

[Document Name] Description

[Title of Invention] PRODUCTION METHOD FOR BRANCHED
CONJUGATED DIENE-BASED POLYMER, RUBBER COMPOSITION,
PRODUCTION METHOD FOR RUBBER COMPOSITION, AND PRODUCTION
METHOD FOR TIRE

[Technical Field]

[0001]

The present invention relates to a production method for a branched conjugated diene-based polymer, a rubber composition, a production method for a rubber composition, and a production method for a tire.

[Background Art]

[0002]

There have been increasing demands for reduction of fuel consumption in vehicles from the viewpoint of an environmental load. In particular, a vehicle tire is required to be improved for low fuel consumption in a material used for a tread portion in direct contact with the ground.

Recently, development of a material having low rolling resistance, namely, having a low hysteresis loss property, has been demanded.

At the same time, there is a trend toward weight reduction of a tire, and for this purpose, it is

necessary to reduce the thickness of a tire tread portion, and simultaneously, a material having high abrasion resistance is required for a tire tread portion.

On the other hand, a material used for the tire tread portion is required, from the viewpoint of safety, to be excellent in wet skid resistance and have practically sufficient fracture performance.

[0003]

An example of a material meeting the aforementioned various requirements includes a rubber material containing a rubber-like polymer and a reinforcing filler such as carbon black or silica.

When a rubber material containing silica is used, balance between a low hysteresis loss property (an index of low fuel consumption) and wet skid resistance can be improved. Besides, dispersibility of silica in a rubber material is improved through introduction of a functional group having affinity or reactivity with silica into a molecular end of a rubber-like polymer having high mobility, and in addition, the mobility of the molecular end of the rubber-like polymer is reduced through a bond to a silica particle, and thus, a hysteresis loss can be reduced.

On the other hand, as a method for improving abrasion resistance, a method in which the molecular weight of a rubber-like polymer is increased can be employed. When the molecular weight of a rubber-like

polymer is increased, however, workability in kneading the rubber-like polymer and a reinforcing filler tends to be deteriorated.

In consideration of these circumstances, an attempt has been made to introduce a branch structure into a rubber-like polymer in order to increase the molecular weight without impairing the workability.

[0004]

For example, a resin composition of a modified conjugated diene-based polymer and silica obtained by reacting alkoxysilane having an amino group with an active end of a conjugated diene-based polymer has been conventionally proposed.

In addition, a modified conjugated diene-based polymer into which a branch structure has been introduced obtained through a coupling reaction between a polymer active end and a polyfunctional silane compound has been proposed (see, for example, Patent Literature 1 and Patent Literature 2).

[Citation Literature]

[Patent Literature]

[0005]

[Patent Literature 1]

International Publication No. WO 2007/114203

[Patent Literature 2]

International Publication No. WO 2016/133154

[Summary of Invention]

[Technical Problem]

[0006]

In the method for introducing a branch structure into a conjugated diene-based polymer in which a coupling reaction is caused between a polymer active end and a polyfunctional silane compound, however, a branch number of a modified conjugated diene-based polymer thus obtained largely depends on the number of groups of the polyfunctional silane compound reactable with the polymer active end, and does not exceed the number of the reactable groups. From the viewpoint of synthesizability, there is a limit in the number of reactable groups that can be imparted to one polyfunctional silane, and hence, there arises a problem that there is a limit in the branch number of the modified conjugated diene-based polymer to be obtained.

[0007]

Therefore, an object of the present invention is to provide a production method for a branched conjugated diene-based polymer by which a conjugated diene-based polymer having a larger branch number can be produced than in a case where a branch structure is introduced into a conjugated diene-based polymer by using a modifier or a coupling agent alone by introducing a branch point into a main chain, and in which polymer design freedom is

so high that the lengths of a main chain and a side chain can be adjusted, whereby providing a production method for a branched conjugated diene-based polymer excellent in low fuel consumption performance, abrasion resistance, wet skid resistance, and fracture strength.

[Solution to Problem]

[0008]

The present inventors have made earnest studies to solve the above-described problems of the related art, resulting in finding a production method for a branched conjugated diene-based polymer in which a branch point can be introduced into a main chain by reacting a conjugated diene-based polymer having an active end with a specific styrene derivative used as a branching agent, and thus, the present invention was accomplished.

Specifically, the present invention is as follows.

[0009]

[1] A production method for a branched conjugated diene-based polymer, comprising:

a polymerizing step of obtaining a conjugated diene-based polymer having an active end by polymerizing or copolymerizing a conjugated diene compound, or a conjugated diene compound and an aromatic vinyl compound with an alkali metal compound or an alkaline earth metal compound used as a polymerization initiator; and

a branching step of introducing a branch structure by reacting a styrene derivative as a branching agent with the active end of the conjugated diene-based polymer.

[2] The production method for a branched conjugated diene-based polymer according to [1], further comprising: a step of adding a conjugated diene compound and/or an aromatic vinyl compound to a reaction system during and/or after the branching step.

[3] The production method for a branched conjugated diene-based polymer according to [1] or [2], further comprising:

a reaction step of reacting a coupling agent or a polymerization terminator with the active end of the conjugated diene-based polymer resulting from the branching step.

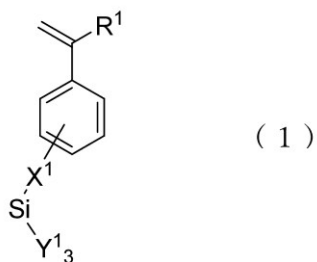
[4] The production method for a branched conjugated diene-based polymer according to [3], wherein the coupling agent has a nitrogen atom-containing group.

[5] The production method for a branched conjugated diene-based polymer according to [3], wherein the polymerization terminator has a nitrogen atom-containing group.

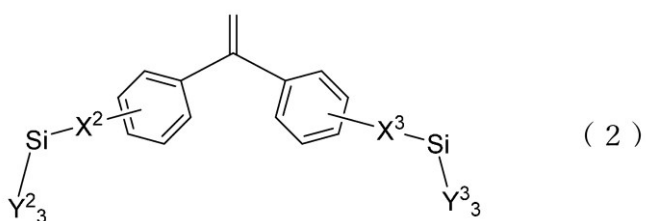
[6] The production method for a branched conjugated diene-based polymer according to [3] or [5], wherein the polymerization terminator is an alkoxy compound having a nitrogen atom-containing group.

[7] The production method for a branched conjugated diene-based polymer according to any one of [1] to [6], wherein the styrene derivative is a compound represented by the following formula (1) and/or formula (2):

[0010]



[0011]



[0012]

wherein R^1 represents any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms, and may have a branch structure in a part thereof;

X^1 , X^2 and X^3 represent a single bond, or an organic group containing any one selected from the group consisting of carbon, hydrogen, nitrogen, sulfur, and oxygen; and

Y^1 , Y^2 and Y^3 represent any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom, are respectively independent, and may be the same or different.

[0013]

[8] The production method for a branched conjugated diene-based polymer according to [7], wherein, in the formula (1), R^1 represents a hydrogen atom, and Y^1 represents any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom.

[9] The production method for a branched conjugated diene-based polymer according to [7], wherein, in the formula (2), X^1 represents a single bond, and Y^2 represents any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom.

[10] The production method for a branched conjugated diene-based polymer according to [7], wherein, in the formula (1), R^1 represents a hydrogen atom, and Y^1 represents an alkoxy group having 1 to 20 carbon atoms, or a halogen atom.

[11] The production method for a branched conjugated diene-based polymer according to [7], wherein, in the formula (2), Y^2 represents an alkoxy group having 1 to 20 carbon atoms, or a halogen atom, and Y^3 represents an

alkoxy group having 1 to 20 carbon atoms, or a halogen atom.

[12] The production method for a branched conjugated diene-based polymer according to [7], wherein, in the formula (1), R^1 represents a hydrogen atom, and Y^1 represents an alkoxy group having 1 to 20 carbon atoms.

[13] The production method for a branched conjugated diene-based polymer according to [7], wherein, in the formula (1), R^1 represents a hydrogen atom, X^1 represents a single bond, and Y^1 represents an alkoxy group having 1 to 20 carbon atoms.

