(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 March 2020 (12.03.2020)

WIPO | PCT

(10) International Publication Number
WO 2020/048930 A1

(51) International Patent Classification:
B60C 1/00 (2006.01) ***C08F 236/10*** (2006.01)
C08L 9/06 (2006.01) ***C07F 7/10*** (2006.01)
C08F 4/48 (2006.01)

(21) International Application Number:
PCT/EP2019/073369

(22) International Filing Date:
02 September 2019 (02.09.2019)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
18461604.3 03 September 2018 (03.09.2018) EP

(71) Applicants: SYNTHOS S.A. [PL/PL]; ul. Chemikow 1, 32-600 OSWIECIM (PL). **SYNTHOS DWORY 7 SPOLKA Z OGRANICZONA ODPOWIEDZIALNOSCIA SPOLKA JAWNA** [PL/PL]; ul. Chemikow 1, 32-600 OSWIECIM (PL).

(72) Inventors: SIOLEK, Maria; ul. Ulanska 9/18, 40-887 KATOWICE (PL). **KOZAK, Radoslaw**; ul. Gwarecka 17/7, 41-500 CHORZOW (PL). **WEDA, Pawel**; ul. Sztygarska 3a/3, 44-193 KNUROW (PL). **BOGACZ, Robert**; ul. Bielska 163, 32-652 BULOWICE (PL). **SKROK, Tomasz**; ul. Górna Droga 4/301, 02-495 WARSZAWA (PL). **WALENIA, Malgorzata**; ul. Marmurowa 4/6, 70-747 SZCZECIN (PL).

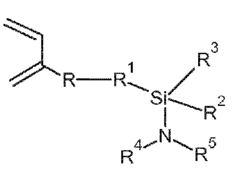
(74) Agent: EISENFÜHR SPEISER PATENTANWÄLTE RECHTSANWÄLTE PARTGMBB; Johannes-Brahms-Platz 1, 20355 Hamburg (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

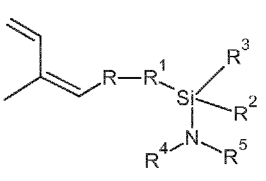
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

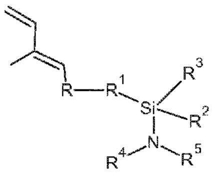
(54) Title: AMINOSILYL-FUNCTIONALIZED CONJUGATED DIENES, THEIR PREPARATION AND THEIR USE IN THE PRODUCTION OF RUBBERS



(IIIa)



(IIIb)



(IIIc).

(57) Abstract: The invention relates to aminosilyl-functionalized conjugated dienes, their preparation and their use in the production of rubbers. Further, the invention relates to rubbers and rubber compositions, and tires produced therefrom. The functionalized conjugated dienes are selected from the group of compounds of formula (Ilia), (Nib), (lllc)

WO 2020/048930 A1

Aminosilyl-functionalized conjugated dienes, their preparation and their use in the production of rubbers

The present invention relates to aminosilyl-functionalized conjugated dienes, their preparation and their use in the production of rubbers. Further, the invention relates to rubbers and rubber compositions, and tires produced therefrom.

A variety of conjugated diene monomers is known that can be used in the production of synthetic rubbers. However, there is a need in the art for further conjugated diene monomers that can be used in advantageous polymerization processes, or that confer advantageous properties to the rubbers produced from such conjugated diene monomers.

State of the art

P. P. Choudhury and M. E. Welker (Molecules 2015, 20, 16892-16907) report the preparation of 2-silicon-substituted 1,3-dienes via Grignard chemistry. The authors further report the use of the 2-silicon-substituted 1,3-dienes in one pot metathesis/Diels-Alder reactions in regio- and diastereoselective fashions.

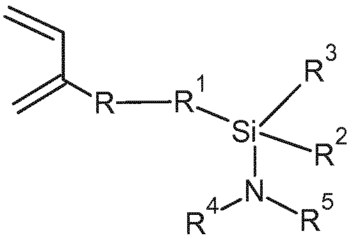
EP 3 159 346 A1 teaches aminosilane-functionalized diene compounds that are useful as modifying monomers in the polymerization of conjugated diene monomers, optionally together with aromatic vinyl monomers, thus producing polymers, specifically elastomeric polymers, which can be used in rubber articles such as tires.

WO2016/162473 A1 and WO2016/162528 A1 disclose aminosilyl-functionalized styrenes and methods for their preparation, as well as the use of the styrene derivatives in the preparation of copolymers thereof.

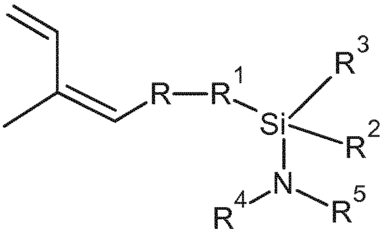
EP 3 064 546 A1 teaches the use of vinylsilanes in the production of rubbers. EP 2 857 446 A1 teaches a conjugated diene polymer derived from conjugated diene, a monomer unit V^1-S^1, and a monomer unit V^2-A^2, where V^1 and V^2 each represent a hydrocarbyl group containing a polymerizable carbon-carbon double bond, S^1 represents a substituted silyl group, and A^2 is an amino group or a nitrogen-containing heterocycle group.

Accordingly, it was an object of the invention to provide conjugated diene monomers for the production of synthetic rubbers. These conjugated diene monomers should be based on easily accessible starting materials, and should be accessible via simple synthetic routes. Moreover, the conjugated diene monomers should be universally applicable, i.e. in a variety of different polymerization processes, and should confer advantageous properties to the rubbers, rubber compositions, and tires produced therefrom.

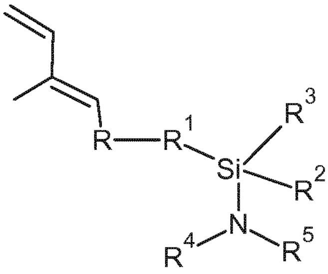
It has now surprisingly been found in accordance with the present invention that this object is solved by the use of specific conjugated dienes having aminosilyl functionalization. The functionalized conjugated dienes of the invention are selected from the group of compounds of formulae (IIIa), (IIIb), (IIIc)



(IIIa),



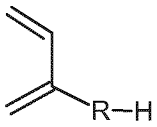
(IIIb),



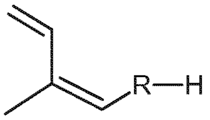
(IIIc),

wherein

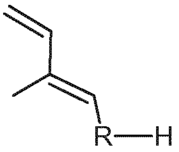
- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



(Ib)



(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms,

- R^1 is selected from

  i) a single bond,

  ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

  iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

  i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

or

  ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom.

The functionalized conjugated dienes of the invention, when used e.g. in the production of solution styrene butadiene rubber (S-SBR) and Ziegler-Natta catalyzed (e.g. neodymium) butadiene rubber (Nd-BR), increase the interaction of the polymer with fillers and thus filler dispersion in the polymer matrix, helping to improve the dynamic and mechanical properties of tire tread compounds.

In a first aspect, the present invention relates to methods for the preparation of a functionalized conjugated diene.

In a second aspect, the invention relates to the functionalized conjugated diene.

In a third aspect, the invention relates to the use of the functionalized conjugated dienes in the production of an elastomeric copolymer.

In a fourth aspect, the invention relates to a process for the production of copolymer component comprising coupled copolymer and terminally modified copolymer.

In a fifth aspect, the invention relates to a process for producing an elastomeric copolymer comprising anionic polymerization conditions.

In a sixth aspect, the invention relates to a process for producing an elastomeric copolymer comprising Ziegler-Natta polymerization conditions.

In a seventh aspect, the invention relates to an elastomeric copolymer.

In an eighth aspect, the invention relates to a method for producing a rubber.

In a ninth aspect, the invention relates to a rubber.

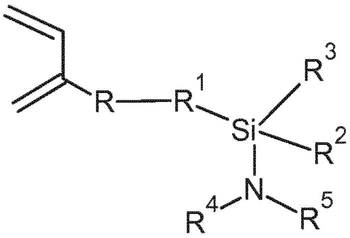
In a tenth aspect, the invention relates to a rubber composition.

In an eleventh aspect, the invention relates to a tire component.

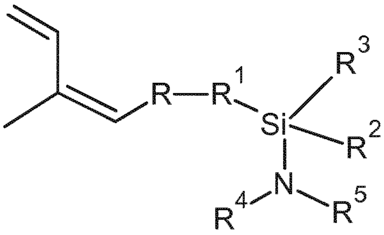
Finally, in a twelfth aspect, the invention relates to a tire.

Detailed description of the invention

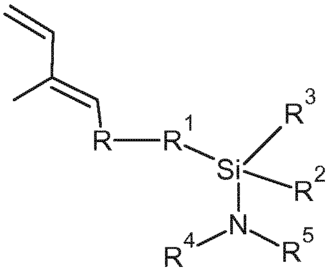
In a first embodiment of the first aspect, the invention relates to a method for the preparation of a functionalized conjugated diene selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)



(IIIa),



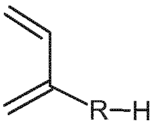
(IIIb),



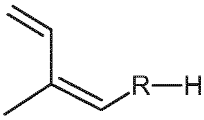
(IIIc),

wherein

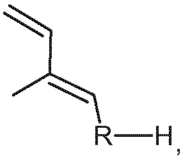
- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



(Ib)



(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms,

- R^1 is selected from

  i) a single bond,

  ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

  iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

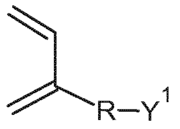
- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

  i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

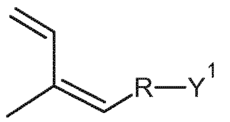
or

  ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom,

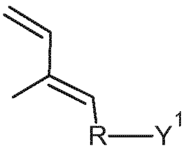
the method comprising reacting, under Grignard conditions, a conjugated diene halide selected from the group of compounds of formula (IIa), (IIb), (IIc)



(IIa)



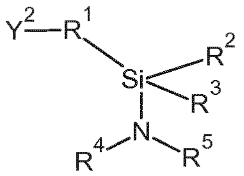
(IIb)



(IIc),

wherein Y^1 is selected from fluorine, chlorine, bromine, and iodine atoms (and Y^1 is preferably a chlorine atom),

with a compound of formula (IV)



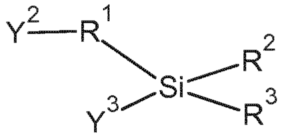
(IV),

wherein Y^2 is selected from fluorine, chlorine, bromine, and iodine atoms.

