen (H2) concentration range in the presence of a metallocene catalyst and a propylene homo- or copolymer having a defined bulk density.

Background

Polypropylene copolymers like propylene-ethylene copolymers are a group of interesting materials for a wide usage in different applications, which require a combination of good cost/performance ratio. The properties of the propylene-ethylene copolymers depend *inter alia* on the properties and nature of the catalyst used in the polymerization process, e.g. its morphology.

Therefore, there is a general interest to control the (co)polymer's powder morphology during polymerisation processes of polypropylene (co)polymers. In the polypropylene polymerisation processes of the prior art, the original morphology of the catalyst and how to start the catalyst are crucial for the final (co)polymer powder morphology. A non-ideal start could lead to non-ideal final powder morphology.

Consequently, in order to avoid abrupt changes, e.g. variations of polymerization conditions, in the environment of the catalyst and to avoid the occurrence of an initial overreaction, a prepolymerization reactor is typically installed before a main polymerization reactor. During the prepolymerization, the catalyst is started under moderate conditions so as to retain the morphology of the growing polymer. The moderate conditions are catalyst- and process-specific. Further, in the prepolymerization step a more controlled catalyst/support break-up (fragmentation) is achieved. This has a significant influence on the powder morphology of the formed polymer.

It is also known that the morphology of the polymer particle is determined by the shape of the supported catalyst particle by the so-called replica effect.

Therefore, there is the constant need for further improving the polymerisation processes of polypropylene in view of maintaining a good polymer powder morphology.

Object of the present invention

It is therefore an object of the present invention to provide a process for the polymerisation of propylene which overcomes the problems mentioned above.

It is a further object of the present invention to provide a process for the polymerisation of propylene and maintaining, and preferably improving, the polymer powder morphology.

It is a further object of the present invention to provide a propylene homo- or copolymer obtained by the inventive process and having an improved morphology, and in particular a defined bulk density.

Definitions

The term '*copolymer of [monomer]*' as used herein denotes a polymer the majority by weight of which derives from the [monomer] units (i.e. at least 50 wt.% [monomer] relative to the total weight of the copolymer).

Summary of the invention

It now has been surprisingly found that above-mentioned object can be achieved by a process for the production of a polypropylene homo- or copolymer, preferably a polypropylene homopolymer, the process comprising the steps of

a) prepolymerising propylene in a first reactor in the presence of hydrogen and a metallocene catalyst yielding a first polypropylene homo- or copolymer fraction, preferably yielding a first polypropylene homopolymer fraction, wherein a ratio of the feed of hydrogen to the feed of propylene is in the range of 0.01 to 0.08 mol/kmol, and wherein the first reactor is maintained at a temperature of from 15 to 29°C,

b) transferring the first polypropylene homo- or copolymer fraction to a second reactor,

c) polymerising in the second reactor propylene in the presence of the first polypropylene homo- or copolymer fraction, yielding a second polypropylene homo- or copolymer fraction, preferably yielding a second polypropylene homopolymer fraction, wherein an average residence time in the second reactor is from 10 to 40 min,

d) withdrawing the polypropylene homo- or copolymer comprising the first and the second polypropylene homo- or copolymer fraction from the second reactor or transferring the polypropylene homo- or copolymer to a third reactor, preferably transferring the polypropylene homo- or copolymer to a third reactor,

wherein the metallocene catalyst comprises a metallocene complex, and the metallocene complex is an organometallic compound (C), the organometallic compound (C) has the following formula (Ia):

$(L)_2R_nMX_2$ (Ia)

wherein

"M" is Zr or Hf;

each "X" is a σ-ligand;

each "L" is an optionally substituted cyclopentadienyl, indenyl or tetrahydroindenyl;

"R" is $SiMe_2$ bridging group linking said organic ligands (L);

"n" is 0 or 1, preferably 1.

The invention is based on the surprising finding that the morphology or the development of the morphology of the obtained polymer powder can be improved by operating the prepolymerisation reactor at a certain temperature range between 15 and 29 °C and feeding hydrogen and propylene in a ratio of 0.01 to 0.08 mol/kmol into the prepolymerisation reactor.

The invention has a number of advantages. The above operation conditions yield not only prepolymerisation degrees of 100 to 600 g polypropylene per g catalyst, but also achieve a bulk density of larger than 320 kg/m^3 for the polypropylene homo- or copolymer. Furthermore, an optimised morphology of the polymerisation catalyst and thus process stability, also in terms of product quality, is achieved.

According to the present invention, step a) is a prepolymerisation step. The purpose of the prepolymerisation is to polymerise a small amount of polymer onto the catalyst at a low temperature and/or a low monomer concentration. The

prepolymerisation step is typically conducted as slurry polymerization. Using the prepolymerisation step it may be possible to improve the performance of the catalyst in slurry and/or modify the properties of the final polymer. Use of the catalyst in the prepolymerisation step offers the advantage of minimizing leaching of catalyst components.

If used, the slurry polymerization in step a) is preferably a bulk polymerization. By “bulk polymerization” is meant that the polymerization is conducted using a monomer in liquid form, thus essentially in the absence of an inert diluent. However, as it is known to a person skilled in the art the monomers used in commercial production are never pure but always contain impurities, such as aliphatic hydrocarbons. For instance, the propylene monomer may contain up to 5 % of propane as an impurity. As propylene is consumed in the reaction and also recycled from a reaction effluent back to the polymerization, the impurities, which may be inert components, tend to accumulate, and thus the reaction medium may experience an increase in the concentration of said impurities reaching values to even up to 40 wt.%. It is to be understood, however, that such a polymerization process, wherein impurities are present, should still be construed as a “bulk polymerization” process, as defined above.

The slurry polymerisation, preferably the bulk polymerisation, may be conducted in any known reactor used for slurry polymerisation. Such reactors typically include a continuous stirred tank reactor and a loop reactor.

It is especially preferred to conduct the prepolymerisation of step a) in a loop reactor.

Preferably, the first reactor is a loop reactor. In such reactors, the slurry is circulated with a high velocity along a closed pipe by using a circulation pump. Loop reactors are continuous reactors, generally known in the art and examples are given, for instance, in US-A-4582816, US-A-3405109, US-A-3324093, EP-A-479186 and US-A-5391654. It is thus preferred to conduct the prepolymerisation step as a slurry polymerisation in a loop reactor.

The average amount of monomer is typically such that from 0.1 to 1000 g of monomer per one gram of solid catalyst component is polymerised in the prepolymerisation step. As the person skilled in the art knows, catalyst particles

recovered from a continuous prepolymerisation reactor do not all contain the same amount of prepolymer. Instead, each particle has its own characteristic amount, which depends on the residence time of that particle in the prepolymerisation reactor. As the residence time of catalyst particles in the reactor vary, e.g. some particles remain in the reactor for a relatively long time and some for a relatively short time, the amount of prepolymer on various particles may consequently be different. It can even happen that some individual particles may even contain an amount of prepolymer outside the above indicated limits. However, the average amount of prepolymer on the catalyst typically is within said limits.

It is understood within the scope of the invention, that the amount of polymer produced in the prepolymerisation typically lies within 0.1 – 0.3 wt.% with respect to the polypropylene homo- or copolymer.

Preferably, step a) is carried out under the indicated conditions such that the first polypropylene homo- or copolymer fraction is produced in an amount of from 0.1 to 0.3 wt.% with respect to the polypropylene homo- or copolymer.

Preferably, in step a) the temperature in the first reactor is between 20 and 28 °C, more preferably between 21 and 27 °C, most preferably between 22 and 26 °C.

Preferably, in step a) the pressure in the first reactor is preferably from 1 to 150 bar, more preferably 35 to 60 bar, even more preferably 50 to 60 bar, and most preferably 53 to 57 bar.