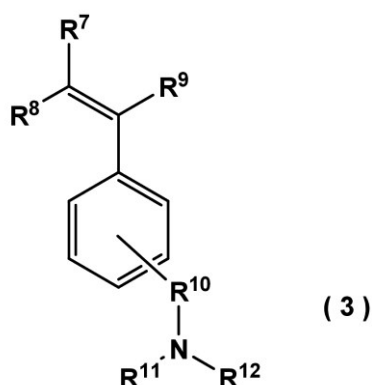
[14] The production method for a branched conjugated diene-based polymer according to [7], wherein, in the formula (2), X^2 represents a single bond, Y^2 represents an alkoxy group having 1 to 20 carbon atoms, or a halogen atom, X^3 represents a single bond, and Y^3 represents an alkoxy group having 1 to 20 carbon atoms, or a halogen atom.

[15] The production method for a branched conjugated diene-based polymer according to any one of [1] to [14], further comprising:

a step of copolymerizing a nitrogen atom-containing vinyl compound, or copolymerizing a conjugated diene compound and a nitrogen atom-containing vinyl compound, or a conjugated diene compound, a vinyl aromatic compound, and a nitrogen atom-containing vinyl compound, in the polymerizing step.

[16] The production method for a branched conjugated diene-based polymer according to [15], wherein the nitrogen atom-containing vinyl compound is a compound represented by the following formula (3) or (4):

[0014]



[0015]

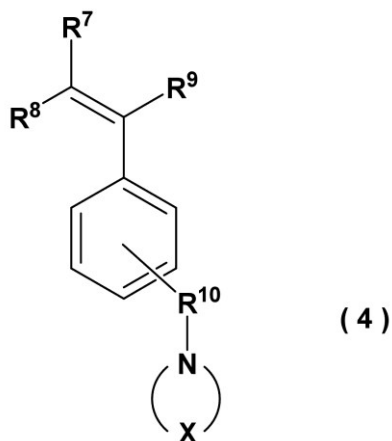
wherein R⁷ to R⁹ each independently represent any one selected from the group consisting of hydrogen, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms;

R¹⁰ represents a single bond, or a divalent hydrocarbon group having 1 to 6 carbon atoms, in which the chain is optionally interrupted by any of NR¹³, O, and S; and

R¹¹ to R¹³ each independently represent any one selected from the group consisting of an alkyl group having 1 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, and a trisubstituted silyl group having, on

silicon, an alkyl group having 1 to 30 carbon atoms and/or an aryl group having 6 to 30 carbon atoms;

[0016]



[0017]

wherein R⁷ to R⁹ each independently represent any one selected from the group consisting of hydrogen, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms;

R¹⁰ represents a single bond, or a divalent hydrocarbon group having 1 to 6 carbon atoms, in which the chain is optionally interrupted by any of NR¹³, O, and S;

R¹³ each independently represents any one selected from the group consisting of an alkyl group having 1 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, and a trisubstituted silyl group having, on silicon, an alkyl group having 1 to 30 carbon atoms and/or an aryl group having 6 to 30 carbon atoms;

X represents a divalent hydrocarbon group having 3 to 10 carbon atoms, in which the chain is optionally interrupted by any of NR¹⁴, O, and S and which corresponds to a saturated ring-forming moiety in which all carbon-carbon bonds are single bonds or an unsaturated ring-forming moiety in which at least some of carbon-carbon bonds are double bonds; and

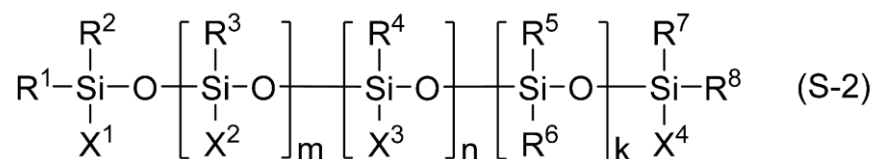
R¹⁴ represents an alkyl group having 1 to 30 carbon atoms or an aryl group having 6 to 30 carbon atoms.

[0018]

[17] The production method for a branched conjugated diene-based polymer according to any one of [3] to [16], wherein, in the reaction step,

the active end of the conjugated diene-based polymer resulting from the branching step is reacted with a coupling agent represented by the following formula (S-2):

[0019]



[0020]

wherein R¹ to R⁸ each independently represent any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms and an aryl group having 6 to 20 carbon atoms, and may be the same or different;

X^1 and X^4 satisfy the following (i) or (ii):

(i) one of X^1 and X^4 represents a group selected from the group consisting of an alkoxysilyl group having 1 to 5 carbon atoms, a 2-pyrrolidonyl group-containing hydrocarbon group, and an epoxy group-containing group having 4 to 12 carbon atoms, and the other represents a group derived from such a group, or a single bond; or

(ii) X^1 and X^4 represent an alkyl group having 1 to 6 carbon atoms or an aryl group having 6 to 12 carbon atoms, and X^1 and X^4 may be the same or different;

some of X^2 represent a group selected from the group consisting of an alkoxysilyl group having 1 to 5 carbon atoms, a 2-pyrrolidonyl group-containing hydrocarbon group, and an epoxy group-containing group having 4 to 12 carbon atoms, and the others represent a group derived from such a group, or a single bond;

X^3 represents a group containing 2 to 20 alkylene glycol repeating units; and

m represents an integer of 3 to 200, n represents an integer of 0 to 200, and k represents an integer of 0 to 200.

[0021]

[18] A branched conjugated diene-based polymer which is a copolymer of a conjugated diene compound, or a conjugated diene compound and an aromatic vinyl compound, with a nitrogen atom-containing vinyl compound, and which

has a main chain branch structure derived from a styrene derivative, in a polymer main chain.

[19] A rubber composition comprising:

a rubber component comprising 10% by mass or more of the branched conjugated diene-based polymer according to [18], and

5.0 parts by mass or more and 150 parts by mass or less of a filler with respect to 100 parts by mass of the rubber component.

[20] A production method for a rubber composition, comprising:

a step of obtaining a branched conjugated diene-based polymer by the production method according to any one of [1] to [17];

a step of obtaining a rubber component containing 10% by mass or more of the branched conjugated diene-based polymer; and

a step of obtaining a rubber composition by causing 5.0 parts by mass or more and 150 parts by mass or less of a filler to be contained with respect to 100 parts by mass of the rubber component.

[21] A production method for a tire, comprising:

a step of obtaining a rubber composition by the production method for a rubber composition according to [20]; and

a step of obtaining a tire by molding the rubber composition.

[Advantageous Effect of Invention]

[0022]

According to the present invention, a production method for a branched conjugated diene-based polymer by which a branched conjugated diene-based polymer having a larger branch number can be produced by introducing a branch point into a main chain than in a case using a coupling agent alone, and in which polymer design freedom is so high that the lengths of a main chain and a side chain can be adjusted can be provided, and thus, a production method for a branched conjugated diene-based polymer excellent in low fuel consumption performance, abrasion resistance, wet skid resistance, and fracture strength can be provided.

[Description of Embodiment]

[0023]

Now, an embodiment for practicing the present invention (hereinafter referred to as the "present embodiment") will be described in detail.

It is noted that the following present embodiment is merely an example for describing the present invention and the present invention is not limited to the following description but may be variously modified within the scope thereof.

[0024]

[Production Method for Branched Conjugated Diene-based Polymer]

A production method for a branched conjugated diene-based polymer of the present embodiment includes:

a polymerizing step of obtaining a conjugated diene-based polymer having an active end by polymerizing or copolymerizing a conjugated diene compound, or a conjugated diene compound and an aromatic vinyl compound with an alkali metal compound or an alkaline earth metal compound used as a polymerization initiator; and

a branching step of introducing a branch structure by reacting a styrene derivative as a branching agent with the active end of the conjugated diene-based polymer.

The conjugated diene-based polymer contained in a branched conjugated diene-based polymer may be any one of a homopolymer of a single conjugated diene compound, a polymer, namely, a copolymer, of different kinds of conjugated diene compounds, and a copolymer of a conjugated diene compound and an aromatic vinyl compound.

According to the production method for a branched conjugated diene-based polymer of the present embodiment, a conjugated diene-based polymer having a larger branch number can be produced by introducing a branch point into a main chain than in a case of introducing a branch structure into a conjugated diene-based polymer by using

a coupling agent alone, and in addition, the lengths of a main chain and a side chain can be adjusted.

[0025]

(Polymerizing Step)

In the polymerizing step of the production method for a branched conjugated diene-based polymer of the present embodiment, a conjugated diene-based polymer having an active end is obtained by polymerizing or copolymerizing a conjugated diene compound or a conjugated diene compound and an aromatic vinyl compound with an alkali metal compound or an alkaline earth metal compound used as a polymerization initiator.

