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(71) Applicant: TOTAL RESEARCH & TECHNOLOGY

FELUY [BE/BE]; Zone Industrielle C, B-7181 Seneffe (BE).

(72) Inventors: SIGWALD, Armelle; Rue de Namur 116, 1400

NIVELLES (BE). SYPASEUTH, Fanni; c/o Total Research & Technology Feluy Zone Industrielle C, 7181 Seneffe (BE). VANTOMME, Aurélien; Rue des Combattants 30, 7070 Mignault (BE). WELLE, Alexandre; Rue Vital Casse 2A, 1490 Court-St-Etienne (BE).

(74) Agent: GARCIA MARTIN, Margarita; Zone Industrielle

C, 7181 Seneffe (BE).

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(54) Title: MONOVINYLDENE AROMATIC POLYMER COMPOSITIONS AND METHOD OF MAKING THEM

(57) Abstract: The present invention relates to a monovinylidene aromatic polymer composition, and a method of making such a composition. More in particular, the monovinylidene aromatic polymer composition comprises an elastomer, preferably a rubber-like elastomer.



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MONOVINYLIDENE AROMATIC POLYMER COMPOSITIONS AND METHOD OF MAKING THEM

FIELD OF INVENTION

The present invention relates to a monovinylidene aromatic polymer composition, and a
5 method of making such a composition. More in particular, the monovinylidene aromatic
polymer composition comprises an elastomer, preferably a rubber-like elastomer.

BACKGROUND OF THE INVENTION

Monovinylidene aromatic polymers, and especially syndiotactic monovinylidene aromatic
10 polymers such as syndiotactic polystyrene (sPS), are typically blended with other
(co-)polymer(s), such as ethylene-styrene interpolymer (ESI), to obtain or improve certain
properties, such as impact resistance. Blending is typically done by melt blending, wherein
both polymers are melted, after which they are kneaded to form the blend, where after said
blend is extruded and pelletized. Other methods of blending involve twin-screw extrusion,
15 solution mixing, latex blending, some methods providing more homogeneous blends than
others. These blending techniques are herein referred to as “physical blending”. All these
methods involve high energy consumption, time and/or use of large volumes of solvents.

Therefore, there is a need for less energy consuming production methods of forming the
monovinylidene aromatic polymer compositions. There is also a need for less time consuming
20 production methods for monovinylidene aromatic polymer compositions. There is also a need
for less solvent consuming production methods for monovinylidene aromatic polymer
compositions. There is also a need for production methods for monovinylidene aromatic
polymer compositions which provide highly homogeneous monovinylidene aromatic polymer
compositions. There is a need for monovinylidene aromatic polymer compositions with highly
25 compatible components.

SUMMARY OF THE INVENTION

The invention provides in at least one of the above named needs by using the same catalyst
system in both the formation of the elastomer, preferably the rubber-like elastomer, and in the
formation of the monovinylidene aromatic polymer. By using one single catalyst system in both
30 formation reactions, the monovinylidene aromatic polymer composition can be obtained as a
chemical blend. The term “chemical blend” as used herein, refers to a composition comprising
at least two components, wherein the second component is formed from a reagent mixture
comprising already the first component. Such production processes may provide highly
uniform compositions, and/or compositions that upon solidification and/or compacting have
35 nodules of one component highly homogeneous distributed in a matrix of the other component.

Preferably, said nodules are highly homogeneous in size. In some preferred embodiments, the nodules comprise and/or are formed by the elastomer, preferably the rubber-like elastomer. In some preferred embodiments, the matrix comprises and/or is formed by monovinylidene aromatic polymer. Preferably, the chemical blending avoids the need for a physical blending
5 step to obtain a monovinylidene aromatic polymer composition. In some embodiments, after reaction, a polymer fluff is obtained, which may be precipitated and compacted.

Using the same catalyst in the formation reaction of the elastomer, preferably the rubber-like elastomer, and the monovinylidene aromatic polymer preferably allows for using a single reaction vessel in both formation reactions. Preferably, the same reaction vessel comprising
10 the reaction product from the formation of the elastomer, preferably the rubber-like elastomer is used as reaction vessel in the formation of the monovinylidene aromatic polymer; such a process can be seen as a one-pot-two-step reaction for the provision of monovinylidene aromatic polymer composition.

According to a first aspect, the present invention provides a process for manufacturing a
15 monovinylidene aromatic polymer composition in a reactor, comprising the steps of:

a1) providing a monomer mixture to the reactor, wherein said monomer mixture comprises an α -olefin or diene, and preferably wherein said monomer mixture further comprises at least one first vinyl aromatic hydrocarbon monomer;

b1) providing a catalyst system to the reactor;

20 a2) polymerizing at least part of the monomer mixture with the catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;

c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor after the formation of the rubber-like elastomer; and,

25 c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the same catalyst system under polymerization conditions in the reactor to form a monovinylidene aromatic polymer;

thereby obtaining the monovinylidene aromatic polymer composition.

According to a second aspect, the present invention provides a process for manufacturing a
30 monovinylidene aromatic polymer composition in a reactor, comprising the steps of:

c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor;

b1) providing a catalyst system to the reactor;

c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the catalyst system under polymerization conditions in the reactor to form a monovinylidene
35 aromatic polymer;

a1) providing a monomer mixture to the reactor, wherein said monomer mixture comprises an α -olefin or diene, and preferably wherein said monomer mixture further comprises at least one first vinyl aromatic hydrocarbon monomer; and,

a2) polymerizing at least part of the monomer mixture with the same catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;

thereby obtaining the monovinylidene aromatic polymer composition.

In some embodiments, the process comprises the step of at least partially removing the α -olefin or diene from the reactor after step a2) and preferably before step c2), preferably before step c1).

In some embodiments, the first vinyl aromatic hydrocarbon monomer is the same as the second vinyl aromatic hydrocarbon monomer.

In some embodiments, the first and/or the second vinyl aromatic hydrocarbon monomer is styrene.

In some embodiments, the α -olefin or diene is ethylene.

In some embodiments, the catalyst system comprises a rare earth element, preferably a light rare earth element.

In some embodiments, at least 60.0 %, preferably at least 80.0 %, preferably at least 90.0 %, preferably at least 95.0 %, preferably at least 99.0 %, preferably at least 99.5 %, preferably at least 99.9 % of the metallic centres in the catalyst system are rare earth elements, preferably a light rare earth elements. These metallic centres result in a more random type of elastomer compared to the titanium, zirconium, hafnium, or vanadium metallic centres. Hence, such catalyst systems leave a typical microstructure. It has been found that a more random type of elastomer provides a better compatibility with other polymers, preferably when said other polymer is a polyolefin or a polydiene.

In some embodiments, the catalyst system comprises an element selected from the list comprising neodymium (Nd), yttrium (Y), scandium (Sc), lanthanum (La), samarium (Sm), praseodymium (Pr); preferably the catalyst system comprises Nd and/or Y; preferably the catalyst system comprises Nd.

In some embodiments, at least 60.0 %, preferably at least 80.0 %, preferably at least 90.0 %, preferably at least 95.0 %, preferably at least 99.0 %, preferably at least 99.5 %, preferably at least 99.9 % of the metallic centres in the catalyst system are metals selected from the list comprising neodymium (Nd), yttrium (Y), scandium (Sc), lanthanum (La), samarium (Sm), and

praseodymium (Pr); preferably selected from Nd and/or Y; preferably Nd. These metallic centres result in a more random type of elastomer compared to the titanium, zirconium, hafnium, or vanadium metallic centres.

In some embodiments, at most 10.0 %, preferably at most 5.0 %, preferably at most 2.0 %, preferably at most 1.0 %, preferably at most 0.5 % of the metallic centres in the catalyst system are titanium, zirconium, hafnium, and vanadium. In some embodiments, at most 10.0 %, preferably at most 5.0 %, preferably at most 2.0 %, preferably at most 1.0 %, preferably at most 0.5 % of the metallic centres in the catalyst system are titanium. These metallic centres result in a more blocky type of elastomer compared to the rare earth metallic centres.

In some embodiments, the catalyst system comprises a metallocene catalyst component of the general formula (II),



wherein,

Cp is a cyclopentadienyl, optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, a hydrocarbyl having 1 to 20 carbon atoms, and SiR''_3 wherein R'' is 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;

Flu is a fluorenyl, optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, a hydrocarbyl having 1 to 20 carbon atoms, and SiR'''_3 wherein R''' is 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;

M is a rare earth metal;

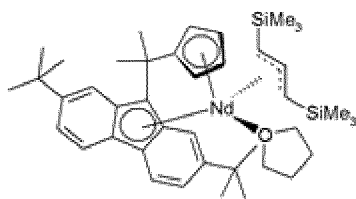
ether is a donor solvent molecule;

R'' is a structural bridge between Cp and Flu (9-position) imparting stereorigidity to the component;

each R' is the same or different, and is hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms; and,

wherein n is 0, 1 or 2.

In some embodiments, the catalyst system comprises a compound according to formula (III):



(III).

In some embodiments, the monovinylidene aromatic polymer is a syndiotactic monovinylidene aromatic polymer having at least 70% rrrrr hexads, preferably at least 75% rrrrr hexads, preferably at least 80% rrrrr hexads, preferably at least 85% rrrrr hexads, preferably at least 90% rrrrr hexads, preferably at least 95% rrrrr hexads, determined by $^{13}\text{C}\{^1\text{H}\}$ NMR.

In another aspect, the invention provides in a monovinylidene aromatic polymer composition comprising:

- an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or a diene; and,

- a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer,

characterized in that the composition is a chemical blend of the elastomer, preferably the rubber-like elastomer and the monovinylidene aromatic polymer, preferably a chemical blend of the elastomer, preferably the rubber-like elastomer, the monovinylidene aromatic polymer and a third polymer;

preferably wherein the chemical blend is obtained by a process according to an embodiment according to the invention.

In another aspect, the invention provides in a monovinylidene aromatic polymer composition comprising:

- an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or a diene;

- a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer; and,

- a third polymer, preferably a homopolymer of the α -olefin or the diene.

In another aspect, the invention provides in a process for manufacturing the monovinylidene aromatic polymer composition according to an embodiment of the invention, said process being a process according to an embodiment of the invention, further comprising the step of physical blending a third polymer in the monovinylidene aromatic polymer composition.

In another aspect, the invention provides in the use of hemi-metallocene catalyst, a metallocene catalyst or post-metallocene catalyst in a catalyst system in at least two different polymerization reactions carried out in the same reactor, wherein:

- at least one polymerization reaction is the polymerization of vinyl aromatic hydrocarbon monomer to form a monovinylidene aromatic polymer; and,
- wherein at least one polymerization reaction is the polymerization of a monomer mixture, said monomer mixture comprises vinyl aromatic hydrocarbon monomer and an α -olefin or a diene;

preferably in a process according to an embodiment of the invention.

- 10 Preferred embodiments of one aspect of the invention are preferred embodiments of the other aspects of the invention.

DESCRIPTION OF THE DRAWINGS

FIG. 1 shows the different chemical shifts in a $^{13}\text{C}\{^1\text{H}\}$ NMR spectra for a styrene-ethylene copolymer.

- 15 **FIG. 2a** depicts a SEM image of a physical blend of syndiotactic polystyrene with a styrene-ethylene copolymer.

FIG. 2b depicts a SEM image of a monovinylidene aromatic polymer composition according to an embodiment of the invention.

- 20 **FIG. 2c** depicts a SEM image of a monovinylidene aromatic polymer composition according to an embodiment of the invention.

FIG. 3 depicts a detail of the NMR spectrum of a styrene homopolymer.

DETAILED DESCRIPTION OF THE INVENTION

- Before the present method used in the invention is described, it is to be understood that this invention is not limited to particular compositions, articles, methods, processes, and uses described, as such compositions, articles, methods, processes, and uses may, of course, vary.

It is also to be understood that the terminology used herein is not intended to be limiting, since the scope of the present invention will be limited only by the appended claims.

- When describing the compositions, articles, methods, processes, and uses of 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 polymer" means one polymer or more than one polymer.

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. The terms "comprising", "comprises" and "comprised of" also include the term "consisting of".

- 5 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
10 range recited herein is intended to include all sub-ranges subsumed therein.

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
15 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
20 embodiments are meant to be within the scope of the invention, and form different embodiments, as would be understood by those in the art. For example, in the following claims and statements, any of the embodiments can be used in any combination.

Unless otherwise defined, all terms used in disclosing the invention, including technical and scientific terms, have the meaning as commonly understood by one of ordinary skill in the art
25 to which this invention belongs. By means of further guidance, definitions for the terms used in the description are included to better appreciate the teaching of the present invention.

Preferred statements (features) and embodiments of the compositions, articles, processes 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 embodiments unless clearly
30 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 1 to
77 with any other statement and/or embodiments in the description.

- 35 1. A process for manufacturing a monovinylidene aromatic polymer composition in a reactor, comprising the steps of:

- a1) providing a monomer mixture to the reactor, wherein said monomer mixture comprises an α -olefin or diene, and preferably wherein said monomer mixture further comprises at least one first vinyl aromatic hydrocarbon monomer;
- b1) providing a catalyst system to the reactor;
- 5 a2) polymerizing at least part of the monomer mixture with the catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;
- c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor after the formation of the rubber-like elastomer; and,
- 10 c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the same catalyst system under polymerization conditions in the reactor to form a monovinylidene aromatic polymer;
- thereby obtaining the monovinylidene aromatic polymer composition.

2. A process for manufacturing a monovinylidene aromatic polymer composition in a reactor, comprising the steps of:
- 15

- a1) providing a monomer mixture to the reactor, wherein said monomer mixture comprises at least one first vinyl aromatic hydrocarbon monomer and an α -olefin or diene;
- b1) providing a catalyst system to the reactor;
- 20 a2) polymerizing at least part of the monomer mixture with the catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;
- c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor after the formation of the rubber-like elastomer; and,
- 25 c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the same catalyst system under polymerization conditions in the reactor to form a monovinylidene aromatic polymer;
- thereby obtaining the monovinylidene aromatic polymer composition.