Preferably, a ratio of the feed of hydrogen to the feed of propylene is in the range of 0.02 to 0.07 mol/kmol.

In step a) a comonomer is preferably present in the first reactor. Preferably, the comonomer in step a) is ethylene.

The average residence time in the first reactor in step a) is typically from 0.05 to 0.5 h, preferably from 0.1 to 0.4 h, more preferably from 0.2 to 0.3 h. As it is well known in the art the average residence time τ can be calculated from equation (1) below:

$$\tau = \frac{V_R}{Q_o} \qquad \text{equation (1)}$$

wherein

V_R is the volume of the reaction space (in case of a loop reactor, the volume of the reactor, in case of the fluidized bed reactor, the volume of the fluidized bed)

Q_o is the volumetric flow rate of a product stream (including the polymer product and the fluid reaction mixture).

As used herein, the production rate of the polypropylene produced (kg PP/h) is measured for the first or second reactor, respectively, by their respective energy balance. Typically production rates in the first reactor are 0.5 to 2.0 kg PP / h.

The prepolymerisation degree in the first reactor is calculated by diving the production rate in the first reactor by the catalyst feed to the first reactor. The catalyst feed in the first reactor is typically 1.0 to 3.0 g catalyst / h. As a result the prepolymerisation degree is typically and preferably of from 50 to 2000 g PP/g catalyst, more preferably 200 to 1000 g PP/g catalyst and most preferably 300 to 700 g PP/g catalyst.

The slurry may be withdrawn from the first reactor either continuously or intermittently. A preferred way of intermittent withdrawal is the use of settling legs where slurry is allowed to concentrate before withdrawing a batch of the concentrated slurry from the reactor. The use of settling legs is disclosed, among others, in US-A-3374211, US-A-3242150 and EP-A-1310295. Continuous withdrawal is disclosed, among others, in EP-A-891990, EP-A-1415999, EP-A-1591460 and WO-A-2007/025640. The continuous withdrawal is advantageously combined with a suitable concentration method, as disclosed in EP-A-1310295 and EP-A-1591460. It is preferred to withdraw the slurry from the first reactor continuously.

Preferably, the slurry withdrawn from the first reactor is directly transferred into the second reactor to produce the second polypropylene homo- or copolymer fraction. By “directly” it is meant that the slurry is introduced from the first reactor into the second reactor without any separation step in between (e.g. a flash separation step).

In step b) the first polypropylene homo- or copolymer fraction obtained in step a) is transferred to a second reactor, preferably directly transferred to a second reactor. Preferably, the first polypropylene homo- or copolymer fraction is transferred to the second reactor in slurry form. The slurry preferably comprises the first polypropylene homo- or copolymer fraction, unreacted monomer and the metallocene catalyst.

Similar to step a), step c) in the second reactor is preferably conducted as a slurry polymerisation, the slurry polymerisation preferably being a bulk polymerisation. Preferably, the second reactor is a loop reactor.

Preferably, the reactor temperature in step c) is in the range of 60 to 100 °C, more preferably 65 to 90 °C, most preferably 70 to 85 °C. Respectively, the polymerisation in step c) is preferably carried out at a reactor pressure in the range of 1 to 100 bar, more preferably 20 to 80 bar, more preferably 30 to 70 bar.

Preferably, the metallocene catalyst used in step a) is present in the second reactor during the polymerisation in step c). This is accomplished by transferring, preferably via slurry, the metallocene catalyst used in step a) into the second reactor. If needed, fresh metallocene catalyst may be added into the second reactor in step c).

In steps a) and/or c), one or more comonomers selected from alpha olefins having 2 or 4 to 10 carbon atoms or mixtures thereof are preferably present in the reactor. Preferably, the one or more comonomers are alpha olefins having 2 or 4 carbon atoms, more preferably having 2 carbon atoms, most preferably being ethylene.

Hydrogen is typically introduced into the polymerisation stage in step c) in case there is a desire to control the MFR_2 of the second propylene homo- or copolymer fraction. The amount of hydrogen needed to reach the desired MFR_2 depends on the catalyst used and the polymerisation conditions, as it will be appreciated by the skilled worker.

In addition to the amount needed to control the MFR_2, it is also often necessary to introduce additional hydrogen into the second reactor, in case that the melt index of the polypropylene homo- or copolymer needs to be controlled. Suitably,

the hydrogen feed to the second reactor is controlled to maintain constant hydrogen to propylene ratio. Good results have been obtained by maintaining a ratio of the feed of hydrogen to the feed of propylene within in the range of from 0.1 to 5.0 mol/kmol.

Preferably, in step c) a ratio of the feed of hydrogen to the feed of propylene is in the range of from 0.1 to 5.0 mol/kmol, more preferably of from 0.2 to 2.0 mol/kmol, more 0.3 to 1.0 mol/kmol.

The average residence time in the second reactor in step c) is typically from 10 to 40 min, preferably from 15 to 35 min. Reference is made to equation (1) above. The production rate is suitably controlled with the catalyst feed rate. It is also possible to influence the production rate by suitable selection of the propylene monomer concentration. The desired monomer concentration can then be achieved by suitably adjusting the propylene feed rate.

In a preferred embodiment, the polymerisation process of the invention does not recover the comonomer.

The production split between the first polypropylene homo- or copolymer fraction of step a) and the second polypropylene homo- or copolymer fraction of step c) is preferably in the range of from 0.1 to 10 wt.%, more preferably of from 0.5 to 5 wt.%, and most preferably of from 1 to 3 wt.%.

In step d) the polypropylene homo- or copolymer is either withdrawn from the second reactor or transferred to a third reactor. Preferably, the polypropylene homo- or copolymer is transferred to a third reactor.

The polypropylene homo- or copolymer comprises the first polypropylene homo- or copolymer fraction produced in the first reactor and the second polypropylene homo- or copolymer fraction produced in the second reactor.

The polypropylene homo- or copolymer preferably has a melt flow rate, MFR_2, from 50 to 90 g/10min, preferably from 60 to 80 g/10min, measured according to ISO 1133.

As discussed above, the polypropylene homo- or copolymer withdrawn from the second reactor is preferably transferred to a third reactor. Preferably, the third reactor is a gas phase reactor, more preferably a fluidized bed gas phase reactor.

For gas phase reactors, the reaction temperature used will generally be in the range 60 to 100 °C, the reactor pressure will generally be in the range 1 to 100 bar. The gas used will commonly be a non-reactive gas such as nitrogen or low boiling point hydrocarbons such as propane together with monomer (e.g. propylene). Preferably, one or more comonomers selected from alpha olefins having 2 or 4 to 10 carbon atoms or mixtures thereof are preferably present in the third reactor. Preferably, the one or more comonomers are alpha olefins having 2 or 4 carbon atoms, more preferably having 2 carbon atoms, i.e. ethylene.

Preferably, the process of the invention further comprises a third reactor downstream of the second reactor, more preferably a third reactor downstream of the second reactor and a fourth reactor downstream of the third reactor, and most preferably a third reactor downstream of the second reactor, a fourth reactor downstream of the third reactor and a fifth reactor downstream of the fourth reactor, for further polymerisation of the the polypropylene homo- or copolymer.

The fourth reactor and/or the fifth reactor are preferably a gas phase reactor, more preferably a fluidized bed gas phase reactor. The temperature and pressure in the fourth reactor and/or the fifth reactor are preferably the same as described for the third reactor above. Also, the residence time and/or the one or more comonomers present in the fourth reactor and/or the fifth reactor are preferably the same as described for the second reactor above.

A suitable process is the above-identified slurry-gas phase process, such as developed by Borealis and known as the Borstar® technology. In this respect, reference is made to the EP applications EP 0 887 379 A1 and EP 0 517 868 A1.

