

DESCRIPTION

Modified Conjugated Diene-Based Polymer, Production
Method Therefor, Polymer Composition,
Crosslinked Polymer, and Tire

TECHNICAL FIELD

[0001]

The present disclosure relates to a modified conjugated diene-based polymer, a production method therefor, a polymer composition, a crosslinked polymer, and a tire.

BACKGROUND ART

[0002]

A conjugated diene-based polymer produced through polymerization of a conjugated diene compound exhibits good properties (e.g., thermal resistance, abrasion resistance, mechanical strength, and processability). Thus, the conjugated diene-based polymer has been used in various industrial products, including pneumatic tires, vibration-proof rubbers, and hoses.

[0003]

A pneumatic tire is required to achieve excellent low fuel consumption performance. In order to meet such a requirement, various modified conjugated diene-based polymers have been proposed, in which a functional group capable of interacting with silica is bonded to the polymerization initiation terminal or polymerization end terminal of a

conjugated diene-based polymer chain (see, for example, Patent Documents 1 to 4). Such a terminal-modified conjugated diene-based polymer exhibits higher affinity to a reinforcing filler (e.g., carbon black or silica), as compared with an unmodified conjugated diene-based polymer. Thus, such a modified conjugated diene-based polymer can achieve low-heat-generating property and improved low fuel consumption performance.

RELATED-ART DOCUMENT

Patent Document

[0004]

Patent Document 1: Japanese Patent Application Laid-Open (*kokai*) No. 2003-171418

Patent Document 2: International Patent Publication WO 2013/94629

Patent Document 3: International Patent Publication WO 2015/152038

Patent Document 4: International Patent Publication WO 2005/021637

SUMMARY OF THE INVENTION

Technical Problem

[0005]

In view of, for example, recent environmental circumstances (e.g., global warming due to carbon dioxide emission), increasing awareness about resource saving and

energy saving, and economic situations (e.g., an increase in the price of gasoline), rubber materials for automobile tires have been required to achieve low fuel consumption performance (low-heat-generating property) superior to that of conventional ones. In addition to low fuel consumption performance, such a rubber material is required to achieve well-balanced properties for tires, including processability and wet grip property.

[0006]

In view of the foregoing, an object of the present disclosure is to provide a modified conjugated diene-based polymer capable of preparing a rubber composition exhibiting excellent processability and a vulcanized rubber achieving excellent low fuel consumption performance and wet grip property.

Solution to Problem

[0007]

In order to solve the aforementioned problems, the present disclosure provides a modified conjugated diene-based polymer, a production method therefor, a polymer composition, a crosslinked polymer, and a tire, which are described below.

[0008]

[1] A modified conjugated diene-based polymer comprising, at one terminal of a conjugated diene-based polymer chain, a polymer block having a structure derived from at least one compound selected from the group consisting of the following

vinylsilane compound (A) and aromatic vinyl compound (B):

(A) a vinylsilane compound having a group $-\text{SiR}^1\text{R}^2\text{R}^3$, wherein R^1 represents a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen, and R^2 and R^3 each represent a hydrocarbyl group or a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen; and

(B) an aromatic vinyl compound containing at least one atom selected from the group consisting of a nitrogen atom, a phosphorus atom, and a sulfur atom, wherein active hydrogen is not bonded to the nitrogen atom, the phosphorus atom, or the sulfur atom.

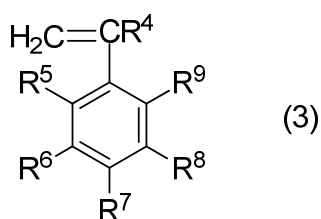
[2] A method for producing a modified conjugated diene-based polymer, the method comprising:

polymerizing a monomer group X containing at least one compound selected from the group consisting of the aforementioned vinylsilane compound (A) and aromatic vinyl compound (B) and a conjugated diene compound in the presence of a polymerization initiator, thereby preparing a polymer block having an active terminal; and

polymerizing a monomer group Y containing a conjugated diene compound in the presence of the polymer block having the active terminal, thereby forming a conjugated diene-based polymer chain bonded to the polymer block.

[3] A method for producing a modified conjugated diene-based polymer, the method comprising:

polymerizing a monomer group Z containing a styrene-based compound represented by formula (3) in the presence of a polymerization initiator, thereby preparing a polymer block having an active terminal:



wherein R^4 represents a hydrogen atom or a methyl group, R^5 to R^9 each represent a hydrogen atom or a hydrocarbyl group, and at least one of R^5 to R^9 has a hydrogen atom at a benzylic position;

polymerizing a monomer group Y containing a conjugated diene compound in the presence of the polymer block having the active terminal, thereby forming a conjugated diene-based polymer chain bonded to the polymer block; and

reacting the polymer block, at a benzylic position of a monomer unit derived from the styrene-based compound, with at least one compound selected from the group consisting of the aforementioned vinylsilane compound (A) and aromatic vinyl compound (B).

[4] A polymer composition comprising a modified conjugated diene-based polymer of the aforementioned [1] or a modified conjugated diene-based polymer produced by a method of the aforementioned [2] or [3], an inorganic filler, and a

crosslinking agent.

[5] A crosslinked polymer produced through crosslinking of a polymer composition of the aforementioned [4].

[6] A tire obtained by employing a crosslinked polymer of the aforementioned [5] as a tread material, a sidewall material, or both.

EFFECTS OF THE INVENTION

[0009]

The modified conjugated diene-based polymer and modified conjugated diene-based polymer production method of the present disclosure can prepare a vulcanized rubber achieving excellent low fuel consumption performance, processability, and wet grip property.

DESCRIPTION OF EMBODIMENTS

[0010]

The modified conjugated diene-based polymer of the present disclosure has, at one terminal of a conjugated diene-based polymer chain, a polymer block having a structure derived from at least one compound selected from the group consisting of the following vinylsilane compound (A) and aromatic vinyl compound (B) (hereinafter the structure may be referred to as "specific structure [F]"):

(A) a vinylsilane compound having the group " $-\text{SiR}^1\text{R}^2\text{R}^3$ ";
and

(B) an aromatic vinyl compound containing at least one

atom selected from the group consisting of a nitrogen atom, a phosphorus atom, and a sulfur atom, wherein active hydrogen is not bonded to the nitrogen atom, the phosphorus atom, or the sulfur atom.

The modified conjugated diene-based polymer can be produced by method 1 or 2 described below. Embodiments of the present disclosure will next be described in detail.

[0011]

[Method 1]

Method 1 includes steps (1-1) and (1-2). Step (1-1) involves polymerizing a monomer group X containing at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B) and a conjugated diene compound in the presence of a polymerization initiator, thereby preparing a polymer block having an active terminal. Step (1-2) involves polymerizing a monomer group Y containing a conjugated diene compound in the presence of the polymer block having the active terminal, thereby forming a conjugated diene-based polymer chain bonded to the polymer block. Hereinafter, the polymer block having the active terminal may be referred to as an "initiator block."

[0012]

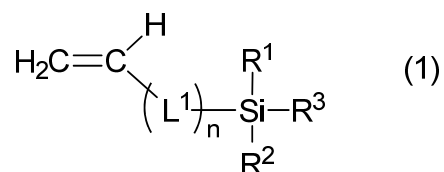
<Step (1-1)>

(Monomer group X)

Vinylsilane compound (A)

The vinylsilane compound (A) is a vinylsilane compound

having a group "-SiR¹R²R³", and is preferably represented by the following formula (1):



wherein R¹ represents a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen, R² and R³ each represent a hydrocarbyl group or a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen, L¹ represents a hydrocarbyl group, and n is 0 or 1.

[0013]

R¹ has at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom. Such a heteroatom is not bonded to active hydrogen, and may be protected with a protective group. As used herein, the term "active hydrogen" refers to a hydrogen atom bonded to an atom other than a carbon atom, preferably a hydrogen atom having a binding energy lower than that of a carbon-hydrogen bond of polymethylene. The term "protective group" refers to a functional group for transforming R¹ into an inactive functional group. Examples of the protective group include tri-substituted hydrocarbylsilyl groups.

[0014]

Specific examples of R^1 include a nitrogen-containing group in which two hydrogen atoms of a primary amino group are substituted by two protective groups, a nitrogen-containing group in which one hydrogen atom of a secondary amino group is substituted by one protective group, $-R^{33}-NR^{31}R^{32}$ (R^{31} and R^{32} each represent a hydrocarbyl group, R^{31} and R^{32} may be bonded to each other to form a cyclic structure with the nitrogen atom, and R^{33} represents a single bond or a hydrocarbylene group), an imino group, an oxygen-containing group in which one hydrogen atom of a hydroxy group is substituted by one protective group, a phosphorus-containing group in which two hydrogen atoms of a primary phosphino group are substituted by two protective groups, a phosphorus-containing group in which one hydrogen atom of a secondary phosphino group is substituted by one protective group, a tertiary phosphino group, and a sulfur-containing group in which one hydrogen atom of a thiol group is substituted by one protective group. In view of high affinity of the modified conjugated diene-based polymer to silica, R^1 is preferably a group containing at least one of a nitrogen atom and an oxygen atom, more preferably a group containing a nitrogen atom.

[0015]

If R^1 is a group $-R^{33}-NR^{31}R^{32}$ (hereinafter may be referred to as a "substituted amino group"), the hydrocarbyl group represented by R^{31} or R^{32} is preferably a C1 to C10

alkyl group, more preferably a C1 to C5 alkyl group. R^{31} and R^{32} taken together may represent a ring together with the nitrogen atom to which R^{31} and R^{32} bond. Examples of the ring (cyclic amino group) include a 1-pyrrolidinyl group, a 1-piperidino group, a 1-hexamethyleneimino group, a 1-octamethyleneimino group, a pyridyl group, and a 1-imidazolyl group.

The hydrocarbylene group represented by R^{33} is preferably a C1 to C20 alkanediyl group, more preferably a C1 to C10 alkanediyl group.

[0016]

The aforementioned description regarding R^1 is applied to the case where R^2 or R^3 is a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen. The hydrocarbyl group represented by R^2 or R^3 is preferably a C1 to C20 alkyl group, a C3 to C20 cycloalkyl group, or a C6 to C20 aryl group. In view of the affinity of the modified conjugated diene-based polymer to a filler, at least two of R^1 to R^3 are preferably a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen.

Examples of L^1 include a C1 to C20 alkanediyl group, a C3 to C20 cycloalkylene group, and a C6 to C20 arylene group. In the formula (1), n is preferably 0.

[0017]

The vinylsilane compound (A) is preferably at least one species selected from the group consisting of a substituted-amino-group-containing vinylsilane compound and a hydrocarbyloxy-group-containing vinylsilane compound.

Specific examples of the substituted-amino-group-containing vinylsilane compound include

(dialkylamino)dialkylvinylsilane,
[bis(trialkylsilyl)amino]dialkylvinylsilane,
(dialkylamino)di(alkoxyalkyl)vinylsilane, a cyclic aminodialkylvinylsilane compound,
(dialkylamino)dialkylvinylphenylsilane,
bis(dialkylamino)alkylvinylsilane,
bis[bis(trialkylsilyl)amino]alkylvinylsilane,
bis(dialkylamino)alkoxyalkylvinylsilane, bis(cyclic amino)alkylvinylsilane,
bis(dialkylamino)alkylvinylphenylsilane,
tris(dialkylamino)vinylsilane, and
tris(dialkylamino)vinylphenylsilane. Specific examples of the hydrocarbyloxy-group-containing vinylsilane compound include trihydrocarbyloxyvinylsilane, dialkoxyalkylvinylsilane, dialkoxyarylvinylsilane, monoalkoxydialkylvinylsilane, monoalkoxydiarylvinylsilane, and monoalkoxyalkylarylvinylsilane.