3. A process for manufacturing a monovinylidene aromatic polymer composition in a reactor, comprising the steps of:
- 30

- c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor;
- b1) providing a catalyst system to the reactor;
- c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the catalyst system under polymerization conditions in the reactor to form
- 35 a monovinylidene aromatic polymer;

- a1) providing a monomer mixture to the reactor, wherein said monomer mixture comprises an α -olefin or diene, and preferably wherein said monomer mixture further comprises at least one first vinyl aromatic hydrocarbon monomer; and,
- a2) polymerizing at least part of the monomer mixture with the same catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;
- thereby obtaining the monovinylidene aromatic polymer composition.

4. A process for manufacturing a monovinylidene aromatic polymer composition in a reactor, comprising the steps of:

- c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor;
- b1) providing a catalyst system to the reactor;
- c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the catalyst system under polymerization conditions in the reactor to form a monovinylidene aromatic polymer;
- a1) providing a monomer mixture to the reactor, wherein said monomer mixture comprises at least one first vinyl aromatic hydrocarbon monomer and an α -olefin or diene; and,
- a2) polymerizing at least part of the monomer mixture with the same catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;
- thereby obtaining the monovinylidene aromatic polymer composition.

5. The process according to any one of statements 1 to 4 or in some embodiments, wherein the step b1) can be performed before, during, or after step a1) or c1); whichever step a1) or c1) is performed first.

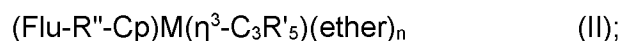
6. The process according to any one of statements 1 to 5, wherein in step b1) the catalyst system is provided to the reactor comprising already at least part of the monomer mixture or vinyl aromatic hydrocarbon monomer.

7. The process according to any one of statements 1 to 6 or in some embodiments, wherein during step a2) the partial pressure of the α -olefin and/or diene in the reaction mixture is maintained.

8. The process according to any one of statements 1 to 7 or in some embodiments, wherein during step a2) the pressure in the reactor is maintained by controlling the amount of α -olefin and/or diene in the reaction mixture.

9. The process according to any one of statements 1 to 8 or in some embodiments, wherein the process comprises the step of at least partially removing the α -olefin or diene from the reactor after step a2) and preferably before step c2), preferably before step c1).
10. The process according to any one of statements 1 to 9 or in some embodiments, wherein the process comprises the step of completely removing the α -olefin or diene from the reactor after step a2) and preferably before step c2), preferably before step c1).
11. The process according to any one of statements 1 to 10 or in some embodiments, wherein the process comprises the step of activating the catalyst system before step a2) or step c2), which ever step is performed first.
12. The process according to any one of statements 1 to 11 or in some embodiments, wherein a third polymer is formed in step a2), preferably a homopolymer, preferably a homopolymer of the α -olefin or the diene.
13. The process according to any one of statements 1 to 12 or in some embodiments, wherein the first vinyl aromatic hydrocarbon monomer is the same as the second vinyl aromatic hydrocarbon monomer.
14. The process according to any one of statements 1 to 13 or in some embodiments, wherein the first and/or the second vinyl aromatic hydrocarbon monomer is according to formula (I)
- $$\text{H}_2\text{C}=\text{CR}-\text{Ar} \quad (\text{I});$$
- wherein R is hydrogen or an alkyl group having from 1 to 4 carbon atoms, and wherein Ar is an aromatic radical of at least 6 to at most 14 carbon atoms, preferably 6 to 10 carbon atoms, preferably wherein the first and the second vinyl aromatic hydrocarbon monomer are the same.
15. The process according to any one of statements 1 to 14 or in some embodiments, wherein the first and/or the second vinyl aromatic hydrocarbon monomer is selected from the list comprising: styrene, alpha-methylstyrene, ortho-methylstyrene, meta-methylstyrene, para-methylstyrene, vinyl toluene, para-t-butylstyrene, vinyl naphthalene, divinylbenzene, para-chlorostyrene, meta-chlorostyrene, ortho-chlorostyrene, 2,4-dimethylstyrene, 4-vinylbiphenyl, and vinylanthracene, preferably wherein the first and the second vinyl aromatic hydrocarbon monomer are the same.
16. The process according to any one of statements 1 to 15, wherein the first and/or the second vinyl aromatic hydrocarbon monomer is styrene.

17. The process according to any one of statements 1 to 16 or in some embodiments, wherein the first and the second vinyl aromatic hydrocarbon monomer are styrene.
18. The process according to any one of statements 1 to 17 or in some embodiments, wherein the first and the second vinyl aromatic hydrocarbon monomer are styrene, and wherein the α -olefin is ethylene.
19. The process according to any one of statements 1 to 18 or in some embodiments, wherein the catalyst system comprises a rare earth element, preferably a light rare earth element.
20. The process according to any one of statements 1 to 19 or in some embodiments, wherein the catalyst system comprises an element selected from the list comprising neodymium (Nd), yttrium (Y), scandium (Sc), lanthanum (La), samarium (Sm), praseodymium (Pr); preferably wherein the catalyst system comprises Nd and/or Y; preferably wherein the catalyst system comprises Nd.
21. The process according to any one of statements 1 to 20 or in some embodiments, wherein the catalyst system comprises a hemi-metallocene catalyst, a metallocene catalyst, or a post-metallocene catalyst, preferably a metallocene catalyst or a hemi-metallocene catalyst, preferably a hemi-metallocene catalyst.
22. The process according to any one of statements 1 to 21 or in some embodiments, wherein the catalyst system comprises a constrained geometry metallocene or a bridged metallocene.
23. The process according to any one of statements 1 to 22 or in some embodiments, wherein the catalyst system is activated by a cocatalyst, methylaluminoxane (MAO) or a borane.
24. The process according to any one of statements 1 to 23 or in some embodiments, wherein the catalyst system comprises a metallocene catalyst component of the general formula (II),



wherein,

Cp is a cyclopentadienyl, optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, a hydrocarbyl having 1 to 20 carbon atoms, and SiR''_3 wherein R'' is 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;

Flu is a fluorenyl, optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, a hydrocarbyl having 1 to 20

carbon atoms, and SiR'''_3 wherein R''' is 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;

M is a rare earth metal;

ether is a donor solvent molecule;

R'' is a structural bridge between Cp and Flu (9-position) imparting stereorigidity to the component;

each R' is the same or different, and is hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms; and,

wherein n is 0, 1 or 2.

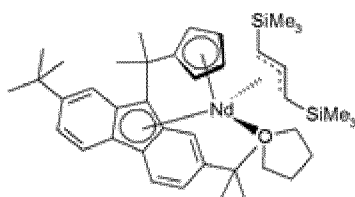
25. The process according to any one of statements 1 to 24 or in some embodiments, wherein no activating agent is added to the catalyst system.

26. The process according to any one of statements 1 to 25 or in some embodiments, wherein M is a rare earth element, preferably a light rare earth element, for example wherein M is selected from the list comprising neodymium (Nd), yttrium (Y), scandium (Sc), lanthanum (La), samarium (Sm), praseodymium (Pr), preferably wherein M is Nd and/or Y; preferably wherein M is Nd.

27. The process according to any one of statements 1 to 26 or in some embodiments, wherein the catalyst system comprises $(\text{Cp-CMe}_2\text{-Flu})\text{Y}(\text{C}_3\text{H}_5)(\text{THF})$, $(\text{Cp-CMe}_2\text{-Flu})\text{Y}(2\text{-Me-C}_3\text{H}_4)(\text{THF})$, $(\text{Cp-CMe}_2\text{-Flu})\text{Y}(2\text{-Me-C}_3\text{H}_4)(\text{THF})$, $(\text{Cp-CMe}_2\text{-Flu})\text{La}(\text{C}_3\text{H}_5)(\text{THF})$, $(\text{Cp-CMe}_2\text{-Flu})\text{Nd}(\text{C}_3\text{H}_5)(\text{THF})$, $(\text{Cp-CMe}_2\text{-Flu})\text{Sm}(\text{C}_3\text{H}_5)(\text{THF})$, $[(3\text{-}t\text{-Bu-C}_5\text{H}_3)\text{-CMe}_2\text{-Flu}]\text{YCl}(\text{THF})$, or $[(3\text{-}t\text{-Bu-C}_5\text{H}_3)\text{-CMe}_2\text{-Flu}]\text{Y}(\text{C}_3\text{H}_5)(\text{THF})$.

28. The process according to any one of statements 1 to 27 or in some embodiments, wherein the catalyst system comprises $[(\text{Cp})\text{-CMe}_2\text{-(2,7-}t\text{Bu-Flu)}]\text{Nd}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2](\text{THF})$.

29. The process according to any one of statements 1 to 28 or in some embodiments, wherein the catalyst system comprise a compound according to formula (III):



(III);

30. The process according to any one of statements 1 to 29 or in some embodiments, wherein the catalyst system comprises a cocatalyst.

31. The process according to any one of statements 1 to 30 or in some embodiments, wherein the cocatalyst is an alkylmagnesium of formula MgR^b_2 , wherein each R^b can be the same or different independently selected from halogens, alkoxy or alkyl.
32. The process according to any one of statements 1 to 31 or in some embodiments, wherein
5 said alkylmagnesium of formula MgR^b_2 is dialkylmagnesium.
33. The process according to any one of statements 1 to 32 or in some embodiments, wherein said alkylmagnesium of formula MgR^b_2 is selected from the group comprising: di-iso-butyl magnesium, di-ethyl magnesium, di-methyl magnesium, and methyl-ethyl magnesium, preferably wherein said alkylmagnesium of formula MgR^b_2 is di-butyl -magnesium.
- 10 34. The process according to any one of statements 1 to 33 or in some embodiments, wherein the monovinylidene aromatic polymer is a syndiotactic monovinylidene aromatic polymer.
35. The process according to any one of statements 1 to 34 or in some embodiments, wherein the monovinylidene aromatic polymer is a syndiotactic monovinylidene aromatic polymer having at least 70% rrrr hexads, preferably at least 75% rrrr hexads, preferably at least
15 80% rrrr hexads, preferably at least 85% rrrr hexads, preferably at least 90% rrrr hexads, preferably at least 95% rrrr hexads, determined by $^{13}\text{C}\{^1\text{H}\}$ NMR.
36. The process according to any one of statements 1 to 35 or in some embodiments, wherein the weight average molecular weight of the monovinylidene aromatic polymer is at least 10,000 Da, preferably at least 50,000 Da, preferably at least 100,000 Da, preferably at
20 least 150,000 Da, preferably at least 175,000 Da, preferably at least 200,000 Da, determined by high temperature gel permeation chromatography (GPC).
37. The process according to any one of statements 1 to 36 or in some embodiments, wherein the molecular weight distribution (weight average molecular weight (M_w) / number average molecular weight (M_n)) of the monovinylidene aromatic polymer is at least 1.0 to
25 at most 15.0, preferably at least 1.1 to at most 10.0, preferably at least 1.5 to at most 7.5, preferably at least 1.7 to at most 5.0, preferably at least 2.0 to at most 3.0, determined by high temperature gel permeation chromatography (GPC).
38. The process according to any one of statements 1 to 37 wherein the melting temperature (T_m) of the monovinylidene aromatic polymer is at least 150°C to at most 270°C , preferably at least 200°C to at most 265°C , preferably at least 220°C to at most 260°C , preferably at least 240°C to at most 255°C , preferably around 250°C , determined by
30 differential scanning calorimetry (DSC) with a heating and cooling rate of $10^\circ\text{C}/\text{min}$ in the range 30°C to $+300^\circ\text{C}$ in the second heating cycle.

39. The process according to any one of statements 1 to 38 or in some embodiments, wherein the monomer mixture comprises α -olefins, preferably wherein the monomer mixture consists of α -olefins and vinyl aromatic hydrocarbon monomers.
40. The process according to any one of statements 1 to 39 or in some embodiments, wherein the α -olefin is an olefin having from 2 to 8 carbon atoms.
41. The process according to any one of statements 1 to 40 or in some embodiments, wherein the monomer mixture in step a1 comprises ethylene.
42. The process according to any one of statements 1 to 41 or in some embodiments, wherein the α -olefin is ethylene.
43. The process according to any one of statements 1 to 42 or in some embodiments, wherein the elastomer, preferably the rubber-like elastomer, is a copolymer.
44. The process according to any one of statements 1 to 43 or in some embodiments, wherein the elastomer, preferably the rubber-like elastomer, is an ethylene-styrene copolymer.
45. The process according to any one of statements 1 to 44 or in some embodiments, wherein the elastomer, preferably the rubber-like elastomer, is an ethylene styrene random copolymer.
46. The process according to any one of statements 1 to 45 or in some embodiments, wherein the glass transition temperature (T_g) of the elastomer, preferably the rubber-like elastomer, is at most -10°C, preferably at most -15°C, preferably at most -18°C, preferably at most -20°C, preferably at most -25°C, preferably at most -27°C, preferably at most -30°C, determined by differential scanning calorimetry (DSC) with a heating and cooling rate of 10°C/min in the range -85°C to + 300°C.
47. The process according to any one of statements 1 to 46 or in some embodiments, wherein the vinyl aromatic hydrocarbon monomer content of the elastomer, preferably the rubber-like elastomer, is at least 5.0% by weight, preferably at least 10.0% by weight, preferably at least 20.0% by weight, preferably at least 30.0% by weight, preferably at least 35.0% by weight, wherein the % by weight is based on the total weight of the elastomer, preferably the rubber-like elastomer.
48. The process according to any one of statements 1 to 47 or in some embodiments, wherein the vinyl aromatic hydrocarbon monomer content of the elastomer, preferably the rubber-like elastomer, is at most 75.0% by weight, preferably at most 65.0% by weight, preferably at most 60.0% by weight, preferably at most 55.0% by weight, preferably at most 50.0%

by weight, wherein the % by weight is based on the total weight of the elastomer, preferably the rubber-like elastomer.