It will be appreciated that the propylene polymers obtained with the inventive process may contain standard polymer additives. These typically form less than 5.0 wt.%, such as less than 2.0 wt.% of the polymer material. Additives, such as antioxidants, phosphites, cling additives, pigments, colorants, fillers, anti-static agent, processing aids, clarifiers and the like may thus be added during the polymerisation process. These additives are well known in the industry and their use will be familiar to the artisan. Any additives which are present may be added

as an isolated raw material or in a mixture with a carrier polymer, i.e. in so called master batch.

The polypropylene homo- or copolymer is manufactured in accordance with the process of the invention in the presence of a metallocene catalyst, more preferably at least one metallocene catalyst. A metallocene catalyst typically comprises a metallocene/activator reaction product impregnated in a porous support at maximum internal pore volume. The metallocene catalyst comprises a ligand which is typically bridged, and a transition metal of group IVa to VIa, and an organoaluminium compound. The catalytic metal compound is typically a metal halide.

The metallocene catalyst used in accordance to the present invention may be any supported metallocene catalyst suitable for the production of polypropylene copolymers.

It is preferred that the metallocene catalyst comprises a metallocene complex, a cocatalyst system comprising a boron-containing cocatalyst and/or aluminoxane cocatalyst, and a support, the support preferably comprising or consisting of silica.

Examples of suitable metallocene compounds are given, among others, in EP 629631, EP 629632, WO 00/26266, WO 02/002576, WO 02/002575, WO 99/12943, WO 98/40331, EP 776913, EP 1074557 and WO 99/42497, EP2402353, EP2729479 and EP2746289.

The metallocene complex is ideally an organometallic compound (C) which comprises a transition metal (M) of Group 3 to 10 of the Periodic Table (IUPAC 2007) or of an actinide or lanthanide. The term "an organometallic compound (C)" in accordance with the present invention includes any metallocene compound of a transition metal which bears at least one organic (coordination) ligand and exhibits the catalytic activity alone or together with a cocatalyst. The transition metal compounds are well known in the art and the present invention covers compounds of metals from Group 3 to 10, e.g. Group 3 to 7, or 3 to 6, such as Group 4 to 6 of the Periodic Table, (IUPAC 2007), as well lanthanides or actinides.

In an embodiment the organometallic compound (C) has the following formula (I):

$(L)_mR_nMX_q$ (I)

wherein

"M" is a transition metal (M) transition metal (M) of Group 3 to 10 of the Periodic Table (IUPAC 2007);

each "X" is independently a monoanionic ligand, such as a σ-ligand;

each "L" is independently an organic ligand which coordinates to the transition metal "M";

"R" is a bridging group linking said organic ligands (L);

"m" is 1, 2 or 3, preferably 2;

"n" is 0, 1 or 2**,** preferably 1;

"q" is 1, 2 or 3, preferably 2; and

m+q is equal to the valency of the transition metal (M).

"M" is preferably selected from the group consisting of zirconium (Zr), hafnium (Hf), or titanium (Ti), more preferably selected from the group consisting of zirconium (Zr) and hafnium (Hf).

In a more preferred definition, each organic ligand (L) is independently

(a) a substituted or unsubstituted cyclopentadienyl or a bi- or multicyclic derivative of a cyclopentadienyl which optionally bear further substituents and/or one or more hetero ring atoms from a Group 13 to 16 of the Periodic Table (IUPAC); or

(b) an acyclic η^1- to η^4- or η^6-ligand composed of atoms from Groups 13 to 16 of the Periodic Table, and in which the open chain ligand may be fused with one or two, preferably two, aromatic or non-aromatic rings and/or bear further substituents; or

(c) a cyclic η^1- to η^4- or η^6-, mono-, bi- or multidentate ligand composed of unsubstituted or substituted mono-, bi- or multicyclic ring systems selected from aromatic or non-aromatic or partially saturated ring systems, such ring systems

containing optionally one or more heteroatoms selected from Groups 15 and 16 of the Periodic Table.

Organometallic compounds (C), preferably used in the present invention, have at least one organic ligand (L) belonging to the group (a) above. Such organometallic compounds are called metallocenes.

More preferably at least one of the organic ligands (L), preferably both organic ligands (L), is (are) selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl, which can be independently substituted or unsubstituted.

Further, in case the organic ligands (L) are substituted it is preferred that at least one organic ligand (L), preferably both organic ligands (L), comprise one or more substituents independently selected from C_1 to C_{20} hydrocarbyl or silyl groups, which optionally contain one or more heteroatoms selected from groups 14 to 16 and/or are optionally substituted by halogen atom(s),

The term C_1 to C_{20} hydrocarbyl group, whenever used in the present application, includes C_1 to C_{20} alkyl, C_2 to C_{20} alkenyl, C_2 to C_{20} alkynyl, C_3 to C_{20} cycloalkyl, C_3 to C_{20} cycloalkenyl, C_6 to C_{20} aryl, C_7 to C_{20} alkylaryl or C_7 to C_{20} arylalkyl groups or mixtures of these groups such as cycloalkyl substituted by alkyl.

Further, two substituents, which can be same or different, attached to adjacent C-atoms of a ring of the ligands (L) can also be taken together to form a further mono or multicyclic ring fused to the ring.

Preferred hydrocarbyl groups are independently selected from linear or branched C_1 to C_{10} alkyl groups, optionally interrupted by one or more heteroatoms of groups 14 to 16, like O, N or S, and substituted or unsubstituted C_6 to C_{20} aryl groups.

Linear or branched C_1 to C_{10} alkyl groups, optionally interrupted by one or more heteroatoms of groups 14 to 16, are more preferably selected from methyl, ethyl, propyl, isopropyl, tertbutyl, isobutyl, C_{5-6} cycloalkyl, OR, SR, where R is C_1 to C_{10} alkyl group,

C_6 to C_{20} aryl groups are more preferably phenyl groups, optionally substituted with 1 or 2 C_1 to C_{10} alkyl groups as defined above.

By "σ-ligand" is meant throughout the invention a group bonded to the transition metal (M) via a sigma bond.

Further, the ligands “X” are preferably independently selected from the group consisting of hydrogen, halogen, C_1 to C_{20} alkyl, C_1 to C_{20} alkoxy, C_2 to C_{20} alkenyl, C_2 to C_{20} alkynyl, C_3 to C_{12} cycloalkyl, C_6 to C_{20} aryl, C_6 to C_{20} aryloxy, C_7 to C_{20} arylalkyl, C_7 to C_{20} arylalkenyl, -SR'', -Pr''$_3$, -SiR''$_3$, -OSiR''$_3$ and -NR''$_2$, wherein each R'' is independently hydrogen, C_1 to C_{20} alkyl, C_2 to C_{20} alkenyl, C_2 to C_{20} alkynyl, C_3 to C_{12} cycloalkyl or C_6 to C_{20} aryl.

More preferably “X” ligands are selected from halogen, C_1 to C_6 alkyl, C_5 to C_6 cycloalkyl, C_1 to C_6 alkoxy, phenyl and benzyl groups.

The bridging group “R” may be a divalent bridge, preferably selected from –R'$_2$C-, –R'$_2$C-CR'$_2$-, –R'$_2$Si-, -R'$_2$Si-Si R'$_2$-, -R'$_2$Ge-, wherein each R’ is independently a hydrogen atom, C_1 to C_{20} alkyl, C_2 to C_{10} cycloalkyl, tri(C_1-C_{20}-alkyl)silyl, C_6-C_{20}-aryl, C_7- C_{20} arylalkyl and C_7- C_{20}-alkylaryl.

