The present disclosure provides the following method for producing a modified conjugated diene-based polymer, modified conjugated diene-based polymer, polymer composition, crosslinked body, and tire.

[0009]

[1] A method for producing a modified conjugated diene-based polymer, which comprises reacting a conjugated diene-based polymer having an active chain end, obtained by polymerizing a monomer containing a conjugated diene compound in the presence of an initiator that contains at least either of an alkali metal compound or an alkaline earth metal compound, with a compound [M] having at least two groups selected from the group consisting of a group "-C(R^1)=N-A^1" and a group "-N=C(R^1)-A^1", where R^1 is a hydrogen atom or a hydrocarbyl group and A^1 is a monovalent group having an alkoxysilyl group.

[2] A modified conjugated diene-based polymer, which is a reaction product between a conjugated diene-based polymer having an active chain end and a compound [M] having two or more groups in total of at least either of a group "-CR^1=N-A^1" or a group "-N=CR^1-A^1" (where R^1 is a hydrogen atom or a hydrocarbyl group and A^1 is a monovalent group having an alkoxysilyl group).

[3] A polymer composition containing a modified conjugated diene-based polymer obtained by the production method according to [1] or a modified conjugated diene-based polymer according to [2], silica, and a crosslinking agent.

[4] A crosslinked body, which is obtained by crosslinking the polymer composition according to [3].

[5] A tire wherein at least a tread or a sidewall is formed using the polymer composition according to [3].

[6] A compound represented by the following formula (1).

Effects of the Invention

[0010]

Based on the present disclosure, a modified conjugated diene-based polymer which has high Mooney viscosity and good shape stability and which exhibits excellent processability when converted into a polymer composition without pseudo-crosslinking can be obtained. Accordingly, the modified conjugated diene-based polymer exhibiting good properties can be obtained in as few steps as possible with preventing an increase in the number of production steps. Moreover, based on the modified conjugated diene-based polymer of the present disclosure, dispersibility of silica can be made satisfactory and a crosslinked rubber having excellent low heat build-up can be obtained.

Embodiments for Carrying Out the Invention

[0011]

The modified conjugated diene-based polymer of the present disclosure is a reaction product between a conjugated diene-based polymer having an active chain end and a compound [M] having at least two groups selected from the group consisting of a group "-C(R^1)=N-A^1" and a group "-N=C(R^1)-A^1", where R^1 is a hydrogen atom or a hydrocarbyl group and A^1 is a monovalent group having an alkoxysilyl group. The modified conjugated diene-based polymer can be produced by the method including the following polymerization step and modification step. The following will describe the items relating to the embodiments of the present disclosure in detail.

[0012]

<Polymerization Step>

This step is a step of polymerizing a monomer containing a conjugated diene compound to obtain a conjugated diene-based polymer having an active chain end. Examples of the conjugated diene compound to be used for the polymerization include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 2-phenyl-1,3-butadiene, 3-methyl-1,3-pentadiene and 2-chloro-1,3-butadiene. Among these, 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene are preferable.

[0013]

The conjugated diene-based polymer may be a homopolymer of the conjugated diene compound, but is preferably a copolymer of the conjugated diene compound and an aromatic vinyl compound from the viewpoint of improving the strength of the resulting rubber. Examples of the aromatic vinyl compound to be used for the polymerization include styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, α-methylstyrene, 2,4-dimethylstyrene, 2,4-diisopropylstyrene, 4-t-butylstyrene, 5-t-butyl-2-methylstyrene, vinylethylbenzene, divinylbenzene, trivinylbenzene, divinylnaphthalene, t-butoxystyrene, vinylbenzyldimethylamine, (4-vinylbenzyl) dimethylaminoethyl ether, N,N-dimethylaminoethylstyrene, N,N-dimethylaminomethylstyrene, 2-ethylstyrene, 3-ethylstyrene, 4-ethylstyrene, 2-t-butylstyrene, 3-t-butylstyrene, 4-t-butylstyrene, vinylxylene, vinylnaphthalene, vinylpyridine, diphenylethylene and a tertiary amino group-containing diphenylethylene (e.g., 1-(4-N,N-dimethylaminophenyl)-1-phenylethylene) . Of these, as the aromatic vinyl compound, styrene and α-methylstyrene are particularly preferable.

substantially maintain the monomer in a liquid phase. Such a pressure may be achieved by a method of pressurizing the reactor using an inert gas to the polymerization reaction, for example.