In the polymerizing step, the polymerization is performed preferably by a growth reaction by a living anionic polymerization reaction, and thus, a conjugated diene-based polymer having an active end can be obtained.

[0026]

<Polymerization Initiator>

As the polymerization initiator, an alkali metal compound or an alkaline earth metal compound is used.

As the polymerization initiator, an organic lithium-based compound is preferably used, and an organomonolithium compound is more preferably used.

Examples of the organomonolithium compound include, but are not limited to, an organomonolithium compound of a low molecular weight compound, and an organomonolithium compound of a soluble oligomer.

As the organomonolithium compound, with respect to a bonding mode between an organic group and lithium thereof, any one of, for example, a compound having a carbon-lithium bond, a compound having a nitrogen-lithium bond, and a compound having a tin-lithium bond can be used.

[0027]

An amount of the polymerization initiator to be used is preferably determined on the basis of the molecular weight of a target conjugated diene-based polymer.

A ratio of the amount of a monomer such as a conjugated diene compound to be used to the amount of the polymerization initiator to be used relates to the degree of polymerization of the target conjugated diene-based polymer. In other words, there is a tendency that it relates to the number average molecular weight and/or the weight average molecular weight.

Accordingly, in order to increase the molecular weight of the conjugated diene-based polymer, adjustment may be made to reduce the amount of the polymerization initiator, and in order to reduce the molecular weight, the adjustment may be made to increase the amount of the polymerization initiator.

[0028]

From the viewpoint that it is used as one method for introducing a nitrogen atom into a conjugated diene-based polymer, the organomonolithium compound is preferably an

alkyl lithium compound having a substituted amino group or dialkylamino lithium.

In this case, a conjugated diene-based polymer having, at a polymerization starting end, a nitrogen atom of an amino group is obtained.

[0029]

The substituted amino group refers to an amino group having no active hydrogen or having a structure in which active hydrogen is protected.

Examples of an alkyl lithium compound containing an amino group having no active hydrogen include, but are not limited to, 3-dimethylaminopropyl lithium, 3-diethylaminopropyl lithium, 4-(methylpropylamino)butyl lithium and 4-hexamethyleneiminobutyl lithium.

Examples of an alkyl lithium compound containing an amino group having a structure in which active hydrogen is protected include, but are not limited to, 3-bis(trimethylsilyl)aminopropyl lithium and 4-trimethylsilylmethylaminobutyl lithium.

[0030]

Examples of the dialkylamino lithium include, but are not limited to, lithium dimethylamide, lithium diethylamide, lithium dipropylamide, lithium dibutylamide, lithium di-n-hexylamide, lithium diheptylamide, lithium diisopropylamide, lithium dioctylamide, lithium-di-2-ethylhexylamide, lithium didecylamide, lithium ethylpropylamide, lithium

ethylbutylamide, lithium ethylbenzylamide, lithium methylphenethylamide, lithium hexamethyleneimide, lithium pyrrolidide, lithium piperidide, lithium heptamethyleneimide, lithium morpholide, 1-lithioazacyclooctane, 6-lithio-1,3,3-trimethyl-6-azabicyclo[3.2.1] octane, and 1-lithio-1,2,3,6-tetrahydropyridine.

[0031]

Such an organomonolithium compound having a substituted amino group can be reacted with a small amount of a polymerizable monomer, such as 1,3-butadiene, isoprene or styrene, to be used as an organomonolithium compound of an oligomer soluble in normal hexane or cyclohexane.

[0032]

From the viewpoint of the industrial availability and the controllability of the polymerization reaction, the organomonolithium compound is preferably an alkyl lithium compound. In this case, a conjugated diene-based polymer having an alkyl group at a polymerization starting end can be obtained.

Examples of the alkyl lithium compound include, but are not limited to, n-butyllithium, sec-butyllithium, tert-butyllithium, n-hexyllithium, benzyllithium, phenyllithium, and stilbene lithium.

From the viewpoint of the industrial availability and the controllability of the polymerization reaction,

the alkyl lithium compound is preferably n-butyllithium or sec-butyllithium.

[0033]

One of these organomonolithium compounds may be singly used, or two or more of these may be used together. Alternatively, another organic metal compound may be used together.

Examples of such another organic metal compound include alkaline earth metal compounds, other alkali metal compounds, and other organic metal compounds.

Examples of the alkaline earth metal compounds include, but are not limited to, organic magnesium compounds, organic calcium compounds and organic strontium compounds. Other examples include compounds of alkoxides, sulfonates, carbonates and amides of alkaline earth metals.

Examples of the organic magnesium compounds include dibutyl magnesium and ethyl butyl magnesium.

Examples of the other organic metal compounds include organic aluminum compounds.

[0034]

Examples of a polymerization reaction mode employed in the polymerizing step include, but are not limited to, batch and continuous polymerization reaction modes.

In the continuous mode, one reactor or two or more connected reactors can be used. As a reactor for the continuous mode, for example, a tank or tubular reactor

equipped with a stirrer can be used. In the continuous mode, preferably, a monomer, an inert solvent and a polymerization initiator are continuously fed to the reactor, a polymer solution containing a polymer is obtained in the reactor, and the polymer solution is continuously discharged.

As a reactor for the batch mode, for example, a tank reactor equipped with a stirrer is used. It is preferable, in the batch mode, that a monomer, an inert solvent and a polymerization initiator are fed to the reactor, the monomer is continuously or intermittently additionally fed if necessary during the polymerization, a polymer solution containing a polymer is obtained in the reactor, and the polymer solution is discharged after completing the polymerization.

In the production method for a branched conjugated diene-based polymer of the present embodiment, in order to obtain a conjugated diene-based polymer having an active end at a high ratio in the polymerizing step, the continuous mode in which a polymer is continuously discharged to be supplied to a next reaction in a short period of time is preferably employed. In the continuous mode, the number of reactors is not especially limited, and one reactor or two or more connected reactors can be used. A reactor capable of obtaining a sufficient contact between a monomer and a polymerization initiator in a solution is preferably used, and a tank or tubular

reactor equipped with a stirrer is used. The number of reactors can be appropriately selected, and one reactor is preferably used from the viewpoint of saving space in a manufacturing facility, or two or more reactors are preferably used from the viewpoint of improving productivity. When two or more reactors are used, it is more preferable that a branching agent is added in a second or following reactor.

[0035]

In the polymerizing step for a conjugated diene-based polymer, the polymerization is performed preferably in an inert solvent.

Examples of the inert solvent include hydrocarbon-based solvents such as saturated hydrocarbons and aromatic hydrocarbons. Specific examples of the hydrocarbon-based solvent include, but are not limited to, aliphatic hydrocarbons such as butane, pentane, hexane and heptane; alicyclic hydrocarbons such as cyclopentane, cyclohexane, methylcyclopentane and methylcyclohexane; aromatic hydrocarbons such as benzene, toluene and xylene; and a hydrocarbon containing a mixture of any of these.

Impurities of allenes and acetylenes are preferably treated with an organic metal compound before the solvent is supplied to the polymerization reaction because thus, a conjugated diene-based polymer having an active end in a high concentration tends to be obtained, and a modified

conjugated diene-based polymer having a high modification ratio tends to be obtained.

[0036]

In the polymerizing step, a polar compound (polar material) may be added. Thus, an aromatic vinyl compound can be randomly copolymerized with a conjugated diene compound. In addition, the polar compound tends to be usable also as a vinylation agent for controlling a microstructure of a conjugated diene portion. Besides, it tends to be advantageous for, for example, acceleration of the polymerization reaction.

[0037]

Examples of the polar compound include, but are not limited to, ethers such as tetrahydrofuran, diethyl ether, dioxane, ethylene glycol dimethyl ether, ethylene glycol dibutyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, dimethoxybenzene, and 2,2-bis(2-oxolanyl)propane; tertiary amine compounds such as tetramethylethylenediamine, dipiperidinoethane, trimethylamine, triethylamine, pyridine, and quinuclidine; alkali metal alkoxide compounds such as potassium-tert-amylate, potassium-tert-butylate, sodium-tert-butylate, and sodium amylate; and phosphine compounds such as triphenylphosphine.

One of these polar compounds may be singly used, or two or more of these may be used together.

[0038]

The amount of the polar compound to be used is not especially limited but can be selected in accordance with the purpose or the like, and is preferably 0.01 mol or more and 100 mol or less per mole of the polymerization initiator.

Such a polar compound (a vinylation agent) can be used, as a microstructure modifier for a conjugated diene portion of the conjugated diene-based polymer, in an appropriate amount in accordance with a desired amount of bound vinyl.

