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(54) Title: PROCESS FOR PREPARING PROPYLENE POLYMERS HAVING LONG CHAIN BRANCHES

(57) Abstract: The present invention relates to a process for the preparation of long chain branched propylene polymers via a polymerization of propylene, preferably under slurry or bulk conditions, in the presence of a catalyst system comprising a supported bridged metallocene catalyst and at least one alpha,omega-diene compound. The invention moreover relates to long chain branched propylene polymers obtained by the present process.

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PROCESS FOR PREPARING PROPYLENE POLYMERS HAVING LONG CHAIN BRANCHES

FIELD OF THE INVENTION

The present invention relates to a process for preparing propylene polymers having long chain branches via a polymerization of propylene in the presence of a catalyst system comprising a supported bridged metallocene catalyst and a diene compound. The process has the advantage of allowing the control of long chain branching in propylene polymers thereby allowing the preparation of propylene polymers with tailored properties. The present invention also relates to long chain branched propylene polymers obtained by the present process.

BACKGROUND OF THE INVENTION

A widespread representative of polyolefins is polypropylene (PP), known for its higher melting point, lower density, chemical resistance, rigidity, impact strength and low cost. For these properties, the PP can be used in many manufacturing processes such as compression, foaming, thermoforming, blow moulding, injection moulding, rotational moulding and extrusion coating. PP occurs in two basic types (linear, branched) and is usually processed in a melt state. The key problem with processing of conventional linear PP is its low melt strength, which may limit processing window considerably, and restrict the use of polypropylene in a number of applications. Highly linear PP, especially those polypropylene resins with narrow polydispersity (metallocene-based resins), are also energetically demanding from the point of view of their processing.

Considerable progress has been made to enhance melt strength and processability of polypropylene by introduction of long chain branches (herein also “LCBs” or “LCB”). In addition, in the case of polypropylene, certain processes like blow molding and production of foams are very difficult. LCBs are known to increase the bubble stability of PP which in turn helps the aforementioned processes. On the other hand, the extensive presence of LCBs in PP can also lead to poorer mechanical properties.

Long chain branching is a key resin parameter as it has huge effects on rheology but remains very difficult to control. It is mainly linked to the used catalyst structure in combination with the process. However, with existing approaches, it remains difficult to obtain a polyolefin with a certain desired amount of long chain branching.

The amount of long chain branching can be modified with post reaction treatment such as electron beam radiation, gamma radiation, UV radiation or by utilizing peroxides, however leading to increased costs. For instance, it is known that electron beam irradiation significantly modifies the structure of a polypropylene molecule. The irradiation of polypropylene results in chain scission and grafting (or branching) which can occur simultaneously. Up to a certain level of irradiation dose, it is possible to produce a modified polymer molecule having free-end long branches, otherwise known as long chain branching, starting from a linear polypropylene molecule. Another post-reactor treatment of polypropylene includes for instance curing by peroxides. For instance, the use of peroxides in the extrusion process can be applied to control the molecular weight distribution by scission of the chains. In such cases the, rearrangements and cross-linking events can take place which can lead to the formation of LCB and increase processability and mechanical properties. However, above-named post reactor treatments may cause polymer degradation and affect the positive properties of PP. Moreover, such methods are intrinsically expensive, and also difficult to steer in order to control the amount of LCBs.

In the light of the above, there is therefore a demand for processes for preparing propylene polymers having tailored properties and especially having a controlled amount of long chain branching. There is in particular a demand in the art for an improved process to prepare propylene polymers having long chain branches, and preferably having controlled amounts of long chain branches.

It is therefore an object of the present invention to provide a process for preparing propylene polymers having long chain branches which is more controllable. It is also an object of the present invention to provide a process for preparing propylene polymers having long chain branches which is widely applicable and less expensive.

It is in particular an object of the present invention to provide a process for preparing propylene polymers with long chain branches during polymer synthesis. In other words, it is an object to provide an “in-reactor” process for preparing propylene polymers having long chain branches. Another object of the present invention to provide a process that allows in reactor production of propylene polymers having tailored amounts, e.g. low amounts of long chain branches.

SUMMARY OF THE INVENTION

It has now surprisingly been found that the above objectives can be attained either individually or in any combination by using the specific and well-defined process as disclosed herein for preparing propylene polymers with long chain branches.

In a first aspect, the present invention provides a process for preparing propylene polymers having long chain branches, said process comprising the steps of

feeding into at least one reactor propylene monomer and optionally one or more alpha-olefins comonomer(s), a catalyst system, optionally a hydrocarbon diluent, optionally hydrogen and an alkylaluminum of formula AlR^b_x, wherein x is an integer selected from 1 to 3 and each R^b is independently selected from halogen, alkoxy or alkyl, and polymerizing in said at least one reactor, the propylene monomer and optionally one or more alpha-olefins comonomer(s), in the presence of said catalyst system, said optional hydrocarbon diluent, said optional hydrogen and said alkylaluminum, thereby producing propylene polymers having long chain branches,

wherein said catalyst system comprises

a. at least one bridged metallocene catalyst which is immobilized on an inert support, and
b. at least one diene compound, wherein said diene compound is an alpha,omega-diene of formula (I)

$$H_2C=CH-(CR^a_2)_m-HC=CH_2 \text{ (I)}$$

wherein m is an integer of at least 3, and preferably from 3 to 16, and

wherein each R^a is independently hydrogen or a C_1-C_{10} alkyl.

Said process allows to fine-tune the amount of long chain branching in propylene polymer during the polymerization process. The present process also allows a reduction of costs as compared to conventional (e.g. post reactor treatment) methods. The present invention also provides the ability to use a process as disclosed herein as a “plug and play system”, wherein LCBs are generated only when needed, e.g. on existing and already established polymerization systems.

The invention also encompasses a catalyst system suitable for catalyzing a polymerisation process for preparing propylene polymers having long chain branches, comprising

a. at least one bridged metallocene catalyst which is immobilized on an inert support, and preferably a bridged metallocene catalyst as defined herein, and
b. at least one diene compound, wherein said diene compound is an alpha,omega-diene of formula (I)

$$H_2C=CH-(CR^a_2)_m-HC=CH_2 \text{ (I)}$$

wherein m is an integer of at least 3, and preferably from 3 to 16, and

wherein each R^a is independently hydrogen or a C_1-C_{10} alkyl, and

preferably a diene compound as defined herein.

The present invention also encompasses propylene polymers having long chain branches obtained by the process according to the first aspect of the invention or obtained by a process using a catalyst system as provided herein.

The present process brings a solution for the “in-reactor” production of propylene polymers having long chain branches in a controlled way, e.g. by using one single catalyst system.

The independent and dependent claims set out particular and preferred features of the invention. Features from the dependent claims may be combined with features of the independent or other dependent claims as appropriate.

The present invention will now be further described. In the following passages, different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 represents a van Gurp-Palmen plot (phase angle versus complex shear modulus) of a number of polypropylene resins as prepared according to example 4.

Figure 2 illustrates the relationship between the g_{rheo} value (indicative for LCB formation) and the amount of diene (1,7-octadiene) used during polymerisation as determined in accordance with example 5.

Figure 3 represents a van Gurp-Palmen plot (phase angle versus complex shear modulus) of a number of polypropylene resins as prepared according to example 5.

Figure 4 compares shear thinning characteristics (Tanδ vs angular frequency plots) of a number of polypropylene resins as prepared according to example 5.

Figure 5 illustrates melt strength values for a number of polypropylene resins as prepared according to example 5.

Figure 6 represents GPC profiles of a number of polypropylene resins as prepared according to example 5.

DETAILED DESCRIPTION OF THE INVENTION

When describing the invention, the terms used are to be construed in accordance with the following definitions, unless a context dictates otherwise.

As used herein, the singular forms "a", "an", and "the" include both singular and plural referents unless the context clearly dictates otherwise. By way of example, "a resin" means one resin or more than one resin.

The terms "comprising", "comprises" and "comprised of" as used herein are synonymous with "including", "includes" or "containing", "contains", and are inclusive or open-ended and do not exclude additional, non-recited members, elements or method steps. It will be appreciated that the terms "comprising", "comprises" and "comprised of" as used herein comprise the terms "consisting of", "consists" and "consists of".

The recitation of numerical ranges by endpoints includes all integer numbers and, where appropriate, fractions subsumed within that range (e.g. 1 to 5 can include 1, 2, 3, 4 when referring to, for example, a number of elements, and can also include 1.5, 2, 2.75 and 3.80, when referring to, for example, measurements). The recitation of end points also includes the end point values themselves (e.g. from 1.0 to 5.0 includes both 1.0 and 5.0). Any numerical range recited herein is intended to include all sub-ranges subsumed therein.

All references cited in the present specification are hereby incorporated by reference in their entirety. In particular, the teachings of all references herein specifically referred to are incorporated by reference.

Reference throughout this specification to “one embodiment” or “an embodiment” means that a particular feature, structure or characteristic described in connection with the embodiment is included in at least one embodiment of the present invention. Thus, appearances of the phrases “in one embodiment” or “in an embodiment” in various places throughout this specification are not necessarily all referring to the same embodiment, but may. Furthermore, the particular features, structures or characteristics may be combined in any suitable manner, as would be apparent to a person skilled in the art from this disclosure, in one or more embodiments. Furthermore, while some embodiments described herein include some but not other features included in other embodiments, combinations of features of different embodiments are meant to be within the scope of the invention, and form different embodiments, as would be understood by those in the art.

Preferred statements (features) and embodiments, resins and uses of this invention are set herein below. Each statement and embodiment of the invention so defined may be combined with any other statement and/or embodiment unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features or statements indicated as being preferred or advantageous. Hereto, the present invention is in particular captured by any one or any combination of one or more of the below numbered aspects and embodiments, with any other statement and/or embodiment.

1. A process for preparing propylene polymers having long chain branches, said process comprising the steps of

   feeding into at least one reactor propylene monomer and optionally one or more alpha-olefins comonomer(s), a catalyst system, optionally an hydrocarbon diluent, optionally hydrogen and an alkylaluminum of formula AlR^b_x, wherein x is an integer selected from 1 to 3 and each R^b is independently selected from halogen, alkoxy or alkyl, and

polymerizing in said at least one reactor, the propylene monomer and optionally one or more alpha-olefins comonomer(s), in the presence of said catalyst system, said optional hydrocarbon diluent, said optional hydrogen and said alkylaluminum, thereby producing propylene polymers having long chain branches,

wherein said catalyst system comprises

a. at least one bridged metallocene catalyst which is immobilized on an inert support, and

b. at least one diene compound, wherein said diene compound is an alpha,omega-diene of formula (I)

$$H_2C=CH\text{-}(CR^a{}_2)_m\text{-}HC=CH_2 \text{ (I)}$$

wherein m is an integer of at least 3, and preferably from 3 to 16, and

wherein each R^a is independently hydrogen or a C_1-C_{10} alkyl.

2. Process according to statement 1, wherein said diene compound is an alpha,omega-diene of formula (I), wherein m is an integer from 3 to 16, and wherein each R^a is hydrogen.

3. Process according to statement 1 or 2 wherein said diene compound is selected from the group consisting of 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, and 1,13-tetradecadiene, and preferably is 1,7-octadiene, or 1,8-nonadiene, or 1,9-decadiene.

4. Process according to any one of statements 1 to 3, wherein said diene compound is applied at a concentration of at most 1000 ppm, or at most 750 ppm, or at most 600 ppm, or at most 500 ppm, or at most 400 ppm, or at most 350 ppm.

5. Process according to any one of statements 1 to 4, wherein said diene compound is applied at a concentration of at least 10 ppm, or at least 15 ppm, or at least 20 ppm, or at least 50 ppm.

6. Process according to any one of statements 1 to 5, wherein said at least one bridged metallocene catalyst is a compound according to formula (II):

$$R^1(Ar)_2M^1Q^1{}_2 \text{ (II)},$$

wherein said metallocene catalyst according to formula (II) has two Ar bound to M^1,

wherein M^1 is a transition metal selected from the group consisting of titanium, zirconium, hafnium, and vanadium; and preferably is zirconium;

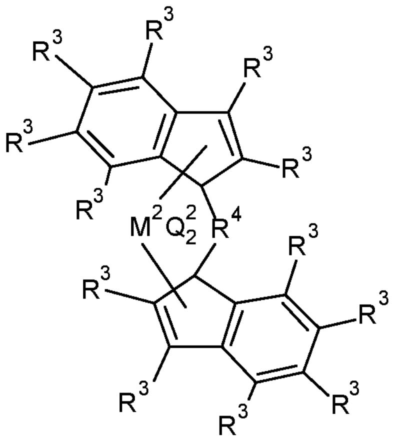
wherein Ar is an aromatic ring, group or moiety and wherein each Ar is independently selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, and fluorenyl, and preferably is selected from the group consisting of indenyl and tetrahydroindenyl,

wherein each of said groups may be optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, SiR^2_3 wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms, and wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl, and P;

wherein each Q^1 is independently selected from the group consisting of halogen, alkyl, heteroalkyl, cycloalkyl, aryl, alkylaryl, aralkyl, alkoxy, cycloalkoxy, aralkoxy, $-COOR^5$ wherein R^5 is hydrogen or alkyl, $-N(R^6)_2$ wherein R^6 is selected from the group consisting of hydrogen, alkyl and COR^7 wherein R^7 is alkyl, and $-CO-(NR^8)_2$ wherein R^8 is H or alkyl, and

wherein R^1 is a divalent group or moiety bridging the two Ar groups and is selected from the group consisting of C_1-C_{20} alkylene, dialkyl germanium, silicon, siloxane, alkylphosphine, and an amine, and wherein said R^1 is optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, SiR^2_3 wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms and wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl, and P.

7. Process according to any one of statements 1 to 6, wherein said at least one bridged metallocene catalyst is a compound according to formula (II), wherein each Ar is independently selected from the group consisting of indenyl and tetrahydroindenyl.
8. Process according to any one of statements 1 to 7, wherein said bridged metallocene catalyst is a compound of formula (III):



(III)

wherein each R^3 in formula (III) is selected independently from hydrogen or a hydrocarbyl having 1 to 20 carbon atoms,

wherein R^4 is a divalent group or moiety bridging the two indenyls and is selected from the group consisting of C_1-C_4 alkylene, dialkyl germanium, silicon, siloxane, alkyl phosphine and amine; and wherein said R^4 is optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, SiR^2_3 wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms and a hydrocarbyl having 1 to 20 carbon atoms.

wherein each Q^2 is independently selected from the group consisting of halogen, alkyl, heteroalkyl, cycloalkyl, aryl, alkylaryl, aralkyl, alkoxy, cycloalkoxy, aralkoxy, $-COOR^5$ wherein R^5 is hydrogen or alkyl, $-N(R^6)_2$ wherein R^6 is selected from the group consisting of hydrogen, alkyl and COR^7 wherein R^7 is alkyl, and $-CO-(NR^8)_2$ wherein R^8 is H or alkyl, and

wherein M^2 is a transition metal selected from the group consisting of titanium, zirconium, hafnium, and vanadium.

9. Process according to statement 8, wherein M^2 is zirconium.

10. Process according to statement 8 or 9, wherein said bridged metallocene catalyst is a compound of formula (III), wherein each Q^2 is a halogen.