49. The process according to any one of statements 1 to 48 or in some embodiments, wherein the vinyl aromatic hydrocarbon monomer content of the elastomer, preferably the rubber-like elastomer, is at least 5.0% by weight to at most 75.0% by weight, preferably at least 10.0% by weight to at most 65.0% by weight, preferably at least 20.0% by weight to at most 60.0% by weight, preferably at least 35.0% by weight to at most 55.0% by weight, preferably at least 25.0% by weight to at most 50.0% by weight, wherein the % by weight is based on the total weight of the elastomer, preferably the rubber-like elastomer.
50. The process according to any one of statements 1 to 49 or in some embodiments, wherein the α -olefin monomer content together with the diene monomer content, which ever one is present, of the elastomer, preferably the rubber-like elastomer, is at least 25.0% by weight, preferably at least 35.0% by weight, preferably at least 45.0% by weight, preferably at least 55.0% by weight, preferably at least 60.0% by weight, wherein the % by weight is based on the total weight of the elastomer, preferably the rubber-like elastomer.
51. The process according to any one of statements 1 to 50 or in some embodiments, wherein the α -olefin monomer content together with the diene monomer content, which ever one is present, of the elastomer, preferably the rubber-like elastomer, is at most 95.0% by weight, preferably at most 90.0% by weight, preferably at most 80.0% by weight, preferably at most 75.0% by weight, preferably at most 65.0% by weight, wherein the % by weight is based on the total weight of the elastomer, preferably the rubber-like elastomer.
52. The process according to any one of statements 1 to 51 or in some embodiments, wherein the α -olefin monomer content together with the diene monomer content, which ever one is present, of the elastomer, preferably the rubber-like elastomer is at least 25.0% by weight to at most 90.0% by weight, preferably at least 35.0% by weight to at most 85.0% by weight, preferably at least 45.0% by weight to at most 80.0% by weight, preferably at least 55.0% by weight to at most 75.0% by weight, preferably at least 60.0% by weight to at most 65.0% by weight, wherein the % by weight is based on the total weight of the elastomer, preferably the rubber-like elastomer.
53. The process according to any one of statements 1 to 52 or in some embodiments, wherein the monovinylidene aromatic polymer composition comprises at least 70.0% by weight of the monovinylidene aromatic polymer, preferably at least 75.0% by weight of the monovinylidene aromatic polymer, preferably at least 80.0% by weight of the

monovinylidene aromatic polymer, preferably at least 85.0% by weight of the monovinylidene aromatic polymer, preferably at least 90.0% by weight of the monovinylidene aromatic polymer, preferably at least 95.0% by weight of the monovinylidene aromatic polymer, preferably at least 99.0% by weight of the monovinylidene aromatic polymer, wherein the % by weight is based on the total weight of the monovinylidene aromatic polymer composition.

54. The process according to any one of statements 1 to 53 or in some embodiments, wherein the monovinylidene aromatic polymer composition comprises at most 75.0% by weight of the monovinylidene aromatic polymer, preferably at most 80.0% by weight of the monovinylidene aromatic polymer, preferably at most 85.0% by weight of the monovinylidene aromatic polymer, preferably at most 90.0% by weight of the monovinylidene aromatic polymer, preferably at most 95.0% by weight of the monovinylidene aromatic polymer, preferably at most 99.0% by weight of the monovinylidene aromatic polymer, preferably at most 99.5% by weight of the monovinylidene aromatic polymer, wherein the % by weight is based on the total weight of the monovinylidene aromatic polymer composition.

55. The process according to any one of statements 1 to 54 or in some embodiments, wherein the monovinylidene aromatic polymer composition comprises at least 70.0% by weight to at most 99.5% by weight of the monovinylidene aromatic polymer, preferably at least 75.0% by weight to at most 99.0% by weight of the monovinylidene aromatic polymer, preferably at least 80.0% by weight to at most 95.0% by weight of the monovinylidene aromatic polymer, preferably at least 85.0% by weight to at most 90.0% by weight of the monovinylidene aromatic polymer, wherein the % by weight is based on the total weight of the monovinylidene aromatic polymer composition.

56. The process according to any one of statements 1 to 55 or in some embodiments, wherein the monovinylidene aromatic polymer composition comprises at least 1.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at least 5.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at least 10.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at least 15.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at least 20.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at least 25.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at least 30.0% by weight of the elastomer, preferably the rubber-like elastomer, wherein the % by weight is based on the total weight of the monovinylidene aromatic polymer composition.

57. The process according to any one of statements 1 to 56 or in some embodiments, wherein the monovinylidene aromatic polymer composition comprises at most 45.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at most 40.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at most 35.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at most 30.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at most 25.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at most 20.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at most 15.0% by weight of the elastomer, preferably the rubber-like elastomer, wherein the % by weight is based on the total weight of the monovinylidene aromatic polymer composition.
58. The process according to any one of statements 1 to 57 or in some embodiments, wherein the monovinylidene aromatic polymer composition comprises at least 1.0% by weight to at most 45.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at least 5.0% by weight to at most 40.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at least 10.0% by weight to at most 35.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at least 15.0% by weight to at most 30.0% by weight of the elastomer, preferably the rubber-like elastomer, preferably at least 20.0% by weight to at most 25.0% by weight of the elastomer, preferably the rubber-like elastomer, wherein the % by weight is based on the total weight of the monovinylidene aromatic polymer composition.
59. The process according to any one of statements 1 to 58 or in some embodiments, wherein the monovinylidene aromatic polymer composition may comprise from at least 0.0% by weight to at most 10.0% by weight third polymer, preferably from at least 0.1% by weight to at most 8.0% by weight third polymer, preferably from at least 0.2% by weight to at most 2.0% by weight third polymer, preferably from at least 0.3% by weight to at most 5.0% by weight third polymer, preferably from at least 0.4% by weight to at most 2.0% by weight third polymer, preferably from at least 0.5% by weight to at most 1.0% by weight third polymer, based on the total weight of the composition.
60. The process according to any one of statements 1 to 59 or in some embodiments, wherein the melting temperature (T_m) of the third polymer is at most 150°C, preferably at most 140°C, preferably at most 130°C, preferably at most 125°C, preferably at most 120°C, determined by differential scanning calorimetry (DSC) with a heating and cooling rate of 10°C/min in the range -85°C to + 300°C in the second heating cycle.
61. The process according to any one of statements 1 to 60 or in some embodiments, wherein the melting temperature (T_m) of the elastomer, preferably the rubber-like elastomer is at

least 100°C, preferably at least 105°C, preferably at least 110°C, preferably at least 115°C, preferably at least 120°C, determined by differential scanning calorimetry (DSC) with a heating and cooling rate of 10°C/min in the range -85°C to + 300°C in the second heating cycle.

- 5 62. The process according to any one of statements 1 to 61 or in some embodiments, wherein the melting temperature (T_m) of the third polymer is at least 100°C to at most 150°C, preferably at least 105°C to at most 140°C, preferably at least 110°C to at most 130°C, preferably at least 115°C to at most 125°C, preferably around 120°C, determined by differential scanning calorimetry (DSC) with a heating and cooling rate of 10°C/min in the
10 range -85°C to + 300°C in the second heating cycle.
63. The process according to any one of statements 1 to 62 or in some embodiments, wherein the monovinylidene aromatic polymer composition may comprise from at least 0.5% by weight to at most 25.0% by weight rubber-like elastomer, preferably from at least 1.0% by weight to at most 20.0% by weight rubber-like elastomer, preferably from at least 2.0% by weight to at most 15.0% by weight rubber-like elastomer, preferably from at least 3.0% by weight to at most 12.0% by weight rubber-like elastomer, preferably from at least 4.0% by weight to at most 10.0% by weight rubber-like elastomer, preferably from at least 5.0% by weight to at most 7.0% by weight rubber-like elastomer, based on the total weight of the composition.
- 15 64. The process according to any one of statements 1 to 63 or in some embodiments, wherein the monovinylidene aromatic polymer composition comprises nodules formed by the elastomer, preferably the rubber-like elastomer.
- 20 65. The process according to any one of statements 1 to 64 or in some embodiments, wherein the average diameter of the nodules is at most 10.0 μm , preferably at most 7.5 μm , preferably at most 5.0 μm .
- 25 66. Monovinylidene aromatic polymer composition comprising:
- an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or a diene; and,
 - 30 - a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer;
- characterized in that the composition is a chemical blend of the elastomer, preferably the rubber-like elastomer and the monovinylidene aromatic polymer, preferably a chemical

blend of the elastomer, preferably the rubber-like elastomer, the monovinylidene aromatic polymer and a third polymer.

67. Monovinylidene aromatic polymer composition according to statement 66 or in some embodiments, wherein the chemical blend is obtained by a process according to any one of statements 1 to 65 or in some embodiments.

68. Monovinylidene aromatic polymer composition according to statement 66 or 67 or in some embodiments, further defined by the characterizing portion of any one of statements 1 to 65 or in some embodiments.

69. Monovinylidene aromatic polymer composition comprising:

- an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or a diene;
- a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer; and,
- a third polymer, preferably a homopolymer of the α -olefin or the diene.

70. Monovinylidene aromatic polymer composition comprising:

- a third polymer, preferably a homopolymer of the α -olefin or the diene; and,
- a chemical blend of:
 - an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or a diene; and,
 - a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer.

71. A process for manufacturing the monovinylidene aromatic polymer composition according to statement 69 or 70 or in some embodiments, said process being a process according to any one of statements 1 to 65 or in some embodiments, further comprising the step of physical blending a third polymer in the monovinylidene aromatic polymer composition.

72. The process according to statement 71 or in some embodiments, wherein the step of physical blending comprises co-extrusion and/or melt blending.

73. Use of the same hemi-metallocene catalyst, a metallocene catalyst or post-metallocene catalyst in a catalyst system in at least two different polymerization reactions carried out in the same reactor.

74. Use according to statement 73 or in some embodiments, wherein at least one polymerization reaction is the polymerization of vinyl aromatic hydrocarbon monomer to form a monovinylidene aromatic polymer.

75. Use according to any one of statements 73 to 74 or in some embodiments, wherein at least one polymerization reaction is the polymerization of a monomer mixture, said monomer mixture comprising vinyl aromatic hydrocarbon monomer, and an α -olefin or a diene.

76. Use according to any one of statements 73 to 75 or in some embodiments, wherein:

- at least one polymerization reaction is the polymerization of vinyl aromatic hydrocarbon monomer to form a monovinylidene aromatic polymer; and,
- wherein at least one polymerization reaction is the polymerization of a monomer mixture, said monomer mixture comprises vinyl aromatic hydrocarbon monomer and an α -olefin or a diene.

77. Use according to any one of statements 73 to 76 or in some embodiments, further defined by the characterizing portion of any one of statements 1 to 72 or in some embodiments.

The invention relates to a process for manufacturing a monovinylidene aromatic polymer composition in a reactor, comprising the steps of:

- a1) providing a monomer mixture to the reactor, wherein said monomer mixture comprises an α -olefin or diene, and preferably wherein said monomer mixture further comprises at least one first vinyl aromatic hydrocarbon monomer;
- b1) providing a catalyst system to the reactor;
- a2) polymerizing at least part of the monomer mixture with the catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;
- c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor after the formation of the rubber-like elastomer; and,
- c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the same catalyst system under polymerization conditions in the reactor to form a monovinylidene aromatic polymer;

thereby obtaining the monovinylidene aromatic polymer composition.

The same inventive concept provides for a process for manufacturing a monovinylidene aromatic polymer composition in a reactor, comprising the steps of:

- c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor;
- b1) providing a catalyst system to the reactor;

- c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the catalyst system under polymerization conditions in the reactor to form a monovinylidene aromatic polymer;
- a1) providing a monomer mixture to the reactor, wherein said monomer mixture comprises an α -olefin or diene, and preferably wherein said monomer mixture further comprises at least one first vinyl aromatic hydrocarbon monomer; and,
- a2) polymerizing at least part of the monomer mixture with the same catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;

10 thereby obtaining the monovinylidene aromatic polymer composition.

As used herein, the terms “first vinyl aromatic hydrocarbon monomer” and “second vinyl aromatic hydrocarbon monomer” do not necessarily denote the order in which they are used. The first vinyl aromatic hydrocarbon monomer is used to prepare an elastomer, while the second vinyl aromatic hydrocarbon monomer is used to prepare a monovinylidene aromatic polymer. The “first vinyl aromatic hydrocarbon monomer” and “second vinyl aromatic hydrocarbon monomer” may be different or the same, preferably the same.

Such processes provide a monovinylidene aromatic polymer composition comprising monovinylidene aromatic polymer and elastomer, preferably rubber-like elastomer. The direct result of using the same catalyst system for both polymerization steps a2) and c2) is a chemical blend of the formed polymers, as the first formed polymer is present when the second polymer is formed. Preferably, upon solidification of the composition, the monovinylidene aromatic polymer in the composition may form a matrix, with nodules embedded in said matrix, the nodules being formed by the elastomer. It has been found that such monovinylidene aromatic polymer compositions are highly compatible with other polymers, so that a physical blend of the monovinylidene aromatic polymer composition and a third polymer can be achieved with less solvent and/or less heating and/or less kneading. In other words it is easier to obtain a more homogeneous blend of monovinylidene aromatic polymer composition and said third polymer. These effects are more pronounced, when said third polymer is at least partially made up of monomers that have been used in step c1) and/or a1)

30 In some embodiments, the term “providing” means “adding”.

Preferably, a solid is obtained at the end of the process, possible after a solidification step, e.g. cooling, precipitation or solvent evaporation. In some embodiments, the solid obtained at the end of the process may be grinded and extruded. In some embodiments, the solid can be compacted and/or extruded. In some embodiments, the solid does not have to undergo a

physical blend step to form a composition with homogeneously distributed nodules dispersed in a matrix.

In some embodiments, steps a2) and c2) are performed in the same reactor or reaction vessel. The term “reactor” or “reaction vessel” as used herein refers to any reactor suitable for polymerisation reactions. Examples of reactors are batch containers, pipe reactors, two or more serially connected reactors, preferably batch type reactors, continuous reactor, continuous stirred-tank reactors, plug flow reactors, fluidized bed reactors and the like.

In some embodiments, the reactor is a batch reactor.

In some embodiments, step a2) is performed in a first reactor vessel reactor, and step c2) is performed in the second reactor vessel, wherein the first reactor vessel and the second reactor vessel are serially connected to each other.