[0025]

The conjugated diene-based polymer having an active chain end can be obtained by such a polymerization reaction. The weight average molecular weight (Mw) of the resulting conjugated diene-based polymer in terms of polystyrene, which is determined by gel permeation chromatography (GPC), is preferably 5.0×10^4 to 1.0×10^6. When the Mw is less than 5.0×10^4, the tensile strength, low heat build-up, and abrasion resistance of the crosslinked polymer are prone to decrease. When the Mw is more than 1.0×10^6, the processability of the rubber composition obtained using the modified polymer tends to decrease. Mw is more preferably 8.0×10^4 to 8.0×10^5, and still more preferably 1.0×10^5 to 5.0×10^5.

[0026]

Regarding the conjugated diene-based polymer having an active chain end, the vinyl bond content in the butadiene unit is preferably 30 to 70% by mass, more preferably 33 to 68% by mass, and still more preferably 35 to 65% by mass. When the vinyl bond content is less than 30% by mass, the grip performance tends to decrease. When the vinyl bond content exceeds 70% by mass, the abrasion resistance of the resulting vulcanized rubber tends to decrease. Incidentally, the term "vinyl bond content" used herein is a value showing a content ratio of the structural unit having a 1,2-bond to the total structural units of butadiene in the conjugated diene-based polymer and is a value measured by ^{1}H-NMR.

[0027]

<Modification Step>

In this step, the active chain end of the conjugated diene-based polymer obtained by the above polymerization step is reacted with the compound [M]. By using a compound having at least two groups selected from the group consisting of a group "-C(R^1)=N-A^1" and a group "-N=C(R^1)-A^1", where R^1 is a hydrogen atom or a hydrocarbyl group and A^1 is a monovalent group having an alkoxysilyl group (hereinafter also referred to as "specific imino group") as a modifier, a modified conjugated diene-based polymer which has a large number of branches of polymer chains and is modified with a group that interacts with silica can be obtained through the modification step.

[0028]

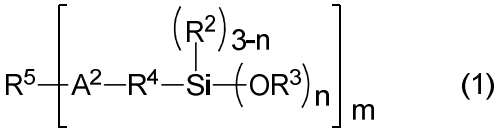
In the specific imino group, examples of the hydrocarbyl group of R^1 include

an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 20 carbon atoms, an alkenyl group having 2 to 20 carbon atoms and an aryl group having 6 to 20 carbon atoms. As long as A^1 has an alkoxysilyl group, the structure except for the group in A^1 is not particularly limited, but A^1 is preferably a group further having a methylene group or a polymethylene group, and more preferably a group which has a methylene group or a polymethylene group and an alkoxysilyl group and is bound to the nitrogen atom or carbon atom that constitutes the carbon-nitrogen double bond with the methylene group or polymethylene group. The number of the specific imino groups in the compound [M] is sufficiently 2 or more, and preferably 2 to 6. Incidentally, a plurality of R^1 and A^1 in the compound [M] may be the same or different.

[0029]

Particularly, the compound [M] is preferably a compound represented by the following formula (1):

[Chem 1]



(1)

wherein R^2 and R^3 are each independently a hydrocarbyl group having 1 to 20 carbon atoms, R^4 is an alkanediyl group having 1 to 20 carbon atoms, A^2 is a group "*-$C(R^1)$=N-" or a group "*-N=$C(R^1)$-" (where R^1 is a hydrogen atom or a hydrocarbyl group and "*" represents that it is a bond to be bound to R^5); R^5 is an m-valent hydrocarbyl group having 1 to 20 carbon atoms or an m-valent group having 1 to 20 carbon atoms, which has at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, and a sulfur atom and does not have an active hydrogen; n is an integer of 1 to 3 and m is an integer of 2 to 10; and a plurality of R^2, R^3, R^4, A^2, and n may be the same or different.