11. Process according to any one of statements 8 to 10, wherein said bridged metallocene catalyst is a compound of formula (III),

    wherein M^2 is zirconium,

    wherein each Q^2 is a halogen,

wherein each R^3 independently is hydrogen or a hydrocarbyl having 1 to 20 carbon atoms, and

wherein R^4 is a divalent group or moiety bridging the two indenyls and is selected from the group consisting of C_1-C_4 alkylene and silicon, and wherein said R^4 is optionally substituted with one or more substituents each independently selected from the group consisting of halogen and a hydrocarbyl having 1 to 20 carbon atoms.

12. Process according to any one of statements 8 to 11, wherein said bridged metallocene catalyst is a compound of formula (III):

    wherein M^2 is zirconium,

    wherein each Q^2 is a halogen, preferably chlorine or fluorine,

    wherein each R^3 independently is hydrogen or is selected from a group consisting of linear or branched C_1-C_{20} alkyl; C_3-C_{20}cycloalkyl; C_5-C_{20}aryl; C_6-C_{20}alkylaryl, C_6-C_{20}arylalkyl, and any combinations thereof,

    wherein R^4 is a divalent group or moiety bridging the two indenyls and is selected from the group consisting of C_1-C_4 alkylene and silicon, and wherein said R^4 is optionally substituted with one or more substituents each independently selected from halogen or from the group consisting of linear or branched C_1-C_{20}alkyl; C_3-C_{20}cycloalkyl; C_5-C_{20}aryl; C_6-C_{20}alkylaryl; C_6-C_{20}arylalkyl, and any combinations thereof.

13. Process according to one of statements 8 to 12, wherein said bridged metallocene catalyst is a compound of formula (III):

    wherein M^2 is zirconium,

    wherein each Q^2 is a chlorine,

    wherein each R^3 independently is hydrogen or is selected from a group consisting of linear or branched C_1-C_{20} alkyl; C_3-C_{20}cycloalkyl; C_5-C_{20}aryl; C_6-C_{20}alkylaryl, C_6-C_{20}arylalkyl, and any combinations thereof,

    wherein R^4 is a divalent group or moiety bridging the two indenyls and is selected from the group consisting of C_1-C_4 alkylene and silicon, and wherein said R^4 is optionally substituted with one or more substituents each independently selected from the group consisting of linear or branched C_1-C_{20}alkyl C_3-C_{20}cycloalkyl; C_5-C_{20}aryl; C_6-C_{20}alkylaryl; C_6-C_{20}arylalkyl, and any combinations thereof.

14. Process according to any one of statements 1 to 13, wherein said alkylaluminum of formula AlR^b_x is trialkylaluminum.
15. Process according to any one of statements 1 to 14, wherein said alkylaluminum of formula AlR^b_x is selected from the group comprising Tri-Iso-Butyl Aluminum (TIBAl),Tri-Ethyl Aluminum (TEAl), Tri-Methyl Aluminum (TMA), and Dimethyl-Ethyl Aluminum, and preferably is TIBAl or TEAl.
16. Process according to any one of statements 1 to 15, wherein said inert support is a silica.
17. Process according to any one of statements 1 to 16, wherein said diene compound is not provided on said inert support.
18. Process according to any one of statements 1 to 17, wherein said polymerisation is carried out in a slurry or in a suspension, optionally in the presence of a diluent, preferably an hydrocarbon diluent.
19. Process according to any of one of statements 1 to 18, wherein said polymerisation is carried out in gas phase.
20. Process according to any one of statements 1 to 19, wherein said polymerization step is carried out in one or more reactors preferably selected from continuous stirred-tank reactor, loop reactor, gas phase, or autoclave.
21. Process according to any one of statements 1 to 20, wherein said process is carried out in one single reactor.
22. Process according to any one of statements 1 to 20, wherein said process is carried out in two or more reactors, connected in series.
23. Process according to any one of statements 1 to 20 and 22, wherein said process is carried out in a double loop reactor.
24. Process according to any one of statements 1 to 23, wherein said bridged metallocene catalyst is pre-contacted with said compound of formula (I) before feeding to said at least one reactor.
25. Process according to any one of statements 1 to 24, wherein said bridged metallocene catalyst is pre-contacted with said alkylaluminum of formula AlR^b_x before feeding to said at least one reactor.
26. Process according to any one of statements 1 to 25, wherein the one or more alpha-olefins comonomers are selected from the group comprising ethylene, 1-butene, 1-pentene, 1-hexene and 1-octene, and preferably wherein said comonomer is ethylene.
27. Process according to any one of statements 1 to 26, wherein said propylene polymer has a rheology long chain branching index (g_{rheo}) lower than 0.95, preferably lower than 0.90, preferably lower than 0.88, preferably lower than 0.85, such as lower than

0.75, such as lower than 0.70, such as lower than 0.65, as determined by the method disclosed in the example section.

28. Process according to any one of statements 1 to 27, wherein said propylene polymer has a rheology long chain branching index (g_{rheo}) higher than 0.35, such as higher than 0.40, or higher than 0.45, or higher than 0.50, or higher than 0.55, as determined by the method disclosed in the example section.
29. A catalyst system suitable for catalyzing a polymerisation process for preparing propylene polymers having long chain branches, comprising
    a. at least one bridged metallocene catalyst which is immobilized on an inert support, and
    b. at least one diene compound, wherein said diene compound is an alpha,omega-diene of formula (I)

$$H_2C{=}CH\text{-}(CR^a{}_2)_m\text{-}HC{=}CH_2 \ (I)$$

wherein m is an integer of at least 3, and preferably from 3 to 16, and

wherein each R^a is independently hydrogen or a C_1-C_{10} alkyl.

30. Catalyst system according to statement 29 wherein said bridged metallocene catalyst is as defined in any of one of statements 1 and 6 to 13.
31. Catalyst system according to statement 29 or 30, wherein said diene compound is as defined in any of one of statements 1 to 3.
32. Catalyst system according to any one of statements 29 to 31, wherein said inert support is a silica.
33. Catalyst system according to any one of statements 29 to 32, wherein said diene compound is not provided on said inert support.
34. Use of a catalyst system according to any one of statements 29 to 33 in a process for preparing propylene polymers having long chain branches.
35. Use of a catalyst system according to any one of statements 29 to 34 in a process for preparing propylene polymers having long chain branches as defined in any one of statements 1 to 28.
36. Propylene polymer having long chain branches obtained by a process according to any one of statements 1 to 28 or obtained by a process using a catalyst system according to any one of statements 29 to 33.
37. Propylene polymer having long chain branches according to statement 36, wherein said propylene polymer has a rheology long chain branching index (g_{rheo}) lower than 0.95, preferably lower than 0.90, preferably lower than 0.88, preferably lower than 0.85,

such as lower than 0.75, such as lower than 0.70, such as lower than 0.65, as determined by the method disclosed in the example section.

38. Propylene polymer having long chain branches according to statement 36 or 37, wherein said propylene polymer has a rheology long chain branching index (g_{rheo}) higher than 0.35, such as higher than 0.40, or higher than 0.45, or higher than 0.50, or higher than 0.55, as determined by the method disclosed in the example section.
39. Propylene polymer having long chain branches according to any one of statements 36 to 38, wherein said propylene polymer has a MI2, as determined according to ISO 1133:2005 Method B, condition M, at a temperature 230 °C, and a 2.16 kg load using a die of 2.096 mm, comprised between 0.5 and 150 g/10 min, such as between 0.5 and 100 g/10 min, such as between 0.5 and 50 g/10 min, or 0.5 and 25 g/10 min.
40. Propylene polymer having long chain branches according to any one of statements 36 to 39, wherein said propylene polymer has a ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) [M_w/M_n] of at most 5.7, or at most 5.5, or at most 5.0 or at most 4.5, or at most 4.0.
41. Propylene polymer having long chain branches according to any one of statements 36 to 40, wherein said propylene polymer has a ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) [M_w/M_n] of at least 2.0, preferably at least 2.2, preferably at least 2.3, preferably at least 2.4, preferably at least 2.5, preferably at least 2.6, preferably at least 3.0.
42. Use of an alpha,omega-diene of formula (I) as defined in any one of statements 1 to 3 in a polymerization process for preparing propylene polymers having long chain branches, wherein said alpha,omega-diene compound is used in combination with at least one bridged metallocene catalyst which is immobilized on an inert support, preferably a silica support, and preferably at least one bridged metallocene catalyst as defined in any one of statements 1 and 6-13.
43. Use according to statement 42, for preparing a propylene polymer having long chain branches, preferably a propylene polymer as defined in any one of statements 37 to 41.
44. Use according to statement 42 or 43, wherein said alpha,omega-diene is used in said polymerisation process at a concentration of at most 1000 ppm, or at most 750 ppm, or at most 600 ppm, or at most 500 ppm, or at most 400 ppm, or at most 350 ppm.
45. Use according to any one of statements 42 to 44, wherein said alpha,omega-diene is used in said polymerisation process at a concentration of at least 10 ppm, or at least 15 ppm, or at least 20 ppm, or at least 35 ppm, or at least 50 ppm.

46. Use according to any one of statements 42 to 45, wherein said alpha,omega-diene is used as in a slurry or bulk polymerisation process for preparing propylene polymers having long chain branches.
47. Use according to any one of statements 42 to 45, wherein said alpha,omega-diene is used in a gas phase polymerisation process for preparing propylene polymers having long chain branches.
48. Use according to any one of statements 42 to 47, wherein said diene is not provided on said inert support.
49. An article made of a propylene polymer according to any one of statements 37 to 41, such as a thermoformed article.

The present invention provides a process for preparing propylene polymers having long chain branches. Long Chain Branches (LCBs) are ramifications in the linear structures of polymers. They differ from Short Chain Branches (SCBs) by their length (typically less than 40 carbons to longer than the average critical entanglement distance) and by how they affect rheological properties of the polymer. Whereas SCBs influence thermal and mechanical properties, LCBs modify the melt rheological behaviour, increasing for example the melt strength of the polymer.

In virtue of their intrinsic nature, metallocenes are able to produce some LCBs, while ZN catalyst generally aren’t. The inventors have now shown that the generation of LCBs can be further fined-tuned and/or steered by the use of an alpha,omega-diene compound, as defined herein, during polymerisation.

The present invention provides propylene polymers having long chain branches. The terms “propylene polymer”, “propylene polymers”, “PP” or “polypropylene” as used herein are synonymous and may be used interchangeably.

The terms “propylene polymer” or “polypropylene” may in certain embodiments encompasses copolymers of propylene and one or more alpha-olefins as defined herein.

Thereto, the process according to the invention comprises the steps of

(i) feeding into at least one reactor propylene monomer and optionally one or more alpha-olefins comonomer(s), a catalyst system, optionally a hydrocarbon diluent, optionally hydrogen and an alkylaluminum of formula $AlR^b{}_{x,}$ wherein x is an integer selected from 1 to 3 and each R^b is independently selected from halogen, alkoxy or alkyl, and
(ii) polymerizing in said at least one reactor, the propylene monomer and optionally one or more alpha-olefins comonomer(s), in the presence of said catalyst system, said optional hydrocarbon diluent, said optional hydrogen and said alkylaluminum, thereby producing propylene polymers having long chain branches,

wherein said catalyst system comprises

a) at least one bridged metallocene catalyst which is immobilized on an inert support, and
b) at least one diene compound, wherein said diene compound is an alpha,omega-diene of formula (I)

$$H_2C=CH-(CR^a{}_2)_m-HC=CH_2 \text{ (I)}$$

wherein m is an integer of at least 3, and preferably from 3 to 16, and

wherein each R^a is independently hydrogen or a C_1-C_{10}alkyl.

The term "metallocene catalyst" is used herein to describe any transition metal complexes comprising metal atoms bonded to one or more ligands. The metallocene catalysts are compounds of Group IV transition metals of the Periodic Table such as titanium, zirconium, hafnium, etc., and have a coordinated structure with a metal compound and ligands composed of one or two groups of cyclopentadienyl, indenyl, tetrahydroindenyl, fluorenyl or their derivatives. The structure and geometry of the metallocene can be varied to adapt to the specific need of the producer depending on the desired polymer. Metallocenes comprise a single metal site, which allows for more control of branching and molecular weight distribution of the polymer. Monomers are inserted between the metal and the growing chain of polymer. Specifically, for this invention the catalyst needs to be a “bridged metallocene catalyst”.

In one embodiment the bridged metallocene catalyst can be represented by formula (II):

$$R^1(Ar)_2M^1Q^1{}_2 \text{ (II)},$$

wherein said metallocene catalyst according to formula (II) has two Ar bound to M^1,

wherein M^1 is a transition metal selected from the group consisting of titanium, zirconium, hafnium, and vanadium; and preferably is zirconium;

wherein Ar is an aromatic ring, group or moiety and wherein each Ar is independently selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, and fluorenyl, preferably consisting of indenyl and tetrahydroindenyl

wherein each of said groups may be optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, $SiR^2{}_3$ wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms, and wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl, and P;

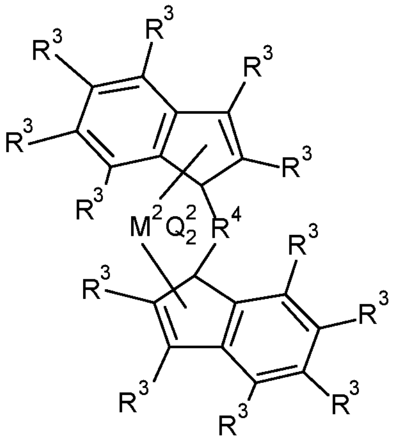
wherein each Q^1 is independently selected from the group consisting of halogen, alkyl, heteroalkyl, cycloalkyl, aryl, alkylaryl, aralkyl, alkoxy, cycloalkoxy, aralkoxy, $-COOR^5$ wherein

R^5 is hydrogen or alkyl, $-N(R^6)_2$ wherein R^6 is selected from the group consisting of hydrogen, alkyl and COR^7 wherein R^7 is alkyl, and $-CO-(NR^8)_2$ wherein R^8 is H or alkyl, and

wherein R^1 is a divalent group or moiety bridging the two Ar groups and is selected from the group consisting of C_1-C_{20} alkylene, dialkyl germanium, silicon, siloxane, alkylphosphine, and an amine, and wherein said R^1 is optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, SiR^2_3 wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms and wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl, and P.

In some preferred embodiments, the bridged metallocene catalyst as used herein is represented by formula (II), wherein each Ar is independently selected from the group consisting of indenyl and tetrahydroindenyl. Preferably, said bridged metallocene catalyst comprises a bridged bis(indenyl) and/or a bridged bis(tetrahydrogenated indenyl) component. Most preferably said bridged metallocene catalyst comprises a bridged bis(indenyl) component.

In more preferred embodiments, the metallocene catalyst is a bridged metallocene catalyst of formula (III):



(III)

wherein each R^3 in formula (III) is selected independently from hydrogen or a hydrocarbyl having 1 to 20 carbon atoms,

wherein R^4 is a divalent group or moiety bridging the two indenyls and is selected from the group consisting of C_1-C_4 alkylene, dialkyl germanium, silicon, siloxane, alkyl phosphine and amine; and wherein said R^4 is optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, SiR^2_3 wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms.

wherein each Q^2 is independently selected from the group consisting of halogen, alkyl, heteroalkyl, cycloalkyl, aryl, alkylaryl, aralkyl, alkoxy, cycloalkoxy, aralkoxy, -$COOR^5$ wherein R^5 is hydrogen or alkyl, -$N(R^6)_2$ wherein R^6 is selected from the group consisting of hydrogen, alkyl and COR^7 wherein R^7 is alkyl, and -CO-$(NR^8)_2$ wherein R^8 is H or alkyl, and

wherein M^2 is a transition metal selected from the group consisting of titanium, zirconium, hafnium, and vanadium.