There is a tendency that many of polar compounds simultaneously have a randomizing effect effective in copolymerization of a conjugated diene compound and an aromatic vinyl compound, and can be used as an adjuster for an aromatic vinyl compound distribution, and as an adjuster for a styrene block amount.

As a method for randomizing the conjugated diene compound and the aromatic vinyl compound, for example, a method as described in Japanese Patent Laid-Open No. 59-140211 in which a copolymerization reaction is started with the whole amount of styrene and a part of 1,3-butadiene with the rest of 1,3-butadiene intermittently added during the copolymerization reaction may be employed.

[0039]

In the polymerizing step, a polymerization temperature is preferably a temperature at which living

anionic polymerization proceeds, and from the viewpoint of productivity, is more preferably 0°C or more and 120°C or less.

If the polymerization temperature falls in this range, there is a tendency that a reaction amount of the branching agent and the coupling agent reacted to the active end after completing the polymerization can be sufficiently attained. The polymerization temperature is further preferably 50°C or more and 100°C or less.

[0040]

<Conjugated Diene Compound>

The conjugated diene compound is not especially limited and may be any polymerizable monomer, and examples thereof include, but are not limited to, 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 3-methyl-1,3-pentadiene, 1,3-heptadiene, and 1,3-hexadiene. Among these, from the viewpoint of the industrial availability, 1,3-butadiene and isoprene are preferred. One of these may be singly used, or two or more of these may be used together.

[0041]

<Aromatic Vinyl Compound>

The aromatic vinyl compound may be any copolymerizable monomer with the conjugated diene compound, and examples thereof include, but are not especially limited to, styrene, p-methylstyrene, α -methylstyrene, vinyl ethylbenzene, vinyl xylene,

vinyl naphthalene, and diphenylethylene. Among these, from the viewpoint of the industrial availability, styrene is preferred. One of these may be singly used, or two or more of these may be used together.

[0042]

<Nitrogen Atom-containing Vinyl Compound>

In the production method for a branched conjugated diene-based polymer of the present embodiment, the conjugated diene compound, or the conjugated diene compound and the aromatic vinyl compound, and furthermore a nitrogen atom-containing vinyl compound may also be copolymerized with in the polymerizing step.

In the production method for a branched conjugated diene-based polymer of the present embodiment, a step of copolymerizing the conjugated diene compound, or the conjugated diene compound and the aromatic vinyl compound, and furthermore a nitrogen atom-containing vinyl compound may be performed separately from the polymerizing step and a branching step described below.

Thus, a conjugated diene-based polymer having an active end and a portion derived from a nitrogen atom-containing vinyl compound can be obtained.

In the production method for a branched conjugated diene-based polymer of the present embodiment, a branching step of introducing a branched structure by reacting a styrene derivative as a branching agent described below with the active end of the conjugated

diene-based polymer obtained in the polymerizing step is performed.

A polymer portion other than a portion derived from the nitrogen atom-containing vinyl compound, of the conjugated diene-based polymer obtained in the polymerizing step, may be any one of a homopolymer of a single conjugated diene compound, a polymer, namely, a copolymer, of different kinds of such conjugated diene compounds, and a copolymer of a conjugated diene compound and an aromatic vinyl compound.

According to the production method for a branched conjugated diene-based polymer of the present embodiment, a branched conjugated diene-based polymer having a larger branch number can be produced by introducing a branch point into a main chain than in a case of introducing a branch structure into a conjugated diene-based polymer by using a coupling agent alone, and in addition, the lengths of a main chain and a side chain can be adjusted.

The nitrogen atom-containing vinyl compound can be further copolymerized, and thus, a branched conjugated diene-based polymer having a nitrogen atom in a polymer main chain and having an active end can be obtained.

The nitrogen atom-containing vinyl compound is used in the polymerizing step, and thus, a conjugated diene-based polymer containing a nitrogen atom in a main chain can be obtained. That is, it is largely characterized in that a polymer is modified in advance at a stage before a

reaction step by a branching step described below and a coupling agent described below is performed.

In the production method for a branched conjugated diene-based polymer of the present embodiment, the timing of introducing the nitrogen atom-containing vinyl compound into the branched conjugated diene-based polymer may be before and after branch point formation, namely, both before and after the branching step or any one of before and after the branching step, and a large amount of the nitrogen atom-containing vinyl compound is more preferably introduced after branch point formation from the viewpoint of improvement of low fuel consumption performance.

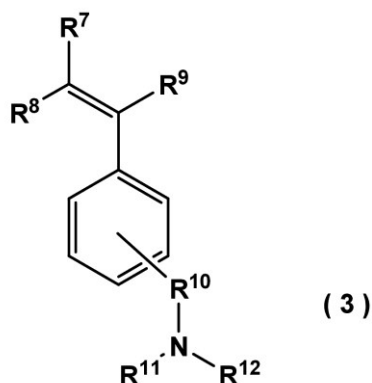
It is preferable for preferentially introducing the nitrogen atom-containing vinyl compound after branch point formation, namely, the branching step that the nitrogen atom-containing vinyl compound and a polymerization monomer are simultaneously added and subjected to polymerization with the initial polymerization temperature being suppressed at 60°C or less, or that the nitrogen atom-containing vinyl compound and a branching agent are simultaneously added. In a case of a continuous polymerization method, it is further preferable that the nitrogen atom-containing vinyl compound and a branching agent are added in a second or following reactor.

[0043]

The nitrogen atom-containing vinyl compound is not especially limited, may be any nitrogen atom-containing vinyl compound which is an anionic polymerizable monomer, and is preferably a compound represented by the following formula (3) or (4) from the viewpoint of reactivity of a target conjugated diene-based polymer with silica.

One of these nitrogen atom-containing vinyl compounds may be singly used, or two or more of these may be used together.

[0044]

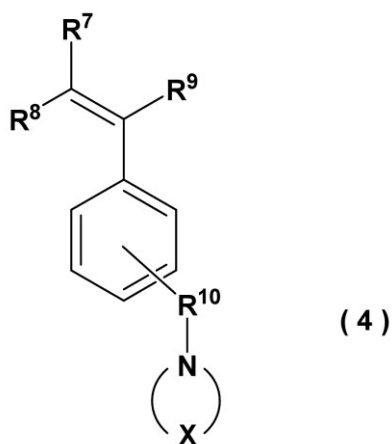


[0045]

In the formula (3), R⁷ to R⁹ each independently represent any one selected from the group consisting of hydrogen, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms, and R¹⁰ represents a single bond, or a divalent hydrocarbon group having 1 to 6 carbon atoms, in which the chain is optionally interrupted by any of NR¹³, O, and S.

R¹¹ to R¹³ each independently represent any one selected from the group consisting of an alkyl group having 1 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, and a trisubstituted silyl group having, on silicon, an alkyl group having 1 to 30 carbon atoms and/or an aryl group having 6 to 30 carbon atoms.

[0046]



[0047]

In the formula (4), R⁷ to R¹⁰ are defined the same as the formula (3), X represents a divalent hydrocarbon group having 3 to 10 carbon atoms, in which the chain is optionally interrupted by any of NR¹⁴, O, and S and which corresponds to a saturated ring-forming moiety in which all carbon-carbon bonds are single bonds or an unsaturated ring-forming moiety in which at least some of carbon-carbon bonds are double bonds.

R¹⁴ represents an alkyl group having 1 to 30 carbon atoms or an aryl group having 6 to 30 carbon atoms.

[0048]

Examples of the compound represented by the formula (3) include, but are not limited to, N,N-dimethylvinylbenzylamine, N,N-diethylvinylbenzylamine, N,N-dipropylvinylbenzylamine, N,N-dibutylvinylbenzylamine, N,N-diphenylvinylbenzylamine, 2-dimethylaminoethylstyrene, 2-diethylaminoethylstyrene, 2-bis(trimethylsilyl)aminoethylstyrene, 1-(4-N,N-dimethylaminophenyl)-1-phenylethylene, N,N-dimethyl-2-(4-vinylbenzyloxy)ethylamine, N¹,N¹,N²-trimethyl-N²-(4-vinylbenzyl)ethane-1,2-diamine, and N,N-dimethyl-2-((4-vinylbenzyl)thio)ethylamine.

Among these, 1-(4-N,N-dimethylaminophenyl)-1-phenylethylene and N,N-dimethylvinylbenzylamine are preferred from the viewpoint that the thus obtained branched conjugated diene-based polymer is excellent in balance among low hysteresis loss property, wet skid resistance, and dynamic elastic modulus when in the form of a vulcanizate including silica.