In a second embodiment of the first aspect, the invention relates to a method for the preparation of a functionalized conjugated diene selected from the group of compounds of formula (IIIa), (IIIb), (IIIc), the method comprising

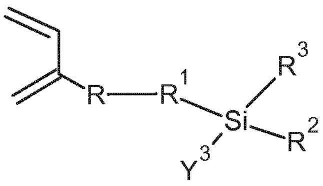
A) reacting, under Grignard conditions, a conjugated diene halide selected from the group of compounds of formula (IIa), (IIb), (IIc)

with a compound of formula (V)

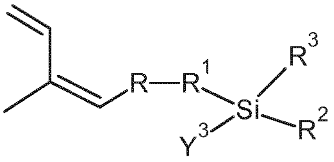


(V),

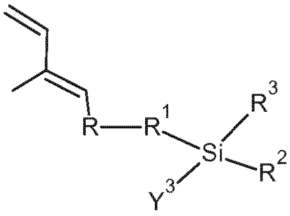
wherein Y^2 and Y^3 are independently selected from fluorine, chlorine, bromine, and iodine atoms, and preferably Y^2 and Y^3 are each chlorine atoms, to result in a compound of formula (VIa), (VIb), (VIc)



(VIa)



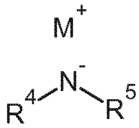
(VIb)



(VIc),

and

B) reacting the compound of formula (VIa), (VIb), (VIc) with an amide of formula (VII)

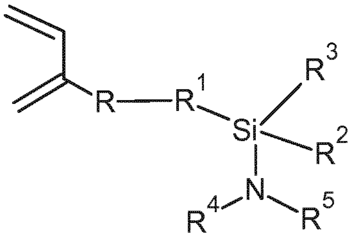


(VII),

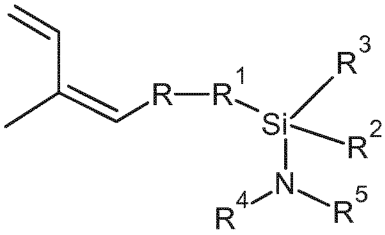
wherein M is an alkali metal selected from lithium, sodium and potassium, and M is preferably sodium.

The preparation of the conjugated diene halide intermediate of formula (IIa), (IIb), (IIc) wherein Y^1 is a chlorine atom may be performed using a chlorinating agent comprising trichloroisocyanuric acid, dichloroisocyanuric acid, an alkali metal salt of dichloroisocyanuric acid, or a mixture thereof. Further details regarding the synthesis of this conjugated diene chloride intermediate are given in PCT/EP2018/070768.

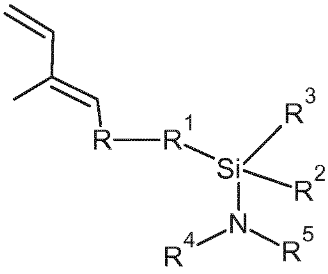
The functionalized conjugated diene of the second aspect of the invention is selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)



(IIIa),



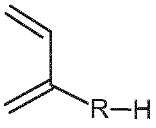
(IIIb),



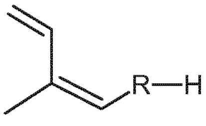
(IIIc),

wherein

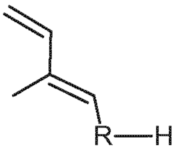
- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



(Ib)



(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms,

- R^1 is selected from

i) a single bond,

ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

  i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

or

  ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom.

In the description of the present invention, an organyl group is any organic substituent group, regardless of functional type, having one free valence at a carbon atom. Preferably, an organyl group contains from 1 to 10 carbon atoms, and optionally one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom, or an aryl, heteroaryl or aralkyl group containing from 6 to 10 carbon atoms, and optionally one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom.

Also, an organylene group is any organic substituent group, regardless of functional type, having two free valences at one carbon atom, or one free valence at each of two carbon atoms.

Preferably, R^1 of the functionalized conjugated diene of the present invention is i) a single bond.

Preferably, R^2, R^3, R^6, R^7, R^8 may be the same or different and represent an organyl group containing from 1 to 10 carbon atoms, and optionally one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom, or an aryl, heteroaryl or aralkyl group containing from 6 to 10 carbon atoms, and optionally one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom.

It is further preferred that R^2, R^3, R^6, R^7, and R^8 are the same or different and represent a linear or branched, saturated or unsaturated hydrocarbyl group (preferably containing from 1 to 10 carbon atoms). Further preferably, R^2, R^3, R^6, R^7, and R^8 are the same or different and represent a linear or branched alkyl, aryl, or alkaryl group; more preferably, R^2, R^3, R^6, R^7, and R^8 are the same or different and represent CH_3 or C_6H_5, in particular R^2, R^3, R^6, R^7, and R^8 all represent CH_3.

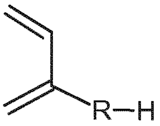
According to the invention, R^4 and R^5 are each a group that at least has a carbon atom bound to the nitrogen atom, i.e. groups R^4 and R^5 are not bound to the nitrogen atom via any heteroatom that may optionally be present in R^4 or R^5.

In embodiment i), R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents a linear, branched or cyclic hydrocarbyl group containing from 1 to 10 carbon atoms, the hydrocarbyl group optionally containing at least one heteroatom selected from a silicon atom, an oxygen atom, and a nitrogen atom; the hydrocarbyl group is saturated or unsaturated.

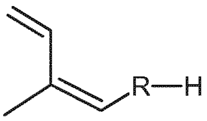
Preferably, i) R^4 and R^5 are the same or different and each R^4 and R^5 independently represents a linear, branched or cyclic, saturated or unsaturated alkyl group containing from 1 to 10 carbon atoms, the alkyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom; or ii) R^4 and R^5 are the same or different and each R^4 and R^5 independently represents an aryl or aralkyl group containing from 6 to 10 carbon atoms, the alkyl group optionally one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom.

It is preferred that R^4 and R^5 are the same and represent a linear, branched or cyclic, saturated or unsaturated alkyl group. More preferably, R^4 and R^5 are the same and represent $–CH(CH_3)_2$ or CH_3. Most preferably, R^4 and R^5 are the same and represent $–CH(CH_3)_2$.

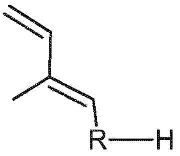
The conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



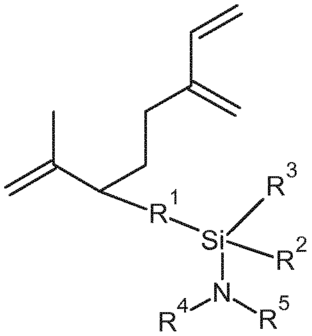
(Ib)



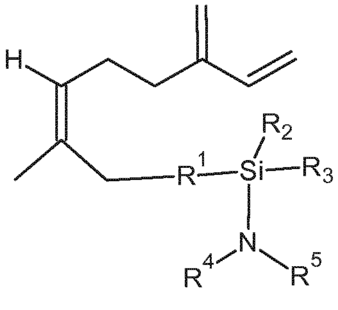
(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived has at least 10 carbon atoms. Preferably, R is a linear or branched, saturated or unsaturated hydrocarbylene, hydrocarbylidene, or hydrocarbylidyne group; more preferably, R is a branched, unsaturated hydrocarbylene group; most preferably, the conjugated diene of formula (IIa), (IIb), (IIc) is selected from terpenes and 4,8-dimethyl-1,3,7-nonatriene. Even more preferably, the terpene is selected from myrcene and ocimene, most preferably the terpene is myrcene selected from α-myrcene and β-myrcene.

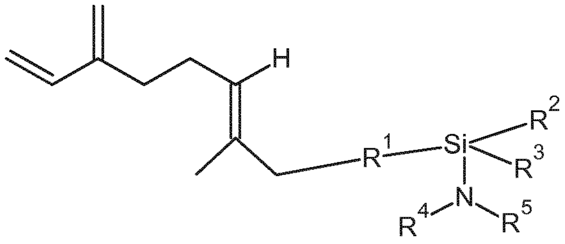
The functionalized conjugated diene according to the invention is in all aspects most preferably a myrcene derivative of formula (VIII), (IX), or (X)



(VIII),

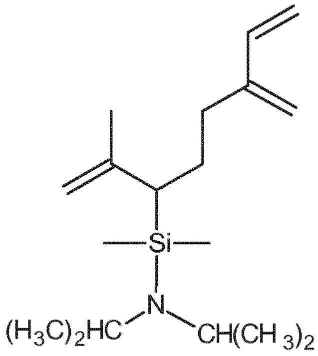


(IX),

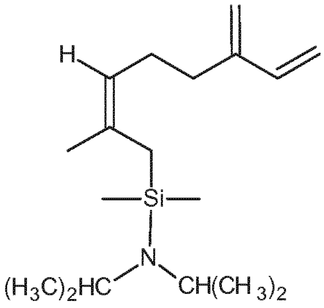


(X).

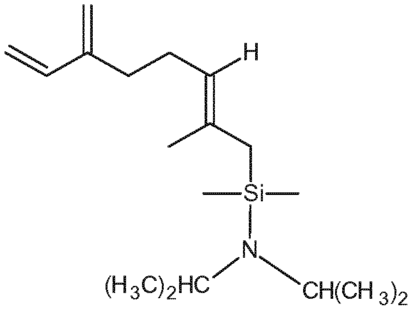
In particular, the myrcene derivative is of formula (VIIIa), (IXa), or (Xa)



(VIIIa),



(IXa),



(Xa).

In a third aspect, the present invention relates to the use of one or more functionalized conjugated dienes of the second aspect in the production of an elastomeric copolymer. The elastomeric copolymer preferably comprises, in addition to one or more units derived from the one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc), units derived from one or more conjugated diene monomers.

The conjugated diene monomer as used in the production of the elastomeric copolymer according to the third aspect of the invention is preferably selected from 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-phenyl-1,3-butadiene, and 4,5-diethyl-1,3-octadiene. More preferably, the conjugated diene monomer is selected from 1,3-butadiene and isoprene, in particular, the conjugated diene monomer is 1,3-butadiene.

Preferably, the use according to the third aspect is in the production of an elastomeric copolymer by 1) anionic polymerization or by 2) coordination polymerization.

It is preferred that the elastomeric copolymer further comprises units derived from one or more vinyl aromatic monomers. The vinyl aromatic monomer is preferably selected from styrene, 1-vinylnaphthalene, 3-methyl styrene, 3,5-diethylstyrene, 4-propylstyrene, 2,4,6-trimethylstyrene, 4-dodecylstyrene, 3-methyl-5-n-hexylstyrene, 4-phenylstyrene, 2-ethyl-4-benzylstyrene, 3,5-diphenylstyrene, 2,3,4,5-tetraethylstyrene, 3-ethyl-1-vinylnaphthalene, 6-isopropyl-1-vinylnaphthalene, 6-cyclohexyl-1-vinylnaphthalene, 7-dodecyl-2-vinylnaphthalene, and α-methyl styrene. More preferably, the vinyl aromatic monomer is selected from styrene, 3-methylstyrene, and α-methylstyrene. In particular, the vinyl aromatic monomer is styrene.

According to the invention, the amount of units derived from the one or more functionalized conjugated dienes selected from of the group of compounds of formula (IIIa), (IIIb), (IIIc) is preferably in a range of from 0.05 to 5 wt.%, based on the weight of the elastomeric copolymer, more preferably in a range of from 0.2 to 1.5 wt.%, most preferably in a range of from 0.4 to 1.2 wt.%, e.g. in a range of from 0.6 to 1.0 wt.%, such as about 0.8 wt.%.

The use according to the third aspect may be of an alkali metal salt derivative of the functionalized conjugated diene selected from the group of compounds of formula (IIIa), (IIIb), (IIIc), as initiator for the anionic copolymerization of one or more conjugated diene monomers, optionally one or more vinyl aromatic monomers, and optionally one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc).

In a fourth aspect, the invention relates to a process for the production of a copolymer component comprising coupled copolymer and terminally modified copolymer, the process comprising the following steps:

(1) providing an initiator component, wherein the initiator component preferably comprises one or more alkali metal salt derivatives of a one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc),

(2) contacting a monomer component comprising

  i) one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc),

  ii) one or more conjugated diene monomers and

  iii) optionally one or more vinyl aromatic monomers,

  with the initiator component, to initiate anionic copolymerization;

(3) continuing copolymerization, to result in a copolymer;

(4) optionally continuing copolymerization of the copolymer, in the presence of one or more functionalized monomers, to result in a functionalized copolymer;

(5) optionally coupling a part of the copolymer of step (3) or the functionalized copolymer of step (4) with one or more coupling agents, to result in coupled copolymer; and

(6) optionally terminally modifying a part of the copolymer of step (3) or the functionalized copolymer of step (4) with one or more terminal modifying agents, to result in terminally modified copolymer.