Each indenyl component may be substituted with R^3 in the same way or differently from one another at one or more positions of either of the fused rings. Each substituent is independently chosen.

As used herein, the term “hydrocarbyl having 1 to 20 carbon atoms” refers to a moiety selected from the group comprising, preferably consisting of, a linear or branched C_1-C_{20} alkyl; C_3-C_{20} cycloalkyl; C_5-C_{20} aryl; C_6-C_{20} alkylaryl and C_6-C_{20} arylalkyl, and any combinations thereof. Exemplary hydrocarbyl groups are methyl, ethyl, *n*-propyl, *n*-butyl, isobutyl, amyl, isoamyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-decyl, *n*-undecyl, *n*-dodecyl, cetyl, cyclopentyl, cyclohexyl, cycloheptyl, 2-ethylhexyl, phenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2-ethylphenyl, 2-*tert*-butylphenyl, 3-*tert*-butylphenyl, 4-*tert*-butylphenyl.

As used herein, the term “alkyl”, by itself or as part of another substituent, refers to straight or branched saturated hydrocarbon group joined by single carbon-carbon bonds having 1 or more carbon atom, for example 1 to 12 carbon atoms, for example 1 to 10 carbon atoms, for example 1 to 6 carbon atoms, for example 1 to 4 carbon atoms. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain. Alkyl groups have the general formula C_nH_{2n+1}. Preferably n in said general formula C_nH_{2n+1} is an integer of at least 1, such as from 1 to 20 or from 1 to 12 or from 1 to 10 or from 1 to 6. Thus, for example, C_{1-12}alkyl means an alkyl of 1 to 12 carbon atoms. Examples of alkyl groups are methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *sec*-butyl, *tert*-butyl, 2-methylbutyl, *n*-pentyl and its chain isomers, *n*-hexyl and its chain isomers, *n*-heptyl and its chain isomers, *n*-octyl and its chain isomers, *n*-nonyl and its chain isomers, *n*-decyl and its chain isomers, *n*-undecyl and its chain isomers, *n*-dodecyl and its chain isomers.

The term “heteroalkyl” as a group or part of a group, refers to an acyclic alkyl wherein one or more carbon atoms are replaced by at least one heteroatom selected from the group comprising O, Si, S, B, and P, with the proviso that said chain may not contain two adjacent heteroatoms. This means that one or more -CH_3 of said acyclic alkyl can be replaced by –OH for example and/or that one or more -CR_2- of said acyclic alkyl can be replaced by O, Si, S, B, and P.

As used herein, the term “cycloalkyl”, by itself or as part of another substituent, refers to a saturated or partially saturated cyclic alkyl radical. Cycloalkyl groups have the general formula C_nH_{2n-1}. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain. Preferably n in said general formula C_nH_{2n-1} is an integer of at least 3, such as from 3 to 20 or from 3 to 12 or from 3 to 10 or from 3 to 6. Examples of C_{3-6}cycloalkyl include cyclopropyl, cyclobutyl, cyclopentyl, or cyclohexyl.

The term “aryl” as used herein by itself or as part of another substituent, refers to an aromatic hydrocarbon of 5-20 carbon atoms derived by the removal of hydrogen from a carbon atom of an aromatic ring system. Examples of aryl groups include, but are not limited to 1 ring, or 2 or 3 rings fused together, of which at least one ring is aromatic. Such ring can be derived from benzene, naphthalene, anthracene, 1,1’-biphenyl, 2,3-dihydro-1H-indenyl, 5,6,7,8-tetrahydronaphthalenyl, 1,2,6,7,8,8a-hexahydroacenaphthylenyl, 1,2-dihydroacenaphthylenyl, and the like. Particular aryl groups are phenyl and naphthyl, especially phenyl.

As used herein, the term “arylalkyl”, by itself or as part of another substituent, refers to an alkyl group as defined herein, wherein a hydrogen atom is replaced by an aryl as defined herein. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain. The arylalkyl group can comprise 6 to 20 carbon atoms, e.g. the alkyl moiety of the arylalkyl group is 1 to 6 carbon atoms and the aryl moiety is 5 to 14 carbon atoms. Typical arylalkyl groups include, but are not limited to, benzyl, 2-phenylethan-1-yl, 2-phenylethen-1-yl, naphthylmethyl, 2-naphthylethyl, and the like.

As used herein, the term “alkylaryl”, by itself or as part of another substituent, refers to an aryl group as defined herein, wherein a hydrogen atom is replaced by an alkyl as defined herein. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group or subgroup may contain. The alkylaryl group can comprise 6 to 20 carbon atoms, e.g. the alkyl moiety of the alkylaryl group is 1 to 6 carbon atoms and the aryl moiety is 5 to 14 carbon atoms. Typical alkylaryl groups include, but are not limited to 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2-ethylphenyl, 2-*tert*-butylphenyl, 3-*tert*-butylphenyl, 4-*tert*-butylphenyl.

As used herein, the term “alkylene”, by itself or as part of another substituent, refers to alkyl groups that are divalent, i.e., with two single bonds for attachment to two other groups. Alkylene groups may be linear or branched and may be substituted as indicated herein. When a subscript is used herein following a carbon atom, the subscript refers to the number of carbon atoms that the named group may contain. For example, C_1-C_{20} alkylene refers to an alkylene having between 1 and 20 carbon atoms. An alkylene group may be a C_1-C_{20} alkylene, or a C_1-

C_{10} alkylene, or a C_1-C_6 alkylene or a C_1-C_4 alkylene. Non-limiting examples of alkylene groups include methylene (-CH_2-), ethylene (-CH_2-CH_2-), methylmethylene (-$CH(CH_3)$-), 1-methyl-ethylene (-$CH(CH_3)$-CH_2-), *n*-propylene (-CH_2-CH_2-CH_2-), 2-methylpropylene (-CH_2-$CH(CH_3)$-CH_2-), 3-methylpropylene (-CH_2-CH_2-$CH(CH_3)$-), *n*-butylene (-CH_2-CH_2-CH_2-CH_2-), 2-methylbutylene (-CH_2-$CH(CH_3)$-CH_2-CH_2-), 4-methylbutylene (-CH_2-CH_2-CH_2-$CH(CH_3)$-), *n*-pentylene and its chain isomers, *n*-hexylene and its chain isomers, *n*-heptylene and its chain isomers, *n*-octylene and its chain isomers, *n*-nonylene and its chain isomers, *n*-decylene and its chain isomers, *n*-undecylene and its chain isomers, *n*-dodecylene and its chain isomers.

Exemplary halogen atoms include chlorine, bromine, fluorine and iodine, wherein fluorine and chlorine are preferred.

Preferred examples of a bridged metallocene catalyst for use in the present invention is represented by the metallocene catalyst of formula X or Y as provided in the example section. The bridged metallocene catalysts used herein are immobilized on a support, more particularly on an inert support. The support can be an inert organic or inorganic solid, which is chemically unreactive with any of the components of the conventional bridged metallocene catalyst. Suitable support materials for the supported catalyst include solid inorganic oxides, such as silica, alumina, magnesium oxide, titanium oxide, thorium oxide, as well as mixed oxides of silica and one or more Group 2 or 13 metal oxides, such as silica-magnesia and silica-alumina mixed oxides. Silica, alumina, and mixed oxides of silica and one or more Group 2 or 13 metal oxides are preferred support materials. Preferred examples of such mixed oxides are the silica-aluminas. Most preferred is a silica compound as inert support.

In a preferred embodiment, the bridged metallocene catalyst is provided on a silica support. The silica may be in granular, agglomerated, fumed or other form.

In some embodiments, the support of the bridged metallocene catalyst is a porous support, and preferably a porous silica support having a surface area comprised between 200 and 900 m^2/g.

In another embodiment, the support of the polymerization catalyst is a porous support, and preferably a porous silica support having an average pore volume comprised between 0.5 and 4 mL/g.

In yet another embodiment, the support of the polymerization catalyst is a porous support, and preferably a porous silica support having an average pore diameter comprised between 50 and 300 Å, and preferably between 75 and 220 Å.

Preferably, the supported bridged metallocene catalyst is activated by an additional activating agent. The activating agent can be any activating agent known for this purpose such as an aluminum-containing activating agent, a boron-containing activating agent or a fluorinated activating agent. The aluminum-containing activating agent may comprise an alumoxane, an alkyl aluminum, a Lewis acid and/or a fluorinated catalytic support.

In some embodiments, alumoxane is used as an activating agent for the bridged metallocene catalyst. The alumoxane can be used in conjunction with a catalyst in order to improve the activity of the catalyst during the polymerization reaction.

As used herein, the term "alumoxane" and "aluminoxane" are used interchangeably, and refer to a substance, which is capable of activating the bridged metallocene catalyst. In some embodiments, alumoxanes comprise oligomeric linear and/or cyclic alkyl alumoxanes. In a further embodiment, the alumoxane has formula (IV) or (V)

R^c-(Al(R^c)-O)$_x$-AlR^c_2 (IV) for oligomeric, linear alumoxanes; or

(-Al(R^c)-O-)$_y$ (V) for oligomeric, cyclic alumoxanes

wherein x is 1-40, and preferably 10-20;

wherein y is 3-40, and preferably 3-20; and

wherein each R^c is independently selected from a C_1-C_8alkyl, and preferably is methyl. In a preferred embodiment, the alumoxane is methylalumoxane (MAO).

In a preferred embodiment, the bridged metallocene catalyst is a supported metallocene-alumoxane catalyst comprising a bridged metallocene catalyst and an alumoxane which are bound on a porous silica support. Preferably, the bridged metallocene catalyst is a bridged bis(indenyl) metallocene catalyst or a bridged bis(tetrahydrogenated indenyl) metallocene catalyst, most preferably a bridged bis(indenyl) metallocene catalyst.

According to the present invention, a process for preparing propylene polymers having long chain branches is provided which is carried out in the presence of a catalyst system comprising a bridged metallocene catalyst and at least one diene compound of formula (I), as defined herein. Said one diene compound is an alpha,omega-diene of formula (I) H_2C=CH-(CR^a_2)$_m$-HC=CH_2 (I), wherein m is an integer of at least 3, and wherein each R^a is independently hydrogen or a C_1-C_{10} alkyl.

In certain embodiments, said diene compound is an alpha,omega-diene of formula (I) wherein m is an integer from 3 to 16, such as from 4 to 12 or from 5 to 10. For instance, m is 3, 4, 5, 6, 7, 8, 9, 10, 11, or 12

In certain embodiments, said diene compound is an alpha,omega-diene of formula (I) wherein each R^a is independently hydrogen or a C_1-C_{10} alkyl group which can be branched or linear. For example, each R^a may be independently chosen from the group comprising methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, iso-butyl, 4-methyl-pentyl, *n*-hexyl and *n*-dodecyl.

In certain embodiments, said diene compound is an alpha,omega-diene of formula (I) wherein each R^a is hydrogen.

In certain embodiments, said diene compound is an alpha,omega-diene of formula (I) wherein each R^a is a C_1-C_{10} alkyl. For example, each R^a may be independently chosen from the group comprising methyl, ethyl, *n*-propyl, iso-propyl, *n*-butyl, iso-butyl, 4-methyl-pentyl, *n*-hexyl and *n*-dodecyl.

In a preferred embodiment, said diene compound is an alpha,omega-diene of formula (I), wherein m is an integer an integer of at least 3, preferably from 3 to 16, more preferably from 4 to 12, and wherein each R^a is hydrogen. Examples of a suitable diene compound for use in a catalyst system as defined herein may be selected from the group comprising but not limited to 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, and 1,13-tetradecadiene. Particularly suitable dienes are selected from the group consisting of 1,7-octadiene, 1,8-nonadiene, and 1,9-decadiene.

In preferred embodiments of the catalyst system, the bridged metallocene catalyst is immobilised on an inert support, preferably silica, while the diene compound is separately provided, and is not provided on said inert support.

In certain embodiments, a diene compound as defined herein is applied in a polymerisation process as described herein, at a concentration of at most 1000 ppm, or at most 750 ppm, or at most 600 ppm, or at most 500 ppm, or at most 400 ppm, or at most 350 ppm.

In certain embodiments, a diene compound as defined herein is applied in a polymerisation process as described herein, at a concentration of at least 10 ppm, such as at least 15 ppm or at least 20 ppm, or at least 35 ppm, at least 50 ppm.

Therefore, the present invention also relates to the use of a diene compound as defined herein in a polymerization process for making propylene polymers having long chain branches, preferably at a concentration of at most 1000 ppm, such as at most 750 ppm, or at most 600 ppm, or at most 500 ppm, or at most 400 ppm, or at most 350 ppm. In certain preferred embodiments, said diene compound as defined herein is used in said polymerization process at a concentration of at least 10 ppm, such as at least 15 ppm, or at least 20 ppm, or at least 35 ppm, at least 50 ppm.

Said diene compounds as defined herein wherein can be used in a slurry, bulk or gas phase polymerization processes for preparing propylene polymers having long chain branches, and preferably in slurry or bulk processes.

According to the present invention, a process for preparing polypropylene having long chain branches is provided which is performed in the presence of a catalyst system comprising a bridged metallocene catalyst and a compound of formula (I) as defined herein, further in the presence of an alkylaluminum of formula AlR^b_x, wherein each R^b is independently selected from the group comprising halogen, and alkoxy and akyl groups preferably having from 1 to 12 carbon atoms, and wherein x is an integer selected from 1 to 3. Non-limiting examples are Tri-*iso*-Butyl Aluminum (TIBAL), Tri-Ethyl Aluminum (TEAL), Tri-Methyl Aluminum (TMA), and Dimethyl-Ethyl Aluminum. Especially suitable are trialkylaluminums, the most preferred being Tri-*iso*-Butyl Aluminum (TIBAL) and Tri-Ethyl Aluminum (TEAL).

A polymerization process for preparing polypropylene having long chain branches according to the present invention may be carried out in a slurry or in a suspension, optionally in the presence of a diluent or in gas phase, or a combination thereof.

Diluents which are suitable for being used in accordance with the present invention are preferably liquid hydrocarbon diluents which may comprise but are not limited to hydrocarbon diluents such as aliphatic, cycloaliphatic and aromatic hydrocarbon solvents, or halogenated versions of such solvents. The preferred solvents are C12 or lower, straight chain or branched chain, saturated hydrocarbons, C5 to C9 saturated alicyclic or aromatic hydrocarbons or C2 to C6 halogenated hydrocarbons. Non-limiting illustrative examples of solvents are *n*-butane, isobutane, *n*-pentane, *n*-hexane, *n*-heptane, cyclopentane, cyclohexane, cycloheptane, methyl cyclopentane, methyl cyclohexane, isooctane, benzene, toluene, xylenes, chloroform, chloroarenes such as chlorobenzene, tetrachloroethylene, dichloroethane and trichloroethane. In a preferred embodiment of the present invention, said diluent is isobutane. However, it should be clear from the present invention that other diluents may as well be applied according to the present invention.