[0018]

The substituted-amino-group-containing vinylsilane compound is preferably a compound of the formula (1) in which

one or two of R¹ to R³ have a substituted amino group and n is 0. Specific examples of the (dialkylamino)dialkylvinylsilane include (dimethylamino)dimethylvinylsilane, (ethylmethylamino)dimethylvinylsilane, and (di-n-propylamino)dimethylvinylsilane. Specific examples of the bis(dialkylamino)alkylvinylsilane include bis(dimethylamino)methylvinylsilane, bis(diethylamino)methylvinylsilane, bis(di-n-propylamino)methylvinylsilane, bis(di-n-butylamino)methylvinylsilane, and bis(dimethylamino)ethylvinylsilane. Specific examples of the bis[bis(trialkylsilyl)amino]alkylvinylsilane include bis[bis(trimethylsilyl)amino]methylvinylsilane and bis[bis(trimethylsilyl)amino]ethylvinylsilane. Specific examples of the bis(dialkylamino)alkoxyalkylvinylsilane include bis(dimethylamino)methoxymethylvinylsilane and bis(dimethylamino)(2-methoxyethyl)vinylsilane. Specific examples of the cyclic aminodialkylvinylsilane include 1-pyrrolidinyldimethylvinylsilane, 1-piperidinyldimethylvinylsilane, 1-hexamethyleneiminodimethylvinylsilane, and 4,5-dihydro-1-imidazolinyldimethylvinylsilane. Specific examples of the bis(cyclic amino)alkylvinylsilane include bis(1-pyrrolidinyl)methylvinylsilane and bis(1-piperidinyl)methylvinylsilane.

[0019]

Specific examples of the hydrocarbyloxy-group-containing vinylsilane compound include trimethoxyvinylsilane, triethoxyvinylsilane, tripropoxyvinylsilane, methyldimethoxyvinylsilane, di(tert-butoxy)phenylvinylsilane, dimethylmethoxyvinylsilane, tert-butoxydiphenylvinylsilane, tert-butoxymethylphenylvinylsilane, and tert-butoxyethylphenylvinylsilane. These vinylsilane compounds (A) may be used singly or in combination of two or more species.

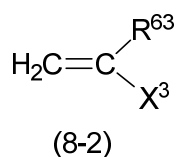
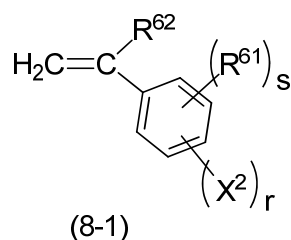
[0020]

Aromatic vinyl compound (B)

In the aromatic vinyl compound (B), none of the nitrogen, phosphorus, and sulfur atoms is bonded to active hydrogen, and each of these atoms may be protected with, for example, a tri-substituted hydrocarbylsilyl group. In view of the dispersibility of a filler, the aromatic vinyl compound (B) is particularly preferably a nitrogen-containing aromatic vinyl compound.

[0021]

Specific examples of preferred nitrogen-containing aromatic vinyl compounds include compounds represented by the following formulae (8-1) and (8-2):



wherein X^2 represents a nitrogen-containing group having no active hydrogen, R^{61} represents a substituent, R^{62} represents a hydrogen atom, a methyl group, or a phenyl group, r is an integer of 1 to 5, s is an integer of 0 to 4, and $r + s \leq 5$; and,

X^3 represents a nitrogen-containing aromatic heterocyclic group (which may have a substituent on the ring moiety), and R^{63} represents a hydrogen atom or a methyl group.

[0022]

In the formula (8-1), X^2 may be in a chain or cyclic form, and X^2 is, for example, a group " $-R^{33}-NR^{31}R^{32}$." Examples of the substituent represented by R^{61} include a C1 to C10 hydrocarbyl group and a C1 to C10 hydrocarbyloxy group. In the formula (8-1), r is preferably 1 or 2, more preferably 1, and s is preferably 0 to 2, more preferably 0 or 1.

In the formula (8-2), X^3 is, for example, a group prepared through removal of one hydrogen atom from the ring moiety of a pyridine ring, a pyrimidine ring, a pyrazine ring, or a quinoline ring. The description regarding R^{61} can be applied to the substituent that may be possessed by the ring moiety.

[0023]

Specific examples of the nitrogen-containing aromatic vinyl compound represented by the formula (8-1) include dihydrocarbylstyrenes, such as 3-dimethylaminostyrene and 4-dimethylaminostyrene; dihydrocarbylaminoalkylstyrenes, such as 4-(diethylaminomethyl)styrene and 4-[2-

(dimethylamino)ethyl]styrene; cyclic-amino-group-containing styrenes, such as 3-(1-pyrrolidinyl)styrene, 4-(1-pyrrolidinyl)styrene, 4-piperidinostyrene, 3-(1-pyrrolidinyl)methylstyrene, 3-(1-pyrrolidinyl)ethylstyrene, 4-(1-pyrrolidinyl)methylstyrene, and 4-(1-pyrrolidinyl)ethylstyrene; and tertiary-amino-group-containing diphenylethylenes, such as 1-(4-dimethylaminophenyl)-1-phenylethylene. Specific examples of the nitrogen-containing aromatic vinyl compound represented by the formula (8-2) include vinylpyridines, such as 3-vinylpyridine and 4-vinylpyridine. These aromatic vinyl compounds (B) may be used singly or in combination of two or more species.

[0024]

Examples of the conjugated diene compound 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. Of these, 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene are preferred. Particularly preferred is 1,3-butadiene from the viewpoint of well-balanced improvements in processability and low hysteresis loss property. These conjugated diene compounds may be used singly or in combination of two or more species.

[0025]

In order to achieve sufficiently high reactivity, the amount of the conjugated diene compound used in the monomer

group X is preferably 5 mass% or more, more preferably 10 mass% or more, still more preferably 15 mass% or more, relative to the total amount of the compounds of the monomer group X. In order to achieve sufficient improvements in tire properties by the vinylsilane compound (A) and the aromatic vinyl compound (B), the maximum amount of the conjugated diene compound used is preferably 70 mass% or less, more preferably 60 mass% or less, still more preferably 50 mass% or less, relative to the total amount of the compounds of the monomer group X.

[0026]

The monomer group X may be polymerized using a solution polymerization method, a vapor-phase polymerization method, or a bulk polymerization method. Among these, a solution polymerization method is particularly preferable. The monomer group X may be polymerized in a batch-wise manner or a continuous manner. When using the solution polymerization method, the monomer group X may be polymerized in an organic solvent in the presence of an initiator, for example.

[0027]

At least one of an alkali metal compound and an alkaline-earth metal compound is preferably used as the initiator for polymerization of the monomer group X. Examples of the initiator include alkylolithiums such as methylolithium, ethylolithium, n-propylolithium, n-butylolithium, sec-butylolithium, and tert-butylolithium, 1,4-dilithiobutane, phenylolithium, stilbenelithium, naphthylolithium, 1,3-bis(1-

lithio-1,3-dimethylpentyl)benzene, 1,3-phenylenebis(3-methyl-1-phenylpentylidene)dilithium, naphthylsodium, naphthylpotassium, di-n-butylmagnesium, di-n-hexylmagnesium, ethoxypotassium, and calcium stearate. Among these, lithium compounds are preferable.

[0028]

The monomer may be polymerized in the presence of a compound that is obtained by mixing at least one of the alkali metal compound and the alkaline-earth metal compound with a compound having a functional group that interacts with silica (hereinafter the compound may be referred to as a "modifying initiator"). The term "functional group that interacts with silica" used herein refers to a group that includes at least one atom (e.g., a nitrogen atom, a sulfur atom, a phosphorus atom, an oxygen atom, or a silicon atom) that interacts with silica. The term "interaction" used herein refers to that a covalent bond is formed between molecules, or an intermolecular force (intermolecular electromagnetic force such as ion-dipole interaction, dipole-dipole interaction, a hydrogen bond, or Van der Waals force) that is weaker than a covalent bond is formed.

[0029]

The modifying initiator is preferably a nitrogen-containing compound (e.g., a secondary amine compound). Specific examples of the nitrogen-containing compound include dimethylamine, diethylamine, dipropylamine, dibutylamine, dodecamethyleneimine, N,N'-dimethyl-N'-trimethylsilyl-1,6-

diaminohexane, piperidine, pyrrolidine, hexamethyleneimine, heptamethyleneimine, dicyclohexylamine, N-methylbenzylamine, di-(2-ethylhexyl)amine, diallylamine, morpholine, N-(trimethylsilyl)piperazine, N-(tert-butyldimethylsilyl)piperazine, and 1,3-ditrimethylsilyl-1,3,5-triazinane. The modifying initiator may be used singly or in combination of two or more species.

[0030]

In the case of polymerization in the presence of the aforementioned mixture, at least one of the alkali metal compound and the alkaline earth metal compound may be preliminarily mixed with the modifying initiator, and the resultant mixture may be added to the polymerization system. Alternatively, at least one of the alkali metal compound and the alkaline earth metal compound and the modifying initiator may be added to the reaction system, and the compound(s) and the modifying initiator may be mixed together in the polymerization system.

[0031]

The monomer group X may be polymerized in the presence of a randomizer for the purpose of, for example, adjustment of the vinyl bond content (i.e., the amount of vinyl bonds) of the polymer block. Examples of the randomizer include dimethoxybenzene, tetrahydrofuran, dimethoxyethane, diethylene glycol dibutyl ether, diethylene glycol dimethyl ether, 2,2-di(tetrahydrofuryl)propane, 2-(2-ethoxyethoxy)-2-methylpropane, triethylamine, pyridine, N-methylmorpholine,

and tetramethylethylenediamine. These randomizers may be used singly or in combination of two or more species.

[0032]

The organic solvent used for polymerization may be any organic solvent that is inert to the reaction. Examples of the organic solvent include aliphatic hydrocarbons, alicyclic hydrocarbons, and aromatic hydrocarbons. In particular, the organic solvent is preferably a C3 to C8 hydrocarbon. Specific examples of the C3 to C8 hydrocarbon include propane, n-butane, isobutane, n-pentane, isopentane, n-hexane, cyclohexane, propene, 1-butene, isobutene, trans-2-butene, cis-2-butene, 1-pentyne, 2-pentyne, 1-hexene, 2-hexene, benzene, toluene, xylene, ethylbenzene, heptane, cyclopentane, methylcyclopentane, methylcyclohexane, 1-pentene, 2-pentene, and cyclohexene. These organic solvents may be used singly or in combination of two or more species.

[0033]

The amounts of the polymerization initiator and the monomer group X used can be determined depending on the number of monomer units forming a target initiator block. Specifically, the amount of the polymerization initiator used is preferably 10 to 2,000 mmol, more preferably 20 to 1,000 mmol, still more preferably 30 to 900 mmol, relative to the total amount (100 g) of the monomers of the monomer group X.

[0034]

In the case of the solution polymerization, the monomer concentration of the reaction solvent is preferably 5 to 50

mass%, more preferably 10 to 30 mass%, for maintaining the balance between productivity and polymerization controllability. The polymerization reaction temperature is preferably -20°C to 150°C, more preferably 0 to 120°C. The polymerization reaction is preferably carried out under a pressure sufficient to maintain the monomer substantially in a liquid phase. Such a pressure can be achieved by, for example, pressurizing the reactor by use of a gas inert to the polymerization reaction.

[0035]

The polymer block having an active terminal is prepared through the above-described polymerization. The resultant polymer block is a copolymer block including a monomer unit derived from at least one monomer of the vinylsilane compound (A) and the aromatic vinyl compound (B) and a monomer unit derived from the conjugated diene compound. The polymer block having the active terminal prepared in step (1-1) is used as a polymerization initiator in the subsequent step (1-2).

[0036]

<Step (1-2)>

(Monomer group Y)

The monomer group Y contains a conjugated diene compound. The conjugated diene compound used for polymerization in this step may be, for example, the compound exemplified in step (1-1). In particular, the conjugated diene compound is preferably at least one of 1,3-butadiene,

isoprene, and 2,3-dimethyl-1,3-butadiene. These conjugated diene compounds may be used singly or in combination of two or more species.

