

CLAIMS

1. A process for preparing a branched elastomeric polymer, said process comprising:

(a) polymerizing at least one conjugated diene and a compound of Formula 1 as defined below, and optionally one or more aromatic vinyl monomers, in the presence of an initiator compound,

(a') polymerizing at least one conjugated diene and optionally one or more aromatic vinyl monomers in the presence of an initiator compound obtainable by reacting a compound of Formula 1 as defined below with an organo-alkali metal compound, or

(a'') reacting a living polymer, obtainable by anionically polymerizing at least one conjugated diene and optionally one or more aromatic vinyl monomers, with a compound of Formula 1 as defined below,

characterized in that (a), (a') and (a'') is carried out in the presence of a stabilizer compound of Formula 2 as defined below;



wherein

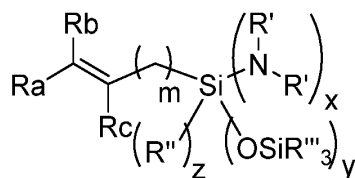
A is an organic group having at least two amino groups;

each B is independently selected from a group $-\text{Si}(\text{R}^1)(\text{R}^2)(\text{R}^3)$, wherein R^1 , R^2 and R^3 are each independently selected from vinyl, butadienyl, methyl, ethyl, propyl, butyl, hexyl, octyl, phenyl and benzyl, with the proviso that at least one of R^1 , R^2 and R^3 is selected from vinyl and butadienyl, wherein each group B is a substituent of an amino group of group A;

at least two of the amino groups of group A are each substituted with at least one group B;

n is an integer of at least 2, preferably an integer selected from 2 to 6; and

all amino groups in group A are tertiary amino groups;



(Formula 2)

wherein

R' is independently selected from C₁-C₁₂ alkyl, C₂-C₁₂ alkenyl, C₆-C₁₈ aryl and C₇-C₁₈ alkylaryl, wherein the two R' groups may be connected to form a ring and the ring may contain, further to the Si-bonded nitrogen atom, one or more of an oxygen atom, a nitrogen atom, an >N(C₁-C₆ alkyl, C₆-C₁₈ aryl, C₇-C₁₈ alkylaryl) group and a sulfur atom;

R'' is selected from C₁-C₆ hydrocarbyl;

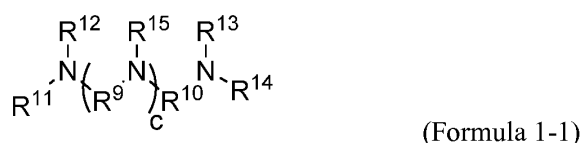
R''' is independently selected from C₁-C₁₈ hydrocarbyl;

R_a, R_b and R_c are independently selected from hydrogen, methyl, ethyl and vinyl;

x is an integer selected from 1 and 2; y is an integer selected from 0, 1 and 2; z is an integer selected from 0, 1 and 2; and x+y+z=3;

m is selected from 0 and 1; with the proviso that, when none of R_a, R_b and R_c is vinyl, then m=0.

2. The process according to claim 1, wherein the compound of Formula 1 is a compound selected from the following Formulas 1-1 to 1-5:

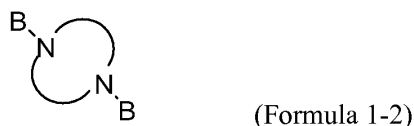


wherein

each of R¹¹, R¹², R¹³, R¹⁴ and R¹⁵ is independently selected from group B, C₁-C₁₈ alkyl, C₆-C₁₈ aryl, optionally C₁-C₄ alkyl-substituted C₃-C₁₂ heteroaryl, C₇-C₁₈ aralkyl, (R⁴)_a-O-(R⁵)_b, wherein each of R⁴ and R⁵ is independently selected from C₁-C₆ alkyl and C₆-C₁₈ aryl and a and b are each integers independently selected from 0 to 4, and -Si(R⁶)(R⁷)(R⁸), wherein each of R⁶, R⁷ and R⁸ is independently selected from methyl, ethyl, propyl, butyl, hexyl, octyl, phenyl and benzyl;