The step of polymerizing propylene is carried out in one or more reactors preferably selected from continuous stirred-tank reactor, loop reactor, gas phase, or autoclave. According to certain embodiments, said process is carried out in one single reactor. According to other embodiments, said process is carried out in two or more reactors, connected in series. For instance, a process of the invention may be carried out in a double loop reactor.

Slurry or bulk polymerization is preferably used to prepare the propylene polymers, preferably in at least one slurry loop reactor or at least one continuously stirred reactor. As used herein, the terms “loop reactor” and “slurry loop reactor” may be used interchangeably herein.

In certain preferred embodiments, the bridged metallocene catalyst is added to the reactor as catalyst slurry. As used herein, the term “catalyst slurry” refers to a composition comprising catalyst solid particles and a diluent. The solid particles can be suspended in the diluent, either spontaneously or by homogenization techniques, such as mixing. The solid particles can be non-homogeneously distributed in a diluent and form sediment or deposit.

As used herein, the term “diluent” refers to any organic diluent, which does not dissolve the synthesized polyolefin. As used herein, the term “diluent” refers to diluents in a liquid state, liquid at room temperature and preferably liquid under the pressure conditions in the reactor. Suitable diluents comprise but are not limited to hydrocarbon diluents such as aliphatic, cycloaliphatic and aromatic hydrocarbon solvents, or halogenated versions of such solvents. Preferred solvents are C_{12} or lower, straight chain or branched chain, saturated hydrocarbons, C_{5-9} saturated alicyclic or aromatic hydrocarbons or C_{2-6} halogenated hydrocarbons. Non-limiting illustrative examples of solvents are *n*-butane, isobutane, *n*-pentane, *n*-hexane, *n*-heptane, cyclopentane, cyclohexane, cycloheptane, methylcyclopentane, methylcyclohexane, isooctane, benzene, toluene, xylenes, chloroform, chloroarenes such as chlorobenzene, tetrachloroethylene, dichloroethane and trichloroethane.

Alternatively, a suitable catalyst slurry diluent may also include a mineral oil, preferably, a mineral oil which is substantially free of impurities which may deleteriously interact with or kill the catalyst. Suitable mineral oils for use in the present context are well known to the skilled person include for instance Finavestan A 360 B, Hydrobrite 550, and Hydrobrite 1000.

In certain embodiments, the bridged metallocene catalyst can be pre-contacted with at least one compound of formula (I) before the catalyst is introduced into the reactor. Hence, in certain embodiments, a process is provided wherein said bridged metallocene catalyst is pre-contacted with said compound of formula (I) before feeding to said at least one reactor. The alkylaluminum of formula AlR^b_x can be introduced into the reactor separately.

Alternatively, the bridged metallocene catalyst can be pre-contacted with an alkylaluminum of formula AlR^b_x before the catalyst is introduced into the reactor. Hence, in certain embodiments, a process is provided wherein said bridged metallocene catalyst is pre-contacted with said alkylaluminum of formula AlR^b_x before feeding to said at least one reactor. The compound of formula (I) can be introduced into the reactor separately.

Alternatively, the bridged metallocene catalyst is pre-contacted before the catalyst is introduced into the reactor with at least one compound of formula (I) and an alkylaluminum of formula AlR^b_x. In such embodiments, a mixture is prepared comprising said the bridged metallocene catalyst, said compound of formula (I) and said alkylaluminum of formula AlR^b_x, and such mixture is fed to the at least one reactor.

Still alternatively, the bridged metallocene catalyst can be introduced into the reactor without any pre-contact with the at least one compound of formula (I) and the alkylaluminum of formula AlR^b_x. Both the compound of formula (I) and the alkylaluminum of formula AlR^b_x can independently and separately be added to the reactor.

In certain embodiments of polymerization reaction according to the invention, one or more alpha-olefin comonomer(s) can be added to the reaction mixture. Preferably said alpha-olefin comonomer is selected from the group comprising ethylene, 1-butene, 1-pentene, 1-hexene and 1-octene, and preferably is ethylene.

The polymerization step can be performed over a wide temperature range. In certain embodiments, the polymerization steps may be performed at a temperature from 20 °C to 125 °C, preferably from 60 °C to 110 °C, more preferably from 70 °C to 100 °C. Said temperature may fall under the more general term of polymerization conditions.

In certain embodiments, the polymerization steps may be performed at a pressure from about 20 bar to about 100 bar, preferably from about 30 bar to about 50 bar. Said pressure may fall under the more general term of polymerization conditions.

The invention also encompasses a catalyst system suitable for catalyzing a polymerisation process for preparing propylene polymers having long chain branches, comprising

a. at least one bridged metallocene catalyst which is immobilized on an inert support, and preferably a bridged metallocene catalyst as defined herein, and

b. a diene compound, wherein said diene compound comprises at least one alpha,omega-diene of formula (I)

$$H_2C{=}CH\text{-}(CR^a{}_2)_m\text{-}HC{=}CH_2 \text{ (II)}$$

wherein m is an integer of at least 3, and preferably from 3 to 16, and wherein each R^a is independently hydrogen or a C_1-C_{10} alkyl, and preferably wherein said diene compound is as defined herein.

The said bridged metallocene catalyst is preferably supported on an inert support as defined herein, preferably a silica support. Said diene compound is usually not provided on a support.

The invention also encompasses the use of a catalyst system as defined herein in a process for preparing propylene polymers having long chain branches, preferably in a process as defined herein.

The invention also encompasses a propylene polymer having long chain branches (herein also “LCB”) obtained by a process as defined herein or obtained by a process using a catalyst system as provided herein.

LCB of propylene polymers according to the present invention may be characterized in terms of their rheology long chain branching index (g_{rheo}). As used herein the long chain branching (LCB) index g_{rheo} can be obtained by rheology according to the formula as described in the example section. A g_{rheo} of less than 1 indicates the presence of long chain branching, the value of g_{rheo} is decreasing with increasing long chain branching.

In some embodiments a propylene polymer as provided herein has a rheology long chain branching index (g_{rheo}) lower than 0.95; preferably lower than 0.90, preferably lower than 0.88, preferably lower than 0.85, such as lower than 0.75, such as lower than 0.70, such as lower than 0.65, as determined by the method disclosed in the example section. In some embodiments, a propylene polymer as provided herein has a rheology long chain branching index (g_{rheo}) higher than 0.35, such as higher than 0.40, or higher than 0.45, or higher than 0.50, or higher than 0.55, as determined by the method disclosed in the example section. In some embodiments, a propylene polymer as provided herein has a rheology long chain branching index (g_{rheo}) comprised between more than 0.35 and less than 0.95. Preferably a propylene polymer as provided herein has a rheology long chain branching index g_{rheo} comprised between more than 0.35 and less than 0.90; such as from at least 0.35 to at most 0.85, or from at least 0.40 to at most 0.80; as determined by the method disclosed in the example section.

In some embodiments, a propylene polymer as provided herein has a MI2, as determined according to ISO 1133:2005 Method B, condition M, at a temperature 230 °C, and a 2.16 kg load using a die of 2.096 mm, comprised between 0.5 and 150 g/10 min, such as between 0.5 and 100 g/10 min, or between 0.5 and 50 g/10 min, or between 0.5 and 25 g/10 min. In some embodiments, a propylene polymer as provided herein has a ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) [M_w/M_n] of at least 2.0, preferably at least 2.2, preferably at least 2.3, preferably at least 2.4, preferably at least 2.5, preferably at least 2.6, preferably at least 3.0. In some embodiments, a propylene polymer as provided herein has a ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) [M_w/M_n] of at most 5.7, such as at most 5.5, or at most 5.0 or at most 4.5, or at most 4.0.

In some embodiments, a propylene polymer provided herein has a ratio of weight average molecular weight (M_w) to number average molecular weight (M_n) [M_w/M_n] of preferably from 2.0 to 5.7, such as from 2.2 to 5.6, such as from 2.4 to 5.0, such as from 2.6 to 4.5, such as from 3.0 to 4.0.

As used herein, the molecular weight (M_n (number average molecular weight), M_w (weight average molecular weight) and molecular weight distributions D (M_w/M_n), and D′ (M_Z/M_W) were determined by size exclusion chromatography (SEC) and in particular by gel permeation chromatography (GPC).

The following examples serve to merely illustrate the invention and should not be construed as limiting its scope in any way. While the invention has been shown in only some of its forms, it should be apparent to those skilled in the art that it is not so limited but is susceptible to various changes and modifications without departing from the scope of the invention.

EXAMPLES

Test methods

The properties cited below were determined in accordance with the following test procedures. Where any of these properties is referenced in the appended claims, it is to be measured in accordance with the specified test procedures. The following test methods were used.

Density

The density was measured according to the method of standard ISO 1183 at a temperature of 23 °C.

Melt flow index

The melt flow index (MI_2) of polypropylene was determined according to ISO 1133:2005 Method B, condition M, at a temperature 230 °C, and a 2.16 kg load using a die of 2.096 mm.

Molecular weight, molecular distribution

The molecular weight (M_n (number average molecular weight), M_w (weight average molecular weight) and molecular weight distributions D (M_w/M_n), and D' (M_z/M_w) were determined by size exclusion chromatography (SEC) and in particular by IR-detected gel permeation chromatography (GPC) at high temperature (145 °C). Briefly, a GPC-IR5MCT from Polymer Char was used: 10 mg polymer sample was dissolved at 160 °C in 10 mL of trichlorobenzene stabilized with 1000 ppm by weight of butylhydroxytoluene (BHT) for 1 h. Injection volume: about 400 µL, automatic sample preparation and injection temperature: 160 °C. Column temperature: 145 °C. Detector temperature: 160 °C. Column set: two Shodex AT-806MS (Showa Denko) and one Styragel HT6E (Waters), columns were used with a flow rate of 1 mL/min. Mobile Phase: trichlorobenzene stabilized with 1000 ppm by weight of butylhydroxytoluene (BHT) filtered through a 0.45 µm PTFE filter. Detector: Infrared detector (2800-3000 cm^{-1}) to measure the concentration, one narrow filter center based at 2928 cm^{-1}, and one narrow filter center based at 2959 cm^{-1}. Calibration: narrow standards of polystyrene (PS) (commercially available).

Calculation for polypropylene of molecular weight M_i of each fraction i of eluted polymer is based on the Mark-Houwink relation $\log_{10}(M_{PP}) = \log_{10}(M_{PS}) -0.25323$ (cut off on the low molecular weight end at $M_{PP} = 1000$).

The molecular weight averages used in establishing molecular weight/property relationships are the number average (M_n), weight average (M_w) and z-average (M_z) molecular weight. These averages are defined by the following expressions and are determined form the calculated M_i:

$$M_n = \frac{\sum_i N_i M_i}{\sum_i N_i} = \frac{\sum_i W_i}{\sum_i W_i / M_i} = \frac{\sum_i h_i}{\sum_i h_i / M_i}$$

$$M_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i} = \frac{\sum_i W_i M_i}{\sum_i W_i} = \frac{\sum_i h_i M_i}{\sum_i h_i}$$

$$M_z = \frac{\sum_i N_i M_i^3}{\sum_i N_i M_i^2} = \frac{\sum_i W_i M_i^2}{\sum_i W_i M_i} = \frac{\sum_i h_i M_i^2}{\sum_i h_i M_i}$$

Here N_i and W_i are the number and weight, respectively, of molecules having molecular weight M_i. The third representation in each case (farthest right) defines how one obtains these averages from SEC chromatograms. hi is the height (from baseline) of the SEC curve at the i_{th} elution fraction and M_i is the molecular weight of species eluting at this increment.

Melt strength

Melt strength is defined as the force required to draw a molten polymer extrudate at a certain rate and at a certain extrusion temperature until breakage of the extrudate whereby the force is applied by take up rollers.

The melt strength (also referred as strength at break) was measured with a Göttfert Rheotens Melt Strength device, model 71-97, in combination with Rheograph Göttfert RG50, both manufactured by Göttfert under the following testing conditions: Rheograph Göttfert (RG50)= Die geometry (L/D): 30 mm/2 mm, 180 ° entrance angle; barrel + die temperature: 190 °C; Piston diameter 12 mm, Piston speed: 0.25 mm/s. Rheotens (model 71-97) Wheels: standard (ridged wheels); Wheel gap: 0.4 mm ; Wheel acceleration: 2 mm/s^2, Strand length: 100.0 mm, Wheel initial speed Vo: 9.0 mm/s. In the Rheotens test, the tensile force required for extension/stretching of an extruded melt filament exiting a capillary die is measured as a function of the wheel take-up velocity that increases continuously at a constant acceleration speed. The tensile force typically increases as the wheel (roller) velocity is increased and above a certain take-up velocity the force remains constant until the filament (strand) breaks.

For each material, Rheotens curves are generated to verify data reproducibility. Polymer was loaded into the barrel and allowed to melt for 360 s at 190 °C before beginning the testing. In fact, the complete amount of material present in the barrel of the Rheograph is extruded through the die and is being picked up by the wheels of the Rheotens device. The strand is let to stabilize between the wheels turning at 9 mm/s, once the strand is stabilized, the force is calibrated to 0 N and the acceleration of the wheels is started. Once the test is started, the speed of the wheels is increased with a 2.0 mm/s^2 acceleration and the tensile force is measured for each given speed. After each strand break, or strand slip between the wheels, the measurement is stopped and the material is placed back between the wheels for a new measurement. A new Rheotens curve is recorded. Measuring continues until all material in the barrel is consumed. In this invention, the average of the tensile force vs. draw ratio for each material is reported.

Differential Scanning Calorimetry (DSC) for Determination of Crystallization and Melting Temperatures.

Peak crystallization temperature (T_c), peak melting temperature (T_m) and heat of fusion (Δ¾) were measured via Differential Scanning using DQ 2000 instrument by TA Instruments, calibrated with indium and using T zero mode. The polymer analysis was performed with a 2 to 10 mg of polymer sample. The sample was first equilibrated at 40 °C and subsequently heated to 220 °C using a heating rate of 20 °C/min (first heat). The sample was held at 220 °C for 3 min to erase any prior thermal and crystallization history. The sample was subsequently cooled down to 30 °C with a constant cooling rate of 20 °C/min (first cool). The sample was held isothermal at 30 °C for 2 min before being heated to 220 °C at a constant heating rate of 20 °C/min (second heat). The exothermic peak of crystallization (first cool) was analyzed using the TA Universal Analysis software and the peak crystallization temperature (T_c) corresponding to 20 °C/min cooling rate was determined. The endothermic peak of melting (second heat) was also analysed using the TA Universal Analysis software and the peak melting temperature (T_m) corresponding to 20 °C/min heating rate was determined. Unless otherwise indicated, reported values of T_c, T_m in this invention refer to a cooling and heating rate of 20 °C/min, respectively.