[0037]

The monomer group Y may contain the conjugated diene compound alone. Preferably, the monomer group Y further contains an aromatic vinyl compound in order to enhance the strength of the resultant rubber. Examples of the aromatic vinyl compound include styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene, α -methylstyrene, 2,4-dimethylstyrene, 2,4-diisopropylstyrene, 4-*t*-butylstyrene, 5-*t*-butyl-2-methylstyrene, vinyl ethylbenzene, divinylbenzene, trivinylbenzene, divinyl naphthalene, *t*-butoxystyrene, vinylbenzyl dimethylamine, (4-vinylbenzyl)dimethylaminoethyl ether, *N,N*-dimethylaminoethylstyrene, *N,N*-dimethylaminomethylstyrene, 2-ethylstyrene, 3-ethylstyrene, 4-ethylstyrene, 2-*t*-butylstyrene, 3-*t*-butylstyrene, vinylxylene, vinyl naphthalene, vinylpyridine, and diphenylethylene. Of these, the aromatic vinyl compound is preferably at least one of styrene and α -methylstyrene. These aromatic vinyl compounds may be used singly or in combination of two or more species.

[0038]

In particular, the monomer group Y preferably contains 1,3-butadiene and styrene for achievement of high livingness during anionic polymerization. Thus, the conjugated diene-based polymer chain in the modified conjugated diene-based

polymer of the present disclosure is preferably a copolymer chain formed of 1,3-butadiene and styrene. The conjugated diene compound and the aromatic vinyl compound are preferably polymerized through random polymerization.

[0039]

The amount of the aromatic vinyl compound used for the polymerization is preferably 3 to 55 mass%, more preferably 5 to 50 mass%, relative to the total amount of the conjugated diene compound and aromatic vinyl compound used for the polymerization, from the viewpoint of a good balance between the low hysteresis loss property and wet grip property of the resultant vulcanized rubber. The amount of the structural unit derived from the aromatic vinyl compound in the polymer is measured by means of ^1H -NMR.

[0040]

The monomer group Y may contain an additional compound other than the conjugated diene compound and the aromatic vinyl compound (hereinafter the additional compound may be referred to as an "additional monomer"). Examples of the additional monomer include acrylonitrile, methyl (meth)acrylate, ethyl (meth)acrylate, 1,5-hexadiene, and 1,6-heptadiene. The amount of the additional monomer used is preferably 10 mass% or less, more preferably 5 mass% or less, relative to the total amount of the monomers used for the polymerization in step (1-2).

[0041]

The monomer group Y is particularly preferably

polymerized by a solution polymerization process as in the case of step (1-1). The polymerization may be performed by a batch or continuous process. In the case of a solution polymerization process, for example, the monomer group Y is polymerized in an organic solvent in the presence of a polymerization initiator and an optional randomizer.

[0042]

In method 1, the polymer block having the active terminal prepared in step (1-1) is used as a polymerization initiator (initiator block) for the polymerization. The total amount of the initiator block(s) used can be appropriately determined depending on the target molecular weight. A single initiator block may be used, or two or more initiator blocks may be used in combination. Specific examples of the randomizer and organic solvent used may be the same as those described above in step (1-1). The conditions for the solution polymerization (e.g., the monomer concentration of the reaction solvent and the polymerization reaction temperature) may be the same as those described above in step (1-1).

[0043]

The above-described polymerization reaction can produce a modified conjugated diene-based polymer in which a polymer block having the specific structure [F] is bonded at one terminal of the conjugated diene-based polymer chain. In the modified conjugated diene-based polymer of the present disclosure, the polymer block includes a monomer unit derived

from at least one of the vinylsilane compound (A) and the aromatic vinyl compound (B). In the monomer unit, a functional group having at least one atom selected from among a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom may be converted, through hydrolysis or a similar reaction, into a group having active hydrogen bonded to at least one atom selected from among the nitrogen atom, the oxygen atom, the phosphorus atom, and the sulfur atom (e.g., an amino group, a hydroxy group, a phosphate group, or a thiol group).

[0044]

[Method 2]

Method 2 includes steps (2-1), (2-2), and (2-3). Step (2-1) involves polymerizing a monomer group Z containing a styrene-based compound represented by the aforementioned formula (3) in the presence of a polymerization initiator, thereby preparing a polymer block (hereinafter may be referred to as a "styrene-based block") having an active terminal. Step (2-2) involves polymerizing the monomer group Y containing a conjugated diene compound in the presence of the styrene-based block having the active terminal, thereby forming a conjugated diene-based polymer chain bonded to the styrene-based block. Step (2-3) involves reacting at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B) with the styrene-based block at a benzylic position of a monomer unit derived from the compound represented by the

formula (3). This method can produce a modified conjugated diene-based polymer having a polymer block at one terminal of the conjugated diene-based polymer chain formed of the monomer group Y, the polymer block having a side chain included the specific structure [F].

[0045]

<Step (2-1)>

(Monomer group Z)

Styrene-based compound

In the aforementioned formula (3), the hydrocarbyl group represented by each of R^5 to R^9 is preferably a C1 to C10 alkyl group. At least one of R^5 to R^9 has a hydrogen atom at a benzylic position. Specific examples of the compound represented by the formula (3) include 2-methylstyrene, 3-methylstyrene, 4-methylstyrene (p-methylstyrene), 2-(4-methylphenyl)-1-propene, and 4-ethylstyrene. Of these, 4-methylstyrene is particularly preferred. These compounds represented by the formula (3) may be used singly or in combination of two or more species.

[0046]

The monomer group Z may contain an additional monomer other than the compound represented by the formula (3), so long as the advantageous effects of the present disclosure are not impaired. Examples of the additional monomer include acrylonitrile, methyl (meth)acrylate, and ethyl (meth)acrylate. The additional monomer may be at least one monomer selected from the group consisting of the vinylsilane

compound (A) and the aromatic vinyl compound (B). In order to increase the introduction efficiency of the specific structure [F], the amount of the additional monomer used is preferably 5 mass% or less, more preferably 2 mass% or less, relative to the total amount of the monomer group Z. In view of an increase in the introduction efficiency of the specific structure [F], the monomer group Z preferably contains only the compound represented by the formula (3).

[0047]

The monomer group Z is particularly preferably polymerized by a solution polymerization process. The polymerization may be performed by a batch or continuous process. In the case of a solution polymerization process, for example, the monomer group Z is polymerized in an organic solvent in the presence of a polymerization initiator. The type of the polymerization initiator and the polymerization conditions may be the same as those described above in step (1-1). The styrene-based block having the active terminal is prepared through the above-described polymerization. The styrene-based block having the active terminal prepared in step (2-1) is used as a polymerization initiator in the subsequent step (2-2).

[0048]

The amounts of the polymerization initiator and the monomer group Y used can be determined depending on the number of monomer units forming a target styrene-based block. Specifically, the amount of the polymerization initiator used

is preferably 10 to 2,000 mmol, more preferably 20 to 1,000 mmol, still more preferably 30 to 900 mmol, relative to the total amount (100 g) of the monomers of the monomer group Y.

[0049]

<Step (2-2)>

Step (2-2) involves polymerizing the monomer group Y in the presence of the styrene-based block having the active terminal, thereby forming a conjugated diene-based polymer chain bonded to the styrene-based block. The monomer group Y and the polymerization conditions used in step (2-2) may be the same as those described above in step (1-2).

[0050]

<Step (2-3)>

Step (2-3) involves reacting at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B) with the styrene-based block at a benzylic position, thereby introducing the specific structure [F] into the styrene-based block.

[0051]

No particular limitation is imposed on the method for introducing the specific structure [F] into the styrene-based block possessed by the conjugated diene-based polymer chain. The specific structure [F] can be introduced by an appropriate combination of customary organic chemical methods. One of these methods involves lithiation at the benzylic position of the aromatic ring in the monomer unit

included in the conjugated diene-based polymer chain and derived from the compound represented by the aforementioned formula (3), and reaction between the active moiety formed at the benzylic position and at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B).

[0052]

For example, the lithiation is performed after completion of the polymerization in step (2-2). Specifically, the conjugated diene-based polymer chain having the styrene-based block bonded thereto is reacted with a lithiating agent in the presence of a promoter (e.g., tetramethylethylenediamine). Examples of the lithiating agent used for the reaction include methyllithium, n-butyllithium, s-butyllithium, and t-butyllithium. No particular limitation is imposed on the amount of the lithiating agent used for the reaction. The amount of the lithiating agent is preferably 0.1 to 20 mole equivalents, more preferably 1 to 10 mole equivalents, relative to 1 mole equivalent of the polymer.

[0053]

The aforementioned lithiation reaction may be, for example, a solution reaction. The solution reaction may be performed by use of a solution containing unreacted monomers after completion of the polymerization reaction without any treatment of the solution. Alternatively, the solution reaction may be performed after isolation of the polymer

contained in the solution and dissolution of the isolated polymer in an appropriate solvent (e.g., cyclohexane). The lithiation reaction temperature is generally equal to the aforementioned polymerization reaction temperature, preferably -20 to 150°C, more preferably 0 to 120°C, particularly preferably 20 to 100°C. The reaction time is preferably 1 minute to 3 hours, more preferably 2 to 30 minutes.

[0054]

The compound that is reacted with the lithiated polymer (hereinafter the compound may be referred to as the "monomer group W") may be only at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B). From the viewpoint of reactivity, the monomer group W preferably contains a conjugated diene compound. The amount of the conjugated diene compound used is preferably 2 to 50 mass%, more preferably 5 to 40 mass%, relative to the total amount of the compounds of the monomer group W, from the viewpoints of introduction of a sufficient amount of the specific structure [F] into the styrene-based block and reactivity.

[0055]

After completion of the lithiation reaction, the conjugated diene-based polymer chain having the styrene-based block is reacted with the monomer group W preferably in a solution. The amount of the monomer group W used for the reaction is preferably 0.1 to 10 mole equivalents, more

preferably 0.3 to 5 mole equivalents, relative to 1 mole equivalent of the lithiating agent used. The reaction temperature is generally equal to the aforementioned polymerization reaction temperature, preferably -20 to 150°C, more preferably 0 to 120°C, still more preferably 20 to 100°C. The reaction time is preferably 1 minute to 5 hours, more preferably 2 minutes to 1 hour.

[0056]

The aforementioned reactions can produce a modified conjugated diene-based polymer in which the polymer block having the specific structure [F] is bonded to one terminal of the conjugated diene-based polymer chain. The modified conjugated diene-based polymer produced by method 2 has a structure in which the polymer block having the monomer unit derived from the styrene-based compound represented by the formula (3) is bonded to one terminal of the conjugated diene-based polymer chain, and the specific structure [F] is bonded at the benzylic position of the styrene-based monomer unit in the polymer block. In a moiety derived from at least one of the vinylsilane compound (A) and the aromatic vinyl compound (B) in the polymer produced by method 2, a functional group having at least one atom selected from among a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom may be converted, through hydrolysis or a similar reaction, into a group having active hydrogen bonded to at least one atom selected from among the nitrogen atom, the oxygen atom, the phosphorus atom, and the sulfur atom.

[0057]

The modified conjugated diene-based polymer produced by method 1 or 2 has a weight average molecular weight (Mw) (in terms of polystyrene) of preferably 5.0×10^4 to 1.0×10^6 as measured by means of gel permeation chromatography (GPC). An Mw of less than 5.0×10^4 may lead to a reduction in the tensile strength, low-heat-generating property, and abrasion resistance of the resultant vulcanized rubber, whereas an Mw exceeding 1.0×10^6 may lead to poor processability of the resultant rubber composition. The Mw is more preferably 8.0×10^4 to 8.0×10^5 , still more preferably 1.0×10^5 to 5.0×10^5 .

[0058]

In the resultant modified conjugated diene-based polymer, the vinyl bond content of the butadiene unit is preferably 30 to 70 mass%, more preferably 33 to 68 mass%, still more preferably 35 to 65 mass%. A vinyl bond content of less than 30 mass% may lead to poor grip property, whereas a vinyl bond content exceeding 70 mass% may lead to a reduction in the abrasion resistance of the resultant vulcanized rubber. As used herein, the term "vinyl bond content" refers to the percentage of the monomer unit having a 1,2-bond relative to all the butadiene-derived monomer units in the modified conjugated diene-based polymer. The vinyl bond content is measured by means of $^1\text{H-NMR}$.