In some embodiments, step a1) b1) and/or c1) involves providing a solvent to the reactor. In some embodiments the solvent is added to the reactor in step a1) and b1), but preferably, solvent is provided to the reactor in step a1) and in step c1).

Suitable solvents comprise but are not limited to hydrocarbon solvents such as aliphatic, cycloaliphatic and aromatic hydrocarbon solvents, or halogenated versions of such solvents. 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 butane, isobutane, pentane, hexane, heptane, cyclopentane, cyclohexane, isohexane, cycloheptane, methyl cyclopentane, methyl cyclohexane, isooctane, benzene, toluene, xylene, chloroform, chlorobenzenes, tetrachloroethylene, dichloroethane and trichloroethane, preferably isohexane.

The term “polymer composition” as used herein refers to an assembly of at least two different polymers. The polymers may differ in

- being a homopolymer or a copolymer;
- the type of monomer residues in the polymer backbone;
- the relative quantities of different monomer residues in the backbone;
- the tacticity of the polymer;
- the branching pattern of the polymers;
- the degree of randomness the polymer;
- the organization of randomness in polymer;
- the arrangement of blocks in the polymer,
- glass transition temperature

- melt temperature, ...

The term “rubber-like elastomer” is an elastomer with have a tensile strength of at most 300 MPa, preferably at most 200 MPa, preferably at most 100 MPa, preferably at most 50 MPa, preferably at most 20 MPa, preferably at most 10 MPa, preferably at most 5 mPa, measured
5 according to ISO 37 (2017).

In some embodiments, the rubber like elastomer has an elongation at break of at least 200%, preferably at least 400%, preferably at least 500%, preferably at least 600%, preferably at least 700% preferably at least 800%, according to ASTM D412-16.

In some embodiments, the step b1) can be performed before, during, or after step a1) or c1);
10 whichever step a1) or c1) is performed first. This might provide some flexibility to the process in the order of adding compounds to the reactor. It may also save time.

In some embodiments, during step a2) the partial pressure of the α -olefin and/or diene in the reaction mixture is maintained.

In some embodiments, during step a2) the pressure in the reactor is maintained by controlling
15 the amount of α -olefin and/or diene in the reaction mixture. In some embodiments, the process comprises the step of at least partially, preferably completely, removing the α -olefin or diene from the reactor after step a2) and preferably before step c2), preferably before step c1). This avoids formation of copolymers with various degrees of incorporation of α -olefin or diene in the polymeric backbone. This may provide more control over the properties of the composition.

20 In some embodiments, the process comprises a single catalyst activation step, preferably before step a2) or step c2), whichever is performed first.

In some embodiments, a third polymer is formed in step a2), preferably a homopolymer, preferably a homopolymer of the α -olefin or the diene. In some embodiments, the catalyst system in step a2) provides:

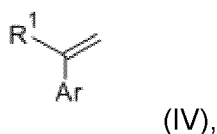
- 25 - the formation of a copolymer comprising vinyl aromatic hydrocarbon residues and α -olefin residues or diene residues; and,
- the formation of a homopolymer, comprising α -olefin residues or the diene residues.

This way a chemical blend is obtained comprising at least three different polymers, i.e. the elastomer, the monovinylidene aromatic polymer, and the third polymer, preferably
30 homopolymer. The presence of the third polymer, preferably a homopolymer, may provide a better compatibility between the elastomer and the monovinylidene aromatic polymer, or better

compatibility when the monovinylidene aromatic polymer composition is further blended with other polymers, for example polyolefins or polydienes, for example polyethylene.

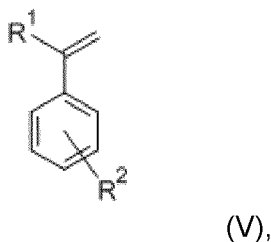
In some embodiments, the first vinyl aromatic hydrocarbon monomer is the same as the second vinyl aromatic hydrocarbon monomer. This may provide a good compatibility between the elastomer and the monovinylidene aromatic polymer. This might avoid repulsion at interfaces between the elastomer and the monovinylidene aromatic polymer. This might also favor the formation of more small nodules instead of fewer big nodules.

In some embodiments, the vinyl aromatic hydrocarbon monomer is a monomer according to formula (IV):



wherein R¹ is H, a halogen or a C₁-C₁₀ hydrocarbon chain.

In some embodiments, the vinyl aromatic hydrocarbon monomer is a monomer according to formula (V):



wherein R¹ is H, a halogen or a C₁-C₁₀ hydrocarbon chain; and, R² is H, a halogen or a C₁-C₁₀ hydrocarbon chain.

In some embodiments, R¹ is H. In some embodiments, R² is H.

In some embodiments, the vinyl aromatic hydrocarbon monomer is selected from the list comprising styrene, divinyl-benzene, alpha-methyl-styrene, para-methyl-styrene, ethyl-vinyl-benzene, vinyl-naphthalene, para-chloro-styrene and or mixtures thereof. Preferably, the vinyl aromatic hydrocarbon is styrene, meaning both R¹ and R² are H.

In some embodiments, the first and/or the second vinyl aromatic hydrocarbon monomer is styrene. Styrene is easily available, cheap, and has no functional groups after being built into the polymer backbone, therefore the obtained polymer is chemically rather non-reactive.

In some embodiments, the first and the second vinyl aromatic hydrocarbon monomer is styrene, and the α-olefin is ethylene. Both monomers are easily available, cheap, and have no

functional groups after being built into the polymer backbone, therefore the obtained polymer is chemically rather non-reactive. This combination may also provide a good compatibility between the elastomeric nodules and the styrene matrix.

5 In some embodiments, the catalyst system comprises a rare earth element, preferably a light rare earth element.

In some embodiments, the catalyst system comprises an element selected from the list comprising neodymium (Nd), yttrium (Y), scandium (Sc), lanthanum (La), samarium (Sm), praseodymium (Pr); preferably the catalyst system comprises Nd and/or Y; preferably the catalyst system comprises Nd.

10 In some embodiments, the catalyst system comprises a constrained geometry metallocene or a bridged metallocene.

In some embodiments, the catalyst system comprises a cocatalyst.

The term cocatalyst as used herein refers to a compound which can activate a catalyst.

15 In some embodiments, the monovinylidene aromatic polymer is a syndiotactic monovinylidene aromatic polymer.

The term "syndiotactic polymer" as used herein refers to a polymer having preferably at least 70% rrrrr hexads, preferably at least 75% rrrrr hexads, preferably at least 80% rrrrr hexads, preferably at least 85% rrrrr hexads, preferably at least 90% rrrrr hexads, preferably at least 95% rrrrr hexads, determined by $^{13}\text{C}\{^1\text{H}\}$ NMR.

20 In some embodiments, the composition comprises at least one homopolymer and at least one copolymer.

The term "copolymer" as used herein is intended to encompass polymers which consist essentially of repeat units deriving from at least two monomers or at least two co-monomers.

25 The terms "interpolymer" and "copolymer" as used herein, are synonyms and can be used interchangeably.

The term "homopolymer" as used herein is intended to encompass polymers which consist essentially of repeat units deriving from the same monomer. Homopolymers may, for example, comprise at least 99.8 % preferably 99.9 % by weight of repeats units derived from of that same monomer, the rest can be regarded as unavoidable imperfections.

In some embodiments, the composition comprises at least one syndiotactic homopolymer and at least one copolymer.

In some embodiments, the composition comprises at least one syndiotactic homopolymer and at least one copolymer, wherein the copolymer comprises the same monomer residue as the syndiotactic homopolymer. This might provide a good compatibility between the two polymers in the liquid state, having an influence on the size and or distribution of nodules. This might also minimizing repulsion effects on the interface between the nodules and matrix.

In some embodiments, the elastomer, preferably the rubber-like elastomer, is a copolymer, preferably a random copolymer.

In some embodiments, the elastomer, preferably the rubber-like elastomer is a thermoplastic elastomers, preferably selected from the list comprising polybutadiene, polyisoprene, polyisobutylene, styrene/butadiene rubber (SBR), styrene/isoprene rubber (SIR), styrene/isoprene/butadiene rubber (SIBR), styrene-butadiene-styrene block copolymer (SBS) preferably having a butadiene/styrene weight ratio of about 90/10 to about 40/60, a styrene-butadiene block copolymer (SB), hydrogenated styrene-butadiene-styrene block copolymer (SEBS), hydrogenated styrene-butadiene block copolymer (SEB), styrene-isoprene-styrene block copolymer (SIS), styrene-isoprene block copolymer (SI), hydrogenated styrene-isoprene block copolymer (SEP), hydrogenated styrene-isoprene-styrene block copolymer (SEPS), styrene-ethylene/butylene-ethylene block copolymer (SEBE), styrene-ethylene-styrene block copolymer (SES), ethylene-ethylene/butylene block copolymer (EEB), ethylene-ethylene/butylene/styrene block copolymer (hydrogenated BR-SBR block copolymer), styrene-ethylene/butylene-ethylene block copolymer (SEBE), ethylene-ethylene/butylene-ethylene block copolymer (EEBE) and mixtures thereof. Preferable the elastomer, preferably the rubber-like elastomer include hydrogenated styrene-butadiene-styrene block copolymer (SEBS), and random copolymers of styrene/butadiene (SBR), block copolymers containing α -olefin and vinyl substituted aromatic hydrocarbons contributed units or hydrogenated versions thereof or block copolymers containing conjugated diene monomers and vinyl substituted aromatic hydrocarbons contributed units or hydrogenated versions thereof.

Preferably, the elastomer, preferably the rubber-like elastomer, is a block copolymer comprising blocks of α -olefin residues and vinyl substituted aromatic hydrocarbons contributed units or hydrogenated versions thereof.

In some embodiments, the elastomer, preferably the rubber-like elastomer, is a copolymer comprising:

- α -olefin and/or diene residues; and,

- optionally vinyl aromatic hydrocarbon residues, e.g. styrene residues.

In some embodiments, the elastomer, preferably the rubber-like elastomer, is a copolymer comprising:

- α -olefin residues, e.g. ethylene residues, propylene residues, butene residues, preferably ethylene residues; and,
- vinyl aromatic hydrocarbon residues, e.g. styrene residues.

In some embodiments, the elastomer, preferably the rubber-like elastomer, is a block copolymer comprising:

- at least one first block, wherein the first block comprises:
 - α -olefin residues and/or diene residues; and
 - optionally vinyl aromatic hydrocarbon residues, e.g. styrene residues;and,
- at least one second block, wherein the second block comprises:
 - vinyl aromatic hydrocarbon residues, e.g. styrene residues; wherein preferably at least 90.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 95.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 98.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 99.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 99.9% of the residues in the second block are vinyl aromatic hydrocarbon residues.

In some embodiments, the elastomer, preferably the rubber-like elastomer, is a block copolymer comprising:

- at least one first block, wherein the first block comprises:
 - α -olefin residues, e.g. ethylene residues, propylene residues, butene residues, preferably ethylene residues; and,
 - vinyl aromatic hydrocarbon residues, e.g. styrene residues;and,
- at least one second block, wherein the second block comprises:
 - vinyl aromatic hydrocarbon residues, e.g. styrene residues; wherein preferably at least 90.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 95.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 98.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 99.0% of the residues in the second block are vinyl aromatic

hydrocarbon residues, preferably at least 99.9% of the residues in the second block are vinyl aromatic hydrocarbon residues.

In some embodiments, the at least one first block comprises a random copolymer of:

- vinyl aromatic hydrocarbon residues, e.g. styrene residues; and,
- α -olefin residues and/or diene residues.

In some embodiments, the at least one first block comprises a random copolymer of:

- vinyl aromatic hydrocarbon residues, e.g. styrene residues; and,
- α -olefin residues and/or diene residues;

and the at least one second block comprises:

- vinyl aromatic hydrocarbon residues, e.g. styrene residues; wherein preferably at least 90.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 95.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 98.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 99.0% of the residues in the second block are vinyl aromatic hydrocarbon residues, preferably at least 99.9% of the residues in the second block are vinyl aromatic hydrocarbon residues.

In some embodiments, the elastomer, preferably the rubber-like elastomer, comprises from at least 20.0% to at most 85.0% by weight α -olefin residues and/or diene residues, preferably from at least 25.0% to at most 75.0% by weight α -olefin residues and/or diene residues, preferably from at least 30.0% to at most 65.0% by weight α -olefin residues and/or diene residues, preferably from at least 35.0% to at most 55.0% by weight α -olefin residues and/or diene residues, preferably from at least 35.0% to at most 45.0% by weight α -olefin residues and/or diene residues, compared to the total weight of the elastomer, preferably the rubber-like elastomer.

In some embodiments, the elastomer, preferably the rubber-like elastomer comprises from at least 80.0% to at most 15.0% by weight vinyl aromatic hydrocarbon residues, preferably from at least 75.0% to at most 25.0% by weight vinyl aromatic hydrocarbon residues, preferably from at least 70.0% to at most 35.0% by weight vinyl aromatic hydrocarbon residues, preferably from at least 65.0% to at most 50.0% by weight vinyl aromatic hydrocarbon residues, preferably from at least 65.0% to at most 55.0% by weight vinyl aromatic hydrocarbon residues, compared to the total weight of the elastomer, preferably the rubber-like elastomer.

In some embodiments, the α -olefin monomers are a C3-C20 alpha-olefins, preferably selected from the list comprising ethylene, propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-

hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, and 1-eicosene.

In some embodiments, the elastomer, preferably the rubber-like elastomer has a glass transition temperature (T_g) of the elastomer, preferably the rubber-like elastomer, is at most 30°C, preferably at most 15°C, preferably at most 0°C, preferably at most -5°C, preferably at most -10°C, preferably at most -20°C, preferably at most -30°C, determined by differential scanning calorimetry (DSC) with a heating and cooling rate of 10°C/min in the range -85°C to + 300°C. This has as advantage that materials made from the composition are less brittle and have a higher impact resistance.