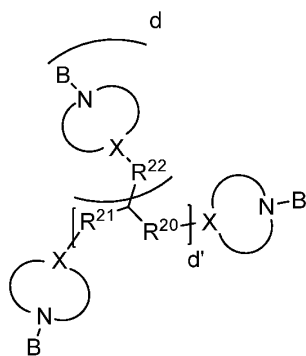
each of R⁹ and R¹⁰ is independently selected from divalent ethyl, propyl, butyl, phenyl and -(CH₂)_{a'}-C₆H₅-(CH₂)_{b'}-, wherein each of a' and b' is an integer independently selected from 0 and 1; and

c is an integer selected from 0, 1, 2 and 3;



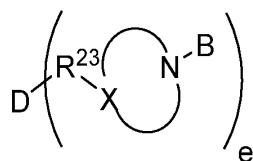
wherein the group -N<>N- is a 5- to 18-membered heterocyclic group which may be saturated or unsaturated and which may be substituted on any carbon atom of the ring with

a C₁-C₆ alkyl group, wherein heteroatomic groups other than the two N atoms expressly shown in Formula 1-2 are selected from -N=, >NR¹⁶, wherein R¹⁶ is selected from group B, C₁-C₆ alkyl, phenyl and benzyl, -O-, -S- and >SiR¹⁷R¹⁸, wherein each of R¹⁷ and R¹⁸ is independently selected from C₁-C₆ alkyl, phenyl and benzyl;



(Formula 1-3)

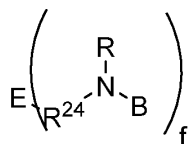
wherein each of R²⁰, R²¹ and R²² is independently selected from a single bond and a divalent C₁-C₁₀ alkyl group, d is an integer selected from 0, 1 and 2, d' is an integer selected from 0 and 1, wherein d is 0 when d' is 0, each group -N<>X- is independently selected from a 5- to 10-membered heterocyclic group which may be saturated or unsaturated and which may be substituted on any carbon atom of the ring with a C₁-C₆ alkyl group, wherein each X is independently selected from -N-, -C= and -CH-, and heteroatomic groups other than the two groups N and X expressly shown in Formula 1-3 are selected from -N=, >NR¹⁶, wherein R¹⁶ is selected from C₁-C₆ alkyl, group B, phenyl and benzyl, -O-, -S- and >SiR¹⁷R¹⁸, wherein each of R¹⁷ and R¹⁸ is independently selected from C₁-C₆ alkyl, phenyl and benzyl;



(Formula 1-4)

wherein D is a 5- to 10-membered carbocyclic or heterocyclic group which may be saturated or unsaturated and which may be substituted on any carbon atom of the ring with a C₁-C₆ alkyl group, wherein heteroatomic groups are selected from -N=, >NR¹⁶, wherein R¹⁶ is selected from C₁-C₆ alkyl, group B, phenyl and benzyl, -O-, -S- and >SiR¹⁷R¹⁸, wherein each of R¹⁷ and R¹⁸ is independently selected from C₁-C₆ alkyl and phenyl, each group -N<>X- is independently selected from a 5- to 10-membered heterocyclic group which may be saturated or unsaturated and which may be substituted on any carbon atom of the ring with a C₁-C₆ alkyl group, wherein each X is independently selected from -N-, -

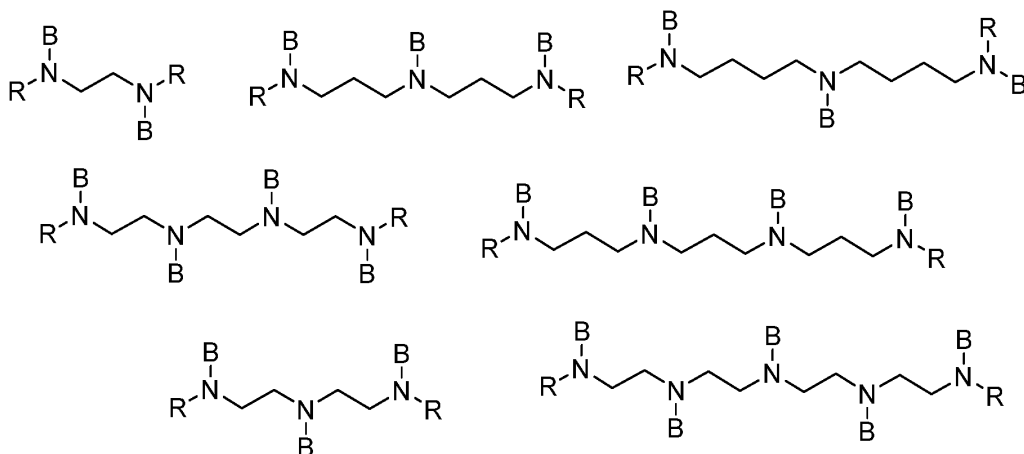
C= and -CH-, R^{23} is selected from a single bond and a divalent C_1 - C_{10} alkyl group, and e is an integer selected from 2, 3 and 4;