In a fifth aspect, the invention relates to a process for producing an elastomeric copolymer comprising subjecting

i) one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc),

ii) one or more conjugated diene monomers, and

iii) optionally one or more vinyl aromatic monomers

to anionic polymerization conditions. Preferably, the anionic polymerization conditions include initiating the polymerization with an alkali metal salt derivative of the one or more functionalized conjugated dienes of formula (IIIa), (IIIb), (IIIc), wherein the alkali metal is selected from lithium, sodium, and potassium.

Using anionic polymerization, copolymers having a linear structure or a star structure may be obtained. Also, branching may be performed with e.g. divinylbenzene. The branching level is difficult to predict since it is difficult to fractionate the specific polymer fractions. Thus, it is more appropriate to define the copolymers as obtained by anionic polymerization by their dispersity index, M_w/M_n, which is typically as follows:

- Linear copolymer: 1.01 to 2.0;

- Coupled copolymer: 1.1 to 3; and

- Branched copolymer: 1.1 to 8.0.

According to the sixth aspect, the invention relates to a process for producing an elastomeric copolymer comprising subjecting

i) one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)

and

ii) one or more conjugated diene monomers

to Ziegler-Natta polymerization conditions.

In the coordination polymerization of conjugated diene (such as 1,3-butadiene), a Ziegler-Natta catalyst is used. Typical catalyst compositions are binary, ternary, or quaternary systems. Binary systems comprise catalytic metal chloride (e.g. chloride of Ni, Co, Ti, Nd, V, Ti, Zr, or Fe) and co-catalyst (e.g. aluminum alkyl or a magnesium alkyl compound). In ternary catalyst systems, a halide-free metal precursor (such as neodymium phosphate) is combined with a co-catalyst (such as aluminium or magnesium alkyl) and a halide donor. Adding halide donors to halide-free catalyst systems significantly increases catalyst activities and *cis*-1,4 or *trans*-1,4 contents. In quaternary catalyst systems, a solubilizing agent for either the metal-salt or for the halide donor is used, in addition to the components as used in ternary systems.

The Ziegler-Natta polymerization conditions consequently preferably include a catalyst system comprising 1) metal chloride and 2) co-catalyst. More preferably, the metal chloride 1) is selected from chlorides of one or more of Ni, Co, Ti, Nd, V, Ti, Zr, and Fe, and the co-catalyst 2) is selected from one or more of aluminium and magnesium alkyl compounds.

Also, the Ziegler-Natta polymerization conditions may include the presence of further monomers.

It is alternatively preferred that the Ziegler-Natta polymerization conditions include a catalyst system comprising 1) non-halide metal compound, 2) co-catalyst, and 3) halide donor compound. The non-halide metal compound 1) is preferably one or more Nd compounds; more preferably the Nd compound is selected from neodymium carboxylates, neodymium alcoholates, neodymium phosphates, neodymium phosphonates, neodymium allyl compounds, neodymium cyclopentadienyl complexes, neodymium amides, and neodymium acetylacetonates.

The most effective catalysts for the production of high cis polybutadiene are ternary systems based on neodymium, where catalyst precursors such as 1) neodymium carboxylates (e.g. neodymium(III) versatate (NdV), neodymium(III) octanoate (NdO), neodymium(III) isooctanoate (NdiO), neodymium(III) naphthenate (NdN); 2) neodymium alcoholates (e.g. $Nd(OBu)_3$, $Nd(O\textit{i}Pr)_3$); 3) neodymium phosphates and phosphonates (e.g. neodymium bis(2-ethylhexyl)phosphate (NdP), bis(2-ethylhexanol)phosphonate); 4) neodymium allyl compounds; 5) neodymium cyclopentadienyl complexes (e.g. monocyclopentadienyl neodymium dichloride ($CpNdCl_2$), monocyclopentadienyl dialkyl neodymium ($CpNdR_2$), monocyclopentadienyl diallyl neodymium ($CpNd(\eta_3{-}C_3H_5)_2$), salts of monoclopentadienyl tris allyl neodymium (e.g $Li[CpNd(\eta_3{-}C_3H_5)_3]$), dicyclopentadienyl neodymium monochloride (Cp_2NdCl), dicyclopentadienyl monoalkyl neodymium (Cp_2NdR), silylene-bridged dicyclopentadienyl neodymium derivatives (e.g. $[R_2Si(Cp)_2]Nd(Cl/R)$); 6) neodymium amides (e.g. $Nd(N(SiMe_3)_2)_3$); or 7) neodymium acetylacetonates are used, in combination with one or more co-catalyst such as: $AlMe_3$ (TMA), $AlEt_3$ (TEA), $Al\textit{i}Bu_3$ (TIBA), $AlOct_3$, methyl alumoxane (MAO), tetraisobutyl dialumoxane (TIBAO), $B(C_6F_5)_3$, modified methyl alumoxane (MMAO), hexaisobutylalumoxane (HIBAO), diisobutylaluminum hydride (DIBAH), MgR_2, $AlPr_3$, $AlBu_3$, $AlHex_3$, $AlOct_3$, $AlDodec_3$, $AlEt_3$, or $AlMe_3$.

Examples for halide donors are $SiCl_4$, ethylaluminium sesquichloride (EASC), diethylaluminium chloride (DEAC), dimethylaluminium chloride, butyl chloride (BuCl), dibutylaluminium chloride, $AlBr_3$, $EtAlCl_2$, and Me_3SiCl.

The copolymer as produced in accordance with the sixth aspect, i.e. by coordination polymerization, preferably has linear structure or branched structure. The polymer structure is dictated by catalyst composition and is typically as follows (M_w/M_n):

- Linear copolymer: 1.5 to 5.0,

- Branched copolymer: 1.5 to 20.0.

According to the seventh aspect, the invention relates to an elastomeric copolymer comprising repeat units that are derived from

A) 0.05 wt.% to 5 wt.%, by weight of the copolymer, of one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc);

B) 45 wt.% to 99.95 wt.%, by weight of the copolymer, of one or more conjugated diene monomers;

C) 0 wt.% to 50 wt.%, by weight of the copolymer, of one or more vinyl aromatic monomers.

The amount of B) conjugated diene monomer in the elastomeric copolymer of the seventh aspect is preferably 50 to 92 wt.%, by weight of the copolymer, more preferably 60 to 90 wt.%, by weight of the copolymer, in particular 65 to 80 wt.%, by weight of the copolymer.

The vinyl aromatic monomer, when present, is preferably selected from styrene, 1-vinylnaphthalene, 3-methylstyrene, 3,5-diethylstyrene, 4-propylstyrene, 2,4,6-trimethylstyrene, 4-dodecylstyrene, 3-methyl-5-n-hexylstyrene, 4-phenylstyrene, 2-ethyl-4-benzylstyrene, 3,5-diphenylstyrene, 2,3,4,5-tetraethylstyrene, 3-ethyl-1-vinylnaphthalene, 6-isopropyl-1-vinylnaphthalene, 6-cyclohexyl-1-vinylnaphthalene, 7-dodecyl-2-vinylnaphthalene, and α-methylstyrene. More preferably, the vinyl aromatic monomer is selected from styrene, 3-methylstyrene and α-methylstyrene. In particular, the vinyl aromatic monomer is styrene.

The amount of C) vinyl aromatic monomer in the elastomeric copolymer according to the seventh aspect of the present invention is preferably 8 to 45 wt.%, by weight of the copolymer, more preferably 10 to 40 wt.%, by weight of the copolymer, in particular 20 to 35 wt.%, by weight of the copolymer.

Alternatively, the elastomeric copolymer comprises less than 1 wt.% C) vinyl aromatic monomer (and preferably no C) vinyl aromatic monomer), and the amount of B) conjugated diene monomer is 95 to 99.95 wt.%, by weight of the copolymer, preferably 98 to 99.6 wt.%, by weight of the copolymer, in particular 99.0 to 99.4 wt.%, by weight of the copolymer.

The conjugated diene monomer in the elastomeric copolymer according to the seventh aspect is preferably selected from 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-phenyl-1,3-butadiene, and 4,5-diethyl-1,3-octadiene. More preferably, the conjugated diene monomer is selected from 1,3-butadiene and isoprene. The conjugated diene monomer is in particular 1,3-butadiene.

The elastomeric copolymer according to the invention may comprise units having a linear structure.

Also, the copolymer may comprise units having a branched structure.

Moreover, the elastomeric copolymer may comprise units having a star structure and being produced by the reaction of metal-terminated living linear copolymer with one or more coupling agents in anionic polymerization conditions. The coupling agent may be

I) a tin halide coupling agent (preferably the tin halide coupling agent is tin tetrachloride),

or

II) a silicon halide coupling agent (preferably the silicon halide coupling agent is selected from silicon tetrachloride, silicon tetrabromide, silicon tetrafluoride, silicon tetraiodide, hexachlorodisilane, hexabromodisilane, hexafluorodisilane, hexaiododisilane, octachlorotrisilane, octabromotrisilane, octafluorotrisilane, octaiodotrisilane, hexachlorodisiloxane, 2,2,4,4,6,6-hexachloro-2,4,6-trisilaheptane-1,2,3,4,5,6-hexakis[2-(methyldichlorosilyl)ethyl]benzene, and alkyl silicon halides of general formula (XI)

$$R^6_n\text{-Si-}X_{4-n} \quad \text{(XI)},$$

wherein R^6 is a monovalent aliphatic hydrocarbon group having 1 to 20 carbon atoms or a monovalent aromatic hydrocarbon group having 6 to 18 carbon atoms; n is an integer of 0 to 2; and X can be a chlorine, bromine, fluorine or iodine atom).

In the elastomeric copolymer according to the seventh aspect, the fraction of units having star structure is preferably between 0 and 75 %, by weight of the copolymer.

According to the eighth aspect, the invention relates to a method for producing a rubber comprising vulcanizing the elastomeric copolymer according to the seventh aspect in the presence of one or more vulcanizing agents.

According to an ninth aspect, the invention relates to a rubber as obtainable according to the method of the eighth aspect.

According to a tenth aspect, the invention relates to a rubber composition comprising x) a rubber component comprising the rubber according to the ninth aspect. Preferably, the rubber composition further comprises y) one or more fillers. The filler is preferably selected from the group consisting of silica and carbon black. Most preferably, the rubber composition comprises y) both silica and carbon black.

In a preferred embodiment of the tenth aspect, the amount of filler component y) in the rubber composition is 10 to 150 parts by mass relative to 100 parts by mass of the rubber component x) (phr). Preferably, the amount of filler component y) is 20 to 140 phr. More preferably, the amount of filler component y) is 30 to 130 phr.

Preferably, the rubber component x) in the rubber composition according to the tenth aspect additionally comprises one or more further rubbery polymers. It is preferred that the further rubbery polymer is selected from the group consisting of natural rubber, synthetic isoprene rubber, butadiene rubber, styrene-butadiene rubber, ethylene-α-olefin copolymer rubber, ethylene-α-olefin-diene copolymer rubber, acrylonitrile-butadiene copolymer rubber, chloroprene rubber and halogenated butyl rubber.