- 10 The invention also relates to a monovinylidene aromatic polymer composition comprising:
- an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or a diene; and,
 - a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer;
- 15 characterized in that the composition is a chemical blend of the elastomer, preferably the rubber-like elastomer and the monovinylidene aromatic polymer, preferably a chemical blend of the elastomer, preferably the rubber-like elastomer, the monovinylidene aromatic polymer and a third polymer.

In some embodiments, the chemical blend is obtained by a process disclosed herein. Preferred
20 embodiments of the process above are also preferred embodiments of the polymer composition.

In some embodiments, the monovinylidene aromatic polymer composition may comprise:

- from at least 0.5 weight % to at most 25.0 weight %, preferably from at least 1.0 weight % to at most 15.0 weight %, preferably from at least 2.0 weight % to at most 10.0 weight %,
25 %, preferably from at least 4.0 weight % to at most 7.0 weight % of the elastomer, preferably the rubber-like elastomer; and,
- from at least 70.0 weight % to at most 99.5 weight %, preferably from at least 85.0 weight % to at most 99.0 weight %, preferably from at least 90.0 weight % to at most 98.0 weight %, preferably from at least 93.0 weight % to at most 96.0 weight % of the
30 monovinylidene aromatic polymer;

wherein the weight % is relative to the total weight of the composition.

Preferably, the amount of each polymer in the monovinylidene aromatic polymer composition is determined after chemical separation.

In some embodiments, the composition may comprise a third polymer, which third polymer may comprise α -olefin and/or diene residues, wherein preferably at least 90.0% of the residues in the third polymer are α -olefin residues and/or diene residues, preferably at least 95.0% of the residues in the third polymer are α -olefin residues and/or diene residues, preferably at least 98.0% of the residues in the third polymer are α -olefin residues and/or diene residues, preferably at least 99.0% of the residues in the third polymer are α -olefin residues and/or diene residues, preferably at least 99.9% of the residues in the third polymer are α -olefin residues and/or diene residues.

In some embodiments, the monovinylidene aromatic polymer composition may comprise from at least 0.0% by weight to at most 5.0% by weight third polymer, preferably from at least 0.1% by weight to at most 4.0% by weight third polymer, preferably from at least 0.2% by weight to at most 2.0% by weight third polymer, preferably from at least 0.3% by weight to at most 1.0% by weight third polymer, preferably from at least 0.4% by weight to at most 0.8% by weight third polymer, preferably from at least 0.5% by weight to at most 0.7% by weight third polymer, based on the total weight of the composition.

In some embodiments, the third polymer is a homopolymer, preferably a homopolymer of the α -olefin or the diene, preferably a polyolefin, preferably ethylene.

In some embodiments, the monovinylidene aromatic polymer composition may comprise from at least 0.5% by weight to at most 25.0% by weight elastomer, preferably rubber-like elastomer, preferably from at least 1.0% by weight to at most 20.0% by weight elastomer, preferably rubber-like elastomer, preferably from at least 2.0% by weight to at most 15.0% by weight elastomer, preferably rubber-like elastomer, preferably from at least 3.0% by weight to at most 12.0% by weight elastomer, preferably rubber-like elastomer, preferably from at least 4.0% by weight to at most 10.0% by weight elastomer, preferably elastomer, preferably rubber-like elastomer, preferably from at least 5.0% by weight to at most 7.0% by weight elastomer, preferably rubber-like elastomer, based on the total weight of the composition.

In some embodiments, the monovinylidene aromatic polymer composition may comprise:

- an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or a diene;
- a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer; and,
- a third polymer, preferably a homopolymer of the α -olefin or the diene.

In some embodiments, the monovinylidene aromatic polymer composition may comprise:

- from at least 0.5 weight % to at most 25.0 weight % rubber-like elastomer;

- from at least 70.0 weight % to at most 99.5 weight % monovinylidene aromatic polymer; and,
 - from at least 0.0 weight % to at most 5.0 weight % third polymer;
- wherein the weight % is relative to the total weight of the composition.

5 In some embodiments, the monovinylidene aromatic polymer composition may comprise:

- a third polymer, preferably a homopolymer of the α -olefin or the diene; and,
- a chemical blend of:
 - an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or
 - 10 a diene; and,
 - a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer.

The invention also relates to the use of hemi-metallocene catalyst, a metallocene catalyst or post-metallocene catalyst in a catalyst system in at least two different polymerization reactions

15 carried out in the same reactor. Such use allows for a two-step-one-pot polymerization of a monovinylidene aromatic polymer composition, comprising a monovinylidene aromatic polymer chemically blended with an elastomer, preferably a rubber-like elastomer. In some embodiments, the use results in a process disclosed herein. Preferred embodiments of the process above are also preferred embodiments of the use.

20 In some embodiments, at least 60.0 %, preferably at least 80.0 %, preferably at least 90.0 %, preferably at least 95.0 %, preferably at least 99.0 %, preferably at least 99.5 %, preferably at least 99.9 % of the metallic centres in the catalyst system are rare earth elements, preferably a light rare earth elements.

In some embodiments, at least one polymerization reaction is the polymerization of vinyl

25 aromatic hydrocarbon monomer to form a monovinylidene aromatic polymer.

In some embodiments, at least one polymerization reaction is the polymerization of a monomer mixture, said monomer mixture comprises vinyl aromatic hydrocarbon monomer and an α -olefin or a diene.

In some embodiments, at least one polymerization reaction is the polymerization of vinyl

30 aromatic hydrocarbon monomer to form a monovinylidene aromatic polymer; and, at least one polymerization reaction is the polymerization of a monomer mixture, said monomer mixture comprises vinyl aromatic hydrocarbon monomer and an α -olefin or a diene.

EXAMPLES

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.

5 Test methods:

Chemical separation

A Kumagawa extractor was applied. 10 g of the ground composition was weighed in the thimble and 400 mL methylethyl ketone (MEK) was added to the round bottom flask. The round bottom flask was heated and the solids in the thimble were extracted with the boiling MEK for 10 5 hours. After extraction the heating was removed and after 1 h, when the MEK cooled to a lower temperature, the cooling water was stopped. The MEK from the still pot was evaporated and the residues were dried in an oven to give the MEK soluble fraction. The MEK insoluble fraction was recovered from the thimble and was also dried in the oven. The % by weight of the fractions were determined as shown in Equation 1 and Equation 2.

15 Equation 1

$$wt\% \text{ MEK soluble} = \frac{m_{MEKS}}{m_{TOT}} \cdot 100 [wt\%]$$

Equation 2

$$wt\% \text{ MEK insoluble} = \frac{m_{MEKIS}}{m_{TOT}} \cdot 100 [wt\%]$$

wherein:

20 m_{MEKS} = mass of MEK soluble fraction [g]

m_{MEKIS} = mass of MEK insoluble fraction [g]

m_{TOT} = mass of total sample [g]

▪ NMR of the copolymers

The microstructure of the copolymers, preferably styrene-ethylene copolymers, was 25 determined by $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy. The samples were prepared by dissolving a sufficient amount of polymer in 1,2,4-trichlorobenzene (TCB 99% spectroscopic grade) at 130°C with occasional agitations to homogenize the sample followed by the addition of hexadeuterobenzene (C6D6, spectroscopic grade) and a minor amount of hexamethyldisiloxane (HMDS, 99.5+%), with HMDS serving as internal standard. Typically,

about 200 to 300 mg of polymer was dissolved in 2.0 ml of TCB, followed by the addition of 0.5 ml of C₆D₆ and 2 to 3 drops of HMDS.

¹³C{¹H} NMR spectra were recorded on a Bruker 400 or 500 MHz with a 10 mm probe under the following conditions:

- 5 Pulse angle: 90°
- Pulse repetition time: 30s
- Spectral width: 25000 Hz centred at 95 ppm
- Data points: 64K
- Temperature: 130°C +/-2°C
- 10 Rotation: 15 Hz
- Scan numbers: 2000 – 4000
- Decoupling sequence: inverse-gated decoupling sequence to avoid NOE effect

- ¹³C{¹H} NMR spectra were obtained by Fourier Transform on 131K points after a light Gaussian multiplication. The spectra were phased, baseline corrected and the chemical shift scale was
- 15 referenced to the internal standard HMDS at 2.03 ppm.

Chemical shifts of signals were peak picked and peaks were integrated, for example as shown in Figure 1 and in Table 1 for a styrene-ethylene copolymer

The person skilled in the art can apply small adjustments on integration limits if necessary.

Chemical shifts are given at +/- 0.05 ppm.

- 20 Specifically for styrene-ethylene copolymers, the total amounts of incorporated styrene and ethylene were determined after considering the different chemical environment of the incorporated co-monomers in various sequences as shown in Figure 1. The resonances of the different carbon atoms in the various styrene-ethylene co-monomer sequences are listed in Table 1. To quantify the total amount of incorporated styrene, resonances at 148-144.5 ppm
- 25 (C_{Arq}) and 126.3 – 125.2 ppm (CH) were considered. As for the incorporated ethylene, the total aliphatic region was considered from which the total amount of styrene previously determined by the aromatic resonances was subtracted. The calculations are summarized in Equation 3- Equation 14, where "Int" stands for integrated area of the peaks at given resonances. The unit
- 30 "E1" is a measure for the randomness of the copolymer, as it represents the amount of single ethylene monomers which are flanked by styrene monomers at either sides in the copolymer backbone.

Equation 3

$$\text{Int}_{\text{total styrene}} = \frac{\text{Int(A)} + \text{Int(B)}}{2}$$

Equation 4

$$5 \quad \text{Int}_{\text{total ethylene}} = \frac{\text{Int(C)} + \text{Int(D)} + \text{Int(E)} + \text{Int(F)} + \text{Int(G)} + \text{Int(H)} - 2 \cdot \text{Int}_{\text{total styrene}}}{2}$$

Equation 5

$$\text{Int}_{\text{blocky styrene}} = \frac{\text{Int(A')} + \text{Int(C')} + \text{Int(D')}}{3}$$

Equation 6

$$\text{Int}_{\text{blocky ethylene}} = \frac{\text{Int(F')}}{2}$$

10 Equation 7

$$\text{Int}_{\text{E1}} = \text{Int(H)}$$

Equation 8

$$\text{mol\%}_{\text{styrene}} = \frac{\text{Int}_{\text{total styrene}}}{\text{Int}_{\text{total styrene}} + \text{Int}_{\text{total ethylene}}} \cdot 100$$

Equation 9

$$15 \quad \text{mol\%}_{\text{ethylene}} = \frac{\text{Int}_{\text{total ethylene}}}{\text{Int}_{\text{total styrene}} + \text{Int}_{\text{total ethylene}}} \cdot 100$$

Equation 10

$$\text{wt\%}_{\text{styrene}} = \frac{\text{Int}_{\text{total styrene}} \cdot M_{\text{styrene}}}{\text{Int}_{\text{total styrene}} \cdot M_{\text{styrene}} + \text{Int}_{\text{total ethylene}} \cdot M_{\text{ethylene}}} \cdot 100$$

Equation 11

$$\text{wt\%}_{\text{ethylene}} = \frac{\text{Int}_{\text{total ethylene}} \cdot M_{\text{ethylene}}}{\text{Int}_{\text{total styrene}} \cdot M_{\text{styrene}} + \text{Int}_{\text{total ethylene}} \cdot M_{\text{ethylene}}} \cdot 100$$

Equation 12

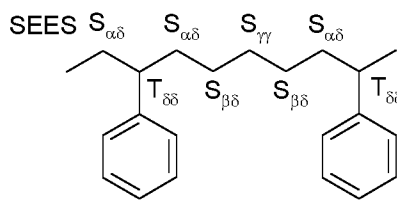
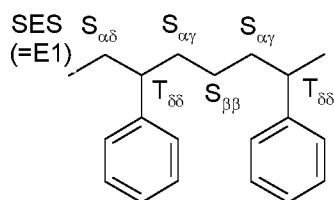
$$\text{blocky styrene\%} = \frac{\text{Int}_{\text{blocky styrene}}}{\text{Int}_{\text{total styrene}}} \cdot 100$$

Equation 13

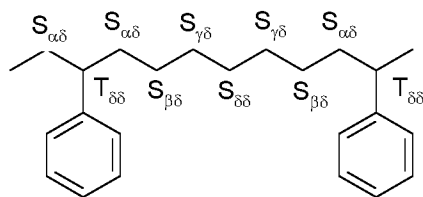
$$\text{blocky ethylene\%} = \frac{\text{Int}_{\text{blocky ethylene}}}{\text{Int}_{\text{total ethylene}}} \cdot 100$$

5 Equation 14

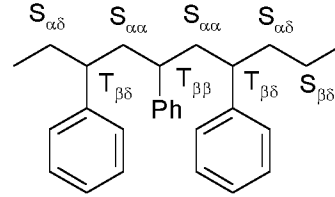
$$\text{E1\%} = \frac{\text{Int}_{\text{E1}}}{\text{Int}_{\text{total ethylene}}} \cdot 100$$



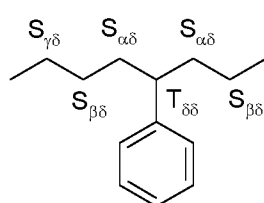
SEEEES



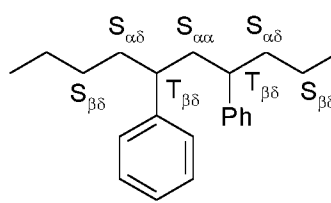
SSSE



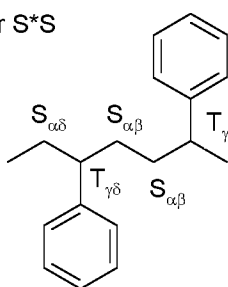
ESE



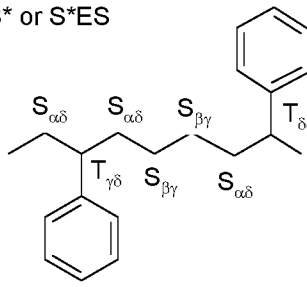
ESSE



SES* or S*S



SEES* or S*ES



Overview 1: differences in chemical environment for styrene ethylene copolymers

Signal	Integration zone in ^{13}C NMR / ppm	Annotation microstructure
A	148 - 144.5	C_{Arq}
A'	145.7 - 145.6	$\text{C}_{\text{Arq}}\text{SSS}$
B	126.3 - 125.2	CH
C	47.4 - 42.7	$\text{T}_{\delta\delta}, \text{T}_{\gamma\delta}, \text{T}_{\gamma\gamma}, \text{S}_{\alpha\alpha}, \text{T}_{\alpha\delta}, \text{T}_{\beta\gamma}$
C'	44.98 - 44.6	$\text{S}_{\alpha\alpha}, \text{SSS}$
D	42.3 - 40.9	$\text{T}_{\beta\beta}$
D'	41.58 - 41.49	$\text{T}_{\beta\beta}, \text{SSS}$
E	38.7 - 35.9	$\text{S}_{\alpha\delta}$ and/or $\text{S}_{\alpha\beta}, \text{S}_{\alpha\gamma}, \text{S}_{\alpha\delta}$
F	30.4 - 28.7	$\text{S}_{\delta\delta}, \text{S}_{\gamma\delta}, \text{S}_{\gamma\gamma}$
F'	30.04 - 29.98	$\text{S}_{\delta\delta}, \text{EEE}$
G	28.3 - 26.8	$\text{S}_{\beta\delta}, \text{S}_{\beta\gamma}$
H	26.4 - 24.6	$\text{S}_{\beta\beta}$
Signal	Integration zone in ^{13}C NMR / ppm	Annotation microstructure

Table 1: ^{13}C NMR integrations zones in chemical shifts of different carbon atoms present in the microstructures of the ethylene / styrene copolymerization products.