[0059]

<Other steps>

Terminal modification step

In steps (1-2) and (2-2), the monomer group Y is polymerized in the presence of the initiator block, to thereby prepare a (modified) conjugated diene-based polymer having an active terminal. The polymerization of the (modified) conjugated diene-based polymer having the active terminal may be terminated by use of, for example, an alcohol as a polymerization terminator. Alternatively, the active terminal of the (modified) conjugated diene-based polymer may be reacted with a compound having an element (not bonded to active hydrogen) capable of interacting with silica and having a functional group capable of reacting with the active terminal of the polymer (hereinafter the compound may be referred to as a "terminal-modifying agent," corresponding to a compound (E)). Such a process produces a modified conjugated diene-based polymer in which one terminal of the conjugated diene-based polymer chain has the polymer block having the specific structure [F], and the other terminal (i.e., the terminal not having the polymer block) has a structure capable of interacting with silica.

[0060]

The "element capable of interacting with silica" is preferably at least one element selected from the group consisting of nitrogen, oxygen, silicon, phosphorus, sulfur, and tin. The term "interaction" refers to formation of a covalent bond between molecules, or formation of an intermolecular force (e.g., an intermolecular electromagnetic

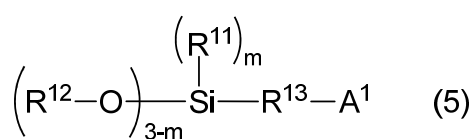
force, such as ion-dipole interaction, dipole-dipole interaction, hydrogen bond, or van der Waals force) weaker than a covalent bond. Examples of the functional group capable of interacting with silica include an amino group, a group having a carbon-nitrogen double bond, a nitrogen-containing heterocyclic group, a phosphino group, a thiol group, and a hydrocarbyloxysilyl group.

[0061]

Specific examples of the terminal-modifying agent include compounds (I) to (V) described below. These terminal-modifying agents may be used singly or in combination of two or more species. As used herein, the term "(thio)carbonyl group" refers to a carbonyl group or a thiocarbonyl group, and the term "iso(thio)cyanate group" refers to an isocyanate group or an isothiocyanate group.

[0062]

(I) Compound (E-1) represented by formula (5);

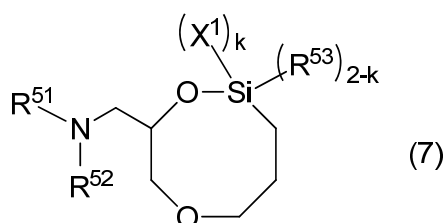


wherein A^1 represents a monovalent functional group that includes at least one atom selected from the group consisting of a nitrogen atom, a phosphorus atom, and a sulfur atom, and does not include active hydrogen, the monovalent functional group being bonded to R^{13} through a nitrogen atom, a phosphorus atom, or a sulfur atom, R^{11} and R^{12} each represent a hydrocarbyl group, R^{13} represents a hydrocarbylene group,

and m is an integer from 0 to 2, provided that a plurality of R^{11} are either identical or different when a plurality of R^{11} are present, and a plurality of R^{12} are either identical or different when a plurality of R^{12} are present.

[0063]

(II) Compound (E-2) represented by formula (7);



wherein R^{51} and R^{52} each represent a substituted or unsubstituted hydrocarbyl group, or R^{51} and R^{52} taken together represent a ring together with the nitrogen atom to which R^{51} and R^{52} bond, R^{53} represents a substituted or unsubstituted hydrocarbyl group, X^1 represents a hydrocarbyloxy group, a halogen atom, or a hydroxy group, and k is an integer of 0 to 2.

[0064]

(III) Compound (E-3) that includes a functional group P and a group Q in its molecule, the functional group P being at least one functional group selected from the group consisting of a cyclic ether group, a (thio)carbonyl group, and an iso(thio)cyanate group, and the group Q including at least one atom selected from the group consisting of a nitrogen atom, a phosphorus atom, an oxygen atom, and a sulfur atom (provided that a nitrogen atom, a phosphorus atom, and a sulfur atom may be protected by a trisubstituted

hydrocarbylsilyl group), and not including active hydrogen, the group Q differing from the functional group P;

(IV) Compound (E-4) that includes two or more iso(thio)cyanate groups in its molecule;

(V) Compound (E-5) that includes silicon-nitrogen bond;
[0065]

The hydrocarbyl group represented by R^{11} and R^{12} in the formula (5) is preferably a C1 to C20 linear or branched alkyl group, a C3 to C20 cycloalkyl group, or a C6 to C20 aryl group.

R^{13} is preferably a C1 to C20 linear or branched alkanediyl group, a C3 to C20 cycloalkylene group, or a C6 to C20 arylene group.

It is preferable that m be 0 or 1 from the viewpoint of improving the reactivity with the conjugated diene-based polymer.

[0066]

A^1 includes at least one atom selected from the group consisting of a nitrogen atom, a phosphorus atom, and a sulfur atom, and is bonded to R^{13} through the nitrogen atom, the phosphorus atom, or the sulfur atom. The nitrogen atom, the phosphorus atom, or the sulfur atom is not bonded to active hydrogen, and may be protected by a protecting group.

Specific examples of A^1 include a nitrogen-containing group in which two hydrogen atoms of a primary amino group are substituted with two protecting groups, a nitrogen-containing group in which one hydrogen atom of a secondary

amino group is substituted with one protecting group, a tertiary amino group, a group having a carbon-nitrogen double bond, a nitrogen-containing heterocyclic group, a phosphorus-containing group in which two hydrogen atoms of a primary phosphino group are substituted with two protecting groups, a phosphorus-containing group in which one hydrogen atom of a secondary phosphino group is substituted with one protecting group, a tertiary phosphino group, and a sulfur-containing group in which one hydrogen atom of a thiol group is substituted with one protecting group. It is preferable that A¹ be a group that includes a nitrogen atom from the viewpoint of affinity to silica.

[0067]

The hydrocarbyl group represented by R⁵¹, R⁵² and R⁵³ in the formula (7) is preferably a C1 to C10 alkyl group, more preferably a C1 to C5 alkyl group. R⁵¹ and R⁵² taken together may represent a ring together with the nitrogen atom to which R⁵¹ and R⁵² bond. Examples of the ring (cyclic amino group) include a 1-pyrrolidinyl group, a 1-piperidino group, a 1-Hexamethyleneimino group, a 1-octamethyleneimino group, a pyridyl group, a 1-imidazolyl group, a 4-methylpiperazinyl group, and a 4-ethylpiperazinyl group.

X¹ is preferably a hydrocarbyl group, more preferably a methyl group and an ethyl group.

[0068]

Specific examples of the compound (E-1) that includes a nitrogen-containing group in which two hydrogen atoms of a

primary amino group are substituted with two protecting groups, or a nitrogen-containing group in which one hydrogen atom of a secondary amino group is substituted with one protecting group, and an alkoxysilyl group, include N,N-bis(trimethylsilyl)aminopropyltrimethoxysilane, N,N-bis(trimethylsilyl)aminopropylmethyldiethoxysilane, N,N',N'-tris(trimethylsilyl)-N-(2-aminoethyl)-3-aminopropyltriethoxysilane, 3-(4-trimethylsilyl-1-piperazino)propylmethyldimethoxysilane, and compounds obtained by substituting the alkyl group or the alkanediyl group included in these compounds with a C1 to C6 alkyl group or a C1 to C6 alkanediyl group.

[0069]

Specific examples of the compound (E-1) that includes a tertiary amino group and an alkoxysilyl group, include 3-(benzylmethylamino)propyltrimethoxysilane, 3-(benzylmethylamino)butyltriethoxysilane, and compounds obtained by substituting the alkyl group or the alkanediyl group included in these compounds with a C1 to C6 alkyl group or a C1 to C6 alkanediyl group.

[0070]

Specific examples of the compound (E-1) that includes a group having a carbon-nitrogen double bond, or a nitrogen-containing heterocyclic group, and an alkoxysilyl group, include N-(1,3-dimethylbutylidene)-3-(triethoxysilyl)-1-propanamine, N-(1-methylpropylidene)-3-(triethoxysilyl)-1-propanamine, N-(4-N,N-dimethylaminobenzylidene)-3-

(triethoxysilyl)-1-propanamine, N-(cyclohexylidene)-3-(triethoxysilyl)-1-propanamine, N-(3-trimethoxysilylpropyl)-4,5-dihydroimidazole, N-(3-trimethoxysilylpropyl)imidazole, 3-hexamethyleneiminopropyltrimethoxysilane, 3-hexamethyleneiminopropylmethyldimethoxysilane, 3-(1-piperidino)propyltrimethoxysilane, 3-(1-hexamethyleneimino)propyltrimethoxysilane, 3-(1-piperazinyl)propyltrimethoxysilane, 3-morpholinopropyltrimethoxysilane, and compounds obtained by substituting the alkyl group or the alkanediyl group included in these compounds with a C1 to C6 alkyl group or a C1 to C6 alkanediyl group.

[0071]

Specific examples of the compound (E-1) that includes a phosphorus-containing group in which two hydrogen atoms of a primary phosphino group are substituted with two protecting groups, a phosphorus-containing group in which one hydrogen atom of a secondary phosphino group is substituted with one protecting group, a tertiary phosphino group, or a sulfur-containing group in which one hydrogen atom of a thiol group is substituted with one protecting group, and an alkoxysilyl group, include P,P-

bis(trimethylsilyl)phosphinopropylmethyldimethoxysilane, P,P-bis(trimethylsilyl)phosphinopropyltrimethoxysilane, 3-dimethylphosphinopropyltrimethoxysilane, 3-dimethylphosphinopropylmethyldimethoxysilane, 3-diphenylphosphinopropyltrimethoxysilane,

3-diphenylphospinopropylmethyldimethoxysilane,
S-trimethylsilylmercaptopropylmethyldimethoxysilane,
S-trimethylsilylmercaptopropyltrimethoxysilane, and
compounds obtained by substituting the alkyl group or the
alkanediyl group included in these compounds with a C1 to C6
alkyl group or a C1 to C6 alkanediyl group.

Examples of the compound (E-1) that includes an
iso(thio)cyanate group, include 3-
isocyanatopropyltrimethoxysilane, and 3-
isocyanatopropyltriethoxysilane.

[0072]

Specific examples of the compound (E-2) include 2,2-
dimethoxy-8-(4-methylpiperazinyl)methyl-1,6-dioxo-2-
silacyclooctane, 2,2-dimethoxy-8-(N,N-diethyl)methyl-1,6-
dioxo-2-silacyclooctane, 2-methoxy 2-methyl-8-(4-
methylpiperazinyl)methyl-1,6-dioxo-2-silacyclooctane, and
compounds obtained by substituting the alkyl group or the
alkanediyl group included in these compounds with a C1 to C6
alkyl group or a C1 to C6 alkanediyl group.

[0073]

The compound (E-3) is preferably that the group Q is a
group having a nitrogen atom that is not bonded to active
hydrogen. In the case of the aforementioned compound (E-3),
specific examples of the compound (E-3) that includes a
cyclic ether group, include epoxyamine compounds such as
N,N,N',N'-tetraglycidyl-1,3-bisaminomethylcyclohexane.
Specific examples of the compound (E-3) that includes a

(thio)carbonyl group include 4-aminoacetophenones such as 4-N,N-dimethylaminobenzophenone; bis(dihydrocarbylaminoalkyl) ketones such as 1,7-bis(methylethylamino)-4-heptanone; dihydrocarbylaminoalkyl (meth)acrylates such as 2-dimethylaminoethyl acrylate; hydrocarbylimidazolidinones such as 1,3-dimethyl-2-imidazolidinone; N-hydrocarbylpyrrolidones such as 1-phenyl-2-pyrrolidone; N-hydrocarbylcaprolactams such as N-methyl- ϵ -caprolactam; N-dihydrocarbylformamides such as N,N-diethylformamide; N,N-dihydrocarbylacetamides such as N,N-dimethylacetamide; (meth)acrylamides such as N,N-dimethylacrylamide. Specific examples of the compound (E-3) that includes an iso(thio)cyanate group include 3-isocyanatopropyltrimethoxysilane.