The tire component according to the eleventh aspect of the invention comprises the rubber composition according to the tenth aspect. Preferably, the tire component is a tire tread.

The tire according to the twelfth aspect of the invention comprises the tire component of the eleventh aspect.

The advantages of the present invention become more apparent from the following examples. Unless indicated otherwise, all percentages are given by weight.

Examples

I. Synthesis of monomers: Example 1a

A reactor of 1 L capacity, equipped with a magnetic stirrer, a dropping funnel and a reflux condenser equipped with a gas introduction attachment and an oil valve (Zaitsev washer), was in an argon atmosphere loaded with magnesium metal (13,2 g, 0.55 mol), followed by the addition of dry and deoxygenated tetrahydrofuran (THF, 200 mL) and diisobutylaluminium hydride (DIBAH) [$(i\text{-Bu})_2AlH$, 1 mL, 5.61 mmol]. This was done at room temperature, with stirring of the reactor contents. The activation of magnesium was conducted until evolution of hydrogen bubbles ceased. Then, (*N,N*-diisopropylamino)dimethylchlorosilane (96.89 g, 0.50 mol) and the remaining part (300 mL) of the solvent were added to the activated magnesium metal. The dropping funnel was filled with chloromyrcene (90.46 g, 0.53 mol). At the initiation step of the reaction, 8.00 mL of chloromyrcene were added dropwise into the mixture (without stirring the reactor contents). When clear symptoms of the reaction proceeding were observed, dosing of the remaining amount of chloromyrcene began with such a rate that the reactor contents boiled gently for about 2 hours. After the dosing of chloromyrcene was completed, the reactor temperature was maintained in the range of 40°C for one hour, followed by cooling to room temperature. To neutralize a small excess of Grignard reagent, 0.6 mL of water were added. Then, the solvent was evaporated from the post-reaction mixture under reduced pressure and 1.0 L of n-hexane were added to the reaction residue. The obtained suspension was filtered off and the precipitate was washed with three portions of n-hexane of 200 mL each. Then, the solvent was evaporated from the obtained filtrate under reduced pressure at 40°C until a constant pressure was achieved. 146.30 g of product were obtained, with a yield of 91 %.

GC-MS: 43 (2.85), 59 (13.97), 73 (12.42), 86 (2.46), 100 (4.14), 116 (37.16), 151 (1.84), 158 (100.00), 159 (14.65), 278 (0.64), 293 (0.35)

II. Synthetic examples for functionalized rubbers

II.1 Application of functionalized myrcene in anionic polymerization

In order to provide more details about the synthesis and properties of elastomers produced according to the present invention, functionalized styrene-butadiene copolymers with exactly controlled micro- and macrostructure and with functional groups are described in Examples 2b, 3b and 4b below, and are compared with a non-functionalized copolymer as described in Comparative Example 1b.

Polymerization

Inertization step:

Cyclohexane (1.2 kg) was added to a nitrogen-purged two-liter reactor and treated with 1 gram of 1.6 M n-butyllithium solution in cyclohexane. The solution was heated to 70°C and vigorously stirred for 10 minutes, to perform cleaning and inertization of the reactor. After that, solvent was removed via a drain valve and nitrogen was purged again.

Example 1b (comparative)

Cyclohexane (820 g) was added to the inerted two-liter reactor, followed by addition of styrene (31 g) and of 1,3-butadiene (117 g). Inhibitor from styrene and 1,3 butadiene was removed. Next, tetramethylethylenediamine (TMEDA, 2.21 mmol) was added, to provide random incorporation of styrene monomer and to increase the vinyl content, from the butadiene-derived units. The solution inside the reactor was heated to 60°C and continuously stirred during the whole process. When the desired temperature was reached, n-butyllithium (0.045 mmol) was added, to perform quenching of residual impurities. Then, n-butyllithium (0.845 mmol) was added to initiate the polymerization process. The reaction was carried out as a isothermic process for 60 minutes. After this time, silicon tetrachloride (5.25×10^{-2} mmol) was added to the polymer solution as a coupling agent. Coupling was performed for 5 minutes. The reaction solution was terminated, using nitrogen-purged isopropyl alcohol (1 mmol), and rapidly stabilized by addition of 2-methyl-4,6-bis(octylsulfanylmethyl)phenol (at 1.0 phr polymer). The polymer solution was treated with isopropanol, and precipitation of polymer occurred. The final product was dried overnight in a vacuum oven.

Example 2b (myrcene derivative from example as comonomer)

Cyclohexane (820 g) was added to the inerted two-liter reactor, followed by addition of styrene (31 g), functionalized myrcene of Example 1a (0.59 g) and 1,3-butadiene (117 g). Inhibitor from styrene and 1,3-butadiene was removed. Next, 2,2-Bis(2-tetrahydrofuryl)propane (DTHFP, 2.52 mmol) was added, to provide random incorporation of styrene monomer and to increase the vinyl content, from the butadiene-derived units. The solution inside the reactor was heated to 60°C and continuously stirred during the whole process. When the desired temperature was reached, n-butyllithium (0.045 mmol) was added, to perform quenching of residual impurities. Then, n-butyllithium (0.845 mmol) was added to initiate the polymerization process. The reaction was carried out as a isothermic process for 60 minutes. After this time, silicon tetrachloride (6.30×10^{-2} mmol) was added to the polymer solution as a coupling agent. Coupling was performed for 5 minutes. The reaction solution was terminated, using nitrogen-purged isopropyl alcohol (1 mmol), and rapidly stabilized by addition of 2-methyl-4,6-bis(octylsulfanylmethyl)phenol (at 1.0 phr polymer). The polymer solution was treated with isopropanol, and precipitation of polymer occurred. The final product was dried overnight in a vacuum oven.

Example 3b (myrcene derivative from example 1a as both initiator component and as comonomer)

Cyclohexane (820 g) was added to the inerted two-liter reactor, followed by addition of styrene (31 g), functionalized myrcene of Example 1a (0.59 g) and 1,3-butadiene (117 g). Inhibitor from styrene and 1,3-butadiene was removed. Next, 2,2-Bis(2-tetrahydrofuryl)propane (DTHFP, 3.69 mmol) was added as a styrene randomizer and to increase the vinyl content, from the butadiene-derived units. The solution inside the reactor was heated to 60°C and continuously stirred during the whole process. When the temperature was reached, n-butyllithium (0.045 mmol) was added to the reactor, to perform quenching of residual impurities.

n-Butyllithium (1.23 mmol) and functionalized myrcene of Example 1a (0.38 g) were mixed together in a burette, the contact time was about 15 min, and then the mixture was added to initiate the polymerization process. The reaction was carried out over 60 minutes, as an isothermic process. After this time, silicon tetrachloride (6.30×10^{-2} mmol) was added to the polymer solution as a coupling agent. Coupling was performed for 5 minutes. The reaction solution was terminated, using nitrogen-purged isopropyl alcohol (1 mmol), and rapidly stabilized by addition of 2-methyl-4,6-bis(octylsulfanylmethyl)phenol (at 1.0 phr polymer). The polymer solution was treated with isopropanol, and precipitation of polymer occurred. The final product was dried overnight in a vacuum oven.

Example 4b (continuous polymerization)

A butadiene-styrene copolymer was prepared in a cascade of three continuous reactors having a volume of 10 L (reactor 1), 20 L (reactor 2) and 10 L (reactor 3), respectively, where each reactor was equipped with a paddle stirrer. The agitation speed was 150-200 rpm and filling factor at the level of 50 %-60 %. Hexane, styrene, 1,3-butadiene, 1,2-butadiene (gel formation prevention additive), DTHFP and functionalized myrcene of Example 1a (the last three reactants as solutions in hexane) were dosed into the first reactor, with flow rates of 10752.00 g/h, 398.00 g/h, 1499.00 g/h, 19.00 g/h, 102.00 g/h and 46,03 g/h, respectively. n-Butyllithium flow rate (as a solution in hexane) was 107.00 g/h, and functionalized myrcene of Example 1a (as a solution in hexane) flow rate was 153,92 g/h. Streams of n-butyllithium and 50/50 by weight of functionalized myrcene of Example 1a were mixed together in the pipe static mixer, before entering the reactor, and the contact time was about 15 min. The temperature in the reactors was between 70°C to 85°C. To obtain branched rubber silicon tetrachloride was added at the reactor 3 inlet, at the entry of static mixer, in a $SiCl_4$/active n-butyllithium ratio of 0.05. The coupling reaction was performed at 70–85°C. At the reactor 3 outlet, 2-methyl-4,6-bis(octylsulfanylmethyl)phenol (as a solution in hexane) was added as an antioxidant (142 g/h).

The polymer solution was subsequently transferred to a stripper. Distilled water, in an amount of double of the total mass of polymer solution, as well as pH regulator and soap were added to the polymer solution, and the stripper contents were then treated with steam. Steam-stripping was carried out until the entire amount of solvent had been removed, and rubber crumbs were obtained. Then, the rubber crumbs were removed from the stripper, cooled to room temperature, milled and dried in a stream of hot air.

Characterization

Vinyl content (%)

Determined by 600 MHz ^{1}H-NMR, based on BS ISO 21561:2005.

Bound styrene content (%)

Determined by 600 MHz ^{1}H-NMR, based on BS ISO 21561:2005.

Molecular weight determination

Gel permeation chromatography was performed via PSS Polymer Standards Service multiple columns (with guard column) using THF as the eluent and for sample preparation. Multi-angle laser light scattering measurements were carried out using a Wyatt Technologies Dawn Heleos II light scattering detector, DAD (PDA) Agilent 1260 Infinity UV-VIS detector and Agilent 1260 Infinity refractive index detector.

Glass transition temperature (°C)

Determined based on PN-EN ISO 11357-1:2009.

Mooney viscosity (ML (1+4)/100°C)

Determined based on ASTM D 1646-07, using a large rotor under the conditions of preheating = 1 minute, rotor operating time = 4 minutes, and temperature = 100°C.

Vulcanization characteristics

Determined based on ASTM D6204, using RPA 2000 Alpha Technologies rubber processing analyzer, operating time = 30 minutes, and temperature = 170°C.

Evaluation and measurement of properties of rubber composition

A vulcanized rubber compound was prepared using a polymer obtained in each of Examples, and was measured for the following test parameters.

i) *Tire predictors (tan δ at 60°C, tan δ at 0°C, tan δ at -10°C)*

A vulcanized rubber compound was used as a test sample and measured for this parameter, using a dynamic mechanical analyzer (DMA 450+ MetraviB) in single shear mode under the conditions of dynamic strain = 2%, frequency = 10 Hz, in the temperature range of from -70 to 70°C, with a heating rate of 2.5 K/min.

ii) *Rebound resilience*

Determined based on ISO 4662.

Table 1 shows the characterization results for the four samples synthesized for this study.