Tacticity determination by NMR

To determine the tacticity of the monovinylidene aromatic polymer, preferably the sPS matrix, styrene homopolymerization samples (sPS) were analyzed by ^{13}C NMR and the methylene region of the spectra was considered to integrate the signals of rrrr, rrrm and rrrmr hexads as well as other unassigned sequences, for styrene the various integration zones age given in Table 2. The tacticity of the monovinylidene aromatic polymer in the composition may be determined by synthesizing monovinylidene aromatic polymer in the absence of rubber-like elastomer, but under exact the same polymerization conditions as if the elastomer, preferably the rubber-like elastomer was present using the same catalyst. An example of the relevant section of the spectrum styrene homopolymer is shown in Figure 3.

Signal	Integration zone in ^{13}C NMR / ppm	Annotation microstructure
I	43.85 - 43.72	rrmr
J	45.37 - 44.47	rrrr
K	45.51 - 45.37	rrrm
L	46.51 - 46.31	rrmr
M	47.5 - 42.5	CH_2 total

Table 2: ^{13}C NMR integrations zones in chemical shifts of different carbon atoms present in the microstructures of styrene homopolymerization product sPS.

Equation 15

$$\%rrrrr = \frac{\text{Int(J)}}{\text{Int(M)}} \cdot 100$$

5 Differential scanning calorimetry (DSC)

DSC (differential scanning calorimetry) measurements were recorded on DSC 1 device by Mettler Toledo within the temperature range of -85 to 300 °C at a heating rate of 10 K/min. The DSC curves were analyzed by STAR^e software. T_g and T_m values were determined on the second heating segments.

10 Gel permeation chromatography (GPC)

GPC measurements were conducted in a PolymerChar instrument using an infrared detector. Materials were dissolved in 1,2,4-trichlorobenzene stabilized with BHT, and the temperature was kept at 160 °C for 1 h. The separation took place in three different columns and the samples were filtered prior to analysis. The calculation used the K and alpha for the sPS which were defined internally.

15 Scanning electron microscopy (SEM)

After cutting the samples, sheets of the materials for the analysis were smoothed in the cryo-microtome at -120 °C. Afterwards the samples were treated with a solution of RuO_4 for two hours and then they were left intact for 48 hours. The samples were glued onto a support and then they were metalized in carbon. Several images were taken at different magnification by detecting the back-scattered electrons (a function of contrast by chemical composition). The polyethylene rich phase is prone to the RuO_4 treatment and therefore the nodules containing polyethylene appear light on the pictures whereas the polystyrene parts remain dark. The average diameter is calculated as the average of all diameters measured at an angle ranging from 0° to 179°. In case the nodules were not clearly separated, values were determined on the agglomerated nodules.

Materials

Styrene-ethylene copolymers

This section relates to preparation of elastomers and monovinylidene aromatic polymers separately.

Styrene-ethylene copolymer 1 (S/E 1)

The catalyst $[(\text{Cp})\text{-CMe}_2\text{-(2,7-tBu-Flu)}]\text{Nd}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2](\text{THF})$ (0.05 mmol), was dissolved in 2.5 mL of MgBu_2 in heptane ($c = 0.99$ M determined by titration, supplied by Sigma Aldrich) in a gas tight syringe. 40 mL styrene, which was degassed with Ar and stored over
 5 molecular sieves (13-X) for the removal of oxygen and water, was added to the 1 L stainless steel reactor through a bed of alumina beads. The filtration was facilitated by pressure difference and the styrene was introduced to the reactor via a Teflon tube. Using pressure difference of N_2 , 150 mL of isohexane ($i\text{C}_6$) was added to the reactor from a solvent tank. The reactor temperature was already at $T = 100$ °C. The catalyst was added to a small addition
 10 funnel attached to the reactor. After the catalyst was added to the reactor, 60 mL $i\text{C}_6$ was used to wash the addition funnel and then stirrer was started at 200 rpm. 60 bar of ethylene was added. The temperature was set to $T = 100$ °C for 30 min reaction time.

After 30 min polymerization the stirring speed was reduced to 100 rpm and the valve to the vent was slowly opened to release the ethylene from the reactor. The reactor was cooled and
 15 the polymer slurry was poured into an $i\text{PrOH}$ solution of Irganox 1010. The rubbery product was filtered and dried in the vacuum oven. Further details are provided in Table 3.

Styrene-ethylene copolymer 2 (S/E 2)

The procedure in S/E 1 was followed with a stirring speed of 500 rpm. Further details are provided in Table 3.

Styrene-ethylene copolymer 3 (S/E 3)

The procedure in S/E 1 was followed with a stirring speed of 800 rpm. Further details are provided in Table 3.

	S/E 1	S/E 2	S/E 3
$m_{\text{cat}} / \text{mg}$	40	40	40
$V_{\text{sty}} / \text{mL}$	40	40	40
$V_{i\text{C}_6} / \text{mL}$	210	210	210
$V_{\text{MgBu}_2} / \text{mL}$	2.5	2.5	2.5
$p_{\text{C}_2} / \text{bar}$	60	60	60
$T / ^\circ\text{C}$	100	100	100
stirring / rpm	800	500	200
t / min	30	30	30
activity / $\text{g} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$	775	675	745
$\text{C}_2 / \text{mol}\%$	70	75.8	72.7

C ₂ / wt%	38.6	45.7	41.8
blocky C ₂ / %	22.7	26	26.7
E1 / \%	9.1	8.3	7.5
blocky PS / \%	8.5	2.8	4.3
T _g	-18.9	-18.6	-20.8
T _{m1}	126	126	126
T _{m2}	n. d.	n. d.	n. d.

Table 3: Conditions of styrene – ethylene copolymerizations and the properties of the obtained products

Polystyrene

Polystyrene 1 (sPS 1)

5 The catalyst $[(\text{Cp})\text{-CMe}_2\text{-(2,7-tBu-Flu)}]\text{Nd}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2](\text{THF})$ (0.05 mmol), was dissolved in 1.5 mL of MgBu_2 in heptane ($c = 0.99$ M determined by titration, supplied by Sigma Aldrich) in a gas tight syringe. 250 mL styrene, which was degassed with Ar and stored over molecular sieves (13-X) for the removal of oxygen and water, was added to the 1 L stainless steel reactor through a bed of alumina beads. The filtration was facilitated by pressure difference and the styrene was introduced to the reactor via a Teflon tube. The reactor temperature was already at $T = 80$ °C. The catalyst was added to a small addition funnel attached to the reactor. After the catalyst was added to the reactor the stirrer was started at 200 rpm. After 30 min polymerization the stirring speed was reduced to 100 rpm and the valve to the vent was opened to release any overpressure from the reactor. The reaction was quenched by adding compressed air to the reactor. Then the mixture was cooled to room temperature. The polymer slurry was poured into an *i*PrOH solution of Irganox 1010. The slurry was filtered and the fluff was dried in the vacuum oven. Further details are provided in Table 4. The tacticity measured for this sPS may be used as the tacticity of the sPS component in the inventive examples, wherever similar polymerisation conditions are used.

20 Polystyrene 2 (sPS 2)

The catalyst $[(\text{Cp})\text{-CMe}_2\text{-(2,7-tBu-Flu)}]\text{Nd}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2](\text{THF})$ (0.05 mmol), was dissolved in 3.0 mL of MgBu_2 in heptane ($c = 0.99$ M determined by titration, supplied by Sigma Aldrich) in a gas tight syringe. 250 mL styrene, which was degassed with Ar and stored over molecular sieves (13-X) for the removal of oxygen and water, was added to the 1 L stainless steel reactor through a bed of alumina beads. The filtration was facilitated by pressure difference and the styrene was introduced to the reactor via a Teflon tube. Using pressure difference of N_2 , 150 mL of *i*C₆ was added to the reactor from a solvent tank. The reactor

temperature was already at $T = 100\text{ }^{\circ}\text{C}$. The catalyst was added to a small addition funnel attached to the reactor. After the catalyst was added to the reactor, 50 mL $i\text{C}_6$ was used to wash the addition funnel and then stirrer was started at 200 rpm. After 90 min polymerization the stirring speed was reduced to 100 rpm and the valve to the vent was opened to release any overpressure from the reactor. Then the mixture was cooled to room temperature. The reaction was quenched by adding compressed air to the reactor. Then the mixture was cooled to room temperature. The polymer slurry was poured into an $i\text{PrOH}$ solution of Irganox 1010. The slurry was filtered and the fluff was dried in the vacuum oven. Further details are provided in Table 4. The tacticity measured for this sPS may be used as the tacticity of the sPS component in the inventive examples, wherever similar polymerisation conditions are used.

	sPS1	sPS2
$m_{\text{cat}} / \text{mg}$	40	40
$V_{\text{sty}} / \text{mL}$	250	250
$V_{i\text{C}_6} / \text{mL}$	0	200
$V_{\text{MgBu}_2} / \text{mL}$	1.5	3.0
$T / ^{\circ}\text{C}$	80	100
stirring / rpm	200	200
t / min	30	90
activity $/\text{g}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$	3058	1615
rrrrr / %	83	86
T_g	90	90
T_{m2}	257	254

Table 4: Conditions of styrene homopolymerizations and the properties of the obtained products

Compositions (sPS + S/E)

This section relates to preparation of monovinylidene aromatic polymers compositions according to different embodiments of the invention.

Inventive Example 1

The catalyst $([(\text{Cp})\text{-CMe}_2\text{-(2,7-tBu-Flu)}]\text{Nd}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2](\text{THF}))$ (0.05 mmol), was dissolved in 2.5 mL of MgBu_2 in heptane ($c = 0.99\text{ M}$ determined by titration, supplied by Sigma Aldrich) in a gas tight syringe. 40 mL styrene, which was degassed with Ar and stored over molecular sieves (13-X) for the removal of oxygen and water, was added to the 1 L stainless steel reactor through a bed of alumina beads. The filtration was facilitated by pressure difference and the styrene was introduced to the reactor via a Teflon tube. Using pressure

difference of N₂, 150 mL of *i*C₆ was added to the reactor from a solvent tank. The reactor temperature was already at *T* = 100 °C. The catalyst was added to a small addition funnel attached to the reactor. After the catalyst was added to the reactor, 60 mL *i*C₆ was used to wash the addition funnel and then stirrer was started at 800 rpm. 60 bar of ethylene was added and maintained during the first polymerisation. The temperature was set to *T* = 100 °C for 30 min reaction time. After 30 min polymerization the stirring speed was reduced to 100 rpm and the valve to the vent was slowly opened to release the ethylene from the reactor. The reactor was flushed with N₂. Afterwards 250 mL of styrene was added to the reactor passing through an alumina column. The temperature was kept at 100 °C for 60 min and the reaction mixture was stirred at 800 rpm. After 60 min the reaction was quenched by adding 40-80 mL of isopropanol (iPrOH) to the reactor. The reactor was left to cool down. The polymer slurry was poured into an iPrOH solution of Irganox 1010. The slurry was filtered and the fluff was dried in the vacuum oven. The fluff was melt-processed before carrying out the SEM experiments. Further details are provided in Table 5.

Inventive Example 2

The procedure in Inventive Example 1 was followed with a stirring speed of 200 rpm in both polymerization steps. Further details are provided in Table 5.

Inventive Example 3

The catalyst ([*(Cp)*-CMe₂-(2,7-*t*Bu-Flu)]Nd[1,3-C₃H₃(SiMe₃)₂](THF)) (0.05 mmol), was dissolved in 2.5 mL of MgBu₂ in heptane (*c* = 0.99 M determined by titration, supplied by Sigma Aldrich) in a gas tight syringe. 40 mL styrene, which was degassed with Ar and stored over molecular sieves (13-X) for the removal of oxygen and water, was added to the 1 L stainless steel reactor through a bed of alumina beads. The filtration was facilitated by pressure difference and the styrene was introduced to the reactor via a Teflon tube. Using pressure difference of N₂, 150 mL of *i*C₆ was added to the reactor from a solvent tank. The reactor temperature was already at *T* = 100 °C. The catalyst was added to a small addition funnel attached to the reactor. After the catalyst was added to the reactor, 60 mL *i*C₆ was used to wash the addition funnel and then stirrer was started at 200 rpm. 50 bar of ethylene was added and maintained during polymerisation. The temperature was set to *T* = 100 °C for 30 min reaction time. After 30 min polymerization the stirring speed was reduced to 100 rpm and the valve to the vent was slowly opened to release the ethylene from the reactor. The reactor was flushed with N₂.

Afterwards 250 mL of styrene was added to the reactor passing through an alumina column. The temperature was kept at 80 °C for 40 min and the reaction mixture was stirred at 800 rpm.