^{13}C NMR/ Tacticity

Tacticity was determined by ^{13}C-NMR spectroscopy. The ^{13}C-NMR spectroscopic analysis was performed at an operative frequency of 125 MHz using a 500 MHz Bruker NMR spectrometer with a high temperature 10 mm cryoprobe under conditions such that the signal intensity in the spectrum is directly proportional to the total number of contributing carbon atoms in the sample. Such conditions are well known to the skilled person and include for example appropriate relaxation time, etc. In practice, the intensity of a signal is obtained from its integral, i.e. the corresponding area. The data were acquired using proton decoupling, 240 scans per spectrum, a pulse repetition delay of 11 s and a spectral width of 26000 Hz at a temperature of 130 °C. The sample was prepared by dissolving a sufficient amount of polymer in 1,2,4-trichlorobenzene (TCB, 99 %, spectroscopic grade) at 130 °C and occasional agitation to homogenize the sample, followed by the addition of hexadeuterobenzene (C_6D_6, spectroscopic grade) and a minor amount of hexamethyldisiloxane (HMDS, 99.5+ %), with HMDS serving as internal standard. To give an example, about 600 mg of polymer were dissolved in 2.0 mL of TCB, followed by addition of 0.5 mL of C_6D_6 and 2 to 3 drops of HMDS.

Following data acquisition, the chemical shifts are referenced to the signal of the internal standard HMDS, which is assigned a value of 2.03 ppm.

The isotacticity is determined by ^{13}C-NMR spectroscopic analysis on the total polymer according to procedures well known in the art. In the spectral region of the methyl groups the signals corresponding to the pentads *mmmm, mmmr, mmrr* and *mrrm* are assigned using published data, for example A. Razavi, Macromol. Symp., vol. 89, pages 345-367. Only the pentads *mmmm, mmmr, mmrr* and *mrrm* are taken into consideration. The other remaining pentads are neglected due to the weak intensity of the corresponding signals. For the signal relating to the mmrr pentad a correction is performed for its overlap with a methyl signal related to 2,1-insertions. The percentage of *mmmm* pentads is then calculated according to

% *mmmm* = AREA*mmmm* / (AREA*mmmm* + AREA*mmmr* + AREA*mmrr* + AREA*mrrm*) * 100

The regiodefects content in the polypropylene is the percentage of 2,1-insertions in the polypropylene.

For propylene homopolymers, the signals corresponding to the 2,1-insertions are identified with the aid of published data, for example H.N. Cheng, J. Ewen, Makromol. Chem., vol. 190 (1989), pages 1931 -1940.

For propylene copolymers, the determination of the percentage of 2,1-insertions is detailed hereunder with respect to ethylene as co-monomer but can be applied with other co-monomers.

The determination of the percentage of 2,1-insertions for a copolymer of propylene with ethylene as comonomer is determined by two contributions:

(i) the percentage of 2,1-insertions as defined above for the propylene homopolymer, and

(ii) the percentage of 2,1-insertions, wherein the 2,1-inserted propylene neighbours an ethylene,

Thus, the total percentage of 2,1-insertions corresponds to the sum of these two contributions. A first area, AREA1, is defined as the average area of the signals corresponding to 2,1-insertions. A second area, AREA2, is defined as the average area of the signals corresponding to 1,2-insertions. The assignment of the signals relating to the 1,2-insertions is well known to the skilled person. The percentage of 2,1-insertions is calculated according to

2,1-insertions (in %) = AREA1 / (AREA1 + AREA2) * 100 with the percentage in 2,1-insertions being given as the molar percentage of 2,1-inserted propylene with respect to total propylene.

The assignments of the signal for case (ii) can be done either by using reference spectra or by referring to the published literature.

Co-monomer content

The total co-monomer content (in particular ethylene (C_2) i.e. % by weight C_2) relative to the total weight of polypropylene can be determined using ^{13}C NMR spectroscopy as is well known to the skilled person.

Small amplitude oscillatory shear (SAOS)

Dynamic shear viscosity (or complex viscosity) as a function of frequency is determined by small-amplitude oscillatory shear (SAOS) rheology. Complex viscosity is measured at 230 °C over an angular frequency range from 0.1 to 200 rad/s using the procedure described below using Small Amplitude Oscillatory Shear (SAOS) testing.

From the data generated by such a test, it is possible to determine the phase or loss angle δ, which is the inverse tangent of the ratio of G" (the loss modulus) to G' (the storage modulus). For a typical linear polymer, the loss angle at low frequencies (or long times) approaches 90° making the loss modulus much larger than the storage modulus. As frequencies increase, more of the chains relax too slowly to absorb energy during the oscillations, and the storage modulus grows relative to the loss modulus. Eventually, the storage and loss moduli become equal and the loss angle reaches 45 °. In contrast, a branched chain polymer relaxes very slowly. Such branched polymers never reach a state where all its chains can relax during an oscillation, and the loss angle never reaches 90° even at the lowest frequency, ω, of the experiments. The loss angle is also relatively independent of the frequency of the oscillations in the SAOS experiment; another indication that the chains cannot relax on these timescales.

In a plot of the phase angle δ versus the measurement frequency ω, polymers that have long chain branches exhibit a plateau in the function of $\delta(\omega)$, whereas linear polymers do not have such a plateau. According to Garcia-Franco et al. (34(10) Macromolecules 3115-3117 (2001)), the plateau in the aforementioned plot will shift to lower phase angles δ when the amount of long chain branching occurring in the polymer sample increases.

Rheological analyses

Long chain branching index g_{rheo}

Rheology long chain branching index g_{rheo} value for propylene polymers according to the invention and/or as described herein was measured according to the following formula:

$$g_{rheo}(iPP) = M_w(COP) / M_w(CY)$$

wherein M_w(COP) [Cross Over Point] and M_w(CY) [Carreau-Yasuda] were obtained from a frequency sweep experiment at a temperature of 230°C, carried out on a ARES-G2 equipment (manufactured by TA Instruments) in the linear viscoelasticity domain; wherein circular frequency (W in rad/s) varies from 0.05-0.1 rad/s to 250-500 rad/s, typically 0.1 to 250 rad/s, and the shear strain is typically 10 %.

$$Mw(COP) = e^{\left(6.9325-0.001954*PI^2-0.2539*\ln(\omega_c)-0.00097*\left(ln(\omega_c)\right)^3\right)}$$

wherein:

$PI = 10^5/Gc$.

G_c : Cross modulus in Pascal (Pa)

ω_c : Cross frequency (rad/s)

$$Mw(CY) = e^{\left(3.6783+0.27444*ln(\eta_0)-0.03674*b*ln(\eta_0)\right)}$$

wherein zero shear viscosity η_0 and b are estimated by fitting with simplified Carreau-Yasuda flow curve (η-W) :

$$\eta = \eta_0 / (1+(\tau W)^b)^{((n-1)/b)}$$

η_0, τ, b and n are parameters from CY model with η_0 being zero-shear viscosity. The parameter, b, is sometimes known as rheological breadth as it is sometimes qualitatively related to molecular weight distribution (MWD). The parameter n is the power exponent (at high W one has power-law behaviour of shear viscosity). The parameter, τ, is related to a relaxation time.

van Gurp-Palmen plot (vGP plot):

Complex modulus, G*, and loss angles, δ, may be obtained from rheological data determined at the test temperature of 230 °C and analyzed using the van Gurp-Palmen treatment (reference: *van Gurp*, *M.* and *Palmen*, *J.*, *Rheology Bulletin*, 1998, *67*(1), *5*–8). The vGP curve is a plot of phase angle δ (= $\tan^{-1}$ [G″/G′]) versus magnitude of the complex modulus, |G*|. In linear polymers, for a decrease of the modulus value, δ will initially drop, it will then pass a minimum, rises again, moves through an inflection point, and finally approaches its limiting value of 90 °. LCB shifts the vGP curve down. The higher the LCB density, the lower the δ values. The area included under the vGP curve can be used as a parameter to evaluate the degree of LCB. In addition, the magnitude of the drop at the apparent plateau caused by LCB is related to the relative length of long-chain branches on the polymer backbone. Low levels of long-chain branching can be detected and quantified on a relative basis, using this methodology.

Tan delta / corrected frequency plots

In the presented examples, corrected frequency plots were established. The corrected frequency is calculated starting from the frequency which is divided by the frequency value of the cross-over point (i.e. the point where G’ and G” meet). Tan delta, which is G”/G’, is then plotted against the corrected frequency. A skilled person is fully familiar on how to establish such plots. As for the van Gurp-Palmen plot, these experiments are very sensitive to LCBs. Since LCBs are responsible for the longer relaxation times, they cause the decrease of value of tanδ at lower corrected frequency. Using the corrected frequency instead of the normal frequency allows the elimination of MWD differences between samples.

TDA/GC analyses

Differential thermal analysis (DTA) coupled with a GC.

Polymer samples, in pellets form, are submitted to a thermic treatment at 150 °C for 15 min in an oven where volatile components are released and carried, with helium flow, to a TENAX sorbent tube cooled to -30 °C. The tube is then heated to 230 °C for 10 min and the compounds are injected in a GC column where they are identified by their retention time. The analysis conditions are as follows.

Chromatographic conditions:

Capillary Column: type: HP-5 or similar

Length : 60m

Internal diameter: 0.32mm

Solid phase type : 5% Ph-Me-siloxane

Solid phase Thickness: 1 µm

Detector : type : F.I.D

Temperature : 280 °C

Air flow : 450 mL/min

Hydrogen flow : 40 mL/min

Make up flow : 30 mL/min (constant)

GC oven Program: Isothermal Temperature 1 : 45 °C

Time of Isotherm 1 : 15 min.

Heating ramp : 10 °C/min

Temperature of Isotherm 2 : 280 °C

Time of Isotherm 2 : 25 min

Recording system : Galaxie. Chromeleon

TDA conditions:

Thermo desorption apparatus : TurboMatrix ATD de Perkin Elmer.

Oven temperature: 150 °C

Desorption time : 15 min.

Trap temperature: low temperature: -30 °C (trapping mode)

high temperature: 230 °C (trap desorption mode)

Trap desorption time: 10 min.

Transfer line temperature : 250 °C

Block valve temperature : 200 °C

Carrier gas pressure : 12,5 psi.

Inlet split flow : 37 mL/min.

Outlet split flow : 16.5 mL/min

Desorption Flow: 20 mL/min

Mode use: MS

Purge time: 1 min.

Run time: 79 min

Example 1: Preparation of supported catalyst 1

The compound rac-Methyl(cyclohexyl)silanediyl-bis[(2-methyl-4-(4-*tert*-butylphenyl)indenyl]zirconium dichloride (CAS number: 888227-55-2) (see below formula X) was used as metallocene catalyst supported on silica which has been previously activated with methylalumoxane (MAO) as described below.

Support preparation

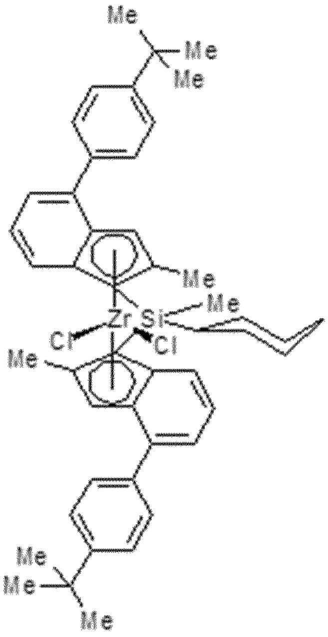
A Ti-impregnated silica support was made as follows. Silica support was heated under nitrogen flow with a desired amount of Ti precursor, i.e. a mixture of 80 wt% of isopropoxide titanium ($Ti(OC_3H_7)_4$) and 20 wt% of tertiary butoxide titanium ($Ti(OC_4H_9)_4$) at 270 °C, then dried at 450 °C. The amount of Ti precursor was chosen in order to reach a Ti content of 4 wt%.

MAO treatment

20 g of the above dried silica support was introduced in a 500 mL round-bottomed flask. Toluene was added and the suspension was stirred at 100 rpm. MAO (30 % by weight in toluene) was dropwise added via a dropping funnel and the resulting suspension was heated at 110 °C (reflux) for 4 h. The amount of added MAO was calculated to reach an Al loading of about 16 wt%. After the reflux, the suspension was cooled down to room temperature and the mixture was filtered through a glass frit. The recovered powder was washed with toluene and iso-hexane before being dried under reduced pressure overnight.

Metallocene treatment

rac-Methyl(cyclohexyl)silanediyl-bis[(2-methyl-4-(4-tert-butylphenyl)indenyl]zirconium dichloride (see formula X below) was dissolved in AlR_3 ($R = C_4H_9$). After 1-hour reaction, the above-obtained MAO-support was slowly added to the metallocene/AlR_3 mixture and mixing was carried out for two hours. The amount of metallocene used was adjusted in order to reach Ti/Zr atomic molar ratio of 18. Solvent was removed by filtration. The obtained catalyst was washed with iso-hexane, filtered and dried at room temperature. Suspension of the resulting catalyst powder in mineral oil was prepared and stored cold.



Formula X

Example 2: Preparation of propylene polymers with long chain branches

In this example, polymerization reactions were performed in an 8-liter reactor comprising an agitator, a temperature controller and inlets for feeding propylene and hydrogen.

In this example, the supported catalyst as described in example 1 was used. The conditions under which the catalyst is applied during polymerisation are listed in **Table 1**.

Table 1

Cocatalyst TEAL (ppm)	H_2 (ppm)	Catalyst Example 1 (mg)	Zr (µmol)	Al/Zr Molar ratio
27	54	25.0	0.41	1427

The reactor was heated at 130 °C and flushed with N_2 during at least 2 hours prior to being used. The reactor was then flushed with 1 L of propylene and cooled to 40 °C.

Subsequently, 3 L of propylene were pushed in the reactor together with the required amount of H_2. Stirring was started. Once the reactor was stabilised, a mixture consisting of 1 mL of TEAL (10 wt% solution in *iso*-hexane), the supported catalyst of example 1, and 1,7-octadiene (CAS Number 3710-30-3), was injected in the reactor together with 1.5 L of propylene. 1,7-octadiene was thus added to the reactor together with the catalyst. The appropriate amount of this diene compound was first diluted in TEAL and then mixed with the catalyst in a syringe. The mixture was then added to the reactor with a flow of propylene. Different amounts of 1,7-octadiene were applied during the different polymerisation reactions reported in this example. For comparison one polymerisation reaction was carried out in the absence of 1,7-octadiene (see **Table 2).**

A pre-polymerisation was carried out at 40 °C for about 5 min.

Then, the reactor was ramped to 70 °C and once the temperature was reached, it was left to react for 1 hour. The reactor was then vented and the polymer was left under a light stream of N_2 to dry. The polymer was then collected and left to dry even further for 2 h. Properties of the resultant polymers were analysed and are listed in **Table 3.**

Table 2

Run	1,7-Octadiene (ppm)	Diene/Zr molar ratio	Fluff	Activity (g/g/h)	Relative	MI_2 (g/10 min)	Bulk density

			Weight (g)		Activity (%)		(g/cc)
CE1	0	-	523.8	20952	100%	38	0.43
Ex1	19	1000	515.1	20602	98%	33	0.43
Ex2	28	1500	450.4	18016	86%	13	0.42
Ex3	56	3000	551.2	22049	105%	14	0.42

Table 3

Run	Mn (kDa)	Mw (kDa)	Mz (kDa)	D (Mw/Mn)	D' (Mz/Mw)	T_m (°C)	T_c (°C)	g_{rheo}
CE1	56	178	516	3.2	2.9	150.7	104.9	nd
Ex1	67	199	466	3	2.3	150.8	110.0	0.78
Ex2	78	238	531	3.1	2.2	151.5	108.5	0.90
Ex3	72	243	552	3.4	2.3	151.6	113.5	0.82

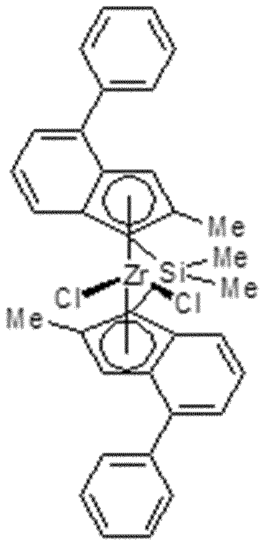
nd = not determined

g_{rheo} values were determined for the polymers of examples 1, 2 and 3. A g_{rheo} value of about 1.0 indicates that no long chain branching are formed. In the present example, all resins in which the diene compound was applied, the formation of LCB was demonstrated in view of a g_{rheo} value which is significantly below 1.0.