[0049]

Examples of the compound represented by the formula (4) include, but are not limited to, 4-(2-pyrrolidinoethyl)styrene, 4-(2-piperidinoethyl)styrene, 4-(2-hexamethyleneiminoethyl)styrene, 4-(2-morpholinoethyl)styrene, 4-(2-thiazinoethyl)styrene, 4-(2-N-methylpiperazinoethyl)styrene, 1-((4-vinylphenoxy)methyl)pyrrolidine, 1-(4-vinylbenzyloxymethyl)pyrrolidine, 1-((4-

vinylbenzyl)thiomethyl)pyrrolidine, and N-methyl-1-(pyrrolidin-1-yl)-N-(4-vinylbenzyl)methylamine.

Among these, 4-(2-pyrrolidinoethyl)styrene is preferred from the viewpoint that the thus obtained branched conjugated diene-based polymer is excellent in balance among low hysteresis loss property, wet skid resistance, and dynamic elastic modulus when in the form of a vulcanizate including silica.

[0050]

An amount of the nitrogen atom-containing vinyl compound to be added in a case of use of the nitrogen atom-containing vinyl compound in the polymerizing step is not especially limited, and can be regulated in accordance with the purpose or the like. For example, such an amount is, but not limited to, preferably 0.5 to 100 mol, more preferably 1 to 20 mol, further preferably 2 to 10 mol per mole of the polymerization initiator.

An amount of the nitrogen atom-containing vinyl compound to be added in the polymerizing step is 0.5 mol or more per mole of the polymerization initiator, and thus a vulcanizate excellent in steering stability is obtained.

On the other hand, such an amount is preferably 100 mol or less per mole of the polymerization initiator from the viewpoint of workability when the thus obtained branched conjugated diene-based polymer is in the form of a rubber composition including silica.

The timing of adding the nitrogen atom-containing vinyl compound in the polymerizing step is not especially limited. Examples of such addition include addition at the same time as addition of the conjugated diene compound, or the conjugated diene compound and the vinyl aromatic compound, or addition in portions during (co)polymerization of the conjugated diene compound, or the conjugated diene compound and the vinyl aromatic compound.

[0051]

(Branching Step)

In the production method for a branched conjugated diene-based polymer of the present embodiment, the branching step of reacting a styrene derivative as a branching agent with the active end of the conjugated diene-based polymer resulting from the polymerizing step is performed.

The branching agent is polymerized with a monomer with retaining polymerization activity, and an active end of another polymer chain is reacted with a functional group of the branching agent, and thus, a branch structure is formed in the polymer. It is possible to form another branch structure by polymerizing and reacting the branched conjugated diene-based polymer in which the branch structure has been thus introduced further with a monomer and the branching agent, and a modified conjugated diene-based polymer can be obtained

through a reaction with a modifier having a functional group, or a polymer chain can be further elongated through a coupling reaction. In this manner, when a styrene derivative that has a functional group reacting with the polymer active end while continuing the polymerization reaction as an aromatic vinyl compound is used as the branching agent, a branched conjugated diene-based polymer can be obtained.

[0052]

<Branching Agent>

From the viewpoints of continuity of the polymerization and prevention of gelation, the styrene derivative used as the branching agent in the branching step needs to have, as a main skeleton, a skeleton having merely one active end remaining in a branch portion after the branching reaction, and a styrene derivative portion formed after the branching reaction needs to have reactivity sufficiently reactive to an active end of another polymer.

That is, the styrene derivative is polymerized in the form of styrene, thus the styrene derivative is incorporated into a main chain with retaining the polymerization activity, another monomer is polymerized with the end having retained activity, and thus, the polymer chain is further elongated. The functional group of the thus incorporated styrene derivative is reacted with an active end of another polymer chain to form a

bond, and thus, a branch structure is formed. When such a reaction repeatedly occurs, branches of the polymer chain increase, so as to make the polymer structure more complicated and to increase the molecular weight.

More specifically, the styrene derivative used as the branching agent is preferably a compound having a vinyl group in a benzene ring, and having a functional group quantitatively reacting with the polymer active end in the living anionic polymerization. The functional group of the styrene derivative and the polymer active end react with each other in a one-on-one manner, the functional group is eliminated to form a single bond, and a polymerization reaction is caused between the vinyl group and another monomer present in the reactor, and thus, a branch structure is formed in the polymer. A functional group excluding the vinyl group of the styrene derivative is a group to be eliminated through a nucleophilic substitution reaction with the polymer active end in the living anionic polymerization, and examples of such a functional group include an alkoxy group, halogen, an ester group, a formyl group, a ketone group, an amide group, an acid chloride group, an acid anhydride group, and an epoxy group.

Since the styrene derivative has the above-described structure, the styrene derivative is incorporated into a main chain with retaining the polymerization activity as styrene, another monomer is polymerized with the end

having retained activity, and thus, the polymer chain is further elongated. Besides, the functional group of the thus incorporated styrene derivative is reacted with an active end of another polymer chain to form a bond, and thus, a branch structure is formed. When such a reaction repeatedly occurs, branches of the polymer chain increase, so as to make the polymer structure more complicated and to increase the molecular weight.

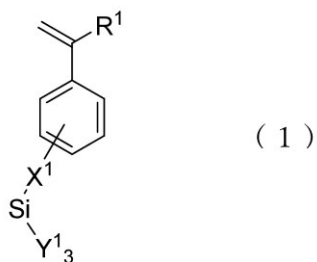
From the viewpoints of the continuity of the polymerization and controllability of the polymer structure, a functional group eliminated after the reaction of the styrene derivative portion with the active end of another polymer chain needs to have small inhibitory action in the polymerization. Here, the term "to have small inhibitory action in the polymerization" means that activity decrease or the like caused, as a side reaction of the anionic polymerization, through a chain transfer reaction, deactivation in the middle of polymerization, increase in a degree of association of the polymer, is small.

The functional group contained in the styrene derivative used as the branching agent needs to be one that does not excessively improve the polymerization activity, and further needs to be one that does not deactivate the polymerization activity. If a polymer is polymerized by the living anionic polymerization, it is significant that the functional group does not have a

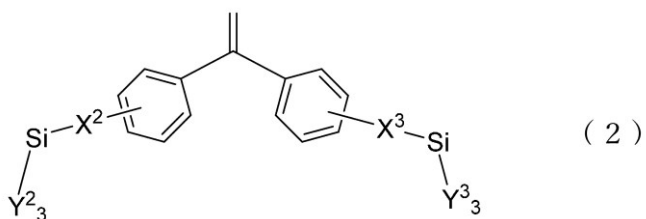
hydrogen atom as a functional group not deactivating the active end and is a hard base according to definition based on Pearson's HSAB principle, and specific examples include an alkoxy group and a halogen group. Not only from the viewpoint of the reactivity with the active end but also from the viewpoint that the eliminated functional group does not inhibit the polymerization, the structure of the styrene derivative to be used as the branching agent in the production method of the present embodiment can be selected among these.

More specifically, from the viewpoint of suppressing a chain transfer reaction, suppressing deactivation of the active end and preventing gelation, a branching agent represented by the following formula (1) having a styrene skeleton as a main skeleton, or the following formula (2) having a diphenylethylene skeleton as a main skeleton is preferably used.

[0053]



[0054]



[0055]

In the formulas (1), (2), R^1 represents any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms, and may have a branch structure in a part thereof.

X^1 , X^2 and X^3 represent a single bond, or an organic group containing any one selected from the group consisting of carbon, hydrogen, nitrogen, sulfur, and oxygen.

Y^1 , Y^2 and Y^3 represent any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom. Y^1 , Y^2 and Y^3 are respectively independent, and may be the same or different.

[0056]

In the styrene derivative used as the branching agent in the branching step, from the viewpoint of improving the branch number in the polymerization, it is preferable that R^1 is a hydrogen atom and Y^1 is any one selected from the group consisting of an alkyl group

having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom in the formula (1).

[0057]

In the present embodiment, in the styrene derivative used as the branching agent in the branching step, from the viewpoint of improving the branch number, it is preferable that X^1 represents a single bond and Y^2 represents any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom in the formula (2).

[0058]

In the present embodiment, in the styrene derivative used as the branching agent in the branching step, from the viewpoints of the continuity of the polymerization and improving the branch number, it is more preferable that R^1 is a hydrogen atom and Y^1 is alkoxy group having 1 to 20 carbon atoms or a halogen atom in the formula (1).