More preferably the bridging group “R” is a divalent bridge selected from –R'$_2$C-, –R'$_2$Si-, wherein each R’ is independently a hydrogen atom, C_1 to C_{20} alkyl, C_2 to C_{10} cycloalkyl, C_6- C_{20}-aryl, C_7- C_{20} arylalkyl and C_7- C_{20}-alkylaryl.

Another subgroup of the organometallic compounds (C) of formula (I) is known as non-metallocenes wherein the transition metal (M), preferably a Group 4 to 6 transition metal, suitably Ti, Zr or Hf, has a coordination ligand other than a cyclopentadienyl ligand.

The term "non-metallocene" used herein means compounds, which bear no cyclopentadienyl ligands or fused derivatives thereof, but one or more non-cyclopentadienyl η-, or σ-, mono-, bi- or multidentate ligand. Such ligands can be chosen e.g. from the groups (b) and (c) as defined above and described e.g. in WO 01/70395, WO 97/10248, WO 99/41290, and WO 99/10353), and further in V. C. Gibson et al., in Angew. Chem. Int. Ed., engl., vol 38, 1999, pp 428 447, the disclosures of which are incorporated in their entirety herein by reference.

However, the organometallic compound (C) of the present invention is preferably a metallocene as defined above.

Metallocenes are described in numerous patents, including EP 0 260 130, WO 97/28170, WO 98/46616, WO 98/49208, WO 98/040331, WO 99/12981, WO 99/19335, WO 98/56831, WO 00/34341, WO00/148034, EP 423 101, EP 537 130, WO2002/02576, WO2005/105863, WO 2006097497, WO2007/116034, WO2007/107448, WO2009/027075, WO2009/054832, WO 2012/001052, and EP 2 532 687, the disclosures of which are incorporated in their entirety herein by reference.

In a preferred embodiment the organometallic compound (C) has the following formula (Ia):

$(L)_2R_nMX_2$ (Ia)

wherein

"M" is Zr or Hf;

each "X" is a σ-ligand;

each "L" is an optionally substituted cyclopentadienyl, indenyl or tetrahydroindenyl;

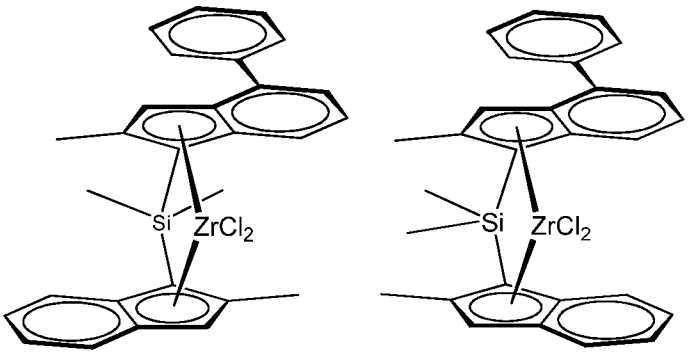
"R" is $SiMe_2$ bridging group linking said organic ligands (L);

"n" is 0 or 1, preferably 1.

The metallocene catalyst complexes of the invention are preferably asymmetrical. Asymmetrical means simply that the two ligands forming the metallocene are different, that is, each ligand bears a set of substituents that are chemically different.

The metallocene catalyst complexes of the invention are typically chiral, racemic bridged bisindenyl C_1-symmetric metallocenes in their anti-configuration. Although such complexes are formally C_1-symmetric, the complexes ideally retain a pseudo-C_2-symmetry since they maintain C_2-symmetry in close proximity of the metal center although not at the ligand periphery. By nature of their chemistry both anti and syn enantiomer pairs (in case of C_1-symmetric complexes) are formed during the synthesis of the complexes. For the purpose of this invention, racemic-anti means that the two indenyl ligands are oriented in opposite directions with respect to the cyclopentadienyl-metal-cyclopentadienyl plane, while racemic-syn means that the two indenyl ligands are oriented in the

same direction with respect to the cyclopentadienyl-metal-cyclopentadienyl plane, as shown in the scheme below.

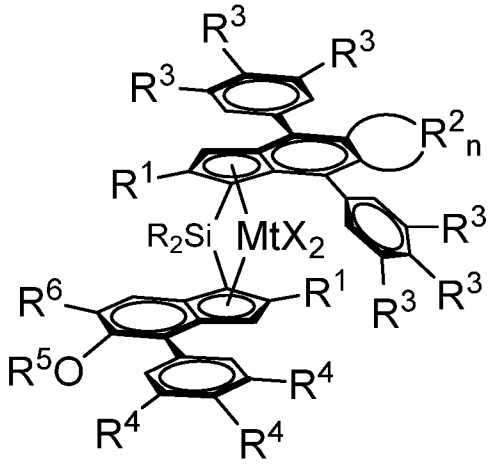


Racemic Anti Racemic Syn

Formula (I), and any sub formulae, are intended to cover both syn- and anti-configurations. Preferred metallocene catalyst complexes are in the anti-configuration.

The metallocene catalyst complexes of the invention are generally employed as the racemic-anti isomers. Ideally, therefore at least 95%mol, such as at least 98%mol, especially at least 99%mol of the metallocene catalyst complex is in the racemic-anti isomeric form.

More preferably, the metallocene catalyst is of formula (II)



Formula (II)

Mt is Hf or Zr;

each X is a sigma-ligand;

each R^1 independently are the same or can be different and are a CH_2-R^7 group, with R^7 being H or linear or branched C_{1-6}-alkyl group, C_{3-8} cycloalkyl group, C_{6-10} aryl group,

each R^2 is independently a –CH=, -CY=, $–CH_2$-, -CHY- or $-CY_2$- group, wherein Y is a C_{1-10} hydrocarbyl group and where n is 2-6,

each R^3 and R^4 are independently the same or can be different and are hydrogen, a linear or branched C_1-C_6-alkyl group, an OY group or a C_{7-20} arylalkyl, C_{7-20} alkylaryl group or C_{6-20} aryl group, whereby at least one R^3 per phenyl group and at least one R^4 is not hydrogen, and optionally two adjacent R^3 or R^4 groups can be part of a ring including the phenyl carbons to which they are bonded,

R^5 is a linear or branched C_1-C_6-alkyl group, C_{7-20} arylalkyl, C_{7-20} alkylaryl group or C_6-C_{20}-aryl group,

R^6 is a $C(R^8)_3$ group, with R^8 being a linear or branched C_1-C_6 alkyl group, and

each R is independently a C_1-C_{20}-hydrocarbyl.

It is preferred if Mt is Zr.

Preferably, each X is independently a hydrogen atom, a halogen atom, C_{1-6} alkoxy group or an R´ group, where R´ is a C_{1-6} alkyl, phenyl or benzyl group. Most preferably, X is chlorine, benzyl or a methyl group. Preferably, both X groups are the same. The most preferred options are two chlorides, two methyl or two benzyl groups, especially two chlorides.

Each R is independently a C_1-C_{20}-hydrocarbyl, such as C_6-C_{20}-aryl, C_7-C_{20}-arylalkyl or C_7-C_{20}-alkylaryl. The term C_{1-20} hydrocarbyl group also includes C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{3-20} cycloalkyl, C_{3-20} cycloalkenyl, C_{6-20} aryl groups, C_{7-20} alkylaryl groups or C_{7-20} arylalkyl groups or mixtures of these groups such as cycloalkyl substituted by alkyl. Unless otherwise stated, preferred C_{1-20} hydrocarbyl groups are C_{1-20} alkyl, C_{4-20} cycloalkyl, C_{5-20} cycloalkyl-alkyl groups, C_{7-20} alkylaryl groups, C_{7-20} arylalkyl groups or C_{6-20} aryl groups.