The results also indicate that, with increasing amounts of diene compound applied, the T_m remained relatively constant while the T_c slightly increased with higher amounts of 1,7-octadiene.

Example 3: Preparation of supported catalyst 2

Dimethylsilylene bis(2-methyl-4-phenyl-inden-1-yl) zirconium dichloride (see below formula Y) was used as metallocene component supported on silica which has been previously activated with methyl-alumoxane (MAO) as described below.



Formula Y

Support preparation

Silica support was dried under a nitrogen flow at 450 °C.

MAO treatment

In a 250 mL round bottom flask conditioned under a light nitrogen flow, 20 g of the above dried silica was introduced in a 500 mL round-bottomed flask. Toluene was added and the suspension was stirred at 100 rpm. MAO (30 % by weight in toluene) was dropwise added via a dropping funnel and the resulting suspension was heated at 110 °C (reflux) for 4 h. The amount of added MAO was calculated to reach an Al loading of about 16 wt%. After the reflux, the suspension was cooled down to room temperature and the mixture was filtered through a glass frit. The recovered powder was washed with toluene and *iso*-hexane before being dried under reduced pressure overnight.

Metallocene treatment

Dimethylsilylene bis(2-methyl-4-phenyl-inden-1-yl) zirconium dichloride (1.25 wt% on support) was dissolved in AlR_3 ($R = C_4H_9$) (ratio Al/Zr = 80). After 1-hour reaction the above-obtained MAO-support was slowly added to the metallocene/AlR_3 mixture and mixing was carried out for two hours. Solvent was removed by filtration. The obtained catalyst was washed with iso-hexane, filtered and dried at room temperature. Suspension of the resulting catalyst powder in mineral oil was prepared and stored cold.

Example 4: Preparation of propylene polymers with long chain branches

In this example, polymerization reactions were performed in an 8-liter reactor comprising an agitator, a temperature controller and inlets for feeding of propylene and hydrogen.

In this example, the **supported catalyst 2** as described in example 3 was used. The conditions under which the catalyst is applied during polymerisation are listed in **Table 4.**

Table 4

Cocatalyst TEAL (ppm)	H_2 (ppm)	Catalyst Example 3 (mg)	Zr (µmol)	Al/Zr Molar ratio
27	54	30.0	0.49	1189

The reactor was heated at 130 °C and flushed with N_2 for at least 2 h prior to being used. The reactor was then flushed with 1 L of propylene and cooled to 40 °C.

Subsequently, 3 L of propylene were pushed in the reactor together with the required amount of H_2. Stirring was started. Once the reactor was stabilised, a mixture consisting of 1 mL of TEAL (10 wt% solution in *iso*-hexane), the supported catalyst of example 2, and the diene compound (1,7-octadiene), was injected in the reactor together with 1.5 L of propylene. 1,7-octadiene was thus added to the reactor together with the catalyst. The appropriate amount of this diene compound was first diluted in TEAL and then mixed with the catalyst in a syringe. The mixture was then added to the reactor with a flow of propylene. Different amounts of 1,7-octadiene were applied during the different polymerisation reactions and for comparison one polymerisation reaction was carried out in the absence of 1,7-octadiene (see **Table 5**).

A pre-polymerisation was carried out at 40 °C for about 5 min.

Then, the reactor was ramped to 70 °C and once the temperature was reached, it was left to react for 1 hour. The reactor was then vented and the polymer was left under a light stream of N_2 to dry. The polymer was then collected and left to dry even further for 2 h.

Reaction conditions and properties of the resultant polymers were analysed and are listed in **Table 5** and **Figure 1**.

Table 5

Run	1,7-Octadiene (ppm)	Diene/Zr ratio	Fluff Weight (g)	Activity (g/g/h)	Relative Activity (%)	MI_2 (g/10 min)	Bulk density (g/cc)
CE2	0	-	641.5	21383	100%	25	0.44
Ex4	11	500	480.0	16000	75%	8.3	0.43

Ex5	22	1000	512.9	17097	80%	8.9	0.44
Ex6	45	2000	527.0	17566	82%	33	0.45
Ex7	67	3000	484.8	16160	76%	8.9	0.46
Ex8	447	20000	263.5	8783	41%	1.3	0.44

Table 5 (continued)

Run	Mn (kDa)	Mw (kDa)	Mz (kDa)	D (Mw/Mn)	D' (Mz/Mw)	T_m (°C)	T_c (°C)	g_{rheo}
CE2	62	221	587	3.6	2.7	149.1	104.0	0.95
Ex4	96	395	997	4.1	2.5	149.6	106.8	0.93
Ex5	87	350	889	4	2.5	150.8	110.1	0.85
Ex6	NF	NF	NF	NF	NF	150.9	115.3	0.70
Ex7	NF	NF	NF	NF	NF	150.4	118.1	0.38
Ex8	NF	NF	NF	NF	NF	151.7	122.0	ND

ND = not determined; NF = not filterable

In this example, activity, MI2 values, g_{rheo} values, and van Gurp-Palmen plots were considered as indicators of good activity and presence of LCBs in the obtained polymers. The presented data also indicate that at the highest amounts of 1,7-octadiene tested, activity and MI_2 value decreased.

g_{rheo} values were determined for the polymers of the comparative example (CE2) and examples 4 to 7. The data obtained shows that g_{rheo} values decrease, pointing to an increase in LCBs, with increasing amounts of 1,7-octadiene. All resins in which the diene compound was applied have a g_{rheo} value that is significantly below 1.0.

Van Gurp-Palmen plots were obtained for all examples and reported in **Figure 1**. The van Gurp-Palmen plots of the polymer produced when using 1,7-octadiene indicate that this compound causes the formation of LCBs. LCB formation is quite efficient as an effect can already be observed at a concentration of 10 ppm of 1,7-octadiene.

This example shows that 1,7-octadiene applied in combination with the supported catalyst of example 3 allows to prepare propylene polymer having LCBs. The amount of LBCs formed is correlated to the amount of 1,7-octadiene introduced in the reactor, hence providing a means for tuning LBC concentration. The results of this example also further indicate that, with increasing amounts of diene applied, the T_m remained relatively constant while the T_c slightly increased with higher amounts of 1,7-octadiene.

Example 5: Preparation of polypropylene with long chain branches

The polymerization reactions in this example were conducted in a loop reactor. Pre-polymerization was performed in a separate smaller loop reactor. The obtained samples were pelletized and analyzed. The polymerization conditions and results are given in **Tables 6-7.**

All resins were prepared under slurry conditions using the supported bridged metallocene catalyst of example 3.

The following example illustrates the use of 1,7-octadiene in a catalyst system for the production of polypropylene having long chain branches. Ten different resins were produced. Nine resins (Resin 1 to 9) were preparing using an increasing amount of 1,7-octadiene. One comparative resin (CE3) was prepared in the absence of 1,7-octadiene. The targeted resins are suitable for application in thermoforming processes.

Different concentrations of 1,7-octadiene were tested. TEAL was applied as co-catalyst in the reaction. For each of the polymerisation runs, the production target was about 350 kg. Details of the operating conditions for preparing polypropylene resins with LCBs are given in **Table 6.**

The catalyst systems applied in the polymerization reactions of this example were prepared as follows. Supported metallocene catalyst, as described in example 3 above, was pre-contacted with TEAL and 1,7-octadiene under the conditions as given below in **Table 6** for the different reactions (see “premix operating conditions”). 1,7-octadiene was diluted in *iso*-hexane. TEAL was added to the mixture as a 10 wt-% solution in *iso*-hexane.

The catalyst system as prepared above was continuous injected in the reactor, together with propylene and hydrogen. Pre-polymerization and polymerization were performed at the operating conditions as indicated in **Table 6**. Properties of the resultant polymers are listed in **Table 7.**

Table 6

			CE3	**Resin**			
				1	**2**	**3**	**4**
CATALYST		(g)	3	3	3	4	4
PREMIX OPERATING CONDITIONS	TEMP	(°C)	19.25	17.34	22.42	25.40	24.82
	Co-catalyst	(type)	TEAl				
		(ppm)	17	14	14	14	14

	Residence time	(min)	2.8	2.8	2.8	2.8	2.8
	Compound	(type)	*Iso*-hexane	1,7-Octadiene			
		(ppm)	0.0	10.0	10.0	20.0	20.0
PRE-POLYMERISATION	TEMP	(°C)	20	20	20	20	20
	Antifouling agent	(type)	Synperonic				
		(ppm)	2.1				
	Residence time	(min)	8.2				
POLYERMISATION	TEMP	(°C)	70				
	H2	(Nl/h)	11.0	12.6	12.4	12.7	12.8
	Activity	(gPP/ gCat/h)	11156.6	10888.4	9768.9	8848.7	8507.8
	H2/C3-		0.21	0.23	0.23	0.23	0.23
	Residence time	(min)	57.0	56.2	54.8	55.1	54.9
ANALYTICAL RESULTS	Bulk Density	(g/cm^3)	0.44	0.43	0.43	0.43	0.42
	MI_2	(g/10 min)	5.7	4.2	3.3	2.8	3.5
Production total		(kg)	370	370	360	382	378
Productivity	(By XRF) (*)	(g/g)	10489	10196	9606	9218	9264

(*) XRF = X-Ray fluorescence

Table 6 (continued)

			Resin				
			5	**6**	**7**	**8**	**9**
CATALYST		(g)	4	4	5	4	4
PREMIX OPERATING CONDITIONS	TEMP	(°C)	20.04	17.79	21.83	21.91	19.73
	Co-catalyst	(type)	TEAl				
		(ppm)	14				
	Residence time	(min)	2.8				
	Compound	(type)	1,7-Octadiene				
		(ppm)	50.0	75.0	152.8	149.3	294.7
PRE-POLYMERISATION	TEMP	(°C)	20	20	20	20	20
	Antifouling agent	(type)	Synperonic				

		(ppm)	2.1				
	Residence time	(min)	8.2				
POLYERMISATION	TEMP	(°C)	70				
	H2	(Nl/h)	12.8	12.8	13.3	14.2	17.7
	Activity	(gPP/gCat/h)	8677.0	8507.8	6886.5	8811.7	8567.0
	H2/C3-		0.23	0.23	0.24	0.25	0.30
	Residence time	(min)	54.6	54.9	55.7	55.1	55.0
ANALYTICAL RESULTS	Bulk Density	(g/cm^3)	0.42	0.42	0.40	0.39	0.41
	MI$_2$	(g/10 min)	3.4	3.5	2.3	3.5	3.4
Production total		(kg)	362	215	359	360	378
Productivity	(By XRF) (*)	(g/g)	8650	8903	7185	9369	9227

(*) XRF = X-Ray fluorescence

Table 7

Analysis			**CE3**	**Resin**			
				1	**2**	**3**	**4**
^{13}C NMR	mmmm	(%)	99.3	99.3	99.2	99.2	99.2
	1,2 C3-	(%)	98.9	98.9	98.9	98.9	98.9
	2,1 C3-	(%)	0.9	0.9	0.9	0.9	0.9
	1,3 C3-	(%)	0.0	0.0	0.0	0.0	0.0
GPC	Mn	(Da)	77128	72402	74310	75475	72608
	Mw	(Da)	299826	280171	302304	320435	301299
	Mz	(Da)	595514	565916	613788	668087	626808
	D		3.9	3.9	4.1	4.2	4.1
	D'		2.0	2.0	2.0	2.1	2.1
DSC	Tm	(°C)	149.7	149.5	149.4	149.1	149.4
	Delta Tm	(J/g)	92.20	107.40	114.80	97.10	108.10
	Tc	(°C)	110.40	110.50	110.10	110.30	109.90
	Delta Tc	(J/g)	-87.20	-87.50	-85.70	-91.90	-87.00
RDA	C-Y	C1 (η°)	3738.9	3132.8	4348.4	5594.3	4688.4
		C2 (λ)	0.0264	0.0231	0.0209	0.0197	0.0167
		C3 (a)	0.4968	0.4863	0.4511	0.3971	0.4081
	COP	Wc1	65	81	63	53	63
		Gc1	38049.8	37961.2	39233.4	36005.1	37489.5
		g_{rheo}	1.00	0.98	0.96	0.93	0.93
TDA/GC	1,7-Octadiene	ppm	0.01 (*)	0.05	0.08	0.15	0.1

(pellets)							

C-Y =Carreau-Yasuda parameter.

COP = Cross over point, i.e. the intersection point between G' and G" curves

(*) this value is considered as background noise and/or derived from impurity in the feed

Table 7 (continued)

Analysis			**Resin**				
			5	**6**	**7**	**8**	**9**
^{13}C NMR	***mmmm***	(%)	99.2	99.2	99.3	99.2	99.3
	1,2 C3-	(%)	98.9	98.9	98.9	98.9	98.9
	2,1 C3-	(%)	0.9	0.9	0.9	0.9	0.9
	1,3 C3-	(%)	0.0	0.0	0.0	0.0	0.0
GPC	Mn	(Da)	69107	68259	67171	66066	58262
	Mw	(Da)	304709	310600	374940	317300	328445
	Mz	(Da)	674000	727839	10333886	834628	1047775
	D		4.4	4.6	5.6	4.8	5.6
	D'		2.2	2.3	2.8	2.6	3.2
DSC	Tm	(°C)	150.20	150.90	151.10	151.30	151.90
	Delta Tm	(J/g)	105.50	94.80	91.70	103.00	102.00
	Tc	(°C)	113.50	115.20	117.40	117.10	120.40
	Delta Tc	(J/g)	-92.40	-91.70	-89.30	-95.40	-91.40
RDA	C-Y	C1 (η°)	5776.8	7459.8	28535.2	10736.0	17659.5
		C2 (λ)	0.0153	0.0151	0.0280	0.0129	0.0111
		C3 (a)	0.3464	0.3003	0.2094	0.2381	0.1852
	COP	Wc1	67	67	37	76	84
		Gc1	36856.1	34940.9	27111.0	31687.5	25590.4
		g_{rheo}	0.84	0.78	0.62	0.66	0.55
TDA/GC (pellets)	1,7-Octadiene	ppm	0.46	0.3	1	0.8	2.3

C-Y =Carreau-Yasuda parameter.