[0030]

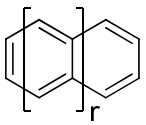
In the above formula (1), examples of the hydrocarbyl groups of R^2 and R^3 include an alkyl group or an allyl group having 1 to 20 carbon atoms, a cycloalkyl group having 3 to 20 carbon atoms and an aryl group having 6 to 20 carbon atoms. Examples of the hydrocarbylene groups of R^4 include an alkanediyl group having 1 to 20 carbon atoms, a cycloalkylene group having 3 to 20 carbon atoms and an arylene group having 6 to 20 carbon atoms. R^4 is preferably linear.

[0031]

The above explanation is applied to R^1 in A^2. n is preferably 2 or 3, and more preferably 3 in view of high effect of improving silica dispersibility.

Examples of the m-valent hydrocarbyl group of R^5 include a group resulting from removal of m pieces of hydrogen atoms from a linear hydrocarbon having 1 to 20 carbon atoms, an alicyclic hydrocarbon having 3 to 20 carbon atoms, and an aromatic hydrocarbon having 6 to 20 carbon atoms. In view of high effect of improving the abrasion resistance of the resulting vulcanized rubber, preferred is a group (aromatic ring group) resulting from removal of m pieces of hydrogen atoms from the ring part of the aromatic hydrocarbon. Examples of the aromatic hydrocarbon include a ring structure represented by the following formula (2) and a multi-ring structure in which two or more ring structures are linked (e.g., a biphenyl group):

[Chem 2]



(2)

wherein r is an integer of 0 to 5.

[0032]

Preferable examples of R^5, which is an m-valent group having 1 to 20 carbon atoms, which has at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, and a sulfur atom and does not have an active hydrogen, include an m-valent heterocyclic group and an m-valent group having a tertiary amine structure. The heterocyclic ring group preferably has a conjugated system and, examples thereof include a group resulting from removal of m pieces of hydrogen atoms from a single ring or condensed ring, such as pyridine, pyrimidine, pyrazine, quinoline, naphthalidine, furan, or thiophene, and a ring part of a structure in which a plurality of the single rings or condensed rings.

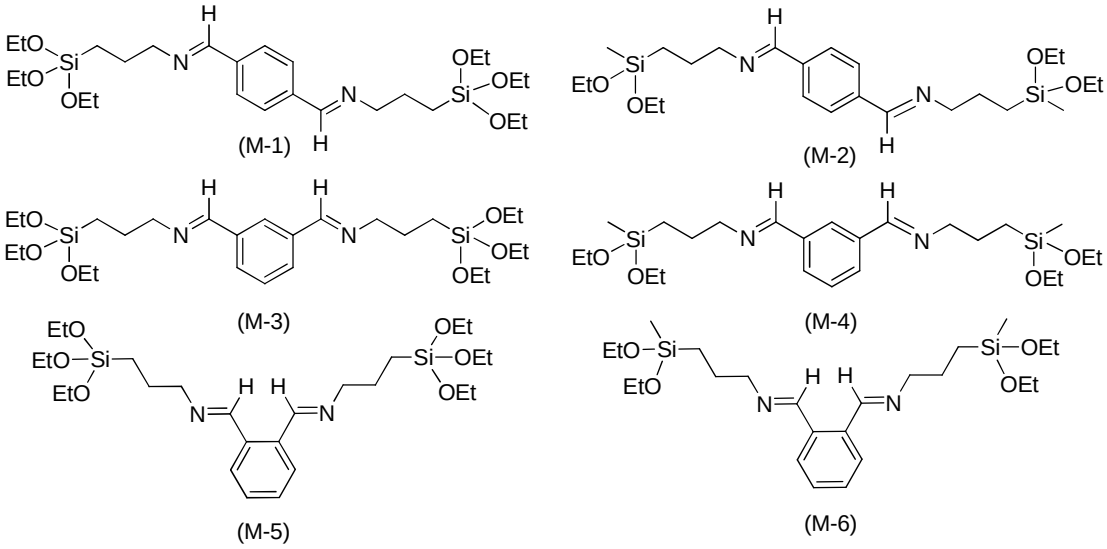
m is an integer of 2 to 10. m is preferably 2 to 6 from the viewpoint of processability of the rubber composition. Incidentally, the term "active hydrogen" used herein refers to a hydrogen atom that is bound to an atom other than a carbon atom, and preferably refers to a hydrogen atom that has a bonding energy lower than that of the carbon-hydrogen bond of polymethylene.