[0074]

Specific examples of the compound (E-4) include 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, diphenylmethane diisocyanate, naphthalene diisocyanate, triphenylmethane triisocyanate, p-phenylene diisocyanate, tris(isocyanatophenyl) thiophosphate, xylene diisocyanate, benzene-1,2,4-triisocyanate, naphthalene-1,2,5,7-tetraisocyanate, and 1,4-phenylene diisothiocyanate.

[0075]

Specific examples of the compound (E-5) include 2-(2,2-dimethoxy-1,2-azasilolidin-1-yl)-N,N-diethylethan-1-amine, 2-(2,2-dimethoxy-1,2-azasilolidin-1-yl)-N,N-dimethyl ethane-1-amine, 3-(2,2-dimethoxy-1,2-azasilolidin-1-yl)-N,N-diethylpropan-1-amine, 2-(2,2-dimethoxy-1-aza-2-

silacyclohexan-1-yl)-N,N-diethylethan-1-amine, 2,2-dimethoxy-1-phenyl-1,2-azasilolidine, N-n-butyl-aza-2,2-dialkoxysilacyclopentane, 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane, 2,2-diethoxy-1-(3-triethoxysilylpropyl)-1-aza-2-silacyclopentane, hexamethyldisilazane, and nonamethyltrisilazane. These terminal-modifying agents may be used singly or in combination of two or more species.

[0076]

The terminal-modifying agent may be a compound (coupling agent) having two or more groups capable of reacting with the active terminal. Inactivation of the active terminal of the conjugated diene-based polymer chain through reaction with the coupling agent can increase the molecular weight of the resultant polymer so as to fall within a desired range. Examples of the coupling agent include succinamide, phthalic amide, dibenzoylpyridine, dibutyldichlorosilane, methyltrichlorosilane, methyldichlorosilane, tetrachlorosilane (silicon tetrachloride), silicon tetrabromide, silicon tetraiodide, trichloromethoxysilane, tribromomethoxysilane, trimethoxysilane, methyltriethoxysilane, tetramethoxysilane, tetraethoxysilane, polyorganosiloxane, 1,5-bis(trichlorosilyl)pentane, 1,6-bis(trichlorosilyl)hexane, dimethyl adipate, dimethyl terephthalate, tetrachlorotin, tetrabromotin, trichlorobutyltin, trichloromethyltin, trichloroethyltin, trichlorophenyltin, trichlorooctyltin,

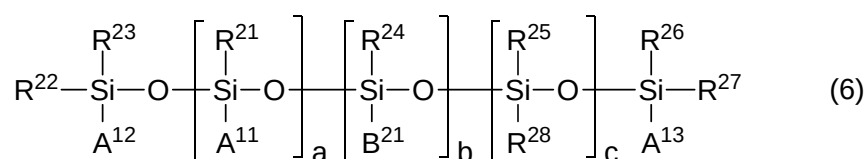
butyltin tris octanoate, dibutyltin bislaurate, ethylene glycol diglycidyl ether, trichlorophosphine, and pyromellitic anhydride.

[0077]

The coupling agent is preferably a polyorganosiloxane having at least one specific functional group selected from the group consisting of an epoxy group, an alkoxy group, a carbonyl group, a 2-pyrrolidonyl group, a vinyl group, and a halogen atom, wherein the total number of the specific functional groups is two or more (hereinafter the polyorganosiloxane may be referred to as a "specific polyorganosiloxane").

[0078]

The specific polyorganosiloxane is a linear, cyclic, or branched compound having a siloxane bond. Specific examples of preferred specific polyorganosiloxanes include compounds represented by the following formula (6):



wherein R^{21} to R^{28} each represent a hydrocarbyl group, A^{11} represents a group having the specific functional group, A^{12} and A^{13} each represent a hydrocarbyl group or a group having the specific functional group, B^{21} represents a group having a polyether structure, a is an integer of 3 to 200, b is an integer of 0 to 200, c is an integer of 0 to 200, and R^{21} to R^{28} , A^{11} , and B^{21} may be identical to or different from one

another between structural units.

[0079]

Examples of the hydrocarbonyl group represented by R^{21} to R^{28} , A^{12} , or A^{13} in the formula (6) include a C1 to C20 linear or branched alkyl group, a C3 to C20 cycloalkyl group, and a C6 to C20 aryl group. Of these, an alkyl group or a phenyl group is preferred.

Examples of the group having the specific functional group represented by A^{11} to A^{13} include a C4 to C12 group having an epoxy group, a C4 to C20 group having a 2-pyrrolidonyl group, a C1 to C5 alkoxy group, a C1 to C5 halogenated alkyl group, a C2 to C5 alkenyl group, a styryl group, and an ester group. Preferred is a C4 to C12 group having an epoxy group, a C4 to C20 group having a 2-pyrrolidonyl group, or a C1 to C5 alkoxy group.

[0080]

Examples of the polyether structure represented by B^{21} include a structure having a C2 to C20 alkylene glycol repeating unit. Specific examples of the structure include a polyethylene glycol structure and a polypropylene glycol structure.

In the formula (6), a is preferably an integer of 20 to 150, more preferably an integer of 30 to 120, in order to sufficiently secure an improvement in the processability of the polymer composition, and to prevent an excessive increase in the viscosity of the specific polyorganosiloxane. In the formula (6), b is preferably 0 to 150, more preferably 0 to

120, and c is preferably 0 to 180, more preferably 10 to 150.

The total number of a, b, and c is preferably 400 or less, more preferably 300 or less, from the viewpoint of ease of handling of the specific polyorganosiloxane. The specific polyorganosiloxane can be prepared by any known synthetic method. The specific polyorganosiloxane may be a commercially available product.

[0081]

The reaction between the conjugated diene-based polymer having the active terminal and the terminal-modifying agent may be, for example, a solution reaction. The solution reaction may be performed by use of a solution containing unreacted monomers after completion of the polymerization reaction. Alternatively, the solution reaction may be performed after isolation of the polymer contained in the solution and dissolution of the isolated polymer in an appropriate solvent (e.g., cyclohexane). The modification reaction may be performed by a batch or continuous process. No particular limitation is imposed on the method of adding the terminal-modifying agent. For example, the terminal-modifying agent may be added at one time or in a divided or continuous manner.

[0082]

In the aforementioned reaction, the amount of the terminal-modifying agent used (or the total amount of two or more terminal-modifying agents used) may be appropriately determined depending on the type of the compound used for the

reaction. For example, in the case of the aforementioned compounds (E-1) to (E-5), the amount of the terminal-modifying agent is preferably 0.1 mole equivalents or more, more preferably 0.3 mole equivalents or more, relative to the metal atom (responsible for the polymerization reaction) of the polymerization initiator. An amount of 0.1 mole equivalents or more can lead to sufficient progress of the modification reaction, and an effective improvement in the dispersibility of silica.

[0083]

In the case where the specific polyorganosiloxane is used for the aforementioned reaction, the amount of the specific polyorganosiloxane is adjusted such that the amount of the specific functional group is preferably 0.01 mol or more, more preferably 0.05 mol or more, relative to 1 mol of the metal atom (responsible for the polymerization) of the polymerization initiator, from the viewpoint of the compatibility between the processability of the polymer composition and the fracture resistance and viscoelasticity of the resultant crosslinked polymer. The maximum amount of the specific polyorganosiloxane is adjusted such that the amount of the specific functional group is preferably less than 1.0 mol, more preferably less than 0.7 mol, relative to 1 mol of the metal atom (responsible for the polymerization) of the polymerization initiator.

[0084]

The terminal modification reaction temperature is

generally equal to the polymerization reaction temperature, and is preferably -20 to 150°C, more preferably 0 to 120°C, particularly preferably 20 to 100°C. A low modification reaction temperature may lead to an increase in the viscosity of the modified conjugated diene-based polymer, whereas a high modification reaction temperature facilitates the inactivation of the active terminal of the polymer. The modification reaction time is preferably 1 minute to 5 hours, more preferably 2 minutes to 1 hour. The conjugated diene-based polymer contained in the reaction solution can be isolated by, for example, a known solvent removal method (e.g., steam stripping) and a drying operation (e.g., thermal treatment).

[0085]

In the case where the specific polyorganosiloxane is used, a polymerization terminator (e.g., an alcohol) or another modifying agent may be added to the polymerization system before reaction between the conjugated diene-based polymer having the active terminal and the specific polyorganosiloxane to thereby inactivate a portion of the conjugated diene-based polymer, for the purpose of adjusting the amount of the conjugated diene-based polymer to be reacted with the specific polyorganosiloxane.

[0086]

In one preferred embodiment of the modified conjugated diene-based polymer of the present disclosure, the polymer block having the specific structure [F] is bonded to one

terminal of the conjugated diene-based polymer chain including a conjugated diene unit and an aromatic vinyl unit, and a structure containing an element capable of interacting with silica is bonded to the other terminal (i.e., the terminal not having the polymer block) of the conjugated diene-based polymer chain. The modified conjugated diene-based polymer effectively achieves improved low fuel consumption performance, processability, and wet grip property of the resultant vulcanized rubber. The polymer may be in a linear or branched form.

[0087]

<Polymer composition>

The polymer composition of the present disclosure contains a rubber component containing the aforementioned modified conjugated diene-based polymer, an inorganic filler, and a crosslinking agent. The amount of the modified conjugated diene-based polymer contained in the polymer composition is preferably 20 mass% or more, more preferably 30 mass% or more, still more preferably 40 mass% or more, relative to the amount of the rubber component contained in the polymer composition. The inorganic filler is preferably at least one of silica and carbon black.

[0088]

Examples of the silica include wet silica (hydrated silica), dry silica (silicic anhydride), colloidal silica, precipitated silica, calcium silicate, and aluminum silicate. Of these, wet silica is particularly preferred from the

viewpoints of an improvement in fracture resistance, and the compatibility between wet grip property and low rolling resistance. The use of high dispersible-type silica is preferred for achieving effective dispersion of the silica in the polymer composition and improvements in physical properties and processability. These silica materials may be used singly or in combination of two or more species.

[0089]

Examples of the carbon black include, but are not particularly limited to, GPF, FEF, HAF, ISAF, and SAF. The use of carbon black as an inorganic filler achieves a good reinforcing effect.

[0090]

The polymer composition may contain, in addition to silica or carbon black, any reinforcing filler (e.g., clay or calcium carbonate). The total amount of silica and carbon black contained in the polymer composition is preferably 20 to 130 parts by mass, more preferably 25 to 110 parts by mass, relative to 100 parts by mass of the total amount of polymer components contained in the polymer composition.

[0091]

Examples of the crosslinking agent include sulfur, sulfur halides, organic peroxides, quinone dioximes, organic polyamine compounds, and alkyl phenolic resins having a methylol group. Sulfur is generally used. The amount of sulfur is preferably 0.1 to 5 parts by mass, more preferably 0.5 to 3 parts by mass, relative to 100 parts by mass of the

total amount of polymer components contained in the polymer composition.

[0092]

The polymer composition of the present disclosure, which contains the above-prepared modified conjugated diene-based polymer of the present disclosure, may contain an additional rubber component different from the modified conjugated diene-based polymer. Examples of the type of the additional rubber component include, but are not particularly limited to, butadiene rubber (BR, such as high cis BR having a cis-1,4 bond content of 90% or more, or BR containing syndiotactic-1,2-polybutadiene (SPB)), styrene butadiene rubber (SBR), natural rubber (NR), isoprene rubber (IR), styrene-isoprene copolymer rubber, and butadiene-isoprene copolymer rubber. The amount of the additional rubber component is preferably 5 to 60 parts by mass, more preferably 10 to 50 parts by mass, relative to 100 parts by mass of the total amount of polymer components contained in the polymer composition.

[0093]

The polymer composition may contain, in addition to the aforementioned components, any additive that is commonly used in a rubber composition for tire. Examples of the additive include an antioxidant, zinc oxide, stearic acid, a softener, a vulcanization accelerator, a silane coupling agent, a compatibilizer, a vulcanization aid, a process oil, a processing aid, and an anti-scorching agent. The amount of

such an additive incorporated into the polymer composition may be appropriately determined, so long as the advantageous effects of the present disclosure are not impaired.