Preferably, both R groups are the same. It is preferred if R is a C_1-C_{10}-hydrocarbyl or C_6-C_{10}-aryl group, such as methyl, ethyl, propyl, isopropyl, tertbutyl, isobutyl, C_{5-6}-cycloalkyl, cyclohexylmethyl, phenyl or benzyl, more preferably both R are a C_1-C_6-alkyl, C_{3-8} cycloalkyl or C_6-aryl group, such as a

C_1-C_4-alkyl, C5-6 cycloalkyl or C_6-aryl group and most preferably both R are methyl or one is methyl and another cyclohexyl. Most preferably the bridge is -$Si(CH_3)_2$-.

Each R^1 independently are the same or can be different and are a CH_2-R^7 group, with R^7 being H or linear or branched C_{1-6}-alkyl group, like methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl and tert.-butyl or C_{3-8} cycloalkyl group (e.g. cyclohexyl) , C_{6-10} aryl group (preferably phenyl).

Preferably, both R^1 groups are the same and are a CH_2-R^7 group, with R^7 being H or linear or branched C_1-C_4-alkyl group, more preferably, both R^1 groups are the same and are a CH_2-R^7 group, with R^7 being H or linear or branched C_1-C_3-alkyl group. Most preferably, both R^1 are both methyl.

Each R^2 is independently a –CH=– -CY=, $–CH_2$-, -CHY- or $-CY_2$- group, wherein Y is a C_{1-10} hydrocarbyl group, preferably a C_{1-4} hydrocarbyl group and where n is 2-6, preferably 3-4.

Each substituent R^3 and R^4 are independently the same or can be different and are hydrogen, a linear or branched C_1-C_6-alkyl group, an OY group or a C_{7-20} arylalkyl, C_{7-20} alkylaryl group or C_{6-20} aryl group, preferably hydrogen, a linear or branched C_1-C_6-alkyl group or C_{6-20} aryl groups, and optionally two adjacent R^3 or R^4 groups can be part of a ring including the phenyl carbons to which they are bonded. More preferably, R^3 and R^4 are hydrogen or a linear or branched C_1-C_4 alkyl group or a OY-group, wherein Y is a is a C_{1-4} hydrocarbyl group. Even more preferably, each R^3 and R^4 are independently hydrogen, methyl, ethyl, isopropyl, tert-butyl or methoxy, especially hydrogen, methyl or tert-butyl, whereby at least one R^3 per phenyl group and at least one R^4 is not hydrogen.

Thus, preferably one or two R^3 per phenyl group are not hydrogen, more preferably on both phenyl groups the R^3 groups are the same, like 3´,5´-di-methyl or 4´- tert-butyl for both phenyl groups.

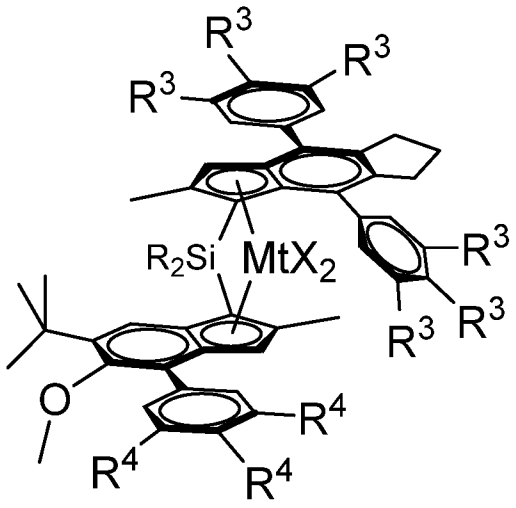
For the indenyl moiety preferably one or two R^4 on the phenyl group are not hydrogen, more preferably two R^4 are not hydrogen and most preferably these two R^4 are the same like 3´,5´-di-methyl or 3´,5´-di-tert-butyl.

R^5 is a linear or branched C_1-C_6-alkyl group such as methyl, ethyl, n-propyl, i-propyl, n-butyl, i-butyl, sec-butyl and tert-butyl, C_{7-20} arylalkyl, C_{7-20} alkylaryl group or C_6-C_{20} aryl group. R^5 is a preferably a linear or branched C_1-C_6 alkyl group or C_{6-20} aryl group, more preferably a linear C_1-C_4 alkyl group, even more preferably a C_1-C_2 alkyl group and most preferably methyl.

R^6 is a $C(R^8)_3$ group, with R^8 being a linear or branched C_1-C_6 alkyl group.

Each R is independently a C_1-C_{20}-hydrocarbyl, C_6-C_{20}-aryl, C_7-C_{20}-arylalkyl or C_7-C_{20}-alkylaryl. Preferably each R^8 are the same or different with R^8 being a linear or branched C_1-C_4-alkyl group, more preferably with R^8 being the same and being a C_1-C_2-alkyl group. Most preferably, all R^8 groups are methyl.

In a further preferred embodiment the organometallic compound (C) has the following formula (III):



Formula (III)

wherein

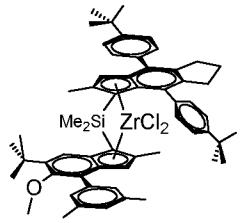
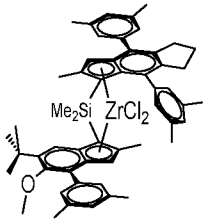
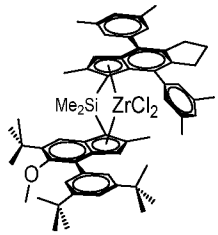
Mt is Zr or Hf, preferably Zr;

each R^3 and R^4 are independently the same or can be different and are hydrogen or a linear or branched C_1-C_6-alkyl group, whereby at least on R^3 per phenyl group and at least one R^4 is not hydrogen.

Specific metallocene catalyst complexes include: rac-anti-dimethylsilanediyl[2-methyl-4,8-bis-(4'-tert-butylphenyl)-1,5,6,7-tetrahydro-s-indacen-1-yl][2-methyl-4-(3',5'-dimethyl-phenyl)-5-methoxy-6-tert-butylinden-1-yl] zirconium dichloride;

rac-anti-dimethylsilanediyl[2-methyl-4,8-bis-(3',5'-dimethylphenyl)-1,5,6,7-tetrahydro-s-indacen-1-yl][2-methyl-4-(3',5'-dimethylphenyl)-5-methoxy-6-tert-butylinden-1 -yl]zirconium dichloride;

rac-anti-dimethylsilanediyl[2-methyl-4,8-bis-(3',5'-dimethylphenyl)-1,5,6,7-tetrahydro-s-indacen-1-yl][2-methyl-4-(3',5'-ditert-butyl-phenyl)-5-methoxy-6-tert-butylinden-1-yl] zirconium dichloride or their corresponding zirconium dimethyl analogues.

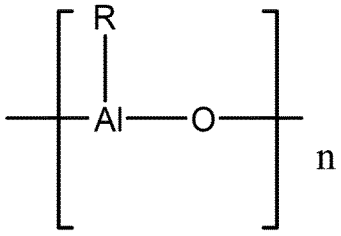
		
MC-1	MC-2	MC-3

The ligands required to form the metallocene catalysts of the invention can be synthesized by any process and the skilled organic chemist would be able to devise various synthetic protocols for the manufacture of the necessary ligand materials. WO2007/116034, for example, discloses the necessary chemistry. Synthetic protocols can also generally be found in WO2002/02576, WO2011/135004, WO2012/084961, WO2012/001052, WO2011/076780 and WO2015/158790.

To form an active catalytic species it is normally necessary to employ a cocatalyst as is well known in the art.

According to the present invention preferably a cocatalyst system comprising a boron containing cocatalyst and/or an aluminoxane cocatalyst is used in combination with the above defined metallocene catalyst.

The aluminoxane cocatalyst can be one of formula (IV):



(IV)

where n is usually from 6 to 20 and R has the meaning below.