[0033]

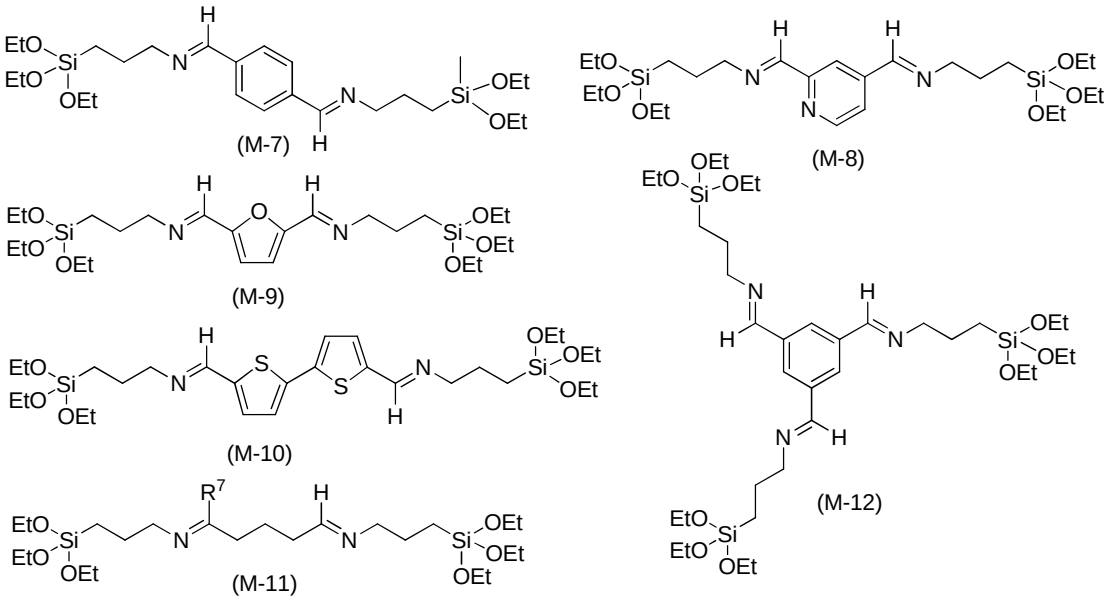
Examples of the compound [M] include compounds represented by the

respective following formulae (M-1) to (M-23). Incidentally, one of the compounds [M] may be used alone or two or more thereof in combination. Note that R^7 in the formula (M-11) represents a hydrogen atom or an alkyl group.

[Chem 3]



[Chem 4]



[Chem 5]

solvent, 4.55 g (33.92 mmol) of terephthalaldehyde, and 15.02 g (67.84 mmol) of 3-aminopropyltriethoxysilane, and refluxed at 120°C using a Dean-Stark apparatus. After water was all removed outside, refluxing was further continued for 2 hours. Thereafter, filtration was performed through a filter and the toluene solvent was distilled off under reduced pressure. After the purity of the product was estimated based on ^{1}H-NMR spectral analysis and GC/MS analysis, the product was used as it was as a modifier for a modified conjugated diene-based polymer.