[0094]

The polymer composition of the present disclosure can be prepared through kneading of the polymer components, the inorganic filler, the crosslinking agent, and an optional component by means of, for example, an open-type kneader (e.g., a roll) or a closed-type kneader (e.g., a Banbury mixer). The polymer composition is prepared into a crosslinked polymer through molding and subsequent crosslinking (vulcanization). The resultant crosslinked polymer can be applied to various rubber products. For example, the crosslinked polymer can be applied to tires (e.g., tire tread, undertread, carcass, sidewall, and bead); sealing materials, such as packing, gasket, weather strip, and O-ring; interior and exterior surface materials for various vehicles, such as automobile, ship, aircraft, and train; building materials; vibration-proof rubbers for industrial machines and facilities; hoses and hose covers, such as diaphragm, roll, radiator hose, and air hose; belts, such as belts for power transmission; linings; dust boots; materials for medical devices; fenders; insulating materials for electric wires; and other industrial products.

[0095]

The production method of the present disclosure can produce a modified conjugated diene-based polymer capable of

preparing a vulcanized rubber that achieves excellent low fuel consumption performance, processability, and wet grip property. Thus, the polymer composition containing the modified conjugated diene-based polymer of the present disclosure is particularly suitable for use as a material of a tire tread or sidewall.

[0096]

The tire can be produced by a customary method. For example, the polymer composition is mixed by means of a kneader to form a sheet, and the sheet is disposed at a predetermined position and vulcanized by a customary method, to thereby form a tread rubber or a sidewall rubber. A pneumatic tire is thereby produced.

Examples

[0097]

The present invention will next be described in detail by way of examples, which should not be construed as limiting the invention thereto. Unless otherwise specified, the units "part(s)" and "%" described in Examples and Comparative Examples refer to "part(s) by mass" and "mass%," respectively. Physical properties are determined as described below.

[0098]

[Evaluation of properties of polymer]

Vinyl bond content (%): determined by means of ^1H -NMR (400 MHz).

Bonded styrene content (%): determined by means of ^1H -NMR (400 MHz).

Weight average molecular weight before modification (peak molecular weight before modification reaction): determined on the basis of a chart of molecular weight (in terms of polystyrene) obtained by means of gel permeation chromatography (GPC). Specific conditions for GPC are as follows.

(GPC conditions)

Chromatograph: HLC-8020 (manufactured by Tosoh Corporation)

Column: two columns of GMH-HR-H (manufactured by Tosoh Corporation) connected in series

Detector: differential refractometer RI-8020 (manufactured by Tosoh Corporation)

Eluent: tetrahydrofuran

Column temperature: 40°C

Mooney viscosity (ML_{1+4} , 100°C): determined according to JIS K6300 by use of an L rotor under the following conditions: preheating: 1 minute, rotor operation time: 4 minutes, temperature: 100°C.

[0099]

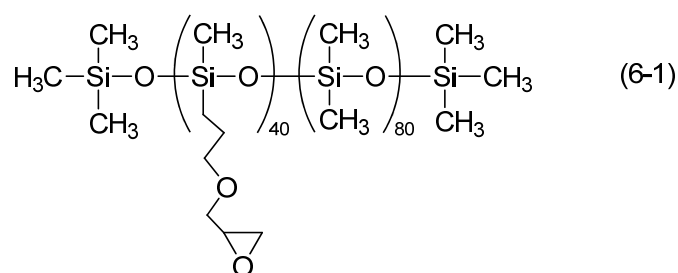
[Example 1-1: Synthesis of modified conjugated diene-based rubber A1 (method 1)]

Cyclohexane (28 g) and tetramethylethylenediamine (8.6 mmol) were added to a 100-mL ampule vial purged with nitrogen, and then n-butyllithium (6.1 mmol) was added

thereto. Subsequently, bis(diethylamino)methylvinylsilane (8.0 g) and 1,3-butadiene (2.0 g) were slowly added to the ampule vial, and then reaction was allowed to proceed in the ampule vial at 60°C for 120 minutes, to thereby prepare a polymer block having an active terminal (hereinafter the polymer block will be referred to as "initiator block 1").

Subsequently, cyclohexane (4,000 g), 1,3-butadiene (357.7 g), and styrene (132.3 g) were added to an autoclave equipped with an agitator in a nitrogen atmosphere, and then the initiator block 1 was entirely added, to thereby initiate polymerization at 40°C. Ten minutes after initiation of the polymerization, 1,3-butadiene (195.3 g) and styrene (14.7 g) were continuously added over 60 minutes. The maximum temperature during polymerization reaction was 60°C. After completion of the continuous addition, the polymerization reaction was continued for 20 minutes. After determination of a polymerization conversion of 95% to 100%, a 20 wt.% solution of 1,6-bis(trichlorosilyl)hexane (0.08 mmol) in cyclohexane was added, and then reaction was allowed to proceed for 10 minutes. Subsequently, a 20 mass% solution of polyorganosiloxane A (0.027 mmol) represented by the following formula (6-1) in xylene was added, and then reaction was allowed to proceed for 30 minutes. Thereafter, methanol (serving as a polymerization terminator) was added in an amount corresponding to 2-fold mole of the n-butyllithium used, to thereby prepare a solution containing a modified conjugated diene-based rubber A1. The solution was

mixed with Irganox 1520L (manufactured by Ciba Specialty Chemicals) serving as an antioxidant (0.15 parts relative to 100 parts of the resultant conjugated diene-based rubber), and then the solvent was removed through steam stripping, followed by vacuum drying at 60°C for 24 hours, to thereby produce a modified conjugated diene-based rubber A1 in a solid form. The polymerization formulation of the modified conjugated diene-based rubber A1 is shown in Table 1, and the properties of the modified conjugated diene-based rubber A1 are shown in Table 2.



[0100]

[Examples 1-2 to 1-7]

The procedure of Example 1-1 was repeated, except that bis(diethylamino)methylvinylsilane was replaced with a polymerizable monomer shown in Table 1, to thereby prepare a polymer block having an active terminal (initiator blocks 2 to 7).

The procedure of Example 1-1 was repeated, except that the initiator block and the type and amount of a compound used for terminal modification were changed as shown in Table 1, to thereby produce modified conjugated diene-based rubbers A2 to A7 (see Table 1). The amount of the initiator blocks 2

to 7 was adjusted as the amount of lithium was 6.1 mmol as in the case of Example 1-1. The properties of the resultant modified conjugated diene-based rubbers A2 to A7 are shown in Table 2.

[0101]

[Table 1]

	Example 1-1	Example 1-2	Example 1-3	Example 1-4	Example 1-5	Example 1-6	Example 1-7	Comparative Example 1-1	Comparative Example 1-2	Comparative Example 1-3
Type of modified conjugated diene-based rubber	A1	A2	A3	A4	A5	A6	A7	P1	P2	P3
Initiator block component										
Type of initiator block	block 1	block 2	block 3	block 4	block 5	block 6	block 7	-	-	-
Cyclohexane (g)	28	28	28	28	28	28	28	-	-	-
Tetramethylethylenediamine (mmol)	8.6	8.6	8.6	8.6	8.6	8.6	8.6	-	-	-
n-Butyllithium (mmol)	6.1	6.1	6.1	6.1	6.1	6.1	6.1	-	-	-
Monomer group X										
: 1,3-Butadiene (g)	2	2	2	2	2	2	2	-	-	-
: X-1 (g)	8	-	-	-	-	8	8	-	-	-
: X-2 (g)	-	8	-	-	-	-	-	-	-	-
: X-3 (g)	-	-	8	-	-	-	-	-	-	-
: X-4 (g)	-	-	-	8	-	-	-	-	-	-
: X-5 (g)	-	-	-	-	8	-	-	-	-	-
Conjugated diene-based polymer chain component										
Cyclohexane (g)	4000	4000	4000	4000	4000	4000	4000	4000	4000	4000
Tetramethylethylenediamine (mmol)	-	-	-	-	-	-	-	7.50	7.50	7.50
Monomer group Y										
: Styrene (g)	132.3	132.3	132.3	132.3	132.3	132.3	132.3	132.3	132.3	132.3
: 1,3-Butadiene (g)	357.7	357.7	357.7	357.7	357.7	357.7	357.7	357.7	357.7	357.7
: Supplemental styrene (g)	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7	14.7
: Supplemental 1,3-butadiene (g)	195.3	195.3	195.3	195.3	195.3	195.3	195.3	195.3	195.3	195.3
n-Butyllithium (mmol)	-	-	-	-	-	-	-	5.40	5.40	5.40
Initiator block	block 1	block 2	block 3	block 4	block 5	block 6	block 7	-	-	-
Terminal-modifying agent										
: N/Si-1 (mmol)	0.08	0.08	0.08	0.08	0.08	-	-	0.08	-	-
: N/Si-2 (mmol)	0.027	0.027	0.027	0.027	0.027	-	-	0.027	-	-
: N/Si-3 (mmol)	-	-	-	-	-	0.51	0.05	-	0.51	0.05
: N/Si-4 (mmol)	-	-	-	-	-	-	2.00	-	-	2.00
Antioxidant (/rubber 100 parts)	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15

[0102]

The abbreviations of compounds shown in Table 1 are as follows.

X-1: bis(diethylamino)methylvinylsilane

X-2: dimethyl-1-piperidinylmethylvinylsilane

X-3: tert-butoxydiphenylvinylsilane

X-4: mixture of 3-1-(pyrrolidinyl)ethylstyrene and 4-1-(pyrrolidinyl)ethylstyrene

X-5: 4-vinylpyridine

N/Si-1: 1,6-bis(trichlorosilyl)hexane

N/Si-2: polyorganosiloxane A (compound represented by the aforementioned formula (6-1))

N/Si-3: silicon tetrachloride

N/Si-4: 3-(benzylmethylamino)propyltrimethoxysilane

[0103]

[Table 2]

Type of modified conjugated diene-based rubber	A1	A2	A3	A4	A5	A6	A7	P1	P2	P3
Bonded styrene content (%)	21	21	21	21	21	21	21	21	21	21
Vinyl bond content (%)	62	63	64	62	62	63	62	62	64	62
Weight average molecular weight before polymerization ($\times 10^4$)	32	33	33	32	34	31	32	32	32	33
Mooney viscosity (ML1+4, 100°C)	53	54	53	52	56	105	82	45	91	75

[0104]

[Comparative Example 1-1: Synthesis of modified conjugated diene-based rubber P1]

Cyclohexane (4,000 g), 1,3-butadiene (357.7 g), and styrene (132.3 g) were added to an autoclave equipped with an agitator in a nitrogen atmosphere, and then tetraethylenediamine (7.5 mmol) and n-butyllithium (5.4

mmol) were added, to thereby initiate polymerization at 40°C. Ten minutes after initiation of the polymerization, 1,3-butadiene (195.3 g) and styrene (14.7 g) were continuously added over 60 minutes. The maximum temperature during polymerization reaction was 60°C. After completion of the continuous addition, the polymerization reaction was continued for 20 minutes. After determination of a polymerization conversion of 95% to 100%, a 20 mass% solution of 1,6-bis(trichlorosilyl)hexane (0.08 mmol) in cyclohexane was added, and then reaction was allowed to proceed for 10 minutes. Subsequently, a 20 mass% solution of polyorganosiloxane A (0.027 mmol) represented by the aforementioned formula (6-1) in xylene was added, and then reaction was allowed to proceed for 30 minutes. Thereafter, methanol (serving as a polymerization terminator) was added in an amount corresponding to 2-fold mole of the n-butyllithium used, to thereby prepare a solution containing a modified conjugated diene-based rubber P1. The solution was mixed with Irganox 1520L (manufactured by Ciba Specialty Chemicals) serving as an antioxidant (0.15 parts relative to 100 parts of the resultant modified conjugated diene-based rubber), and then the solvent was removed through steam stripping, followed by vacuum drying at 60°C for 24 hours, to thereby produce a modified conjugated diene-based rubber P1 in a solid form. The polymerization formulation of the modified conjugated diene-based rubber P1 is shown in Table 1, and the properties of the modified conjugated diene-based

rubber P1 are shown in Table 2.