[0059]

In the present embodiment, in the styrene derivative used as the branching agent in the branching step, from the viewpoints of the continuity of the polymerization and improving the branch number, it is more preferable that Y^2 represents an alkoxy group having 1 to 20 carbon atoms, or a halogen atom, and Y^3 represents an alkoxy

group having 1 to 20 carbon atoms, or a halogen atom in the formula (2).

[0060]

In the present embodiment, in the styrene derivative used as the branching agent in the branching step, it is more preferable, from the viewpoint of continuity of the polymerization, improvement of a branch number, and improvement of a modification ratio, that R^1 is a hydrogen atom, and Y^1 is an alkoxy group having 1 to 20 carbon atoms in the formula (1).

[0061]

In the present embodiment, in the styrene derivative used as the branching agent in the branching step, it is further preferable, from the viewpoint of continuity of the polymerization, improvement of a branch number, and further improvement of a modification ratio, that R^1 is a hydrogen atom, X^1 is a single bond, and Y^1 is an alkoxy group having 1 to 20 carbon atoms in the formula (1).

[0062]

In the present embodiment, in the styrene derivative used as the branching agent in the branching step, from the viewpoints of the continuity of the polymerization, improving the branch number, and further improving the modification ratio, it is still further preferable that X^2 is a single bond, Y^2 is an alkoxy group having 1 to 20 carbon atoms or a halogen atom, X^3 is a single bond, and

Y³ is an alkoxy group having 1 to 20 carbon atoms or a halogen atom in the formula (2).

[0063]

Examples of the branching agent represented by the formula (1) include, but are not limited to, trimethoxy(4-vinylphenyl)silane, triethoxy(4-vinylphenyl)silane, tripropoxy(4-vinylphenyl)silane, tributoxy(4-vinylphenyl)silane, triisopropoxy(4-vinylphenyl)silane, trimethoxy(3-vinylphenyl)silane, triethoxy(3-vinylphenyl)silane, tripropoxy(3-vinylphenyl)silane, tributoxy(3-vinylphenyl)silane, triisopropoxy(3-vinylphenyl)silane, trimethoxy(2-vinylphenyl)silane, triethoxy(2-vinylphenyl)silane, tripropoxy(2-vinylphenyl)silane, tributoxy(2-vinylphenyl)silane, triisopropoxy(2-vinylphenyl)silane, dimethoxymethyl(4-vinylphenyl)silane, diethoxymethyl(4-vinylphenyl)silane, dipropoxymethyl(4-vinylphenyl)silane, dibutoxymethyl(4-vinylphenyl)silane, diisopropoxymethyl(4-vinylphenyl)silane, dimethoxymethyl(3-vinylphenyl)silane, diethoxymethyl(3-vinylphenyl)silane, dipropoxymethyl(3-vinylphenyl)silane, dibutoxymethyl(3-vinylphenyl)silane, diisopropoxymethyl(3-vinylphenyl)silane, dimethoxymethyl(2-vinylphenyl)silane, diethoxymethyl(2-vinylphenyl)silane, dipropoxymethyl(2-vinylphenyl)silane, dibutoxymethyl(2-vinylphenyl)silane, diisopropoxymethyl(2-vinylphenyl)silane,

dimethylmethoxy(4-vinylphenyl)silane, dimethylethoxy(4-vinylphenyl)silane, dimethylpropoxy(4-vinylphenyl)silane, dimethylbutoxy(4-vinylphenyl)silane, dimethylisopropoxy(4-vinylphenyl)silane, dimethylmethoxy(3-vinylphenyl)silane, dimethylethoxy(3-vinylphenyl)silane, dimethylpropoxy(3-vinylphenyl)silane, dimethylbutoxy(3-vinylphenyl)silane, dimethylisopropoxy(3-vinylphenyl)silane, dimethylmethoxy(2-vinylphenyl)silane, dimethylethoxy(2-vinylphenyl)silane, dimethylpropoxy(2-vinylphenyl)silane, dimethylbutoxy(2-vinylphenyl)silane, dimethylisopropoxy(2-vinylphenyl)silane, trimethoxy(4-isopropenylphenyl)silane, triethoxy(4-isopropenylphenyl)silane, tripropoxy(4-isopropenylphenyl)silane, tributoxy(4-isopropenylphenyl)silane, triisopropoxy(4-isopropenylphenyl)silane, trimethoxy(3-isopropenylphenyl)silane, triethoxy(3-isopropenylphenyl)silane, tripropoxy(3-isopropenylphenyl)silane, tributoxy(3-isopropenylphenyl)silane, triisopropoxy(3-isopropenylphenyl)silane, trimethoxy(2-isopropenylphenyl)silane, triethoxy(2-isopropenylphenyl)silane, tripropoxy(2-isopropenylphenyl)silane, tributoxy(2-isopropenylphenyl)silane, triisopropoxy(2-isopropenylphenyl)silane, dimethoxymethyl(4-

isopropenylphenyl)silane, diethoxymethyl (4-
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isopropenylphenyl)silane, dimethylbutoxy(2-isopropenylphenyl)silane, dimethylisopropoxy(2-isopropenylphenyl)silane, trichloro(4-vinylphenyl)silane, trichloro(3-vinylphenyl)silane, trichloro(2-vinylphenyl)silane, tribromo(4-vinylphenyl)silane, tribromo(3-vinylphenyl)silane, tribromo(2-vinylphenyl)silane, dichloromethyl(4-vinylphenyl)silane, dichloromethyl(3-vinylphenyl)silane, dichloromethyl(2-vinylphenyl)silane, dibromomethyl(4-vinylphenyl)silane, dibromomethyl(3-vinylphenyl)silane, dibromomethyl(2-vinylphenyl)silane, dimethylchloro(4-vinylphenyl)silane, dimethylchloro(3-vinylphenyl)silane, dimethylchloro(2-vinylphenyl)silane, dimethylbromo(4-vinylphenyl)silane, dimethylbromo(3-vinylphenyl)silane, dimethylbromo(2-vinylphenyl)silane, trimethoxy(4-vinylbenzyl)silane, triethoxy(4-vinylbenzyl)silane, and tripropoxy(4-vinylbenzyl)silane.

Among these, trimethoxy(4-vinylphenyl)silane, triethoxy(4-vinylphenyl)silane, tripropoxy(4-vinylphenyl)silane, tributoxy(4-vinylphenyl)silane, triisopropoxy(4-vinylphenyl)silane, trimethoxy(3-vinylphenyl)silane, triethoxy(3-vinylphenyl)silane, tripropoxy(3-vinylphenyl)silane, tributoxy(3-vinylphenyl)silane, triisopropoxy(3-vinylphenyl)silane, and trichloro(4-vinylphenyl)silane are preferred, and trimethoxy(4-vinylphenyl)silane, triethoxy(4-vinylphenyl)silane, tripropoxy(4-vinylphenyl)silane,

tributoxy(4-vinylphenyl)silane, triisopropoxy(4-vinylphenyl)silane, trimethoxy(4-vinylbenzyl)silane, and triethoxy(4-vinylbenzyl)silane are more preferred, and trimethoxy(4-vinylphenyl)silane, and triethoxy(4-vinylphenyl)silane are further preferred.

[0064]

Examples of the branching agent represented by the formula (2) include, but are not limited to, 1-bis(4-trimethoxysilylphenyl)ethylene, 1,1-bis(4-triethoxysilylphenyl)ethylene, 1,1-bis(4-tripropoxysilylphenyl)ethylene, 1,1-bis(4-tripentoxysilylphenyl)ethylene, 1,1-bis(4-triisopropoxysilylphenyl)ethylene, 1,1-bis(3-trimethoxysilylphenyl)ethylene, 1,1-bis(3-triethoxysilylphenyl)ethylene, 1,1-bis(3-tripropoxysilylphenyl)ethylene, 1,1-bis(3-tripentoxysilylphenyl)ethylene, 1,1-bis(3-triisopropoxysilylphenyl)ethylene, 1,1-bis(2-trimethoxysilylphenyl)ethylene, 1,1-bis(2-triethoxysilylphenyl)ethylene, 1,1-bis(3-tripropoxysilylphenyl)ethylene, 1,1-bis(2-tripentoxysilylphenyl)ethylene, 1,1-bis(2-triisopropoxysilylphenyl)ethylene, 1,1-bis(4-(dimethylmethoxysilyl)phenyl)ethylene, 1,1-bis(4-(diethylmethoxysilyl)phenyl)ethylene, 1,1-bis(4-(dipropylmethoxysilyl)phenyl)ethylene, 1,1-bis(4-(dimethylethoxysilyl)phenyl)ethylene, 1,1-bis(4-

(diethylethoxysilyl)phenyl)ethylene, 1,1-bis(4-(dipropylethoxysilyl)phenyl)ethylene, 1,1-bis(4-trimethoxysilylbenzyl)ethylene, 1,1-bis(4-triethoxysilylbenzyl)ethylene, 1,1-bis(4-tripropoxysilylbenzyl)ethylene, and 1,1-bis(4-tripentoxysilylbenzyl)ethylene.