Aluminoxanes are formed on partial hydrolysis of organoaluminum compounds, for example those of the formula AlR_3, AlR_2Y and $Al_2R_3Y_3$ where R can be, for example, C_1-C_{10} alkyl, preferably C_1-C_5 alkyl, or C_3-C_{10} cycloalkyl, C_7-C_{12} arylalkyl or alkylaryl and/or phenyl or naphthyl, and where Y can be hydrogen, halogen, preferably chlorine or bromine, or C_1-C_{10} alkoxy, preferably methoxy or ethoxy. The resulting oxygen-containing aluminoxanes are not in general pure compounds but mixtures of oligomers of the formula (III).

The preferred aluminoxane is methylaluminoxane (MAO). Since the aluminoxanes used according to the invention as cocatalysts are not, owing to their mode of preparation, pure compounds, the molarity of aluminoxane solutions hereinafter is based on their aluminium content.

According to the present invention, also a boron containing cocatalyst can be used instead of the aluminoxane cocatalyst or the aluminoxane cocatalyst can be used in combination with a boron containing cocatalyst.

It will be appreciated by the person skilled in the art that where boron based cocatalysts are employed, it is normal to pre-alkylate the complex by reaction thereof with an aluminium alkyl compound, such as TIBA. This procedure is well known and any suitable aluminium alkyl, e.g. $Al(C_1$-C_6 alkyl$)_3$ can be used. Preferred aluminium alkyl compounds are triethylaluminium, tri-isobutylaluminium, tri-isohexylaluminium, tri-n-octylaluminium and tri-isooctylaluminium.

Alternatively, when a borate cocatalyst is used, the metallocene complex is in its alkylated version, that is for example a dimethyl or dibenzyl metallocene complex can be used.

Boron based cocatalysts of interest include those of formula (V)

$$BY_3 \quad (V)$$

wherein Y is the same or different and is a hydrogen atom, an alkyl group of from 1 to about carbon atoms, an aryl group of from 6 to about 15 carbon atoms, alkylaryl, arylalkyl, haloalkyl or haloaryl each having from 1 to 10 carbon atoms in the alkyl radical and from 6-20 carbon atoms in the aryl radical or fluorine, chlorine, bromine or iodine. Preferred examples for Y are methyl, propyl, isopropyl, isobutyl or trifluoromethyl, unsaturated groups such as aryl or haloaryl like phenyl, tolyl, benzyl groups, p-fluorophenyl, 3,5- difluorophenyl, pentachlorophenyl, pentafluorophenyl, 3,4,5-trifluorophenyl and 3,5-di(trifluoromethyl)phenyl. Preferred options are trifluoroborane, triphenylborane, tris(4-fluorophenyl)borane, tris(3,5-difluorophenyl)borane, tris(4-fluoromethylphenyl)borane, tris(2,4,6-trifluorophenyl)borane, tris(penta-fluorophenyl)borane, tris(tolyl)borane, tris(3,5-dimethyl-phenyl)borane, tris(3,5-difluorophenyl)borane and/or tris (3,4,5-trifluorophenyl)borane.

Particular preference is given to tris(pentafluorophenyl)borane.

However it is preferred that borates are used, i.e. compounds containing a borate 3^+ ion.

Such ionic cocatalysts preferably contain a non-coordinating anion such as tetrakis(pentafluorophenyl)borate and tetraphenylborate. Suitable counterions are protonated amine or aniline derivatives such as methylammonium, anilinium, dimethylammonium, diethylammonium, N- methylanilinium, diphenylammonium, N,N-dimethylanilinium, trimethylammonium, triethylammonium, tri-n-butylammonium, methyldiphenylammonium, pyridinium, p-bromo-N,N-dimethylanilinium or p-nitro-N,N-dimethylanilinium.

Preferred ionic compounds which can be used according to the present invention include:

triethylammoniumtetra(phenyl)borate,

tributylammoniumtetra(phenyl)borate,

trimethylammoniumtetra(tolyl)borate,

tributylammoniumtetra(tolyl)borate,

tributylammoniumtetra(pentafluorophenyl)borate,

tripropylammoniumtetra(dimethylphenyl)borate,

tributylammoniumtetra(trifluoromethylphenyl)borate,

tributylammoniumtetra(4-fluorophenyl)borate,

N,N-dimethylcyclohexylammoniumtetrakis(pentafluorophenyl)borate,

N,N-dimethylbenzylammoniumtetrakis(pentafluorophenyl)borate,

N,N-dimethylaniliniumtetra(phenyl)borate,

N,N-diethylaniliniumtetra(phenyl)borate,

N,N-dimethylaniliniumtetrakis(pentafluorophenyl)borate,

N,N-di(propyl)ammoniumtetrakis(pentafluorophenyl)borate,

di(cyclohexyl)ammoniumtetrakist(pentafluorophenyl)borate,

triphenylphosphoniumtetrakis(phenyl)borate,

triethylphosphoniumtetrakis(phenyl)borate,

diphenylphosphoniumtetrakis(phenyl)borate,

tri(methylphenyl)phosphoniumtetrakis(phenyl)borate,

tri(dimethylphenyl)phosphoniumtetrakis(phenyl)borate,

triphenylcarbeniumtetrakis(pentafluorophenyl)borate,

or ferroceniumtetrakis(pentafluorophenyl)borate.

Preference is given to triphenylcarbeniumtetrakis(pentafluorophenyl) borate,

N,N- dimethylcyclohexylammoniumtetrakis(pentafluorophenyl)borate or

N,N- dimethylbenzylammoniumtetrakis(pentafluorophenyl)borate.

It has been surprisingly found that certain boron cocatalysts are especially preferred.

Preferred borates of use in the invention therefore comprise the trityl ion. Thus the use of N,N-dimethylammonium-tetrakispentafluorophenylborate and $Ph_3CB(PhF_5)_4$ and analogues therefore are especially favoured.

According to the present invention, the preferred cocatalysts are aluminoxanes, more preferably methylaluminoxanes, combinations of aluminoxanes with Al-alkyls, boron or borate cocatalysts, and combination of aluminoxanes with boron-based cocatalysts.

Suitable amounts of cocatalyst will be well known to the person skilled in the art.

The molar ratio of boron to the metal ion of the metallocene may be in the range 0.5:1 to 10:1 mol/mol, preferably 1:1 to 10:1 mol/mol, especially 1:1 to 5:1 mol/mol.

The molar ratio of Al in the aluminoxane to the metal ion of the metallocene may be in the range 1:1 to 2000:1 mol/mol, preferably 10:1 to 1000:1 mol/mol, more preferably 50:1 to 900:1 mol/mol, and most preferably 600:1 to 800:1 mol/mol.

The metallocene catalyst used in the polymerisation process of the present invention is preferably used in supported form. The support used comprises, preferably consists of, silica. The person skilled in the art is aware of the procedures required to support a metallocene catalyst.

Especially preferably, the support is a porous material so that the complex may be loaded into the pores of the support, e.g. using a process analogous to those described in WO 94/14856 (Mobil), WO 95/12622 (Borealis) and WO 2006/097497.

The average particle size of the support can be typically from 10 to 100 μm. However, it has turned out that special advantages can be obtained if the support has an average particle size from 15 to 80 μm, preferably from 18 to 50 μm.

The particle size distribution of the support is described in the following. The support preferably has a D_{50} of between 10 and 80 μm, preferably 18 and 50 μm. Furthermore, the support preferably has a D_{10} of between 5 and 30 μm and a D_{90} of between 30 and 90 μm. Preferably, the support has a SPAN value of 0.1 to 1.1, preferably 0.3 to 1.0.

The average particle size of the metallocene catalyst is preferably of from 20 to 50 μm, more preferably of from 25 to 45 μm, and most preferably of from 30 to 40 μm.