Table 1

Example	M_n [g/mol]	M_w [g/mol]	M_w/M_n	Vinyl content [%][1]	Styrene content [%]	%F [%wt.]	MV [1+4]	Tg [°C]
1b (comp.)	222,300	318,800	1.43	62.1	21.3	0	60.3	-26.1
2b	229,100	316,200	1.38	61.5	21.1	0.39	57.3	-24.4
3b	226,400	319,900	1.41	62.3	21.7	0.65	62.4	-25.2
4b	185,800	329,100	1.77	61.9	21.5	0.62	51.8	-23.4

[1] Based on 1,3-butadiene content

Compounding

Using the rubbers obtained in Examples 2b, 3b, 4b and Comparative Example 1b, respectively, compounding was made according to the "compounding recipe of rubber composition" shown in Table 2. The compounding of the solution styrene-butadiene rubber, fillers, and rubber additives was performed in a Banbury type of internal mixer (350E Brabender GmbH& Co. KG) and on a lab-sized two roll mill. The rubber compounds were mixed in two different stages and the final pass was completed on a two roll mill. The first stage was used to mix the polymer with oil, silica, silane coupling agent, 6PPD and activators in several steps. The second stage was to further improve the distribution of the silica along with adding of carbon black, then the compound was allowed to sit for 24 hours. In order to be conditioned for the final pass, the rubber compound was allowed to condition for four hours. The final mixing was performed on a two roll mill. The last step was used to add the cure packages. Then, each compound was vulcanized at 170°C, for $T_{95+1.5}$ minutes (based on RPA results), to obtain vulcanizates. Each vulcanized rubber compound was evaluated and measured for the above-mentioned curing characteristics, tire predictors and rebound resilience. The results are shown in Table 3.

Table 2

Component	**phr**
SBR	75
Polybutadiene rubber[1]	25
Silica[2]	80
Carbon Black[3]	10
Stearic acid	2
Zinc oxide	3
Oil extender[4]	37.5
6PPD[5]	2
Bis[3-(triethoxysilyl)propyl]tetrasulfide[6]	6.4
N-tert-butyl-2-benzothiazole sulfenamide[7]	1.7
1,3-Diphenylguanidine[8]	2
Sulphur	1.5

[1] Synteca 44, a product of Synthos
[2] Zeosil 1165MP, a product of Solvay
[3] ISAF-N234, a product of Cabot Corporation
[4] VivaTec 500, a product of Klaus Dahleke KG
[5] VULKANOX 4020/LG, a product of Lanxess
[6] Si 69, a product of Evonik
[7] LUVOMAXX TBBS, a product of Lehmann & Voss & Co. KG
[8] DENAX, a product of Draslovka a.s.

Table 3

Example	Rebound re-silience (23°C), [%]	Rebound re-silience (70°C), [%]	tan δ (60°C)	tan δ, (0°C)	tan δ, (-10°C)
1c (comp.)	32.2	54.9	0.192	0.514	0.663
2c	34.8	60.7	0.145	0.646	0.756
3c	37.7	66.1	0.134	0.644	0.788
4c	38.2	67.3	0.143	0.682	0.949

It is apparent from these results that in a silica mix, as judged based on the properties in the vulcanized state, SSBR 3b according to the invention imparts to the corresponding rubber composition 3c reinforcement properties which are superior to those obtained with the control SSBR 1b and with the other SSBR 2b according to the invention. Moreover, the data in Table 3 shows that SSBR 4b obtained in continuous polymerization has better reinforcement properties compared to control SSBR 1b and SSBR 2b.

Furthermore, the tire predictors of rubber composition 3c according to the invention are improved relative to those of the control rubber composition 1c and of the rubber compositions 2c and 4c (in terms of rolling resistance) according to the invention. Moreover, said tire predictors are improved for rubber composition 2c according to the invention relative to the control rubber composition 1c. Furthermore, tire predictors are improved for rubber composition 4c according to the invention relative to the control rubber composition 1c; additionally, ice traction and dry traction properties are improved relative to those of rubber compositions 1c, 2c, and 3c.

II.2 Application of functionalized myrcene in coordination polymerization

In order to provide more details about the synthesis and properties of elastomers produced according to the present invention, functionalized butadiene homopolymer with functional groups are described in Examples 6b and 8b below, and are compared with a non-functionalized homopolymer as described in Comparative Examples 5b and 7b. The amounts of starting materials used in these examples are listed in Table 4. The measurement methods and evaluation methods of properties are shown below.

Polymerization (for additional information, see also the above information relating to anionically obtained polymers)

For catalyst composition and procedure, see the following publications:

1. Lars Friebe, Oskar Nuyken and Werner Obrecht, “A Comparison of Neodymium Versatate, Neodymium Neopentanolate and Neodymium Bis(2-ethylhexyl)phosphate in Ternary Ziegler Type Catalyst Systems With Regard to their Impact on the Polymerization of 1,3-Butadiene”, in J. Macromol. Sci. A., (2005), 42, 7, 839-851.

2. Friebe, L., Nuyken, O., Windisch, H., and Obrecht, W. “Polymerization of 1,3-butadiene initiated by neodymium versatate/diisobutylaluminum hydride/ethylaluminum sesquichloride: Kinetics and conclusions about the reaction mechanism”, in Macromol. Chem. Phys., (2002), 203, 8, 1055–1064.

General polymerization description:

A twenty litre reactor was filled with dry 1,3-butadiene and dry solvent (cyclohexane), and functionalized myrcene of Example 1a, and heated to 60°C. Then, catalyst was added in the following sequence: neodymium bis(2-ethylhexyl)phosphate (NdP), diisobutylaluminum hydride (DIBAH) (both 0.1 mol/L solutions in cyclohexane). Polymerization was started by addition of ethylaluminum sesquichloride (EASC) (1.0 mol/L solution in cyclohexane). The solution inside the reactor was heated and continuously stirred during the whole process. The temperature of the reaction mixture was kept between 60 and 90°C. The reaction solution was terminated, using nitrogen-purged isopropyl alcohol, and was rapidly stabilized by the addition of 2-methyl-4,6-bis(octylsulfanylmethyl)phenol (at 1.0 phr polymer).

The polymers were recovered by a conventional recovery operation using steam stripping of the solvent and were dried in a stream of hot air.

Details of the reaction conditions, of the used recipes and characteristics of the obtained polymers are included in Table 4 below.

Table 4. Reactions conditions and obtained polymers characteristics (coordination polymerization), where n_M/n_{Nd} - represents the molar ratio of monomer to neodymium, n_{Cl}/n_{Nd} – represents the molar ratio of chloride to neodymium, n_{DIBAH}/n_{Nd} – represents the molar ratio of DIBAH to neodymium, F% - represents content by weight percent of functionalized myrcene in the polymer chains.

	Reaction conditions						**GPC results**			**FTIR results [%]**			**DSC results**		
Ex.	**T_{init} [°C]**	**Cyclo-hexane [g]**	**1,3-butadiene [g]**	**$n_M/$ n_{Nd}**	**$n_{Cl}/$ n_{Nd}**	**$n_{DIBAH}/$ n_{Nd}**	**Mn [kg/mol]**	**Mw [kg/mol]**	**Mw/Mn**	**Vinyl**	**1,4-cis**	**1,4-trans**	**Tg, °C**	**%F [%wt.][1]**	**MV [1+4]**
5b	60	12000	1500	9250	2	6	156.3	292.3	1.87	0.2	97.8	2.0	-105	0	66
6b	60	12000	1500	9250	2	7	148.1	265.1	1.79	0.3	98.0	1.7	-105	0.98	60
7b	60	12000	1500	9250	2	8	119.2	243.2	2.04	0.3	97.6	2.1	-104	0	43
8b	60	12000	1500	9250	2	8	121.7	244.6	2.01	0.2	97.8	2.0	-104	0.96	45

[1] Theoretical value, some signals from catalyst overlap signals from functionalized diene

Characterization (additional information, see also the above information relating to anionically obtained polymers)

Vinyl content, cis-1,4 content, trans-1,4 content (%)

The microstructure of butadiene rubber was determined by infrared spectroscopy (Thermo Scientific Nicolet Is10). The following peaks were used for quantitative determination of the poly(butadiene) microstructure:

735 cm^{-1} (δ(cis-R–CH=CR–H), →cis-1,4, ε=0.192),

912 cm^{-1} (δ(R–CH=CH–H), →vinyl (1,2), ε=1.0),

965 cm^{-1} (δ(trans-R–CH=CR–H), →trans-1,4, ε=0.769).

The methodology is described in:

1. M. Kraft, Struktur und Absorptionsspektroskopie der Kunststoffe, VCH, Weinheim 1973, p. 93; and

2. E. O. Schmalz, W. Kimmer, Z. Anal. Chem. 1961, 181, 229.

Evaluation and measurement of properties of vulcanized rubber composition **(additional information, see also the above information relating to anionically obtained polymers)**

A vulcanized rubber compound was produced using a polymer obtained in each of the examples, and was measured for the following test parameters

i) *Tire predictors (tan δ at 60°C, tan δ at 0°C, tan δ at -10°C, J" at 30°C)*

A vulcanized rubber composition was used as a test sample and measured for this parameter, using a dynamic mechanical analyzer (DMA 450+ MetraviB) in shear mode under the conditions of tensile strain = 2 %, frequency = 10 Hz, in a temperature range of from -80 to 80°C, with a heating rate of 2.5 K/min.

ii) *Rebound resilience*

Determined based on ISO 4662

iii) *Reinforcement Factor*

Expressed as ratio between Modulus 300 % and Modulus 100 %, Determined based PN-ISO 37:2007 using Zwick/Roel Z005

iv) *Silica dispersion*

Determined based ISO 1134 C, D, E; ASTM D7723, using disperGRADER Alpha Technologies

Compounding (additional information, see also the above information relating to anionically obtained polymers)

Using the rubbers as obtained in Examples 6b and 8b and Comparative Examples 5b and 7b, respectively, compounding was made according to the compounding recipe as shown in Table 5. The compounding of the solution styrene-butadiene rubber, fillers, and rubber additives was performed in a Farrel type of internal mixer (Mixer Farrel BR +1600) and on a lab sized two roll mill. The rubber compounds were mixed in three different stages, first two on internal mixer, and third one (final pass) was completed on a two roll mill.

The first stage was used to mix the rubbers with oil, silica, silane coupling agent, 6PPD and activators in several steps. The second stage was performed to further improve the distribution of the silica along with adding of carbon black, then the compound was conditioned for 24 hours.. The final mixing was performed on a two roll mill. The last step was used to add the cure packages. Then, each compound was vulcanized at 170°C, for $T_{95+1.5}$ minutes (based on RPA results), to obtain vulcanizates. Each vulcanized rubber compound was evaluated and measured for the above-mentioned curing characteristics, Payne effect and tire predictors. The results are shown in Table 6.

Table 5

Component	**phr**	**Mixing stage**
SBR[1]	52	1
Polybutadiene rubber	48	1
Silica[2]	80	1
Carbon Black[3]	5	2
Stearic acid	2	1
Zinc oxide	2	1
Oil extender[4]	28	1
6PPD[5]	2	1
Antioxidant[6]	2	1
Wax[7]	2	1
Bis[3-(triethoxysilyl)propyl]tetrasulfide[8]	6.4	1
N-tert-butyl-2-benzothiazole sulfenamide[9]	1.6	3
1,3-Diphenylguanidine[10]	2	3
Sulphur	1.5	3

[1] Syntion 2150, a product of Synthos R&D, specification: non functionalized rubber, Mn ~ 202 kg/mol, Mw ~395 kg/mol, Mw/Mn = 1.95, styrene content 21.5 %, vinyl 50.6 % (/polymer), Tg ~ -25°C,
[2] Zeosil 1165MP, a product of Solvay,
[3] ISAF-N234, a product of Cabot Corporation,
[4] VivaTec 500, a product of Klaus Dahleke KG,
[5] VULKANOX 4020/LG, a product of Lanxess,
[6] TMQ luvomaxx,
[7] MC Wax 721,
[8] Si 69, a product of Evonik,
[9] LUVOMAXX TBBS, a product of Lehmann & Voss & Co. KG,
[10] DENAX, a product of Draslovka a.s.