After 40 min the reaction was quenched by adding 40-80 mL of iPrOH to the reactor. The reactor was left to cool down. The polymer slurry was poured into an iPrOH solution of Irganox 1010. The slurry was filtered and the fluff was dried in the vacuum oven. The fluff was melt-processed before carrying out the SEM experiments. Further details are provided in Table 5.

5 Inventive Example 4

The catalyst $[(\text{Cp})\text{-CMe}_2\text{-(2,7-tBu-Flu)}]\text{Nd}[1,3\text{-C}_3\text{H}_3(\text{SiMe}_3)_2](\text{THF})$ (0.05 mmol), was dissolved in 2.5 mL of MgBu_2 in heptane ($c = 0.99$ M determined by titration, supplied by Sigma Aldrich) in a gas tight syringe. 40 mL styrene, which was degassed with Ar and stored over molecular sieves (13-X) for the removal of oxygen and water, was added to the 1 L stainless steel reactor through a bed of alumina beads. The filtration was facilitated by pressure difference and the styrene was introduced to the reactor via a Teflon tube. Using pressure difference of N_2 , 150 mL of $i\text{C}_6$ was added to the reactor from a solvent tank. The reactor temperature was already at $T = 100^\circ\text{C}$. The catalyst was added to a small addition funnel attached to the reactor. After the catalyst was added to the reactor, 60 mL $i\text{C}_6$ was used to wash the addition funnel and then stirrer was started at 200 rpm. 50 bar of ethylene was added and maintained during the first polymerisation. The temperature was set to $T = 100^\circ\text{C}$ for 30 min reaction time. After 30 min polymerization the stirring speed was reduced to 100 rpm and the valve to the vent was slowly opened to release the ethylene from the reactor. The reactor was flushed with N_2 .

Afterwards 150 mL of styrene was added to the reactor passing through an alumina column. 100 mL of $i\text{C}_6$ was added by pressure difference of N_2 from a solvent tank. The temperature was kept at 80°C for 40 min and the reaction mixture was stirred at 800 rpm. After 40 min the reaction was quenched by adding 40-80 mL of iPrOH to the reactor. The reactor was left to cool down. The polymer slurry was poured into an iPrOH solution of Irganox 1010. The slurry was filtered and the fluff was dried in the vacuum oven. The fluff was melt-processed before carrying out the SEM experiments. Further details are provided in Table 5.

Inventive Example 5

The procedure in Inventive Example 4 was followed with an ethylene pressure of 60 bar in the first and a reaction temperature of 60°C in the second polymerization step. Further details are provided in Table 5.

Inventive Example 6

The procedure in Inventive Example 4 was followed with an ethylene pressure of 60 bar in the first polymerization step. Further details are provided in Table 5.

step		Inv. Ex 1	Inv. Ex 2	Inv. Ex 3	Inv. Ex 4	Inv. Ex 5	Inv. Ex 6
<i>b1</i>	m_{cat} / mg	40	40	40	40	40	40
<i>a1</i>	V_{sty} / mL	40	40	40	40	40	40
<i>a1</i>	V_{IC6} / mL	210	210	210	210	210	210
<i>b1</i>	V_{MgBu2} / mL	2.5	2.5	2.5	2.5	2.5	2.5
<i>a1</i>	p_{C2} / bar	60	60	50	50	60	60
<i>a2</i>	T / °C	100	100	100	100	100	100
<i>a2</i>	stirring / rpm	800	200	200	200	200	200
<i>a2</i>	t / min	30	30	30	30	30	30
	t_{vent} / min	2.5	2.5	2.5	2.5	2.5	2.5
<i>c1</i>	V_{sty} / mL	250	250	250	150	150	150
<i>c1</i>	V_{IC6} / mL	0	0	0	100	100	100
<i>c2</i>	T / °C	100	100	80	80	60	80
<i>c2</i>	stirring / rpm	800	200	800	800	800	800
<i>c2</i>	t / min	60	60	40	40	40	40
	activity / $\text{g} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$	796	1621	3827	2265	551	756
	C_2 / mol%	24	32.5	9.3	19.3	42.3	35.0
	C_2 / wt%	7.6	11.5	2.7	6.1	16.5	12.6
	blocky C_2 / %	56.1	45.3	25.7	20.7	24.6	29.7
	E1 / %	2.5	4.4	16.9	15.1	10.5	14.9
	blocky PS / %	67.5	64.1	61.9	61.8	32.5	37.7
	T_g	n. d.	n. d.	76	60.5	-22.5	n. d.
	T_{m1}	125.6	125.3	126.5	127	129	126
	T_{m2}	257.6	257.8	253	255	238	225
	MEK sol / wt%	10	12	13	26	73	67
Composition of final product							
	S/E / wt%	6.4	9.0	2.7	8.7	33.1	26.7
	aPS / wt%	5.6	5.1	10.2	17.4	39.7	40.7
	PE / wt%	3.3	5.3	1.3	2.1	4.3	3.5
	sPS / wt%	84.7	80.6	85.8	71.8	22.9	29.1

Table 5: Conditions of styrene – ethylene copolymerizations followed by styrene homopolymerization and the properties of the obtained products

SEM images

After cutting the samples, sheets of the materials for the analysis were smoothed in the cryomicrotome at -120 °C. Afterwards the samples were treated with a solution of RuO_4 for

two hours and then they were left intact for 48 hours. The samples were glued onto a support and then they were metalized in carbon. Several images were taken at different magnification by detecting the back-scattered electrons (a function of contrast by chemical composition). The polyethylene rich phase is prone to the RuO₄ treatment and therefore the nodules containing polyethylene appear light on the pictures whereas the polystyrene parts remain dark.

Figure 2a depicts a SEM image of a physical blend of syndiotactic polystyrene with a styrene-ethylene copolymer. The physical blend comprises 10 wt% of S/E1 and 90 wt% of sPS1 and was prepared by extrusion using a MiniLab twin screw extruder by Haake at 270°C in corotatory configuration.

10 Figure 2b depicts a SEM image of Inventive Example 1, showing a more homogeneous distribution of the E/S nodules in the sPS matrix than Figure 2a. The E/S nodules are also more homogeneous in size than in Figure 2a.

Figure 2c depicts a SEM image of Inventive Example 2, showing a more homogeneous distribution of the E/S nodules in the sPS matrix than Figure 2a. The E/S nodules are also
15 more homogeneous in size than in Figure 2a.

Claims

1. A process for manufacturing a monovinylidene aromatic polymer composition in a reactor, comprising the steps of:
 - a1) providing a monomer mixture to the reactor, wherein said monomer mixture comprises an α -olefin or diene, and wherein said monomer mixture further comprises at least one first vinyl aromatic hydrocarbon monomer;
 - b1) providing a catalyst system to the reactor;
 - a2) polymerizing at least part of the monomer mixture with the catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;
 - c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor after the formation of the rubber-like elastomer; and,
 - c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the same catalyst system under polymerization conditions in the reactor to form a monovinylidene aromatic polymer;thereby obtaining the monovinylidene aromatic polymer composition.
2. A process for manufacturing a monovinylidene aromatic polymer composition in a reactor, comprising the steps of:
 - c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor;
 - b1) providing a catalyst system to the reactor;
 - c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the catalyst system under polymerization conditions in the reactor to form a monovinylidene aromatic polymer;
 - a1) providing a monomer mixture to the reactor, wherein said monomer mixture comprises an α -olefin or diene, and wherein said monomer mixture further comprises at least one first vinyl aromatic hydrocarbon monomer; and,
 - a2) polymerizing at least part of the monomer mixture with the same catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;thereby obtaining the monovinylidene aromatic polymer composition.
3. The process according to any one of claims 1 or 2, wherein the process comprises the step of at least partially removing the α -olefin or diene from the reactor after step a2) and preferably before step c2), preferably before step c1).

4. The process according to any one of claims 1 to 3, wherein the first vinyl aromatic hydrocarbon monomer is the same as the second vinyl aromatic hydrocarbon monomer.
5. The process according to any one of claims 1 to 4, wherein the first and/or the second vinyl aromatic hydrocarbon monomer is styrene.
6. The process according to any one of claims 1 to 5, wherein the monomer mixture in step a1 comprises ethylene.
7. The process according to any one of claims 1 to 6, wherein the catalyst system comprises a rare earth element, preferably a light rare earth element.
8. The process according to any one of claims 1 to 7, wherein the catalyst system comprises an element selected from the list comprising neodymium (Nd), yttrium (Y), scandium (Sc), lanthanum (La), samarium (Sm), praseodymium (Pr); preferably the catalyst system comprises Nd and/or Y; preferably the catalyst system comprises Nd.
9. The process according to any one of claims 1 to 8, wherein the catalyst system comprises a metallocene catalyst component of the general formula (II),



wherein,

Cp is a cyclopentadienyl, optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, a hydrocarbyl having 1 to 20 carbon atoms, and SiR''_3 wherein R'' is 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;

Flu is a fluorenyl, optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, a hydrocarbyl having 1 to 20 carbon atoms, and SiR'''_3 wherein R''' is 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;

M is a rare earth metal;

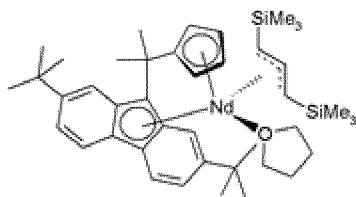
ether is a donor solvent molecule;

R'' is a structural bridge between Cp and Flu (9-position) imparting stereorigidity to the component;

each R' is the same or different, and is hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms; and,

wherein n is 0, 1 or 2.

10. The process according to any one of claims 1 to 9, wherein the catalyst system comprise a compound according to formula (III):



(III).

11. The process according to any one of claims 1 to 10, wherein the monovinylidene aromatic polymer is a syndiotactic monovinylidene aromatic polymer having at least 70% rrrrr hexads, preferably at least 75% rrrrr hexads, preferably at least 80% rrrrr hexads, preferably at least 85% rrrrr hexads, preferably at least 90% rrrrr hexads, preferably at least 95% rrrrr hexads, determined by $^{13}\text{C}\{^1\text{H}\}$ NMR.

12. Monovinylidene aromatic polymer composition comprising:

- an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or a diene; and,
- a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer,

characterized in that the composition is a chemical blend of the elastomer, preferably the rubber-like elastomer and the monovinylidene aromatic polymer, preferably a chemical blend of the elastomer, preferably the rubber-like elastomer, the monovinylidene aromatic polymer and a third polymer; and,

wherein the chemical blend is obtained by a process according to any one of claims 1 to 11.

13. Monovinylidene aromatic polymer composition comprising:

- a third polymer, preferably a homopolymer of the α -olefin or the diene; and,
- a chemical blend of:
 - an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or a diene; and,
 - a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer.

14. A process for manufacturing the monovinylidene aromatic polymer composition according to claim 13, said process being a process according to any one of claims 1 to 11, further comprising the step of physical blending a third polymer in the monovinylidene aromatic polymer composition.

5 15. Use of hemi-metallocene catalyst, a metallocene catalyst or post-metallocene catalyst in a catalyst system in at least two different polymerization reactions carried out in the same reactor, wherein:

- at least one polymerization reaction is the polymerization of vinyl aromatic hydrocarbon monomer to form a monovinylidene aromatic polymer; and,
- 10 - wherein at least one polymerization reaction is the polymerization of a monomer mixture, said monomer mixture comprises vinyl aromatic hydrocarbon monomer and an α -olefin or a diene;

wherein at least 60.0 %, preferably at least 80.0 %, preferably at least 90.0 %, preferably at least 95.0 %, preferably at least 99.0 %, preferably at least 99.5 %, preferably at least 99.9 % of the metallic centres in the catalyst system are rare earth elements, preferably a light rare earth elements,

15 preferably in a process according to any one of claims 1 to 11.

AMENDED CLAIMS
received by the International Bureau
on 02 June 2020 (02.06.2020)

1. A process for manufacturing a monovinylidene aromatic polymer composition in a reactor, comprising the steps of:
 - a1) providing a monomer mixture to the reactor, wherein said monomer mixture
5 comprises an α -olefin or diene, and wherein said monomer mixture further comprises at least one first vinyl aromatic hydrocarbon monomer;
 - b1) providing a catalyst system to the reactor;
 - a2) polymerizing at least part of the monomer mixture with the catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a
10 rubber-like elastomer;
 - c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor after the formation of the rubber-like elastomer; and,
 - c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the same catalyst system under polymerization conditions in the reactor to
15 form a monovinylidene aromatic polymer;thereby obtaining the monovinylidene aromatic polymer composition.
2. A process for manufacturing a monovinylidene aromatic polymer composition in a reactor, comprising the steps of:
 - c1) providing at least a second vinyl aromatic hydrocarbon monomer to the reactor;
 - 20 b1) providing a catalyst system to the reactor;
 - c2) polymerizing at least part of the second vinyl aromatic hydrocarbon monomer with the catalyst system under polymerization conditions in the reactor to form a monovinylidene aromatic polymer;
 - a1) providing a monomer mixture to the reactor, wherein said monomer mixture
25 comprises an α -olefin or diene, and wherein said monomer mixture further comprises at least one first vinyl aromatic hydrocarbon monomer; and,
 - a2) polymerizing at least part of the monomer mixture with the same catalyst system under polymerization conditions in the reactor to form an elastomer, preferably a rubber-like elastomer;
 - 30 thereby obtaining the monovinylidene aromatic polymer composition.
3. The process according to any one of claims 1 or 2, wherein the process comprises the step of at least partially removing the α -olefin or diene from the reactor after step a2) and preferably before step c2), preferably before step c1).