The particle size distribution of the metallocene catalyst is described in the following. The metallocene catalyst preferably has a D50 of from 30 to 80 μm, preferably of from 32 to 50 μm and most preferably of from 34 to 40 μm. Furthermore, the metallocene catalyst preferably has a D10 of at most 29 μm, more preferably of from 15 to 29 μm, more preferably of from 20 to 28 μm, and most preferably of from 25 to 27 μm. The metallocene catalyst preferably has a

D90 of at least 45 µm, more preferably of from 45 to 70 µm and most preferably of from 40 to 60 µm.

The average pore size of the support can be in the range 10 to 100 nm, preferably 20 to 50 nm and the pore volume from 1 to 3 ml/g, preferably 1.5 to 2.5 ml/g. BET surface area of silica support materials are determined according to ASTM D3663 and porosity parameters based on BJH according to ASTM D4641. Examples of suitable support materials are, for instance, ES757 produced and marketed by PQ Corporation, Sylopol 948 produced and marketed by Grace or SUNSPERA DM-L-303 silica produced by AGC Si-Tech Co. Supports can be optionally calcined prior to the use in catalyst preparation in order to reach optimal silanol group content.

All or part of the preparation steps can be done in a continuous manner. The formed catalyst preferably has good stability/kinetics in terms of longevity of reaction, high activity and the catalysts enable low ash contents.

Generally, silica supported polymerisation catalysts show very complex polymerisation behaviour and the polymerisation process can be subdivided into several phases.

During the first minutes of polymerisation the catalyst activity can reach high values resulting in an uncontrollable fragmentation process which in turn can lead to decrease of catalyst activity due to increased external mass and heat transport phenomena. More particularly, the exothermic heat generated due to the polymerisation reaction cannot be properly dissipated, thus, leading to local particle overheating (i.e., the temperature difference between the surface of the growing polymer particles and the bulk temperature attains high values). Therefore, the polymer that is produced on the surface of the growing polymer particle becomes sticky, thus leading to increased risk of particle agglomeration, with concomitant effects on process performance and reactor operability.

A polymerisation kinetic described above requires a new design of the pre-polymerisation process with respect to temperature, monomer concentration and residence time.

In a preferred embodiment of the invention, in the initial phase (first activity peak) the temperature and monomer concentration must be as low as possible to avoid

overheating of the formed polymer and to avoid formation of agglomerates. In the second phase the monomer concentration and the temperature must be as high as possible to accelerate the catalyst fragmentation process.

Experimental Part

Measurement methods

Any parameter mentioned above in the detailed description of the invention is measured according to the tests given below.

a) Melt Flow Rate

The melt flow rate (MFR) is determined according to ISO 1133 and is indicated in g/10 min. The MFR is an indication of the melt viscosity of the polymer. The MFR is determined at 190 °C for polyethylene and 230 °C for polypropylene. The load under which the melt flow rate is determined is usually indicated as a subscript, for instance MFR_2 is measured under 2.16 kg load (condition D).

b) Average Particle size and particle size distribution

The particle size distribution was determined using laser diffraction measurements by Coulter LS 200. The particle size and particle size distribution is a measure for the size of the particles. The D-values (D10 (or d10), D50 (or d50) and D90 (or d90)) represent the intercepts for 10%, 50% and 90% of the cumulative mass of sample. The D-values can be thought of as the diameter of the sphere which divides the sample's mass into a specified percentage when the particles are arranged on an ascending mass basis. For example the D10 is the diameter at which 10% of the sample's mass is comprised of particles with a diameter less than this value. The D50 is the diameter of the particle where 50% of a sample's mass is smaller than and 50% of a sample's mass is larger than this value. The D90 is the diameter at which 90% of the sample's mass is comprised of particles with a diameter less than this value. The D50 value is also called median particle size. From laser diffraction measurements according to ISO 13320 the volumetric D-values are obtained, based on the volume distribution.

The distribution width or span of the particle size distribution is calculated from the D-values D10, D50 and D90 according to equation (3):

$$\text{Span} = (D90-D10)/D50 \quad \text{equation (3)}$$

Sieve fraction is determined by a Camsizer P4 from the Company Retsch Technology GmbH via digital image analysis. The measuring principle is a dynamic image analysis according to ISO 13322-2.

c) *Xylene soluble fraction*

The xylene soluble fraction (XS) is determined according to ISO 16152 at 25 °C.

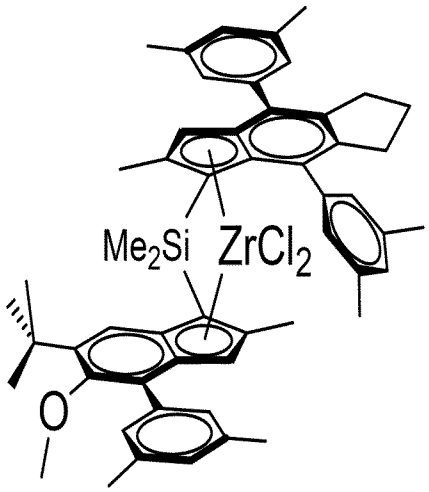
d) *Bulk density*

The bulk density is measured according to ASTM D1895.

Materials

The following catalyst was used in the processes according to the comparative and inventive examples as described in Table 1.

A metallocene catalyst as described in WO 2019/179959 A1 was used, the method of its preparation being detailed hereinbelow.



A steel reactor equipped with a mechanical stirrer and a filter net was flushed with nitrogen and the reactor temperature was set to 20 °C. Next silica grade DM-L-303 from AGC Si-Tech Co, pre-calcined at 600 °C (10 kg) was added from a feeding drum followed by careful pressuring and depressurising with nitrogen using manual valves. Then toluene (43.5 kg) was added. The mixture was stirred

for 30 min. Next 30 wt.% solution of MAO in toluene (17.5 kg) from Lanxess was added via feed line on the top of the reactor within 140 min. The reaction mixture was then heated up to 90 °C and stirred at 90 °C for additional two hours. The slurry was allowed to settle, and the mother liquor was filtered off. The catalyst was washed twice with toluene (43.5 kg) at 90 °C, following by settling and filtration.

Finally, MAO treated SiO2 was dried at 60 °C under nitrogen flow for 2 hours and then for 14 hours under vacuum (~0.5 barg) with stirring. MAO treated support was collected as a free-flowing white powder found to contain 15.0% Al by weight. 30 wt.% MAO in toluene (2 kg) was added into a steel nitrogen blanked reactor via a burette at 20 °C. Toluene (12.8 kg) was then added under stirring. 129 g of the metallocene was added from a metal cylinder followed by flushing with 1 kg toluene. The mixture was stirred for 60 minutes at 20 °C. Trityl tetrakis(pentafluorophenyl) borate (127.2 g) was then added from a metal cylinder followed by a flush with 1 kg of toluene. The mixture was stirred for 1 h at room temperature. The resulting solution was added to a stirred cake of MAO-silica support prepared as described above over ~~1~~2 hour. The cake was stirred for 30 minutes and then allowed to stay without stirring for 30 minutes, followed by drying under N2 flow at 60 °C for 2 h and additionally for 15 h under vacuum (~0.5 barg) under stirring.

Examples

The following examples were carried out in a pilot plant, comprising a reactor sequence consisting of a prepolymerisation loop reactor and a loop reactor. Process and properties are given in table 1 below.