COP = Cross over point, i.e. the intersection point between G' and G" curves

(*) this value is considered as background noise and/or derived from impurity in the feed

Properties of the resultant polymers were analysed. ^{13}C NMR spectroscopic, DSC, GPC, TDA and RDA analyses were carried out as explained in the section above on samples of all obtained resins and results thereof are listed in **Table 7** and **Figures 2 to 6.**

Rheological analyses

RDA/Rheology is a powerful tool to assess the presence of LCBs. The data presented herein show that the addition of 1,7-octadiene during propylene polymerisation profoundly modifies the rheological properties of the resin produced.

g_{rheo} values were determined for all resins. The g_{rheo} value for the reference resin was about 1.0, indicating that no long chain branching was formed in this resin. For resins wherein the diene compound was applied, formation of LCB is demonstrated in view of a g_{rheo} value below 1.0. **Figure 2** illustrates the relationship between the g_{rheo} value (indicative for LCB formation) and the amount of diene compound (1,7-octadiene) used during polymerisation. From the rheological analyses it is further noted that the g_{rheo} value diminishes with higher amounts of diene compound being used during polymerisation. The lower this value the more LCBs are present in the product (**Figure 2**).

In addition to g_{rheo} values also van Gurp-Palmen and tanδ/freq plots give valuable data on the properties of the obtained resins. van Gurp-Palmen plots were established for a number of polypropylene resins, and are reported in **Figure 3**. These plots show that compared to the reference sample (CE3), increasing amounts of 1,7-octadiene applied during polymerisation, cause a decrease in the phase angle, which is a sign of the presence of LCBs.

Also tanδ/angular freq plots are particularly suitable to detect the presence of LCBs. Since LCBs are responsible for longer relaxation times, they cause the decrease of value of tanδ at lower corrected frequency. This is illustrated in **Figure 4** for a number of polypropylene resins.

Figures 3 and **4** further permit to make a distinction between resin 8 and 9 (i.e. respectively using 150 and 300 ppm of 1,7-octadiene).

Melt strength analyses

The melt strength of a number of obtained resins was further analysed. Results of these analyses are reported in **Figure 5**. These analyses show a significant increase of melt strength with increasing amounts of 1,7-octadiene. Figure 5 for instance shows a significant difference between resin 8 (150 ppm) and resin 9 (300 ppm).

NMR and GPC analyses

^{13}C NMR spectroscopic analyses indicate that the diene compound advantageously has no influence over stereo-errors and mis-insertion.

Based on the GPC data it is noted how with increasing amounts of diene compound in the polymerisation reaction, there is an increase in polydispersity of the obtained resins. This is also noted (see **Figure 6**) by the occurrence of a “shoulder” like pattern in the higher values of M. Both observations are indications for the presence of LCB. An interesting additional effect was that longer chains were produced with increasing amounts of diene compound.

DSC analyses

Results of DSC analyses indicated that T_m of the different resins was relatively constant while T_c slightly increased, with increasing amounts of diene compound in the polymerisation reaction.

TDA analyses

TDA analyses were performed on samples of pellets made from the resins as obtained. This analysis consists in heating the pellet samples and trapping all volatile substances which are then analysed by gas chromatography, hence identified. Results of the TDA analyses confirmed that the amount of 1,7-octadiene in pellets of prepared resin is minimal.

Conclusions

Overall, this example provides evidence for the formation of long chain branches in polypropylene prepared using a catalyst system as defined herein, and comprising a supported bridged metallocene catalyst in combination with a diene. In the present example, the diene compound was found to allow the generation of LCBs in metallocene-based polypropylene. The present example shows that there is an increase of LCBs in the produced polymer proportional to the amount of diene used. Also illustrated is that catalyst activity is maintained in the presence of an alpha,omega-diene compound. Using a diene compound induced a widening of the molecular weight distribution of the produced polymer and enabled to increase the melt strength of the final product. Further, in the presented experiments, an increase in T_c proportional to the amount of diene was also observed. Using alpha,omega-diene was found to have a profound effect on the final polymer products, causing an increase in LCB. Effects of the diene compound on activity is negligible.

CLAIMS

1. A process for preparing propylene polymers having long chain branches, said process comprising the steps of

   feeding into at least one reactor propylene monomer and optionally one or more alpha-olefins comonomer(s), a catalyst system, optionally a hydrocarbon diluent, optionally hydrogen and an alkylaluminum of formula $AlR^b{}_x$, wherein x is an integer selected from 1 to 3 and each R^b is independently selected from halogen, alkoxy or alkyl, and

   polymerizing in said at least one reactor, the propylene monomer and optionally one or more alpha-olefins comonomer(s), in the presence of said catalyst system, said optional hydrocarbon diluent, said optional hydrogen and said alkylaluminum, thereby producing propylene polymers having long chain branches,

   wherein said catalyst system comprises

   a. at least one bridged metallocene catalyst which is immobilized on an inert support, and
   b. at least one diene compound, wherein said diene compound is an alpha,omega-diene of formula (I)

      $$H_2C=CH-(CR^a{}_2)_m-HC=CH_2 \text{ (I)}$$

      wherein m is an integer of at least 3, and preferably from 3 to 16, and

      wherein each R^a is independently hydrogen or a C_1-C_{10} alkyl.

2. Process according to claim 1, wherein said diene compound is an alpha,omega-diene of formula (I), wherein m is an integer from 3 to 16, and wherein each R^a is hydrogen.

3. Process according to claim 1 or 2 wherein said diene compound is selected from the group consisting of 1,6-heptadiene, 1,7-octadiene, 1,8-nonadiene, 1,9-decadiene, 1,10-undecadiene, 1,11-dodecadiene, 1,12-tridecadiene, and 1,13-tetradecadiene, and preferably is 1,7-octadiene, or 1,8-nonadiene, or 1,9-decadiene.

4. Process according to any one of claims 1 to 3, wherein said diene compound is applied at a concentration of at most 1000 ppm, or at most 750 ppm, or at most 600 ppm, at most 500 ppm, or at most 400 ppm, or at most 350 ppm.

5. Process according to any one of claims 1 to 4, wherein said diene compound is applied at a concentration of at least 10 ppm, or at least 15 ppm, or at least 20 ppm, or at least 35 ppm, or at least 50 ppm.

6. Process according to any one of claims 1 to 5, wherein said at least one bridged metallocene catalyst is a compound according to formula (II):

   $$R^1(Ar)_2M^1Q^1{}_2 \text{ (II)},$$

   wherein said metallocene catalyst according to formula (II) has two Ar bound to M^1,

   wherein M^1 is a transition metal selected from the group consisting of titanium, zirconium, hafnium, and vanadium;

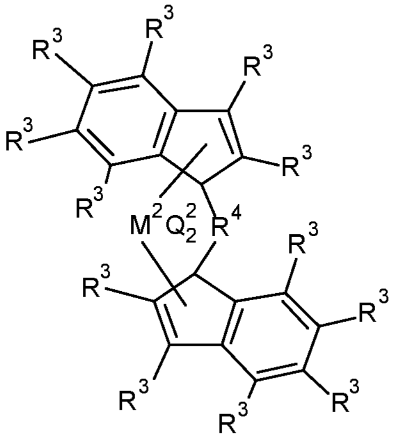
   wherein Ar is an aromatic ring, group or moiety and wherein each Ar is independently selected from the group consisting of cyclopentadienyl, indenyl, tetrahydroindenyl, and fluorenyl,

      wherein each of said groups may be optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, $SiR^2{}_3$ wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms, and wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl, and P;

   wherein each Q^1 is independently selected from the group consisting of halogen, alkyl, heteroalkyl, cycloalkyl, aryl, alkylaryl, aralkyl, alkoxy, cycloalkoxy, aralkoxy, $-COOR^5$ wherein R^5 is hydrogen or alkyl, $-N(R^6)_2$ wherein R^6 is selected from the group consisting of hydrogen, alkyl and COR^7 wherein R^7 is alkyl, and $-CO-(NR^8)_2$ wherein R^8 is H or alkyl, and

   wherein R^1 is a divalent group or moiety bridging the two Ar groups and is selected from the group consisting of C_1-C_{20} alkylene, dialkyl germanium, silicon, siloxane, alkylphosphine, and an amine, and wherein said R^1 is optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, $SiR^2{}_3$ wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms and wherein said hydrocarbyl optionally contains one or more atoms selected from the group comprising B, Si, S, O, F, Cl, and P.

7. Process according to any one of claims 1 to 6, wherein said bridged metallocene catalyst is a compound of formula (III):



(III)

wherein each R^3 in formula (III) is selected independently from hydrogen or a hydrocarbyl having 1 to 20 carbon atoms,

wherein R^4 is a divalent group or moiety bridging the two indenyls and is selected from the group consisting of C_1-C_4 alkylene, dialkyl germanium, silicon, siloxane, alkyl phosphine and amine; and wherein said R^4 is optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, SiR^2_3 wherein R^2 is a hydrocarbyl having 1 to 20 carbon atoms, and a hydrocarbyl having 1 to 20 carbon atoms

wherein each Q^2 is independently selected from the group consisting of halogen, alkyl, heteroalkyl, cycloalkyl, aryl, alkylaryl, aralkyl, alkoxy, cycloalkoxy, aralkoxy, $-COOR^5$ wherein R^5 is hydrogen or alkyl, $-N(R^6)_2$ wherein R^6 is selected from the group consisting of hydrogen, alkyl and COR^7 wherein R^7 is alkyl, and $-CO-(NR^8)_2$ wherein R^8 is H or alkyl, and

wherein M^2 is a transition metal selected from the group consisting of titanium, zirconium, hafnium, and vanadium.

8. Process according to claim 7, wherein said bridged metallocene catalyst is a compound of formula (III)

wherein M^2 is zirconium,

wherein each Q^2 is a halogen,

wherein each R^3 independently is hydrogen or a hydrocarbyl having 1 to 20 carbon atoms, and

wherein R^4 is a divalent group or moiety bridging the two indenyls and is selected from the group consisting of C_1-C_4 alkylene and silicon, and wherein said R^4 is optionally substituted with one or more substituents each independently selected from the group consisting of halogen and a hydrocarbyl having 1 to 20 carbon atoms.

9. Process according to any one of claims 1 to 8, wherein said alkylaluminum of formula AlR^b_x is trialkylaluminum.

10. Process according to any one of claims 1 to 9, wherein said alkylaluminum of formula AlR^b_x is selected from the group comprising Tri-Iso-Butyl Aluminum (TIBAl),Tri-Ethyl Aluminum (TEAl), Tri-Methyl Aluminum (TMA), and Dimethyl-Ethyl Aluminum, and preferably is TIBAl or TEAl.

11. Process according to any one of claims 1 to 10, wherein said inert support is a silica.

12. A catalyst system suitable for catalyzing a polymerisation process for preparing propylene polymers having long chain branches, comprising

    a. at least one bridged metallocene catalyst which is immobilized on an inert support, and preferably a bridged metallocene catalyst as defined in any of claims 6 to 8, and 11, and

    b. at least one diene compound, wherein said diene compound is an alpha,omega-diene of formula (I)

$$H_2C=CH-(CR^a_2)_m-HC=CH_2 \text{ (I)}$$

wherein m is an integer of at least 3, and preferably from 3 to 16, and

wherein each R^a is independently hydrogen or a C_1-C_{10} alkyl, and

preferably wherein said diene compound is as defined in any of claims 2 to 3.

13. Use of a catalyst system according to claim 12 in a process according to any one of claims 1-11.

14. Propylene polymer having long chain branches obtained by a process according to any one of claims 1 to 11 or obtained by a process using a catalyst system according to claim 12.

15. Use of an alpha,omega-diene of formula (I) as defined in any one of claims 1 to 3 in a polymerization process for preparing propylene polymers having long chain branches, wherein said alpha,omega-diene is used in combination with at least one bridged metallocene catalyst which is immobilized on an inert support, and preferably which is as defined in any one of claims 6 to 8 and 11.