(Formula 1-5)

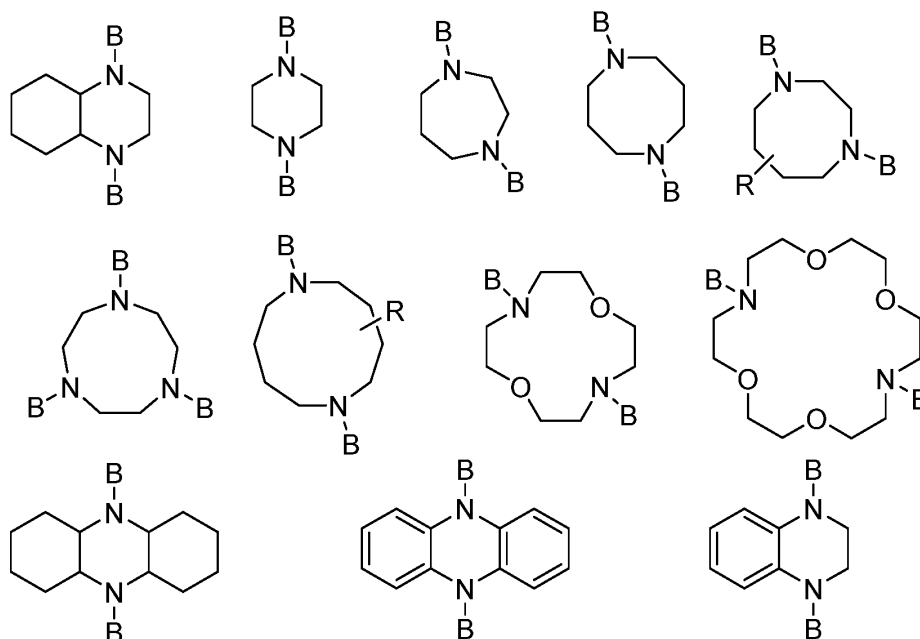
wherein E is a 6- to 10-membered cycloaliphatic or aromatic group, each R^{24} is independently selected from a single bond and C_1 - C_2 alkyl, each R is independently selected from B, C_1 - C_6 alkyl and benzyl, and f is an integer selected from 2 and 3.

3. The process according to claim 1, wherein the compound of Formula 1 is selected from

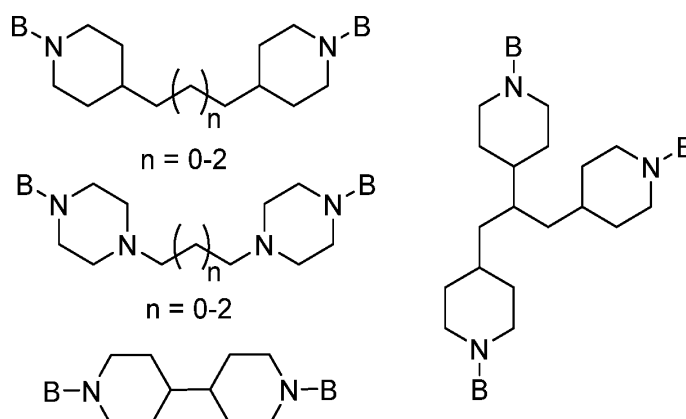


10 wherein each R is independently selected from B, C_1 - C_6 alkyl and benzyl;

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wherein R is a C₁-C₆ alkyl group; and



4. The process according to any one of claims 1 to 3, wherein R''' in Formula 2 is
 5 independently selected from C₁-C₁₈ alkyl, C₂-C₁₈ alkenyl, C₆-C₁₈ aryl and C₇-C₁₈
 alkylaryl, preferably methyl, ethyl, isopropyl, tert-butyl, phenyl and benzyl.
5. The process according to any one of claims 1 to 4, wherein R' in Formula 2 is
 10 independently selected from methyl, ethyl, n-propyl, n-butyl, isobutyl, pentyl, hexyl, octyl
 and benzyl, or the two R' groups are connected to form, together with the Si-bonded
 nitrogen atom, a 5- to 12-membered ring such as a cyclopentylamine group,
 cyclohexylamine group, a cycloheptylamine group, a cyclooctylamine group, a
 cyclododecylamine group, a morpholine group, an oxazolidine group, a thiazolidine group,

a thiamorpholine group, a 4-methylpiperazine group, a 4-ethylpiperazine group, a 4-propylpiperazine group, a 4-butylpiperazine group and a 4-benzylpiperazine group.