Among these, 1,1-bis(4-trimethoxysilylphenyl)ethylene, 1,1-bis(4-triethoxysilylphenyl)ethylene, 1,1-bis(4-tripropoxysilylphenyl)ethylene, 1,1-bis(4-tripentoxysilylphenyl)ethylene, and 1,1-bis(4-triisopropoxysilylphenyl)ethylene are preferred, and 1,1-bis(4-trimethoxysilylphenyl)ethylene is more preferred.

If the branching agent represented by the formula (1) or (2) is used, the branch number is improved, and an effect of improving the abrasion resistance and the workability can be obtained.

[0065]

The timing of adding the branching agent is not especially limited and can be selected in accordance with the purpose or the like, and from the viewpoints of improvement of an absolute molecular weight of the conjugated diene-based polymer and improvement of a coupling ratio, the timing is timing, after adding the polymerization initiator, when a raw material conversion rate is preferably 20% or more, more preferably 40% or more, further preferably 50% or more, still further

preferably 65% or more, and much further preferably 75% or more.

During and/or after the branching step, a monomer corresponding to a desired raw material may be additionally added to a reaction system to continue the polymerizing step after the branching step, or the above-described process may be repeated.

It is noted that the term "after the branching step" refers to after the addition of the branching agent.

The monomer to be additionally added is not especially limited, but is preferably a conjugated diene compound and/or an aromatic vinyl compound. Particularly when the monomer is additionally added in the branching step, from the viewpoint of the improvement of the modification ratio of the conjugated diene-based polymer by reducing steric hindrance at a branch point, it is preferably 5% or more, more preferably 10% or more, further preferably 15% or more, still further preferably 20% or more, and much further preferably 25% or more based on the total amount of conjugated diene-based monomers, for example, the total amount of butadiene, used in the polymerizing step. In such a case, it is preferable, from the viewpoint of the improvement of the modification ratio, that the monomer is additionally added by continuous polymerization process in the branching step in an amount of 5% or more of the total amount of conjugated diene-based monomers, for example,

the total amount of butadiene, used in the polymerizing step.

Since the lengths of a main chain and a side chain can be adjusted in accordance with the timing of adding the branching agent and the amount of the monomer to be additionally added, the polymer design freedom is high.

[0066]

The branch structure of the branched conjugated diene-based polymer obtained in the branching step of the production method for a branched conjugated diene-based polymer of the present embodiment has preferably 3 branches or more and 24 branches or less, more preferably 4 branches or more and 20 branches or less, and further preferably 5 branches or more and 18 branches or less.

If the number of branches is 24 or less, there is a tendency that it is easy to obtain a modified conjugated diene-based polymer through a reaction with a modifier having a functional group, or to further elongate the polymer chain through a coupling reaction, and if the number of branches is 3 or more, the resultant branched conjugated diene-based polymer tends to be excellent in workability and abrasion resistance.

[0067]

An amount of the branching agent to be added is not especially limited, but can be selected in accordance with the purpose or the like, and from the viewpoints of improvement of a rate of an end stopping reaction of the

conjugated diene-based polymer, improvement of the coupling ratio, and continuity of the polymerization after branching, the amount of the branching agent is, in terms of a molar ratio to the amount of the active polymerization initiator, preferably $1/2$ or less and $1/100$ or more, more preferably $1/3$ or less and $1/50$ or more, further preferably $1/4$ or less and $1/30$ or more, further more preferably $1/6$ or less and $1/25$ or more, and still further preferably $1/8$ or less and $1/12$ or more.

[0068]

Furthermore, as described above, during and/or after the branching step, a monomer may be further additionally added to continue the polymerizing step after the branching, or after the additional addition of the monomer, addition of the branching agent and the monomer may be repeated.

If the monomer is additionally added, steric hindrance around the branch point is reduced, and as a result, effects of improving the continuity of the polymerization and improving the coupling ratio and the modification ratio can be obtained. Thus, with the molecular weight of the polymer increased, a branch structure can be formed in a desired position.

The monomer to be additionally added may be aromatic vinyl such as styrene, or a conjugated diene compound such as butadiene, or a mixture of these, and may be the same as or different from the monomer initially

polymerized in the type and ratio, and from the viewpoint of the continuity of the polymerization, is preferably a conjugated diene compound. From the viewpoint of improving heat resistance of the polymer, an aromatic vinyl compound is preferably additionally added.

[0069]

The branched conjugated diene-based polymer obtained in the branching step of the production method of the present embodiment has a Mooney viscosity, measured at 110°C, of preferably 10 or more and 150 or less, more preferably 15 or more and 140 or less, and further preferably 20 or more and 130 or less. The Mooney viscosity is still further preferably 30 or more and 100 or less.

If the Mooney viscosity falls in this range, a branched conjugated diene-based polymer obtained by the production method of the present embodiment tends to be excellent in workability and abrasion resistance.

[0070]

The branched conjugated diene-based polymer obtained in the branching step of the production method of the present embodiment has a weight average molecular weight of preferably 10,000 or more and 1,500,000 or less, more preferably 100,000 or more and 1,000,000 or less, and further preferably 200,000 or more and 900,000 or less.

If the weight average molecular weight falls in this range, a branched conjugated diene-based polymer obtained

by the production method of the present embodiment tends to be excellent in workability, abrasion resistance and balance between these characteristics.

If an unmodified branched conjugated diene-based polymer is to be produced, in order to attain a weight average molecular weight in a range of 100,000 or more and 1,000,000 or less, the amount of the branching agent to be added is controlled to a molar ratio to the amount of the polymerization initiator of $1/3$ or less and $1/50$ or more. Thus, it is necessary to prevent the polymerization initiator from being totally consumed before the coupling step while forming a branch, and to make the number of functional groups of the coupling agent two or more. In order to attain a weight average molecular weight in a range of 200,000 or more and 900,000 or less, it is necessary to control the amount of the branching agent to be added to be a molar ratio to the amount of the polymerization initiator of $1/3$ or less and $1/50$ or more, and to make the number of functional groups of the coupling agent three or more.

If a modified branched conjugated diene-based polymer is to be produced, in order to attain a weight average molecular weight in a range of 100,000 or more and 1,000,000 or less, the amount of the branching agent to be added is controlled to a molar ratio to the amount of the polymerization initiator of $1/3$ or less and $1/50$ or more. Thus, it is necessary to prevent the

polymerization initiator from being totally consumed before the coupling step while forming a branch structure, and to make the number of functional groups of the coupling agent two or more. In order to attain a weight average molecular weight in a range of 200,000 or more and 900,000 or less, it is necessary to control the amount of the branching agent to be added to be a molar ratio to the amount of the polymerization initiator of $1/3$ or less and $1/50$ or more, and to make the number of functional groups of the coupling agent three or more. [0071]

A branched conjugated diene-based polymer obtained by the production method of the present embodiment may be a polymer of a conjugated diene monomer and the branching agent, or may be a copolymer of a conjugated diene monomer, the branching agent, and another monomer.

For example, when the conjugated diene monomer is butadiene or isoprene, and this diene monomer is polymerized with a branching agent containing an aromatic vinyl portion, a polymer chain is what is called polybutadiene or polyisoprene, and a polymer containing a structure derived from an aromatic vinyl in a branched portion is obtained. Owing to such a structure, linearity of each polymer chain can be improved and a crosslink density obtained after vulcanization can be improved, resulting in obtaining an effect of improving the abrasion resistance of the polymer. Therefore, such

a polymer is suitably used for a tire, resin modification, interior/exterior of a vehicle, an anti-vibration rubber, shoes and the like.

When the conjugated diene-based polymer is used in application to a tire tread, a copolymer of a conjugated diene monomer, an aromatic vinyl monomer, and a branching agent is suitably used, and in the copolymer used in this application, the amount of bound conjugated diene is preferably 40% by mass or more and 100% by mass or less, and more preferably 55% by mass or more and 80% by mass or less.