[0105]

[Comparative Examples 1-2 and 1-3]

The procedure of Comparative Example 1-1 was repeated, except that the type and amount of a terminal-modifying agent were changed as shown in Table 1, to thereby produce modified conjugated diene-based rubbers P2 and P3. The properties of the resultant modified conjugated diene-based rubbers P2 and P3 are shown in Table 2.

[0106]

[Example 2-1: Preparation of rubber composition and evaluation of physical properties thereof]

A rubber composition having the formulation shown in Table 3 was prepared from the above-produced modified conjugated diene-based rubber A1. The rubber composition was vulcanized and evaluated for its physical properties. The rubber composition was kneaded and evaluated by the methods described below.

[0107]

[Table 3]

Compounding formulation		Parts by mass
Rubber component		100
Silica	*1	40
Silane coupling agent	*2	4.3
Oil	*3	10
Silica	*1	14
Carbon black	*4	6
Stearic acid		2
Antioxidant	*5	2
Zinc oxide		3
Vulcanization accelerator	*6	1.4
Vulcanization accelerator	*7	1.4
Sulfur		1.6

[0108]

The details of each component in Table 3 are shown below.

*1: Zeosil 1165MP manufactured by Rhodia

*2: Si69 manufactured by Degussa

*3: Fukkol Eramic 30 manufactured by Nippon Oil Corporation

*4: Seast 7HM," manufactured by TOKAI CARBON Co., Ltd.

*5: Nocrac 6C manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.

*6: Nocceler D manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.

*7: Nocceler NS manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.

[0109]

Methods for kneading and evaluating rubber composition

The modified conjugated diene-based rubber A1 produced in Example 1-1 (100 parts) was masticated by means of a Banbury mixer (volume: 250 mL). Subsequently, silica (trade name "Zeosil 1165MP," manufactured by Rhodia, nitrogen

adsorption specific surface area (BET): 163 m²/g) (40 parts), a silane coupling agent (bis(3-(triethoxysilyl)propyl) tetrasulfide, trade name "Si69," manufactured by Degussa) (4.3 parts), and process oil (trade name "Fukkol Eramic 30," manufactured by Nippon Oil Corporation) (10 parts) were added, and the resultant mixture was kneaded at 110°C (initiation temperature) for 1.5 minutes. The kneaded product was mixed with silica (trade name "Zeosil 1165MP," manufactured by Rhodia) (14 parts), carbon black (trade name "Seast 7HM," manufactured by TOKAI CARBON Co., Ltd.) (6 parts), zinc oxide (zinc white No. 1) (3.0 parts), stearic acid (trade name "SA-300," manufactured by Adeka Corporation) (2 parts), and an antioxidant (N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine, trade name "Nocrac 6C," manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.) (2 parts), and the mixture was kneaded for 2.5 minutes. Thereafter, the resultant rubber composition was discharged from the Banbury mixer. The temperature of the rubber composition was 150°C at the time of completion of kneading. After the rubber composition was cooled to room temperature, the rubber composition was kneaded again in the Banbury mixer for 3 minutes and then discharged from the Banbury mixer. Subsequently, the rubber composition was kneaded with sulfur (1.6 parts), and a vulcanization accelerator (mixture of N-t-butyl-2-benzothiazole sulphenamide (trade name "Nocceler NS," manufactured by Ouchi Shinko Chemical Industrial Co.,

Ltd. (1.4 parts) and diphenylguanidine (trade name "Nocceler D," manufactured by Ouchi Shinko Chemical Industrial Co., Ltd. (1.4 parts)) by means of an open roll mill at 50°C, and then a sheet-form rubber composition was discharged therefrom.

[0110]

The rubber composition was press-crosslinked at 160°C for 20 minutes, to thereby prepare a test piece. The test piece was evaluated for processability, wet grip property, and low-heat-generating property as described below. The results are shown in Table 4.

(i) Mooney viscosity: The polymer composition that was not vulcanized was used as a measurement specimen. The Mooney viscosity of the measurement specimen was measured in accordance with JIS K 6300-1 using an L rotor (preheating time: 1 minute, rotor operation time: 4 minutes, temperature: 100°C). A lower value of the mooney viscosity indicates superior processability of the polymer composition.

(ii) Wet grip property: The vulcanized rubber was used as a sample for measurement. An impact resilience test was performed according to JIS K6255 by use of a test piece having a diameter of 29.0 mm and a thickness of 12.5 mm, to thereby determine an impact resilience at 0°C. The impact resilience was indicated by an index relative to that (taken as 100) of the sample (standard) of Comparative Example 2-1. A higher index indicates superior wet grip property of a

tire produced from the vulcanized rubber.

(iii) Low-heat-generating property: The vulcanized rubber was used as a sample for measurement. A test piece having a length of 50 mm, a width of 12.7 mm, and a thickness of 2 mm was tested by means of ARES (manufactured by Rheometrics) under the following conditions (dynamic strain: 2.5%, 10 Hz), to thereby determine a $\tan\delta$ at 60°C. The $\tan\delta$ value was indicated by an index relative to that (taken as 100) of the sample (standard) of Comparative Example 2-1. A lower index indicates superior low-heat-generating property of a tire produced from the vulcanized rubber.

The results of evaluation of these properties are shown in Table 4.

[0111]

[Examples 2-2 to 2-7 and Comparative Examples 2-1 to 2-3]

The procedure of Example 2-1 was repeated, except that the type and amount of a rubber component used were changed as shown in Table 4, to thereby prepare a rubber composition. The prepared rubber composition was vulcanized and evaluated for the aforementioned properties. The results of evaluation of the properties are shown in Table 4.

[0112]

[Table 4]

Evaluation of properties	Example 2-1	Example 2-2	Example 2-3	Example 2-4	Example 2-5	Example 2-6	Example 2-7	Comparative Example 2-1	Comparative Example 2-2	Comparative Example 2-3
Type of modified conjugated diene- based rubber	A1	A2	A3	A4	A5	A6	A7	P1	P2	P3
Mooney viscosity (ML1+4,100℃)	78	77	75	76	75	98	92	65	92	85
Wet grip property (INDEX)	131	126	122	125	199	110	131	100	102	122
Low-heat-generating (INDEX) property	82	84	83	86	88	92	72	100	105	80

[0113]

[Example 3-1: Synthesis of modified conjugated diene-based rubber B1 (method 2)]

(Production of styrene-based block having active terminal)

Cyclohexane (31.8 parts), 4-methylstyrene (14.2 parts), and tetramethylethylenediamine (1.74 parts) were added to a glass reaction vessel in a nitrogen atmosphere. Subsequently, while the mixture was agitated, n-butyllithium (0.96 parts) was added (tetramethylethylenediamine: 1.0 mol per 1 mol of n-butyllithium, 4-methylstyrene: 8.0 mol per 1 mol of n-butyllithium), and then reaction was allowed to proceed at 50°C for 30 minutes, to thereby prepare a solution containing an initiator block; i.e., a styrene-based block having an active terminal (hereinafter the styrene-based block will be referred to as "styrene-based block D"). In order to determine the number of 4-methylstyrene units of the resultant styrene-based block D, an aliquot of the reaction mixture was sampled, and methanol was added to the aliquot for extraction and washing of the catalyst residue, followed by removal of the solvent through evaporation. The number of 4-methylstyrene units (average value) of the styrene-based block D was determined to be 9.0 by means of GPC.

[0114]

(Production of modified conjugated diene-based rubber B1)

Cyclohexane (800 parts), 1,3-butadiene (86.9 parts), styrene (23.1 parts), and tetramethylethylenediamine (0.07

parts) were added to an autoclave in a nitrogen atmosphere. Thereafter, a solution (2.6 parts) containing the above-produced styrene-based block D was added, and then polymerization was initiated at 50°C. The polymerization reaction was continued for 60 minutes. After determination of a polymerization conversion of 95% to 100%, 1-phenyl-2-pyrrolidone (serving as a terminal-modifying agent) (0.12 parts) was added, and then reaction was allowed to proceed for 30 minutes. Subsequently, the temperature was increased to 60°C, tetramethylethylenediamine (3.3 parts) and n-butyllithium (1.88 parts) serving as a lithiating agent were added, and then reaction was allowed to proceed for 60 minutes. Subsequently, bis(diethylamino)methylvinylsilane (1.6 parts) and 1,3-butadiene (0.4 parts) were added, and then reaction was allowed to proceed for 120 minutes. Thereafter, methanol (1.58 parts) was added, and then reaction was allowed to proceed for 30 minutes, to thereby prepare a solution containing a modified conjugated diene-based rubber B1. The resultant solution was mixed with 2,4-bis[(octylthio)methyl]-o-cresol (trade name "Irganox 1520," manufactured by BASF) serving as an antioxidant (0.20 parts relative to 100 parts of the modified conjugated diene-based rubber), and then the solvent was removed through steam stripping, followed by vacuum drying at 60°C for 24 hours, to thereby produce a modified conjugated diene-based rubber B1 in a solid form.

[0115]

[Examples 3-2 to 3-7]

The procedure of Example 3-1 was repeated, except that the polymerization formulation was changed as shown in Table 5, to thereby produce modified conjugated diene-based rubbers B2 to B7. The properties of the modified conjugated diene-based rubbers B2 to B7 are shown in Table 6.

[0116]

[Table 5]

	Example 3-1	Example 3-2	Example 3-3	Example 3-4	Example 3-5	Example 3-6	Example 3-7	Comparative Example 1-1	Comparative Example 1-2	Comparative Example 1-3
Type of modified conjugated diene-based rubber	B1	B2	B3	B4	B5	B6	B7	Q1	Q2	Q3
Conjugated diene-based polymer chain component										
Cyclohexane (parts)	800	800	800	800	800	800	800	800	800	800
Tetramethylethylenediamine (parts)	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07	0.07
Monomer group Y (parts)										
: Styrene	23.1	23.1	23.1	23.1	23.1	23.1	23.1	23.1	23.1	23.1
: 1,3-Butadiene	86.9	86.9	86.9	86.9	86.9	86.9	86.9	86.9	86.9	86.9
n-Butyllithium (parts)	-	-	-	-	-	-	-	5.40	5.40	5.40
Initiator block	block D	block D	block D	block D	block D	block D	block D	-	-	-
Terminal-modifying agent (parts)										
: N/Si-5	0.12	0.12	0.12	0.12	0.12	-	-	0.12	-	-
: N/Si-3	-	-	-	-	-	0.03	0.01	-	0.03	0.01
: N/Si-4	-	-	-	-	-	-	0.14	-	-	0.14
Lithiation (parts)										
: Tetramethylethylenediamine	3.30	3.30	3.30	3.30	3.30	3.30	3.30	-	-	-
: n-Butyllithium	1.88	1.88	1.88	1.88	1.88	1.88	1.88	-	-	-
Monomer group W (parts)										
: W-1	1.60	-	-	-	-	1.60	1.60	-	-	-
: W-2	-	1.60	-	-	-	-	-	-	-	-
: W-3	-	-	1.60	-	-	-	-	-	-	-
: W-4	-	-	-	1.60	-	-	-	-	-	-
: W-5	-	-	-	-	1.60	-	-	-	-	-
: 1,3-Butadiene	0.40	0.40	0.40	0.40	0.40	0.40	0.40	-	-	-
Antioxidant (/rubber 100 parts)	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20

[0117]

The abbreviations of compounds shown in Table 5 are as follows.