Table 6

Ex.	%F [%wt.]	MV [1+4]	tan 6 (60°C)[1]	J'' (30°C)[2], [Pa^{-1}]	G' [Pa]/ E' (-20°C)[3] [MPa]	Rebound[4] at $T_{70°C}$	RI (S300%/S100%)[5]	Silica Dispersion[6] [%]
5c	0	66	0.188	4.63E-08	1.62E+07	59	4.3	81
6c	0.98	60	0.162	5.09E-08	1.18E+07	62	4.7	93
7c	0	43	0.190	5.07E-08	1.62E+07	57	4.2	79
8c	0.96	45	0.157	4.81E-08	1.26E+07	63	4.8	92

[1] Rolling resistance (lower is better)
[2] Dry traction (higher is better)
[3] Winter Traction (lower is better)
[4] Rebound at 70°C (higher is better)
[5] Reinforcement index (higher is better)
[6] Silica dispersion (higher is better)

The rubbers as obtained in Examples 6c and 8c and Comparative Examples 5c and 7c, respectively, were examined and compared to each other (functionalized vs. non-functionalized), see the results presented in Table 6.

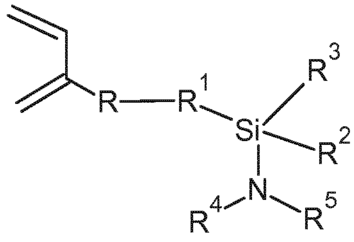
Example 5c was compared with Example 6c, and Example 7c with Example 8c, since they correspond to similar Mooney ranges, namely higher (58, 64) and lower (44, 51).

In each case, tire predictors obtained from DMA, such as rolling resistance, dry traction, winter traction are improved when comparing functionalized (Ex. 6c, 8c – Table 6) and nonfunctionalized (Ex. 5c, 7c – Table 6) rubber, the same is true with respect to rebound at high temperature. The reinforcement index, the ratio of modulus 300 % to modulus 100 %, was also found to be increased, as well as much higher silica dispersion (dispeGRADER). This confirmed a much higher interaction between functionalized *cis*-polybutadiene rubber and filler (silica), as compared to the use of non-functionalized rubber.

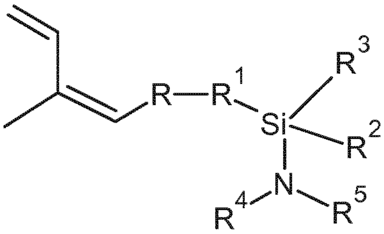
While certain representative embodiments and details have been shown for the purpose of illustrating the subject invention, it will be apparent to those skilled in this art that various changes and modifications can be made therein without departing from the scope of the subject invention, which scope is defined by the following claims.

Claims

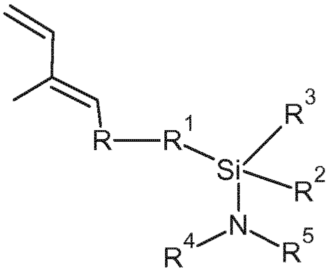
1. A method for the preparation of a functionalized conjugated diene selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)



(IIIa),



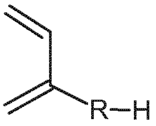
(IIIb),



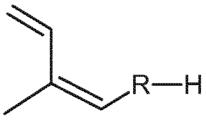
(IIIc),

wherein

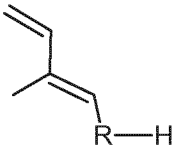
- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



(Ib)



(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms,

- R^1 is selected from

  i) a single bond,

  ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

  iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

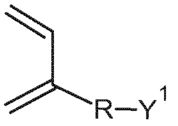
- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

  i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

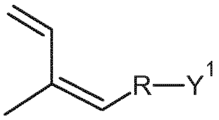
or

  ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom,

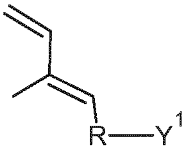
  the method comprising reacting, under Grignard conditions, a conjugated diene halide selected from the group of compounds of formula (IIa), (IIb), (IIc)



(IIa)



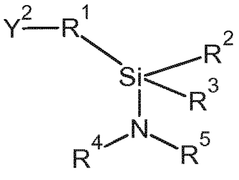
(IIb)



(IIc),

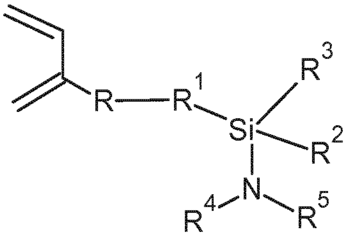
wherein Y^1 is selected from fluorine, chlorine, bromine, and iodine atoms (and Y^1 is preferably a chlorine atom),

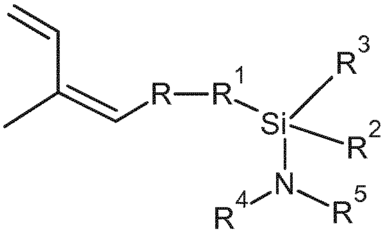
with a compound of formula (IV)

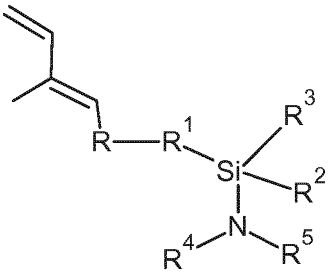

(IV),

wherein Y^2 is selected from fluorine, chlorine, bromine, and iodine atoms.

2. A method for the preparation of a functionalized conjugated diene selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)

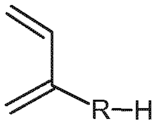

(IIIa),


(IIIb),

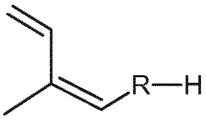

(IIIc),

wherein

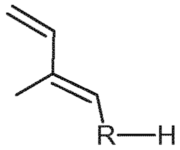
- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



(Ib)



(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms,

- R^1 is selected from

  i) a single bond,

  ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

  iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

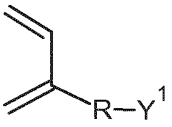
  i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

or

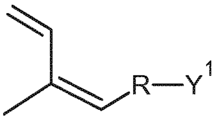
  ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom,

the method comprising

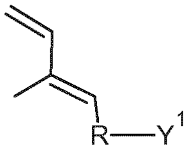
A) reacting, under Grignard conditions, a conjugated diene halide selected from the group of compounds of formula (IIa), (IIb), (IIc)



(IIa)



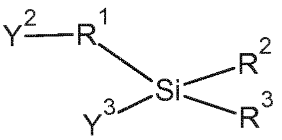
(IIb)



(IIc),

wherein Y^1 is selected from fluorine, chlorine, bromine, and iodine atoms (and Y^1 is preferably a chlorine atom),

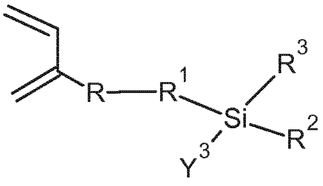
with a compound of formula (V)



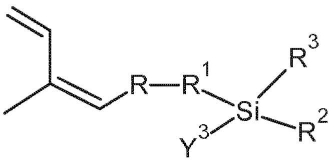
(V),

wherein Y^2 and Y^3 are independently selected from fluorine, chlorine, bromine, and iodine atoms, and preferably Y^2 and Y^3 are each chlorine atoms,

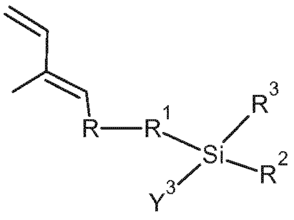
to result in a compound of formula (VIa), (VIb), (VIc)



(VIa)



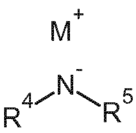
(VIb)



(VIc),

and

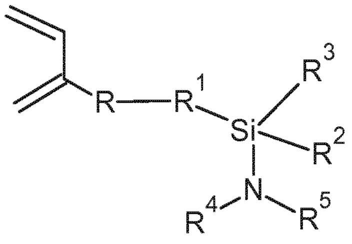
B) reacting the compound of formula (VIa), (VIb), (VIc) with an amide of formula (VII)



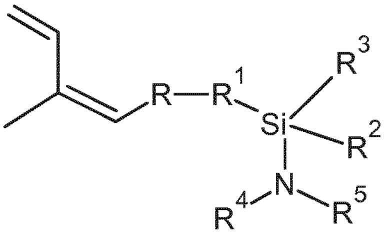
(VII),

wherein M is an alkali metal selected from lithium, sodium, and potassium, and M is preferably sodium.

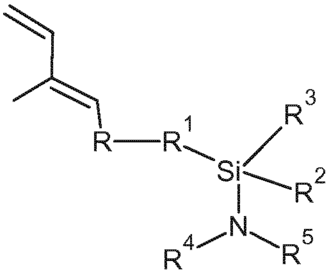
3. A functionalized conjugated diene selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)



(IIIa),



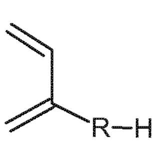
(IIIb),



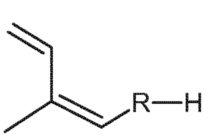
(IIIc),

wherein

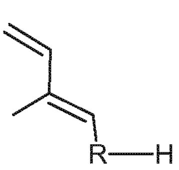
- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



(Ib)



(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms,

- R^1 is selected from

i) a single bond,

ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

or

ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom.

4. The functionalized conjugated diene of claim 3, wherein R^1 is i) a single bond.

5. The functionalized conjugated diene of any of claims 3 or 4, wherein R^2, R^3, R^6, R^7, and R^8 are the same or different and represent a linear or branched, saturated or unsaturated hydrocarbyl group,

preferably wherein R^2, R^3, R^6, R^7, and R^8 are the same or different and represent a linear or branched alkyl, aryl, or alkaryl group,

more preferably wherein R^2, R^3, R^6, R^7, and R^8 are the same or different and represent CH_3 or C_6H_5,

in particular wherein R^2, R^3, R^6, R^7, and R^8 all represent CH_3.

6. The functionalized conjugated diene of any of claims 3 to 5, wherein R^4 and R^5 are the same and represent a linear, branched or cyclic, saturated or unsaturated alkyl group,

preferably wherein R^4 and R^5 are the same and represent $–CH(CH_3)_2$ or CH_3, more preferably wherein R^4 and R^5 are the same and represent –$CH(CH_3)_2$.

7. The functionalized conjugated diene of any of claims 3 to 6, wherein R is a linear or branched, saturated or unsaturated hydrocarbylene, hydrocarbylidene, or hydrocarbylidyne group,

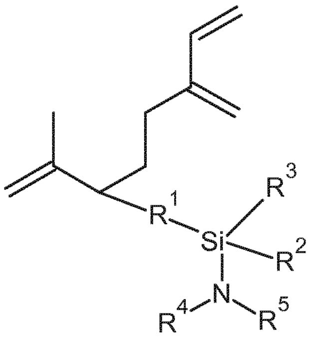
   preferably wherein R is a branched, unsaturated hydrocarbylene group,

   more preferably wherein the starting conjugated diene of formula (Ia), (Ib), (Ic) is selected from terpenes and 4,8-dimethyl-1,3,7-nonatriene,

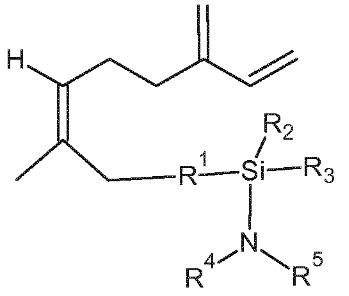
   most preferably wherein the terpene is selected from myrcene and ocimene,

   in particular wherein the terpene is myrcene selected from α-myrcene and β-myrcene.