6. The process according to any one of claims 1 to 5, wherein R" in Formula 2 is selected from C₁-C₆ alkyl and phenyl, preferably methyl.

5 7. The process according to any one of claims 1 to 6, wherein R_a, R_b and R_c in Formula 2 are identical and are preferably hydrogen.

8. The process according to any one of claims 1 to 7, wherein in Formula 2 (i) x, y and z are each 1 and m=0, (ii) x=2, y=0, z=1 and m=0, or (iii) x=1, y=0, z=2 and m=1 and at least one of R_a, R_b and R_c is vinyl.

10 9. The process according to any one of claims 1 to 8, wherein the initiator compound in step (a) or the organo-alkali metal compound in step (a') is selected from methyllithium, ethyllithium, n-butyllithium, s-butyllithium, tert-butyllithium, tert-octyllithium, isopropyllithium, phenyllithium, cyclohexyllithium, 2-butyllithium, 4-phenylbutyllithium, t-butyl dimethylsilyloxypropyllithium, dialkylaminopropyllithium, N-morpholinopropyllithium, sodium biphenylide, sodium naphthalenide, potassium naphthalenide, 1,3-bis(1-(phenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-ethylphenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-methylphenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-propylphenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-(tert-butyl)phenyl)1-lithiohexyl)-benzene, 1,3-bis(1-(4-(diethylamino)phenyl)1-lithiohexyl)-benzene, 1,3-bis(1-(4-(dimethylamino)phenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-ethoxyphenyl)1-lithiohexyl)benzene, 1,3-bis(1-(4-(dimethoxy)phenyl)1-lithiohexyl)benzene, (((dimethylamino)dimethylsilyl)methyl)lithium, (((diethylamino)dimethylsilyl)methyl)lithium, (((dibutylamino)dimethylsilyl)methyl)lithium, (((dihexylamino)dimethylsilyl)methyl)lithium, (((dioctylamino)dimethylsilyl)methyl)lithium, (((dibenzylamino)dimethylsilyl)methyl)lithium, (((dimethyl(piperidin-1-yl)silyl)methyl)lithium, (((dimethyl(morpholino)silyl)methyl)lithium, (((dimethyl(4-methylpiperazin-1-yl)silyl)methyl)lithium, (((dimethyl(4-ethylpiperazin-1-yl)silyl)methyl)lithium, and (((dimethyl(4-benzylpiperazin-1-yl)silyl)methyl)lithium.

15 20 25 30

10. The process according to any one of claims 1 to 9, wherein the stabilizer of Formula 2 is used in an amount of 0.01 to 100 equivalent per equivalent of initiator or living polymer chain end, preferably 0.05 to 20 equivalents per equivalent, more preferably 0.1 to 5 equivalents per equivalent, even more preferably 0.1 to 0.9 equivalents per equivalent.

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11. A branched elastomeric polymer obtainable by a process as defined in any one of claims 1 to 10.

12. A non-vulcanized polymer composition comprising the branched elastomeric polymer as defined in claim 11 and one or more further components selected from (i)

- components which are added to or formed as a result of the polymerization process used for making said polymer, (ii) components which remain after solvent removal from the polymerization process, and (iii) components which are added to the polymer after completion of the polymer manufacturing process, wherein said composition optionally comprises one or more fillers.
- 5 13. The non-vulcanized polymer composition according to claim 12, which comprises one or more extender oils.
14. The non-vulcanized polymer composition according to claim 12 or 13, which comprises one or more vulcanizing agents.
- 10 15. A vulcanized polymer composition which is obtained by vulcanizing the non-vulcanized polymer composition as defined in claim 14.
16. A process for preparing a vulcanized polymer composition, said process comprising vulcanizing the non-vulcanized polymer composition as defined in claim 14.
- 15 17. An article comprising at least one component formed from the vulcanized polymer composition as defined in claim 15, which article is preferably selected from a tire, a tire tread, a tire side wall, a tire carcass, a belt, a gasket, a seal, a hose, a vibration damper, a footwear component, a golf ball and a hose.