N/Si-3: silicon tetrachloride

N/Si-4: 3-(benzylmethylamino)propyltrimethoxysilane

N/Si-5: 1-phenyl-2-pyrrolidone

W-1: bis(diethylamino)methylvinylsilane

W-2: dimethyl-1-piperidinylmethylvinylsilane

W-3: tert-butoxydiphenylvinylsilane

W-4: mixture of 3-1-(pyrrolidinyl)ethylstyrene and 4-1-(pyrrolidinyl)ethylstyrene

W-5: 4-vinylpyridine

[0118]

[Table 6]

Type of modified conjugated diene-based rubber	B1	B2	B3	B4	B5	B6	B7	Q1	Q2	Q3
Bonded styrene content (%)	21	21	21	21	21	21	21	21	21	21
Vinyl bond content (%)	62	63	62	62	64	63	62	63	63	62
Weight average molecular weight before polymerization ($\times 10^4$)	22	23	22	24	21	22	23	21	22	22
Mooney viscosity (ML1+4, 100°C)	33	35	30	35	31	108	63	29	100	61

[0119]

[Comparative Example 3-1: Synthesis of modified conjugated diene-based rubber Q1]

Cyclohexane (800 parts), 1,3-butadiene (86.9 parts), styrene (23.1 parts), and tetramethylethylenediamine (0.15 parts) were added to an autoclave in a nitrogen atmosphere. Thereafter, n-butyllithium (serving as a polymerization initiator) (0.05 parts) was added, and then polymerization was initiated at 50°C. The polymerization reaction was

continued for 60 minutes. After determination of a polymerization conversion of 95% to 100%, N-phenylpyrrolidone (serving as a terminal-modifying agent) (0.12 parts) was added, and then reaction was allowed to proceed for 30 minutes. Subsequently, methanol (serving as a polymerization terminator) (1.58 parts) was added, and reaction was allowed to proceed for 30 minutes, to thereby prepare a solution containing a modified conjugated diene-based rubber Q1. The resultant solution was mixed with 2,4-bis[(octylthio)methyl]-o-cresol (trade name "Irganox 1520," manufactured by BASF) serving as an antioxidant (0.20 parts relative to 100 parts of the modified conjugated diene-based rubber), and then the solvent was removed through steam stripping, followed by vacuum drying at 60°C for 24 hours, to thereby produce a modified conjugated diene-based rubber Q1 in a solid form. The properties of the resultant modified conjugated diene-based rubber Q1 are shown in Table 6.

[0120]

[Comparative Examples 3-2 and 3-3]

The procedure of Comparative Example 3-1 was repeated, except that the type and amount of a terminal-modifying agent were changed as shown in Table 5, to thereby produce modified conjugated diene-based rubbers Q2 and Q3. The properties of the resultant modified conjugated diene-based rubbers Q2 and Q3 are shown in Table 6.

[0121]

[Example 4-1: Preparation of rubber composition and evaluation of physical properties thereof]

A rubber composition having the formulation shown in Table 7 was prepared from the above-produced modified conjugated diene-based rubber B1. The rubber composition was vulcanized and evaluated for its physical properties. The rubber composition was kneaded and evaluated by the methods described below.

[0122]

[Table 7]

Compounding formulation		Parts by mass
Rubber component		96
Silica	*1	48
Silane coupling agent	*2	5.8
Oil	*3	24
Silica	*1	24
Stearic acid		1.9
Antioxidant	*4	1.9
Zinc oxide		2.9
Vulcanization accelerator	*5	1.3
Vulcanization accelerator	*6	1.3
Sulfur		1.5

[0123]

The details of each component in Table 7 are shown below.

*1: Zeosil 1165MP manufactured by Rhodia

*2: Si69 manufactured by Degussa

*3: Fukkol Eramic 30 manufactured by Nippon Oil Corporation

*4: Nocrac 6C manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.

*5: Nocceler D manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.

*6: Nocceler NS manufactured by Ouchi Shinko Chemical

Industrial Co., Ltd.

[0124]

The modified conjugated diene-based rubber B1 produced in Example 3-1 (96 parts) was masticated by means of a Banbury mixer (volume: 250 mL). Subsequently, silica (trade name "Zeosil 1165MP," manufactured by Rhodia, nitrogen adsorption specific surface area (BET): 163 m²/g) (48 parts), a silane coupling agent (bis(3-(triethoxysilyl)propyl) tetrasulfide, trade name "Si69," manufactured by Degussa) (5.8 parts), and process oil (trade name "Fukkol Eramic 30," manufactured by Nippon Oil Corporation) (24 parts) were added, and the resultant mixture was kneaded at 110°C (initiation temperature) for 1.5 minutes. The kneaded product was mixed with silica (trade name "Zeosil 1165MP," manufactured by Rhodia) (24 parts), zinc oxide (zinc white No. 1) (2.9 parts), stearic acid (trade name "SA-300," manufactured by Adeka Corporation) (1.9 parts), and an antioxidant (N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine, trade name "Nocrac 6C," manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.) (1.9 parts), and the mixture was kneaded for 2.5 minutes. Thereafter, the resultant rubber composition was discharged from the Banbury mixer. The temperature of the rubber composition was 150°C at the time of completion of kneading. After the rubber composition was cooled to room temperature, the rubber composition was kneaded again in the Banbury mixer for 3 minutes and then discharged from the

Banbury mixer. Subsequently, the rubber composition was kneaded with sulfur (1.5 parts), and a vulcanization accelerator (mixture of N-t-butyl-2-benzothiazole sulphenamide (trade name "Nocceler NS," manufactured by Ouchi Shinko Chemical Industrial Co., Ltd. (1.3 parts) and diphenylguanidine (trade name "Nocceler D," manufactured by Ouchi Shinko Chemical Industrial Co., Ltd. (1.3 parts)) by means of an open roll mill at 50°C, and then a sheet-form rubber composition was discharged therefrom.

[0125]

The rubber composition was press-crosslinked at 160°C for 20 minutes, to thereby prepare a test piece. The test piece was evaluated for the aforementioned properties (tire performance) as in the case of Example 2-1. The results are shown in Table 8.

[0126]

[Examples 4-2 to 4-7 and Comparative Examples 4-1 to 4-3]

The procedure of Example 4-1 was repeated, except that the type and amount of a rubber component used were changed as shown in Table 8, to thereby prepare a rubber composition. The prepared rubber composition was vulcanized and evaluated for the aforementioned properties. The results of evaluation of the properties are shown in Table 8.

[0127]

[Table 8]

Evaluation of properties	Example 4-1	Example 4-2	Example 4-3	Example 4-4	Example 4-5	Example 4-6	Example 4-7	Comparative Example 4-1	Comparative Example 4-2	Comparative Example 4-3
Type of modified conjugated diene- based rubber	B1	B2	B3	B4	B5	B6	B7	Q1	Q2	Q3
Mooney viscosity (ML1+4,100°C)	69	70	71	68	68	120	80	65	111	75
Wet grip property (INDEX)	130	129	124	125	120	115	134	100	102	120
Low-heat-generating (INDEX) property	78	77	79	78	80	92	72	100	103	82

[0128]

As shown in the aforementioned results, the modified conjugated diene-based rubbers A1 to A7 and B1 to B7 of the Examples achieved well-balanced properties in terms of the processability of a rubber composition and the low fuel consumption performance and wet grip property of a vulcanized rubber, as compared with the modified conjugated diene-based rubbers of the Comparative Examples.

These results demonstrated that a modified conjugated diene-based polymer having at a terminal thereof a polymer block having the specific structure [F] can prepare a rubber composition exhibiting excellent processability and a vulcanized rubber achieving excellent low fuel consumption performance and wet grip property.

CLAIMS

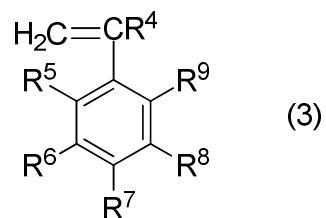
[Claim 1] A modified conjugated diene-based polymer comprising, at one terminal of a conjugated diene-based polymer chain, a polymer block having a structure derived from at least one compound selected from the group consisting of the following vinylsilane compound (A) and aromatic vinyl compound (B),

wherein the polymer block has a side chain including a structure derived from at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B):

(A) a vinylsilane compound having a group " $-\text{SiR}^1\text{R}^2\text{R}^3$ ", wherein R^1 represents a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen, and R^2 and R^3 each represent a hydrocarbyl group or a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen; and

(B) an aromatic vinyl compound containing at least one atom selected from the group consisting of a nitrogen atom, a phosphorus atom, and a sulfur atom, wherein active hydrogen is not bonded to the nitrogen atom, the phosphorus atom, or the sulfur atom.

[Claim 2] The modified conjugated diene-based polymer according to claim 1, wherein the polymer block comprises a monomer unit derived from a styrene-based compound represented by formula (3):



wherein R^4 represents a hydrogen atom or a methyl group, R^5 to R^9 each represent a hydrogen atom or a

hydrocarbyl group, and at least one of R⁵ to R⁹ has a hydrogen atom at a benzylic position; and

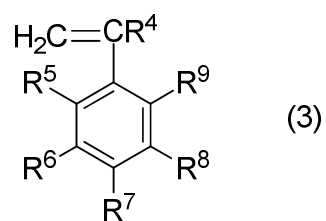
a structure derived from at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B) is bonded to a benzylic position included in the monomer unit derived from the styrene-based compound.

[Claim 3] The modified conjugated diene-based polymer according to claim 1 or 2, wherein the polymer block comprises a monomer unit derived from at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B).

[Claim 4] The modified conjugated diene-based polymer according to any one of claims 1 to 3, wherein the terminal of the conjugated diene-based polymer chain not having the polymer block is bonded to a structure derived from a compound containing at least one element selected from the group consisting of nitrogen, oxygen, silicon, phosphorus, sulfur, and tin.

[Claim 5] A method for producing a modified conjugated diene-based polymer, the method comprising:

polymerizing a monomer group Z containing a styrene-based compound represented by formula (3) in the presence of a polymerization initiator, thereby preparing a polymer block having an active terminal:



wherein R^4 represents a hydrogen atom or a methyl group, R^5 to R^9 each represent a hydrogen atom or a hydrocarbyl group, and at least one of R^5 to R^9 has a hydrogen atom at a benzylic position;

polymerizing a monomer group Y containing a conjugated diene compound in the presence of the polymer block having the active terminal, thereby forming a conjugated diene-based polymer chain bonded to the polymer block; and

reacting the polymer block, at a benzylic position of a monomer unit derived from the styrene-based compound, with at least one compound selected from the group consisting of the following vinylsilane compound (A) and aromatic vinyl compound (B):

(A) a vinylsilane compound having a group " $-\text{SiR}^1\text{R}^2\text{R}^3$ ", wherein R^1 represents a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen, and R^2 and R^3 each represent a hydrocarbyl group or a monovalent group having at least one atom selected from the group consisting of a nitrogen atom, an oxygen atom, a phosphorus atom, and a sulfur atom and having no active hydrogen; and

(B) an aromatic vinyl compound containing at least one atom selected from the group consisting of a nitrogen atom, a phosphorus atom, and a sulfur atom, wherein active hydrogen is not bonded to the nitrogen atom, the phosphorus atom, or the sulfur atom.

[Claim 6] The method for producing a modified conjugated diene-based polymer according to claim 5, wherein a monomer group X containing at least one compound selected from the group consisting of the vinylsilane compound (A) and the aromatic vinyl compound (B) and a conjugated diene compound is reacted with the polymer block at a benzylic position of the monomer unit derived from the styrene-based compound.

[Claim 7] The method for producing a modified conjugated diene-based polymer according to claim 5 or 6, wherein the monomer group Y is polymerized, thereby a conjugated diene-based polymer chain having the polymer block at one terminal of the polymer chain, wherein the other terminal of the polymer chain is an active terminal is prepared; and

the method further comprising:

reacting the conjugated diene-based polymer chain having the active terminal with the following compound (E):

(E) a compound containing at least one specific element which is selected from the group consisting of nitrogen, oxygen, silicon, phosphorus, sulfur, and tin, and which is not bonded to active hydrogen, and having a functional group capable of reacting with the active terminal of the conjugated diene-based polymer chain.

[Claim 8] A polymer composition comprising a modified

conjugated diene-based polymer according to any one of claims 1 to 4, an inorganic filler, and a crosslinking agent.

[Claim 9] A crosslinked polymer produced through crosslinking of a polymer composition according to claim 8.

[Claim 10] A tire obtained by employing a crosslinked polymer according to claim 9 as a tread material, a sidewall material, or both.