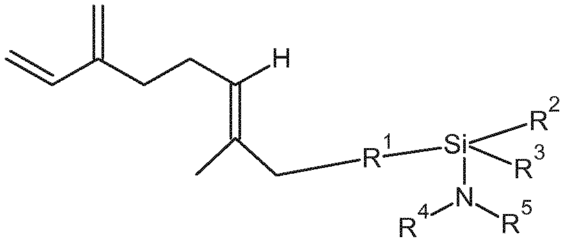
8. The functionalized conjugated diene of claim 7, which is a myrcene derivative of formula (VIII), (IX), or (X)



(VIII),

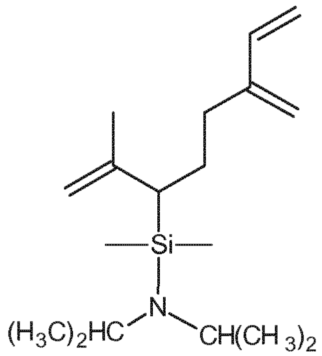


(IX),

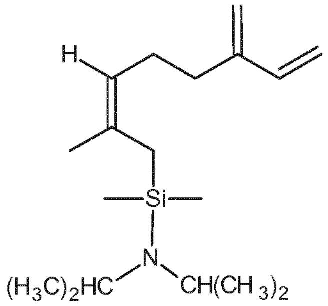


(X),

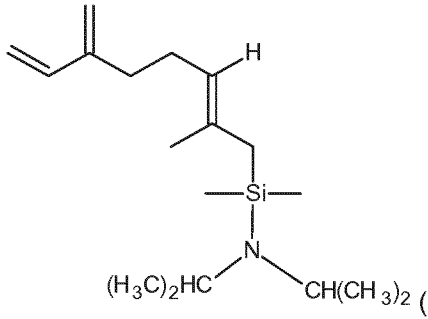
preferably wherein the myrcene derivative is of formula (VIIIa), (IXa), or (Xa)



(VIIIa),



(IXa),



(Xa).

9. Use of one or more functionalized conjugated dienes of any of claims 3 to 8 in the production of an elastomeric copolymer.

10. The use of claim 9, wherein the elastomeric copolymer comprises, in addition to one or more units derived from the one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc), units derived from one or more conjugated diene monomers,

    preferably wherein the conjugated diene monomer is selected from 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-phenyl-1,3-butadiene, and 4,5-diethyl-1,3-octadiene, more preferably wherein the conjugated diene monomer is selected from 1,3-butadiene and isoprene,

in particular wherein the conjugated diene monomer is 1,3-butadiene.

11. The use of claim 9 or claim 10, wherein the production of the elastomeric copolymer is by anionic polymerization or by coordination polymerization.

12. The use of any of claims 9 to 11, wherein the elastomeric copolymer further comprises units derived from one or more vinyl aromatic monomers,

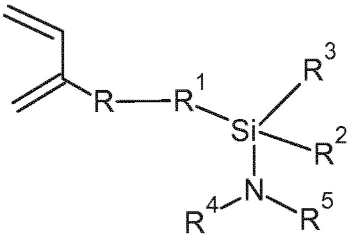
preferably wherein the vinyl aromatic monomer is selected from styrene, 1-vinylnaphthalene, 3-methyl styrene, 3,5-diethylstyrene, 4-propylstyrene, 2,4,6-trimethylstyrene, 4-dodecylstyrene, 3-methyl-5-n-hexylstyrene, 4-phenylstyrene, 2-ethyl-4-benzylstyrene, 3,5-diphenylstyrene, 2,3,4,5-tetraethylstyrene, 3-ethyl-1-vinylnaphthalene, 6-isopropyl-1-vinylnaphthalene, 6-cyclohexyl-1-vinylnaphthalene, 7-dodecyl-2-vinylnaphthalene, and α-methyl styrene,

more preferably wherein the vinyl aromatic monomer is selected from styrene, 3-methylstyrene and α-methylstyrene,

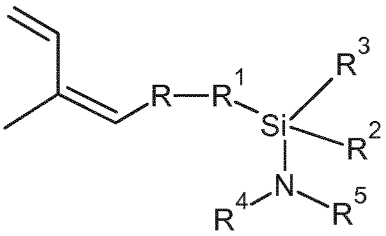
in particular wherein the vinyl aromatic monomer is styrene.

13. The use of any of claims 9 to 12, wherein the amount of units derived from the one or more functionalized conjugated dienes selected from of the group of compounds of formula (IIIa), (IIIb), (IIIc) is in a range of from 0.05 to 5 wt.%, based on the weight of the elastomeric copolymer, more preferably in a range of from 0.2 to 1.5 wt.%, most preferably in a range of from 0.4 to 1.2 wt.%, e.g. in a range of from 0.6 to 1.0 wt.%, such as about 0.8 wt.%.

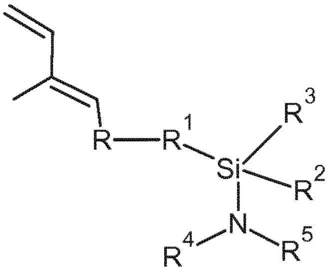
14. The use of an alkali metal salt derivative of a functionalized conjugated diene selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)



(IIIa),



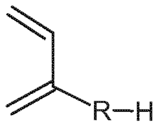
(IIIb),



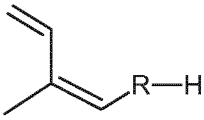
(IIIc),

wherein

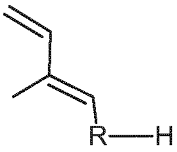
- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



(Ib)



(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms;

- R^1 is selected from

  i) a single bond,

  ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

  iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

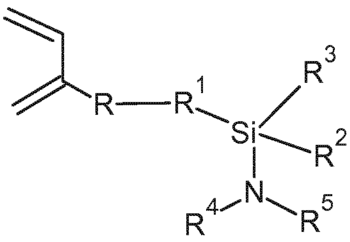
or

ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom,

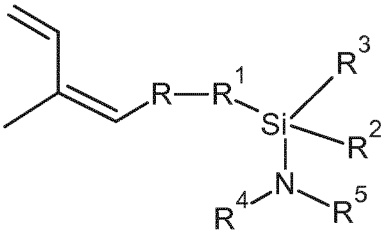
as initiator for the anionic copolymerization of one or more conjugated diene monomers, optionally one or more vinyl aromatic monomers, and optionally one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc).

15. A process for the production of a copolymer component comprising coupled copolymer and terminally modified copolymer, the process comprising the following steps:

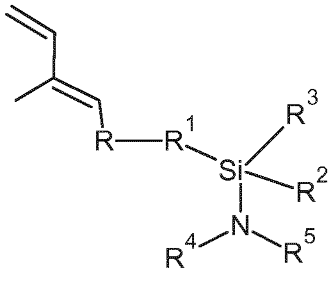
(1) providing an initiator component, wherein the initiator component preferably comprises one or more alkali metal salt derivatives of a one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)



(IIIa),



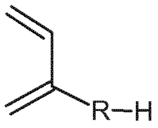
(IIIb),



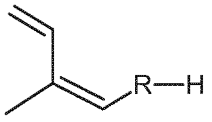
(IIIc),

wherein

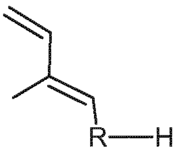
- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



(Ib)



(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms

- R^1 is selected from

  i) a single bond,

  ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

  iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

or

ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom,

wherein the alkali metal is selected from lithium, sodium, and potassium;

(2) contacting a monomer component comprising

i) one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc),

ii) one or more conjugated diene monomers and

iii) optionally one or more vinyl aromatic monomers,

with the initiator component, to initiate anionic copolymerization;

(3) continuing copolymerization, to result in a copolymer;

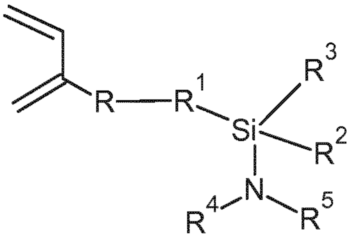
(4) optionally continuing copolymerization of the copolymer, in the presence of one or more functionalized monomers, to result in a functionalized copolymer;

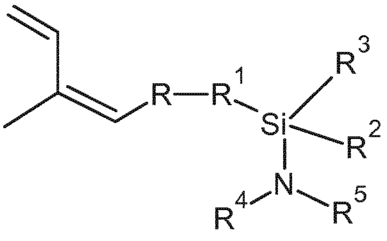
(5) coupling a part of the copolymer of step (3) or the functionalized copolymer of step (4) with one or more coupling agents, to result in coupled copolymer; and

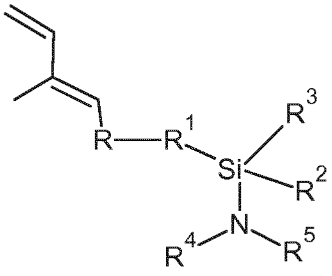
(6) terminally modifying a part of the copolymer of step (3) or the functionalized copolymer of step (4) with one or more terminal modifying agents, to result in terminally modified copolymer.

16. A process for producing an elastomeric copolymer comprising subjecting

i) one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)

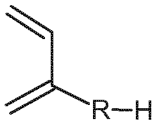

(IIIa),

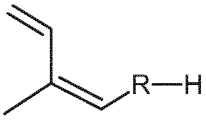

(IIIb),

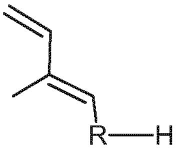

(IIIc),

wherein

- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)


(Ia)


(Ib)


(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms;

- R^1 is selected from

  i) a single bond,

ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

or

ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom,

ii) one or more conjugated diene monomers, and

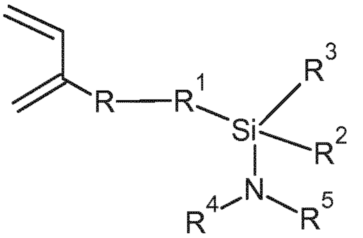
iii) optionally one or more vinyl aromatic monomers

to anionic polymerization conditions,

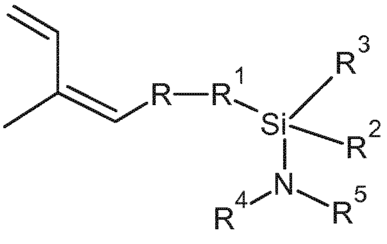
preferably wherein the anionic polymerization conditions include initiating the polymerization with an alkali metal salt derivative of the one or more functionalized conjugated dienes of formula (IIIa), (IIIb), (IIIc), wherein the alkali metal is selected from lithium, sodium, and potassium.

17. A process for producing an elastomeric copolymer comprising subjecting

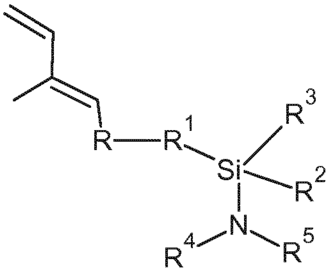
i) one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)



(IIIa),



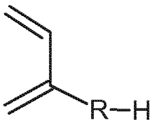
(IIIb),



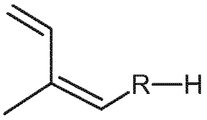
(IIIc),

wherein

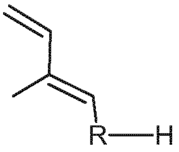
- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



(Ib)



(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms;

- R^1 is selected from

  i) a single bond,

ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

or

ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom,

and

ii) one or more conjugated diene monomers

to Ziegler-Natta polymerization conditions.