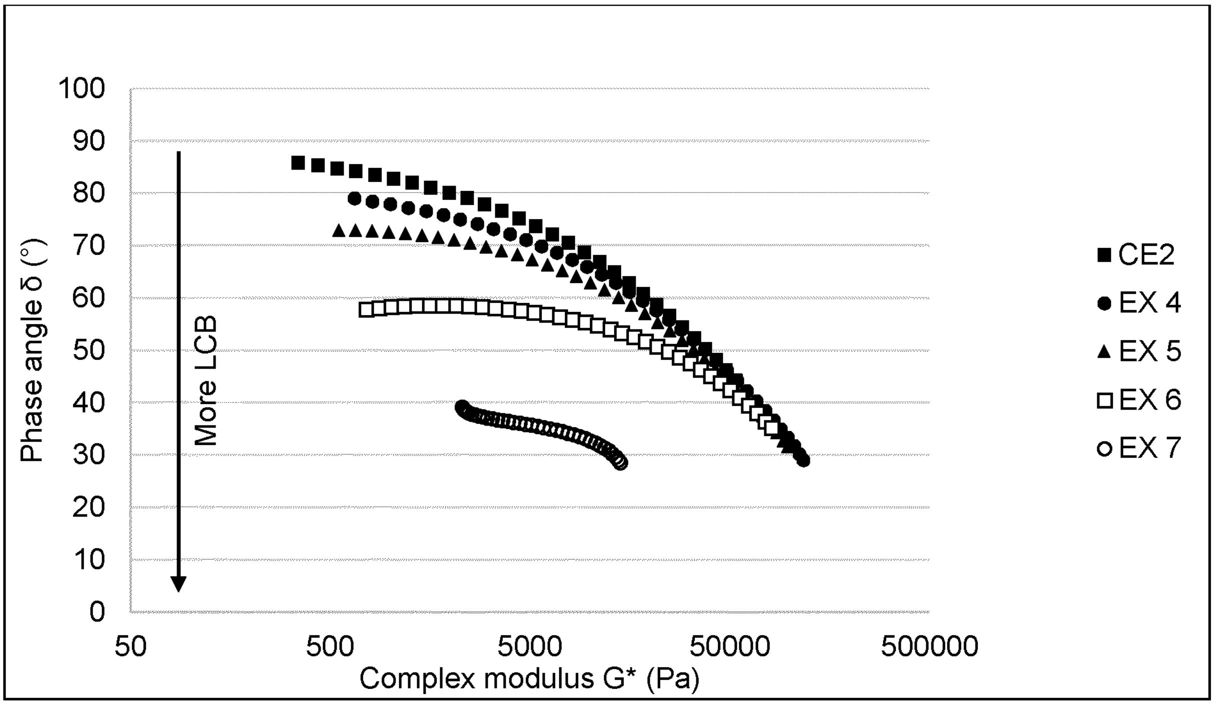


FIGURE 1

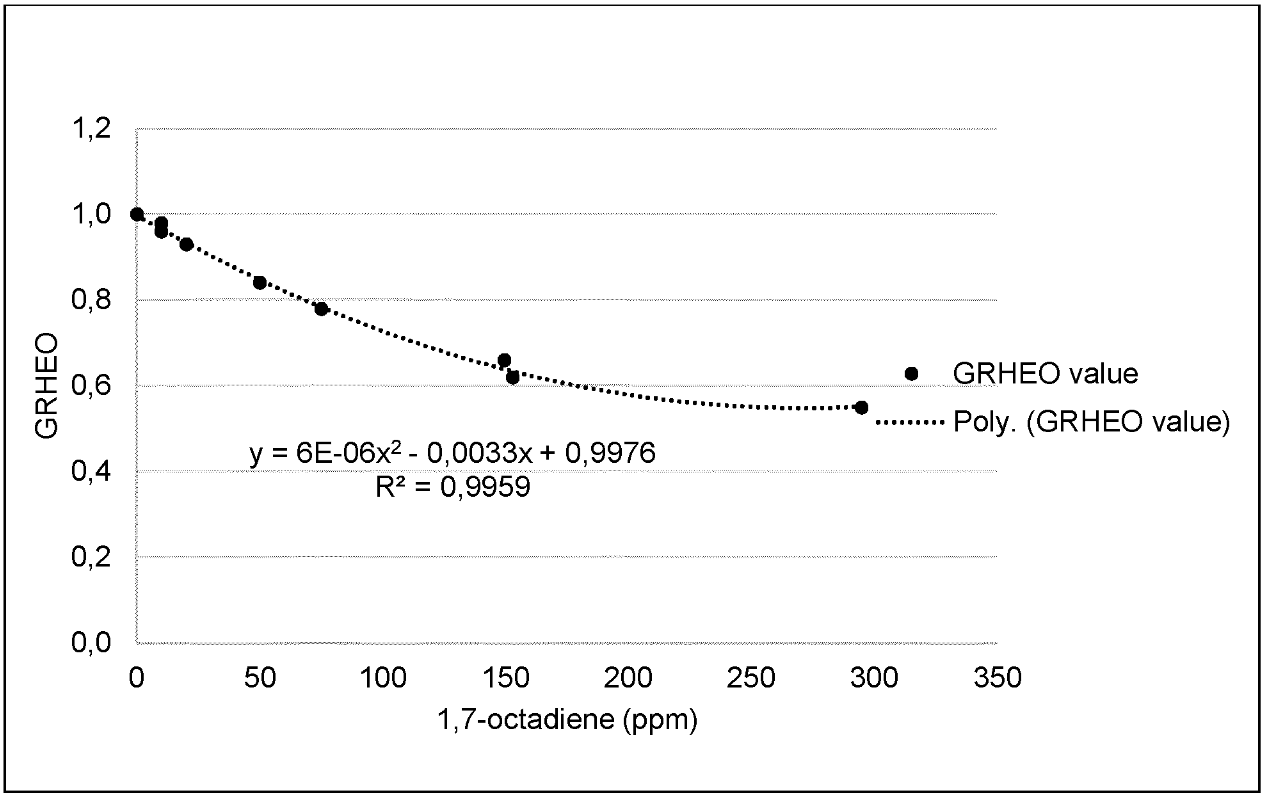


FIGURE 2

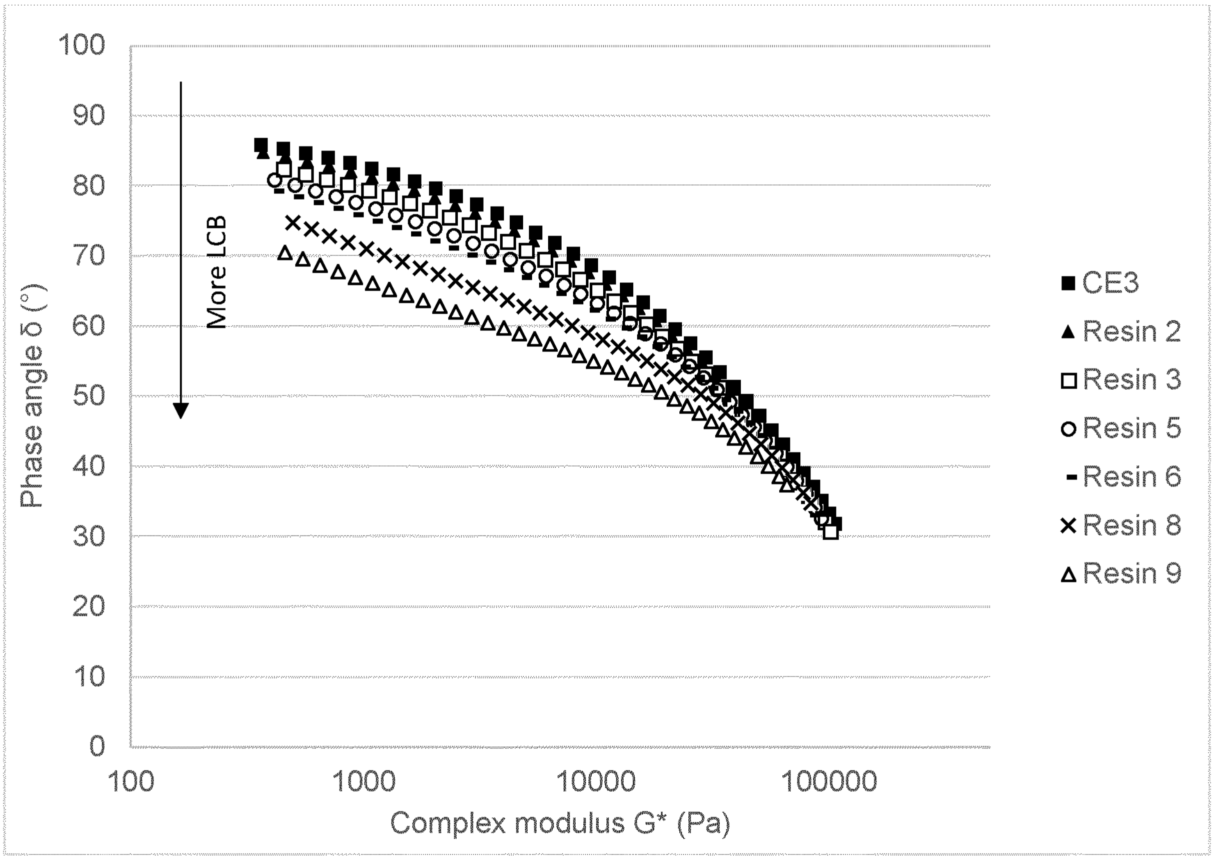


FIGURE 3

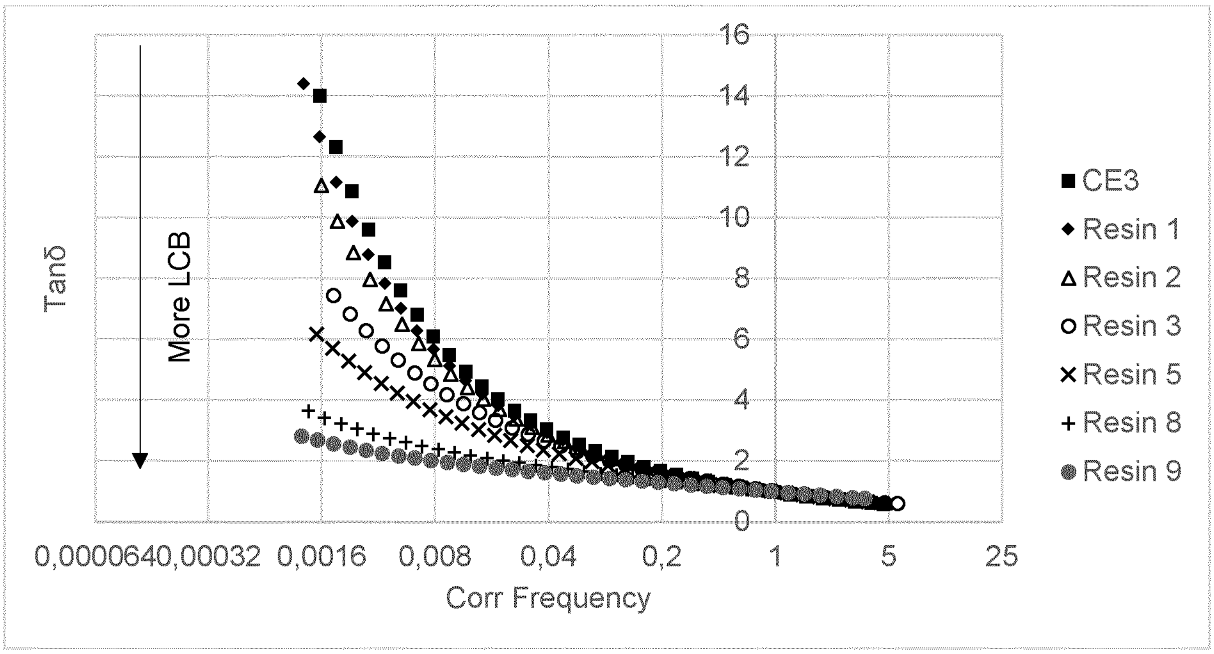


FIGURE 4

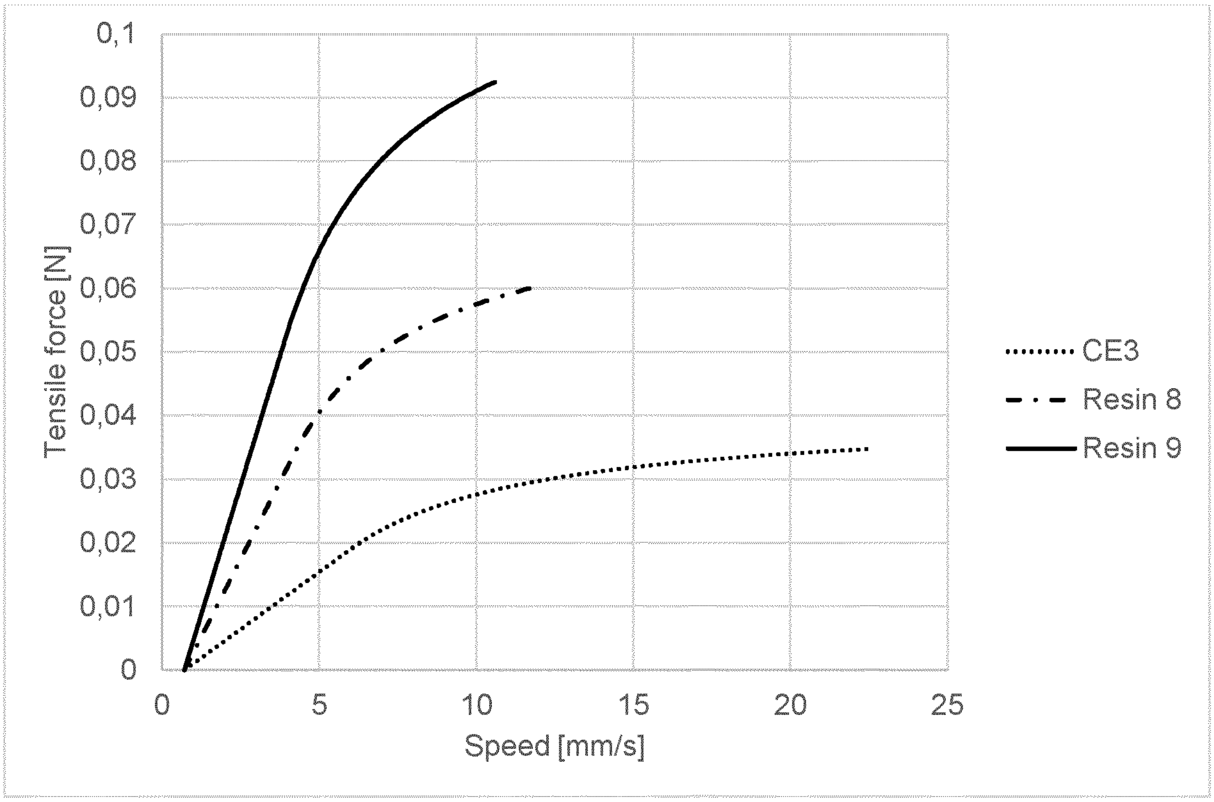


FIGURE 5

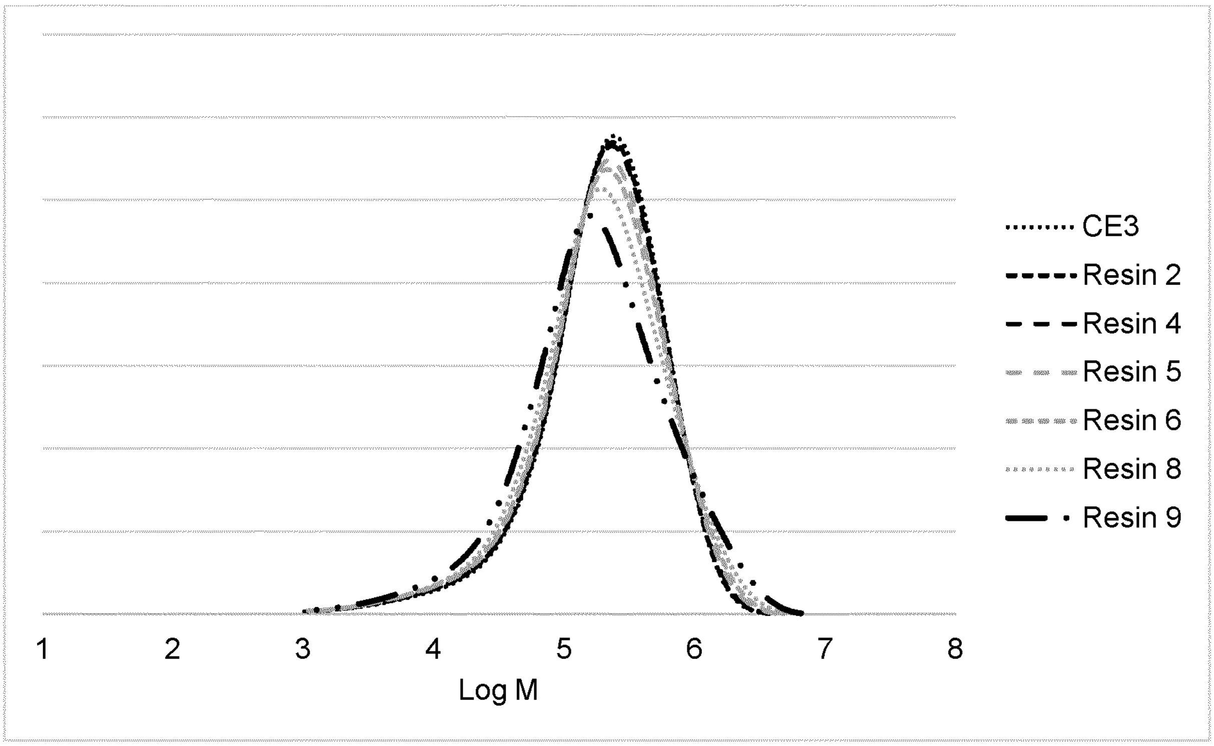


FIGURE 6

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2021/071834

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F210/06
ADD. C08F4/659 C08F2/02

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, WPI 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 2004/046214 A2 (EXXONMOBIL CHEM PATENTS INC [US]; JIANG PEIJUN [US] ET AL.) 3 June 2004 (2004-06-03) tables 5-14, 30 -----	1-15
X	WO 97/08216 A1 (EXXON CHEMICAL PATENTS INC [US]) 6 March 1997 (1997-03-06) tables 1-3 -----	1-15
X	US 2001/007896 A1 (AGARWAL PAWAN KUMAR [US] ET AL) 12 July 2001 (2001-07-12) example cat.C; table 1 -----	1-15
X	EP 0 476 148 A1 (MITSUI TOATSU CHEMICALS [JP]) 25 March 1992 (1992-03-25) examples 3,5,6 ----- -/--	1-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search 18 November 2021	Date of mailing of the international search report 26/11/2021
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