4. The process according to any one of claims 1 to 3, wherein the first vinyl aromatic hydrocarbon monomer is the same as the second vinyl aromatic hydrocarbon monomer.
5. The process according to any one of claims 1 to 4, wherein the first and/or the second vinyl aromatic hydrocarbon monomer is styrene.
6. The process according to any one of claims 1 to 5, wherein the monomer mixture in step a1 comprises ethylene.
7. The process according to any one of claims 1 to 6, wherein the catalyst system comprises a rare earth element, preferably a light rare earth element.
8. The process according to any one of claims 1 to 7, wherein the catalyst system comprises an element selected from the list comprising neodymium (Nd), yttrium (Y), scandium (Sc), lanthanum (La), samarium (Sm), praseodymium (Pr); preferably the catalyst system comprises Nd and/or Y; preferably the catalyst system comprises Nd.
9. The process according to any one of claims 1 to 8, wherein the catalyst system comprises a metallocene catalyst component of the general formula (II),



wherein,

Cp is a cyclopentadienyl, optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, a hydrocarbyl having 1 to 20 carbon atoms, and SiR''_3 wherein R'' is 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;

Flu is a fluorenyl, optionally substituted with one or more substituents each independently selected from the group consisting of halogen, hydrosilyl, a hydrocarbyl having 1 to 20 carbon atoms, and SiR'''_3 wherein R''' is 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;

M is a rare earth metal;

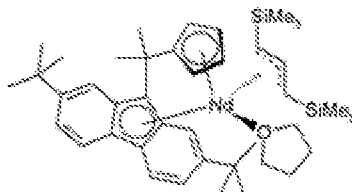
ether is a donor solvent molecule;

R'' is a structural bridge between Cp and Flu (9-position) imparting stereorigidity to the component;

each R' is the same or different, and is hydrogen or a hydrocarbyl having from 1 to 20 carbon atoms; and,

wherein n is 0, 1 or 2.

10. The process according to any one of claims 1 to 9, wherein the catalyst system comprise a compound according to formula (III):



(III).

- 5 11. The process according to any one of claims 1 to 10, wherein the monovinylidene aromatic polymer is a syndiotactic monovinylidene aromatic polymer having at least 70% rrrr hexads, preferably at least 75% rrrr hexads, preferably at least 80% rrrr hexads, preferably at least 85% rrrr hexads, preferably at least 90% rrrr hexads, preferably at least 95% rrrr hexads, determined by $^{13}\text{C}\{^1\text{H}\}$ NMR.
- 10 12. Monovinylidene aromatic polymer composition comprising:
- an elastomer, preferably a rubber-like elastomer, which is preferably the polymerization product of vinyl aromatic hydrocarbon monomer and an α -olefin or a diene; and,
 - a monovinylidene aromatic polymer, which is the polymerization product of vinyl aromatic hydrocarbon monomer,
- 15 characterized in that the composition is a chemical blend of the elastomer, preferably the rubber-like elastomer and the monovinylidene aromatic polymer, preferably a chemical blend of the elastomer, preferably the rubber-like elastomer, the monovinylidene aromatic polymer and a third polymer; and,
- 20 wherein the chemical blend is obtained by a process according to any one of claims 1 to 11.
13. Use of hemi-metallocene catalyst, a metallocene catalyst or post-metallocene catalyst in a catalyst system in at least two different polymerization reactions carried out in the same reactor, wherein:
- 25
- at least one polymerization reaction is the polymerization of vinyl aromatic hydrocarbon monomer to form a monovinylidene aromatic polymer; and,
 - wherein at least one polymerization reaction is the polymerization of a monomer mixture, said monomer mixture comprises vinyl aromatic hydrocarbon monomer and an α -olefin or a diene;

wherein at least 60.0 %, preferably at least 80.0 %, preferably at least 90.0 %, preferably at least 95.0 %, preferably at least 99.0 %, preferably at least 99.5 %, preferably at least 99.9 % of the metallic centres in the catalyst system are rare earth elements, preferably a light rare earth elements,

5 preferably in a process according to any one of claims 1 to 11.

FIGURES

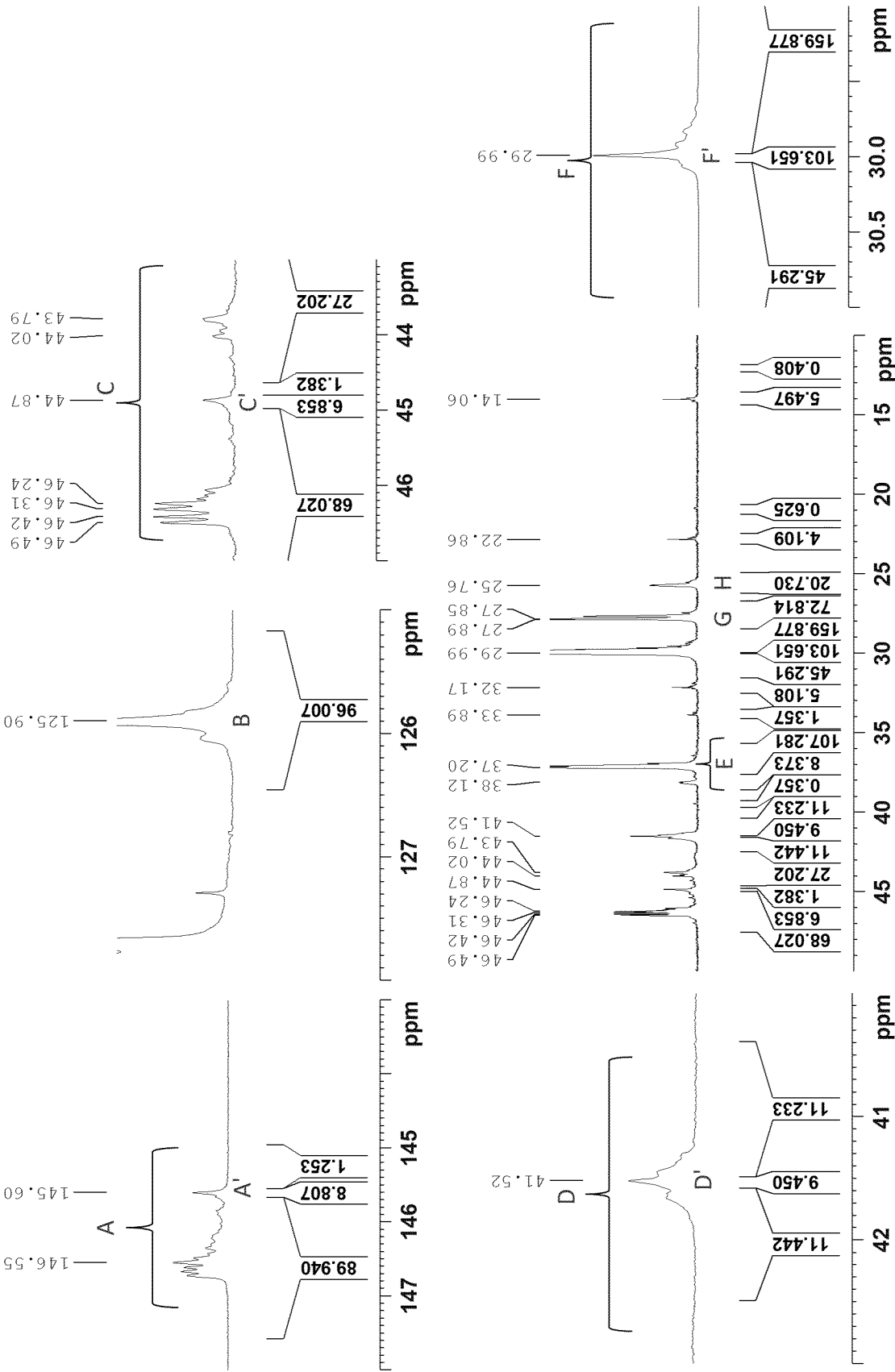
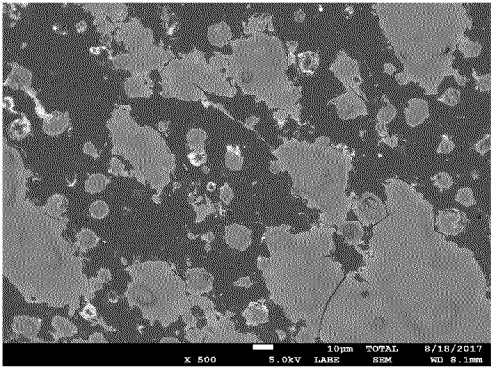
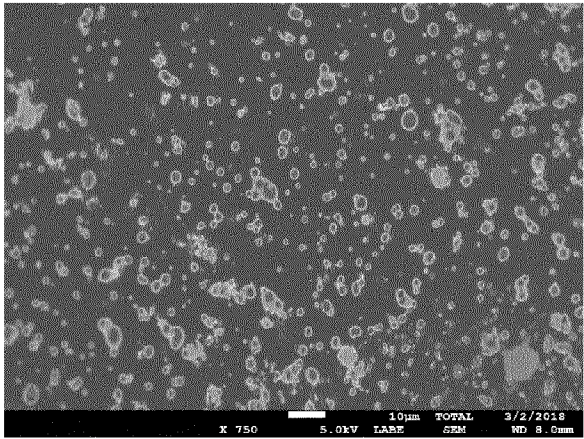


Fig. 1

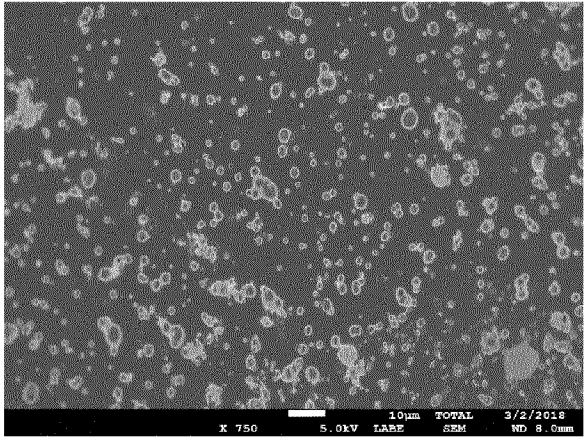


A.

Example not according to the invention (physical blend)



B.



C.

Fig. 2

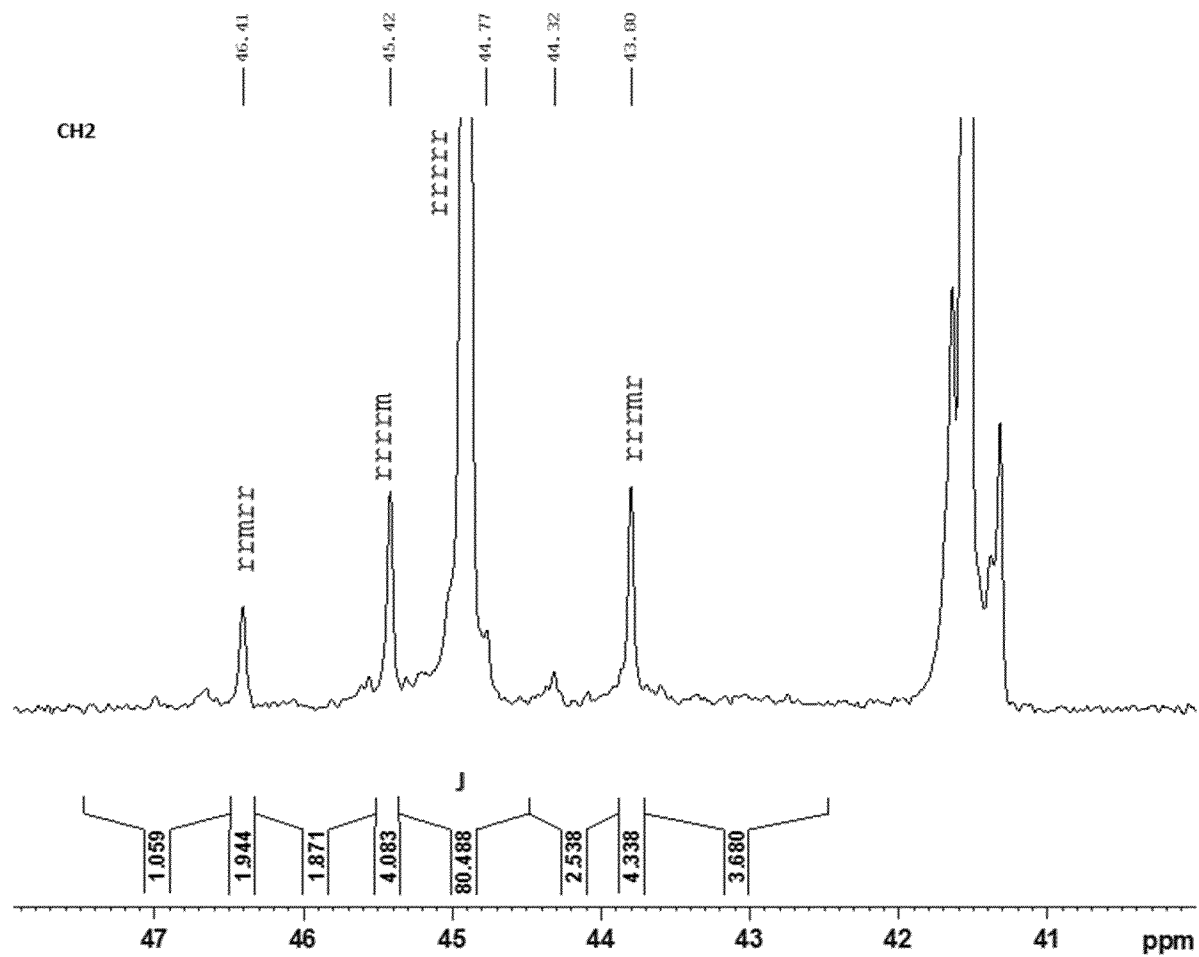


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2020/051738

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C08F4/52	C08F12/08 C08F210/02 C08F2/00 C08L23/08
	C08L25/06	
ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols)		
C08F C08L		
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.
A	CN 1 187 500 A (CHINA PETROCHEMICAL CORP [CN]) 15 July 1998 (1998-07-15) the whole document	1-15
X	----- LU Z ET AL: "COPOLYMERIZATION OF ETHYLENE AND STYRENE WITH SUPPORTED TICL4/NDCL3CATALYST", JOURNAL OF APPLIED POLYMER SCIENCE, JOHN WILEY & SONS, INC, US, vol. 53, no. 11, 12 September 1994 (1994-09-12), pages 1453-1460, XP000464324, ISSN: 0021-8995, DOI: 10.1002/APP.1994.070531107	13
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