18. The process of claim 17, wherein the Ziegler-Natta polymerization conditions include a catalyst system comprising 1) metal chloride and 2) co-catalyst,

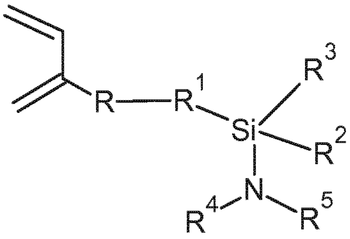
preferably wherein the metal chloride 1) is selected from chlorides of one or more of Ni, Co, Ti, Nd, V, Ti, Zr, and Fe, and the co-catalyst 2) is selected from one or more of aluminium and magnesium alkyl compounds.

19. The process of claim 17, wherein the Ziegler-Natta polymerization conditions include a catalyst system comprising 1) non-halide metal compound, 2) co-catalyst, and 3) halide donor compound,

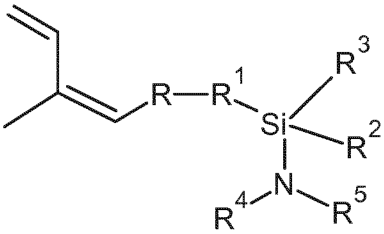
preferably wherein the non-halide metal compound 1) is one or more Nd compounds, more preferably wherein the Nd compound is selected from neodymium carboxylates, neodymium alcoholates, neodymium phosphates, neodymium phosphonates, neodymium allyl compounds, neodymium cyclopentadienyl complexes, neodymium amides, and neodymium acetylacetonates.

20. An elastomeric copolymer comprising repeat units that are derived from

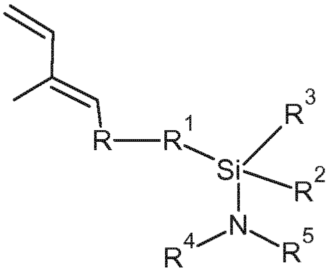
    A) 0.05 wt.% to 5 wt.%, by weight of the copolymer, of one or more functionalized conjugated dienes selected from the group of compounds of formula (IIIa), (IIIb), (IIIc)



(IIIa),



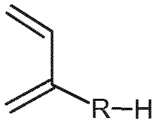
(IIIb),



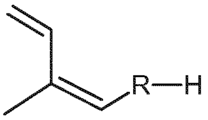
(IIIc),

wherein

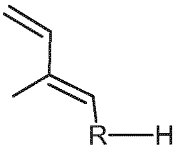
- R is an organylene group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom, and the starting conjugated diene selected from the group of compounds of formula (Ia), (Ib), (Ic)



(Ia)



(Ib)



(Ic),

from which the functionalized conjugated diene of formula (IIIa), (IIIb), (IIIc) is derived, has at least 10 carbon atoms,

- R^1 is selected from

  i) a single bond,

  ii) one or more of an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8; and

  iii) an organylene group optionally containing one or more selected from an oxygen atom, a sulfur atom, a group NR^6, and a group SiR^7R^8;

- R^2, R^3, R^6, R^7, R^8 can be the same or different and represent an organyl group optionally containing one or more heteroatoms selected from an oxygen atom, a sulfur atom, a nitrogen atom, and a silicon atom; and

i) R^4 and R^5 can be the same or different and each R^4 and R^5 independently represents an organyl group optionally containing one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

or

ii) R^4 and R^5 are bonded to each other to form a heterocyclic ring containing the nitrogen atom and at least one carbon atom and, optionally, one or more heteroatoms selected from a silicon atom, an oxygen atom, a sulfur atom, and a nitrogen atom;

B) 45 wt.% to 99.95 wt.%, by weight of the copolymer, of one or more conjugated diene monomers;

C) 0 wt.% to 50 wt.%, by weight of the copolymer, of one or more vinyl aromatic monomers.

21. The elastomeric copolymer of claim 20, wherein the amount of B) conjugated diene monomer is 50 to 92 wt.%, by weight of the copolymer, preferably 60 to 90 wt.%, by weight of the copolymer, in particular 65 to 80 wt.%, by weight of the copolymer.

22. The elastomeric copolymer of claim 20 or claim 21 wherein the vinyl aromatic monomer is selected from styrene, 1-vinylnaphthalene, 3-methylstyrene, 3,5-diethylstyrene, 4-propylstyrene, 2,4,6-trimethylstyrene, 4-dodecylstyrene, 3-methyl-5-n-hexylstyrene, 4-phenylstyrene, 2-ethyl-4-benzylstyrene, 3,5-diphenylstyrene, 2,3,4,5-tetraethylstyrene, 3-ethyl-1-vinylnaphthalene, 6-isopropyl-1-vinylnaphthalene, 6-cyclohexyl-1-vinylnaphthalene, 7-dodecyl-2-vinylnaphthalene, and α-methylstyrene,

    preferably wherein the vinyl aromatic monomer is selected from styrene, 3-methylstyrene and α-methylstyrene,

    in particular wherein the vinyl aromatic monomer is styrene.

23. The elastomeric copolymer of any one of claims 20 to 22 wherein the amount of C) vinyl aromatic monomer is 8 to 45 wt.%, by weight of the copolymer, preferably 10 to 40 wt.%, by weight of the copolymer, in particular 20 to 35 wt.%, by weight of the copolymer.

24. The elastomeric copolymer of claim 20, comprising less than 1 wt.% C) vinyl aromatic monomer (and preferably no C) vinyl aromatic monomer), wherein the amount of B) conjugated diene monomer is 95 to 99.95 wt.%, by weight of the copolymer, preferably 98 to 99.6 wt.%, by weight of the copolymer, in particular 99.0 to 99.4 wt.%, by weight of the copolymer.

25. The elastomeric copolymer of any of claims 20 to 24, wherein the conjugated diene monomer is selected from 1,3-butadiene, isoprene, 1,3-pentadiene, 2,3-dimethyl-1,3-butadiene, 2-methyl-1,3-pentadiene, 2,3-dimethyl-1,3-pentadiene, 2-phenyl-1,3-butadiene, and 4,5-diethyl-1,3-octadiene,

    more preferably wherein the conjugated diene monomer is selected from 1,3-butadiene and isoprene,

    in particular wherein the conjugated diene monomer is 1,3-butadiene.

26. The elastomeric copolymer of any one of claims 20 to 25, wherein the copolymer comprises units having a linear structure.

27. The elastomeric copolymer of any one of claims 20 to 26, wherein the copolymer comprises units having a branched structure.

28. The elastomeric copolymer of any one of claims 20 to 27, wherein the copolymer comprises units having a star structure and being produced by the reaction of metal-terminated living linear copolymer with one or more coupling agents in anionic polymerization conditions,

preferably wherein a.

I) the coupling agent is a tin halide coupling agent, preferably wherein the tin halide coupling agent is tin tetrachloride,

or

II) the coupling agent is a silicon halide coupling agent, preferably wherein the silicon halide coupling agent is selected from silicon tetrachloride, silicon tetrabromide, silicon tetrafluoride, silicon tetraiodide, hexachlorodisilane, hexabromodisilane, hexafluorodisilane, hexaiododisilane, octachlorotrisilane, octabromotrisilane, octafluorotrisilane, octaiodotrisilane, hexachlorodisiloxane, 2,2,4,4,6,6-hexachloro-2,4,6-trisilaheptane-1,2,3,4,5,6-hexakis[2-(methyldichlorosilyl)ethyl]benzene, and alkyl silicon halides of general formula (XI)

$$R^6_n\text{-Si-}X_{4-n} \text{ (XI)},$$

wherein R^6 is a monovalent aliphatic hydrocarbon group having 1 to 20 carbon atoms or a monovalent aromatic hydrocarbon group having 6 to 18 carbon atoms; n is an integer of 0 to 2; and X can be a chlorine, bromine, fluorine or iodine atom,

and/or wherein b. the fraction of units having star structure is between 0 and 75 %, by weight of the copolymer.

29. A method for producing a rubber comprising vulcanizing the elastomeric copolymer according to any one of claims 20 to 28 in the presence of one or more vulcanizing agents.

30. A rubber as obtainable according to the method of claim 29.

31. A rubber composition comprising x) a rubber component comprising the rubber according to claim 30,

    preferably wherein the rubber composition further comprises y) one or more fillers,

    more preferably wherein the filler is selected from the group consisting of silica and carbon black,

    most preferably wherein the rubber composition comprises y) both silica and carbon black.

32. The rubber composition according to claim 31, wherein the amount of filler component y) is 10 to 150 parts by mass relative to 100 parts by mass of the rubber component x) (phr),

    preferably wherein the amount of filler component y) is 20 to 140 phr,

    more preferably wherein the amount of filler component y) is 30 to 130 phr.

33. The rubber composition according to claim 31 or claim 32 wherein the rubber component x) also comprises one or more further rubbery polymers,

    preferably wherein the further rubbery polymer is selected from the group consisting of natural rubber, synthetic isoprene rubber, butadiene rubber, styrene-butadiene rubber, ethylene-α-olefin copolymer rubber, ethylene-α-olefin-diene copolymer rubber, acrylonitrile-butadiene copolymer rubber, chloroprene rubber, and halogenated butyl rubber.

34. A tire component comprising the rubber composition of claim 33,

    preferably wherein the tire component is a tire tread.

35. A tire comprising the tire component of claim 34.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2019/073369

A. CLASSIFICATION OF SUBJECT MATTER
INV. B60C1/00 C08L9/06 C08F4/48 C08F236/10 C07F7/10
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)
B60C 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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 3 159 346 A1 (TRINSEO EUROPE GMBH [CH]) 26 April 2017 (2017-04-26) cited in the application claims 1,9 paragraphs [0001], [0096], [0098], [0100], [0102], [0104], [0106], [0111] - [0114] tables 1,3 -----	1-35
A	EP 3 257 869 A1 (TRINSEO EUROPE GMBH [CH]) 20 December 2017 (2017-12-20) claims 1,8,11-17 paragraphs [0107], [0149], [0154] table 4 -----	1-35

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

☒ See patent family annex.

* Special categories of cited documents :

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

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search 20 September 2019	Date of mailing of the international search report 04/10/2019
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Baekelmans, Didier

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2019/073369

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 3159346 A1	26-04-2017	CN 108350001 A	31-07-2018
		EP 3159346 A1	26-04-2017
		ES 2685917 T3	15-10-2018
		HU E039540 T2	28-01-2019
		JP 2018532743 A	08-11-2018
		PL 3159346 T3	30-11-2018
		TW 201728595 A	16-08-2017
		US 2018291041 A1	11-10-2018
		WO 2017067877 A1	27-04-2017
EP 3257869 A1	20-12-2017	CN 109415447 A	01-03-2019
		EP 3257869 A1	20-12-2017
		ES 2717151 T3	19-06-2019
		HU E042696 T2	29-07-2019
		JP 2019523805 A	29-08-2019
		KR 20190018696 A	25-02-2019
		PL 3257869 T3	31-07-2019
		SG 11201811212S A	30-01-2019
		TW 201821440 A	16-06-2018
		US 2019169406 A1	06-06-2019
		WO 2017216344 A1	21-12-2017