^{1}H-NMR (solvent: $CDCl_3$) chemical shift δ: 8.26 ppm (N=C<u>H</u>-Ph, 2H), 7.73 ppm (hydrogen on benzene ring, 4H), 3.80 ppm (CH_3-C<u>H</u>$_2$-O-, 12H), 3.61 ppm (Si-CH_2-CH_2-C<u>H</u>$_2$-N, 4H), 1.83 ppm (Si-CH_2-C<u>H</u>$_2$-CH_2-N, 4H), 1.20 ppm (C<u>H</u>$_3$-CH_2-O, 18H), 0.67 ppm (Si-C<u>H</u>$_2$-CH_2-CH_2-N, 4H)

[0058]

[Examples 2A to 13A]

The same operations as in Example 1A were performed except for the kinds and charged amounts of the compounds to be used for the synthesis of the compound [M] as shown in the following Table 1 to synthesize compounds (M-2) to (M-13), respectively. ^{1}H-NMR peaks of the compounds (M-2), (M-8), (M-9), and (M-10) were as follows.

- Compound (M-2)

^{1}H-NMR (solvent: $CDCl_3$) chemical shift δ: 8.67 ppm (N=C<u>H</u>-Ph, 2H), 8.10 ppm (hydrogen on benzene ring, 4H), 3.83 ppm (CH_3-C<u>H</u>$_2$-O-, 8H), 3.71 ppm (Si-CH_2-CH_2-C<u>H</u>$_2$-N, 4H), 1.70 ppm (Si-CH_2-C<u>H</u>$_2$-CH_2-N, 4H), 1.21 ppm (C<u>H</u>$_3$-CH_2-O, 12H), 1.02 ppm (Si-C<u>H</u>$_2$-CH_2-CH_2-N, 4H), 0.14 ppm (C<u>H</u>$_3$-Si, 6H)

- Compound (M-8)

^{1}H-NMR (solvent: $CDCl_3$) chemical shift δ: 8.89 to 7.94 ppm (hydrogen on pyridine ring, 3H), 8.28 to 7.50 ppm (N=C<u>H</u>-Py, 2H), 3.83 ppm (CH_3-C<u>H</u>$_2$-O-, 12H), 1.49 ppm (Si-CH_2-CH_2-C<u>H</u>$_2$-N, 4H), 1.40 ppm (Si-CH_2-C<u>H</u>$_2$-CH_2-N, 4H), 1.21 ppm (C<u>H</u>$_3$-CH_2-O, 18H), 0.58 ppm (Si-C<u>H</u>$_2$-CH_2-CH_2-N, 4H))

- Compound (M-9)

^{1}H-NMR (solvent: $CDCl_3$) chemical shift δ: 7.50 ppm (N=C<u>H</u>-Fr, 2H), 6.54 ppm (hydrogen on furan ring, 2H), 3.83 ppm (CH_3-C<u>H</u>$_2$-O, 8H), 1.49 ppm (Si-CH_2-CH_2-C<u>H</u>$_2$-N, 4H), 1.40 ppm (Si-CH_2-C<u>H</u>$_2$-CH_2-N, 4H), 1.21 ppm (C<u>H</u>$_3$-CH_2-O, 12H), 0.58 ppm (Si-C<u>H</u>$_2$-CH_2-CH_2-N, 4H)

- Compound (M-10)

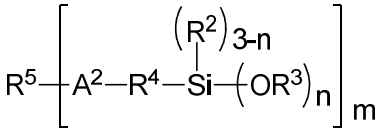
^{1}H-NMR (solvent: $CDCl_3$) chemical shift δ: 7.73 to 7.35 ppm (hydrogen on thiophene ring, 4H), 7.50 ppm (N=C<u>H</u>-Th, 2H), 3.83 ppm (CH_3-C<u>H</u>$_2$-O, 8H), 1.49 ppm (Si-CH_2-

Claims

[Claim 1] A method for producing a modified conjugated diene-based polymer, which comprises reacting a conjugated diene-based polymer having an active chain end, obtained by polymerizing a monomer containing a conjugated diene compound in the presence of an initiator that contains at least either of an alkali metal compound or an alkaline earth metal compound, with a compound [M] having at least two groups selected from the group consisting of a group "-C(R^1)=N-A^1" and a group "-N=C(R^1)-A^1", where R^1 is a hydrogen atom or a hydrocarbyl group and A^1 is a monovalent group having an alkoxysilyl group.