Table 1

Examples		CE1	CE2	IE1	IE2	IE3	IE4	IE5	IE6	IE7
Prepoly reactor										
Temperature	[°C]	30	10	25	25	25	25	25	20	15
Pressure	[kPa]	5180	5155	5219	5193	5206	5202	5227	5177	5165
Catalyst feed	[g/h]	2.1	2.0	2.2	2.1	2.4	2.7	2.9	1.9	2.1
H2 feed (g/h)	[g/h]	0.12	0.12	0.12	0.07	0.15	0.18	0.03	0.12	0.12
C3 feed (kg/h)	[kg/h]	65.4	65.5	65.6	65.4	65.4	65.4	65.6	65.7	65.5
Feed H2/C3	[mol/kmol]	0.04	0.04	0.04	0.02	0.05	0.06	0.01	0.04	0.04
Production rate (kg/h)	[kg/h]	1.2	1.4	1.0	1.1	1.1	1.2	0.6	1.0	1.2
Prep-degree	[gPP/g catalyst]	559	698	471	500	447	429	215	504	564
Loop reactor										
Temperature	[°C]	75	75	75	75	75	75	75	75	75
Pressure	[kPa]	5068	5045	5094	5079	5078	5106	5104	5054	5039
Feed H2/C3 ratio	[mol/kmol]	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Production rate	[kg/h]	31.3	29.7	32.3	29.9	29.0	29.1	26.6	29.2	30.1
Catalyst productivity	[kg/g]	15.1	15.1	15.0	14.7	12.5	11.4	9.9	15.6	14.5
Catalyst activity	[kg/g/h]	38.8	39.3	40.4	37.6	32.2	29.0	24.8	42.5	37.8
Final polymer										
MFR_2	[g/10 min]	82.60	64.60	62.00	72.00	78.20	72.00	60.50	66.60	69.80
Total XS	[wt%]	0.84	1.05	0.78	1.00	0.90	0.86	0.64	0.55	0.74
Bulk Density	[kg/m^3]	346.00	319.00	355.00	342.00	346.00	354.00	339.00	333.00	340.00
Sieve bottom	[%]	0.02	0.04	0.01	0.01	0.03	0.02	0.02	0.02	0.03
Sieve fraction 0.106 mm	[%]	0.08	0.15	0.15	0.10	0.15	0.14	0.11	0.11	0.15
Sieve fraction 0.250 mm	[%]	0.34	0.38	0.69	0.33	0.74	0.74	0.48	0.41	0.56
Sieve fraction 0.355 mm	[%]	15.67	10.68	18.53	12.85	24.24	26.30	13.84	8.42	13.91
Sieve fraction 0.820 mm	[%]	78.70	81.53	73.65	80.29	70.24	68.85	77.90	77.80	79.34
Sieve fraction 2.000 mm	[%]	4.73	7.20	6.93	6.40	4.57	3.95	7.48	13.20	5.91
Sieve fraction > 4.000 mm	[%]	0.46	0.02	0.04	0.02	0.03	0.00	0.17	0.12	0.10

When the process is running at 30°C as for CE1, although giving quite good bulk density, the process was stopped due to plug of convey line between prepolymerisation reactor and loop reactor also due to much more bigger particles (4 mm or above, agglomerates).

However, if the prepolymerisation is running at too low temperature as in comparative example CE2, then the bulk density is low which indicates bad morphology.

As can be seen from IE1 to IE7, the best condition for the process is a temperature of 15 - 29°C with H2/C3 ratio of 0.01-0.08 mol/kmol in the prepolymerisation reactor.

Claims

1. Process for the production of a polypropylene homo- or copolymer, the process comprising the steps of

   a) prepolymerising propylene in a first reactor in the presence of hydrogen and a metallocene catalyst yielding a first polypropylene homo- or copolymer fraction, wherein a ratio of the feed of hydrogen to the feed of propylene is in the range of 0.01 to 0.08 mol/kmol, and wherein the temperature in the first reactor is from 15 to 29°C,

   b) transferring the first polypropylene homo- or copolymer fraction to a second reactor,

   c) polymerising in the second reactor propylene in the presence of the first polypropylene homo- or copolymer fraction, yielding a second polypropylene homo- or copolymer fraction, wherein a residence time in the second reactor is from 10 to 40 min,

   d) withdrawing the polypropylene homo- or copolymer comprising the first and the second polypropylene homo- or copolymer fraction from the second reactor or transferring the polypropylene homo- or copolymer to a third reactor,

   wherein metallocene catalyst comprises a metallocene complex, and the metallocene complex is an organometallic compound (C), the organometallic compound (C) has the following formula (Ia):

   $(L)_2R_nMX_2$ (Ia)

   wherein

   "M" is Zr or Hf;

   each "X" is a σ-ligand;

   each "L" is an optionally substituted cyclopentadienyl, indenyl or tetrahydroindenyl;

   "R" is $SiMe_2$ bridging group linking said organic ligands (L);

   "n" is 0 or 1, preferably 1.

2. The process according to claim 1, wherein in step a) the temperature in the first reactor is between 20 and 28 °C.

3. The process according to any one of the preceding claims, wherein in step a) the pressure in the first reactor is between 1 and 150 bar.

4. The process according to any one of the preceding claims, wherein in step c) the temperature in the second reactor is between 60 and 100 °C.

5. The process according to any one of the preceding claims, wherein in step c) the pressure in the second reactor is between 1 and 150 bar.

6. The process according to any one of the preceding claims, wherein in step a) a comonomer is present in the first reactor.

7. The process according to any one of the preceding claims, wherein in step c) a comonomer is present in the second reactor.

8. The process according to claim 6, wherein the comonomer in step a) is ethylene.

9. The process according to claim 7, wherein the comonomer in step c) is ethylene.

10. The process according to any one of the preceding claims, wherein the metallocene catalyst further comprises a support, wherein the support comprises silica.

11. The process according to any one of the preceding claims, wherein the metallocene catalyst further comprises a cocatalyst system, the cocatalyst system comprising a boron-containing cocatalyst and/or an aluminoxane cocatalyst.

12. The process according to any one of the preceding claims, wherein the first reactor is a loop reactor and/or wherein the second reactor is a loop reactor.

13. The process according to any one of the preceding claims, wherein in step d) the third reactor is a gas phase reactor.

14. Propylene homo- or copolymer obtained by the process according to any one of the preceding claims.

15. The propylene homo- or copolymer according to claim 14, having a bulk density of 320 kg/m^3 or more measured according to ASTM D1895.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/086300

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F110/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2022/034126 A1 (BOREALIS AG [AT]) 17 February 2022 (2022-02-17) page 24, lines 24, 25 page 48 table 1 claims 1-15 -----	1-15
X	WO 2021/233824 A1 (BOREALIS AG [AT]) 25 November 2021 (2021-11-25) page 23, lines 34, 35 page 42 HPP1; table 1 claims 1-18 ----- -/--	1-15

[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 March 2024	28/03/2024

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/086300

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2019/179959 A1 (BOREALIS AG [AT]) 26 September 2019 (2019-09-26) cited in the application	14,15
A	example 2; tables 1-4B claims 1-12	1-13

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2023/086300

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2022034126 A1	17-02-2022	BR 112023002198 A2	03-10-2023
		CN 116134087 A	16-05-2023
		EP 4196526 A1	21-06-2023
		US 2023348705 A1	02-11-2023
		WO 2022034126 A1	17-02-2022
WO 2021233824 A1	25-11-2021	BR 112022023287 A2	20-12-2022
		CN 115667324 A	31-01-2023
		EP 3913005 A1	24-11-2021
		JP 2023526330 A	21-06-2023
		KR 20230009937 A	17-01-2023
		US 2023174759 A1	08-06-2023
		WO 2021233824 A1	25-11-2021
WO 2019179959 A1	26-09-2019	CN 112292406 A	29-01-2021
		EP 3768735 A1	27-01-2021
		ES 2905783 T3	12-04-2022
		JP 7297782 B2	26-06-2023
		JP 2021518462 A	02-08-2021
		KR 20200133264 A	26-11-2020
		SA 520420157 B1	05-06-2023
		US 2021017307 A1	21-01-2021
		WO 2019179959 A1	26-09-2019