[Claim 2] The method for producing a modified conjugated diene-based polymer according to claim 1, wherein the compound [M] is a compound represented by the following formula (1):

[Chem 1]



(1)

wherein R^2 and R^3 are each independently a hydrocarbyl group having 1 to 20 carbon atoms, R^4 is an alkanediyl group having 1 to 20 carbon atoms, and A^2 is a group "*-C(R^1)=N-" or a group "*-N=C(R^1)-" (where R^1 is a hydrogen atom or a hydrocarbyl group and "*" represent a bond to be bound to R^5); R^5 is an m-valent hydrocarbyl group having 1 to 20 carbon atoms or an m-valent group having 1 to 20 carbon atoms, which has at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, and a sulfur atom and does not have an active hydrogen; n is an integer of 1 to 3 and m is an integer of 2 to 10; and a plurality of R^2, R^3, R^4, A^2, and n may be the same or different.

[Claim 3] The method for producing a modified conjugated diene-based polymer according to claim 1 or 2, wherein, on a gel permeation chromatography (GPC) curve obtained from measurement by GPC after the reaction of the conjugated diene-based polymer having an active chain end with the compound [M], an area of peak portion(s) showing 2.5 times or more peak top molecular weight than the peak top molecular weight at a peak having the smallest molecular weight is 40% or more of the total peak area of the GPC curve.

[Claim 4] The method for producing a modified conjugated diene-based polymer according to any one of claims 1 to 3, wherein the peak top molecular weight of a peak having the smallest molecular weight measured by gel permeation chromatography (GPC) after the reaction of the conjugated diene-based polymer having an active chain end with the compound [M] is in the range of 5.0×10^4 to 1.0×10^6.

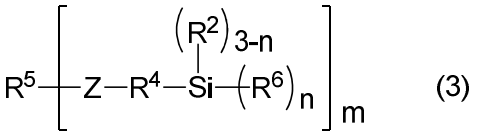
[Claim 5] The method for producing a modified conjugated diene-based polymer according to any one of claims 1 to 4, wherein the monomer further contains an aromatic vinyl compound.

[Claim 6] The method for producing a modified conjugated diene-based polymer according to any one of claims 1 to 5, wherein the monomer is polymerized using a mixture of at least either of an alkali metal compound or an alkaline earth metal compound and a compound having a functional group that interacts with silica, as the initiator.

[Claim 7] A modified conjugated diene-based polymer, which is a reaction product between a conjugated diene-based polymer having an active chain end and a compound [M] having at least two groups selected from the group consisting of a group "-C(R^1)=N-A^1" and a group "-N=C(R^1)-A^1", where R^1 is a hydrogen atom or a hydrocarbyl group and A^1 is a monovalent group having an alkoxysilyl group.

[Claim 8] A modified conjugated diene-based polymer represented by the following formula (3):

[Chem 2]



(3)

wherein R^2 is a hydrocarbyl group having 1 to 20 carbon atoms, R^6 is a hydrocarbyloxy group having 1 to 20 carbon atoms or a modified or unmodified conjugated diene-based polymer chain, R^4 is an alkanediyl group having 1 to 20 carbon atoms, and Z is a group represented by the following formula (4) or (5); R^5 is an m-valent hydrocarbyl group having 1 to 20 carbon atoms or an m-valent group having 1 to 20 carbon atoms, which has at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, and a sulfur atom and does not have an active hydrogen; n is an integer of 1 to 3 and m is an integer of 2 to 10; and a plurality of R^2, R^4, R^6, Z, and n may be the same or different:

[Chem 3]