Besides, an amount of bound aromatic vinyl in a branched conjugated diene-based polymer obtained by the production method of the present embodiment is not especially limited, and is preferably 0% by mass or more and 60% by mass or less, and more preferably 20% by mass or more and 45% by mass or less.

When the amounts of the bound conjugated diene and the bound aromatic vinyl fall in the above-described ranges, the balance between a low hysteresis loss property and wet skid resistance, abrasion resistance and fracture performance obtained when in the form of a vulcanizate tend to be more excellent.

Here, the amount of bound aromatic vinyl can be measured in accordance with UV absorption by a phenyl group, and based on the thus obtained amount, the amount of bound conjugated diene can be also obtained.

Specifically, these amounts can be measured in accordance with a method described later in the examples.

[0072]

In the branched conjugated diene-based polymer obtained by the production method of the present embodiment, the amount of bound vinyl in a conjugated diene bond unit is not especially limited, and is preferably 10% by mol or more and 75% by mol or less, and more preferably 20% by mol or more and 65% by mol or less.

If the amount of bound vinyl falls in the above-described range, the balance between a low hysteresis loss property and wet skid resistance, abrasion resistance, and fracture strength obtained when in the form of a vulcanizate tend to be more excellent.

Here, if the branched conjugated diene-based polymer is a copolymer of butadiene and styrene, the amount of bound vinyl (the amount of a 1,2-bond) in a butadiene bond unit can be obtained by Hampton method (R. R. Hampton, Analytical Chemistry, 21, 923 (1949)). Specifically, it can be measured by a method described in the examples below.

[0073]

As for the microstructure of the branched conjugated diene-based polymer, if the amounts of the aforementioned bonds in the branched conjugated diene-based polymer obtained by the production method of the present

embodiment respectively fall in the above-described ranges and the glass transition temperature of the branched conjugated diene-based polymer is -80°C or more and -15°C or less, there is a tendency that a vulcanizate more excellent in the balance between a low hysteresis loss property and wet skid resistance can be obtained.

The glass transition temperature is defined as a peak top (an inflection point) of a DSC differential curve obtained by recording a DSC curve during temperature increase in a prescribed temperature range in accordance with ISO 22768:2006.

[0074]

If the branched conjugated diene-based polymer obtained by the production method of the present embodiment is a conjugated diene-aromatic vinyl copolymer, the branched conjugated diene-based polymer preferably contains a few or no blocks in which 30 or more aromatic vinyl units are chained. More specifically, if the branched conjugated diene-based polymer obtained by the production method of the present embodiment is a butadiene-styrene copolymer, in employing a known method in which the copolymer is decomposed by Kolthoff method (a method described by I. M. Kolthoff, et al., J. Polym. Sci. 1, 429 (1946)) to analyze the amount of polystyrene insoluble in methanol, blocks in each of which 30 or more aromatic vinyl units are chained are preferably 5.0% by mass or less, and more preferably 3.0%

by mass or less with respect to the total amount of the branched conjugated diene-based polymer.

[0075]

From the viewpoint of improving fuel efficiency, if the branched conjugated diene-based polymer obtained by the production method of the present embodiment is a conjugated diene-aromatic vinyl copolymer, a larger proportion of an aromatic vinyl unit is preferably present singly.

Specifically, if the branched conjugated diene-based polymer obtained by the production method of the present embodiment is a butadiene-styrene copolymer, when the branched conjugated diene-based polymer is decomposed by employing a method through ozonolysis known as a method of Tanaka et al., (Polymer, 22, 1721 (1981)) to analyze a styrene chain distribution by GPC, it is preferable that the amount of isolated styrene, with respect to the whole amount of bound styrene, is 40% by mass or more, and that the amount of a chain styrene structure consisting of 8 or more chained styrene is 5.0% by mass or less.

In this case, a resultant vulcanized rubber tends to attain excellent performance of particularly low hysteresis loss.

[0076]

(Reaction Step)

In the production method for a branched conjugated diene-based polymer of the present embodiment, a step of

performing a coupling reaction on the active end of the conjugated diene-based polymer obtained through the polymerizing step and the branching step with a coupling agent of, for example, a tri- or higher functional reactive compound, such as a step of performing a coupling reaction with a coupling agent containing a silane sulfide compound described below, or a step of performing a reaction on the active end of the conjugated diene-based polymer with a polymerization terminator of, for example, a di- or lower functional reactive compound is preferably performed.

Hereinafter, the step of performing the reaction with a coupling agent (coupling step) and the step of performing the reaction with a polymerization terminator (polymerization termination step) will be together referred to as a reaction step.

In the reaction step, one end of the active end of the conjugated diene-based polymer is reacted with a coupling agent or a polymerization terminator.

[0077]

<Coupling Step>

In the production method for a branched conjugated diene-based polymer of the present embodiment, the conjugated diene-based polymer obtained through the polymerizing step and the branching step is preferably subjected to the coupling reaction with a coupling agent as the reaction step.

Through the coupling reaction, a molecular chain can be efficiently elongated, and if a tri- or higher functional coupling agent is used, a branch can be introduced into the polymer. The function of forming a branch is similar to that of the step using a branching agent, but the coupling step is preferably performed from the viewpoint that a branch can be formed with a desired element such as nitrogen, sulfur, or silicon introduced by using a known coupling agent.

In the coupling step, for example, on the active end of the conjugated diene-based polymer, a tri- or higher functional reactive compound, a coupling agent having a nitrogen atom-containing group, or a coupling agent containing a silane sulfide compound described below (hereinafter sometimes altogether referred to as the "coupling agent") is preferably used.

[0078]

In the reaction step, for example, one end of the active end of the conjugated diene-based polymer is subjected to the coupling reaction with the tri- or higher functional reactive compound, the coupling agent having a nitrogen atom-containing group, or a silane sulfide compound described below, that is, a modifier containing silicon and a sulfur atom, and thus, a branched conjugated diene-based polymer can be obtained.

[0079]

[Tri- or Higher Functional Reactive Compound]

The tri- or higher functional reactive compound used in the reaction step in the production method for a branched conjugated diene-based polymer of the present embodiment is preferably a tri- or higher functional reactive compound having a silicon atom.

[0080]

Examples of the tri- or higher functional reactive compound having a silicon atom include, but are not limited to, a halogenated silane compound, an epoxidized silane compound, a vinylized silane compound, and an alkoxysilane compound.

[0081]

Examples of the halogenated silane compound used as the coupling agent include, but are not limited to, methyl trichlorosilane, tetrachlorosilane, tris(trimethylsiloxy)chlorosilane, tris(dimethylamino)chlorosilane, hexachlorodisilane, bis(trichlorosilyl)methane, 1,2-bis(trichlorosilyl)ethane, 1,2-bis(methyldichlorosilyl)ethane, 1,4-bis(trichlorosilyl)butane, and 1,4-bis(methyldichlorosilyl)butane.

[0082]

Examples of the epoxidized silane compound used as the coupling agent include, but are not limited to, 3-glycidoxypropyltrimethoxysilane, 3-glycidoxypropyltriethoxysilane, 3-

glycidoxypropylmethyldiethoxysilane, and epoxy-modified silicone.

[0083]

Examples of the alkoxysilane compound used as the coupling agent include, but are not limited to, tetramethoxysilane, tetraethoxysilane, triphenoxymethylsilane, 1,2-bis(triethoxysilyl)ethane, and methoxy-substituted polyorganosiloxane.

[0084]

[Coupling Agent having Nitrogen Atom-containing Group]

Examples of the coupling agent having a nitrogen atom-containing group include, but are not limited to, an isocyanate compound, an isothiocyanate compound, an isocyanuric acid derivative, a carbonyl compound having a nitrogen atom-containing group, a vinyl compound having a nitrogen atom-containing group, an epoxy compound having a nitrogen atom-containing group, an alkoxysilane compound having a nitrogen atom-containing group, and a protected amine compound having a nitrogen atom-containing group and capable of forming a primary or secondary amine.

[0085]

In the coupling agent having a nitrogen atom-containing group, a nitrogen atom-containing group can be a functional group derived from an amine-based compound preferably not having active hydrogen, and examples of

the amine-based compound include a tertiary amine compound, and a protected amine compound having the active hydrogen substituted by a protecting group. Other examples of a compound capable of forming a nitrogen atom-containing group include an imine compound represented by a general formula, $-N=C$, and an alkoxy silane compound bonded to the nitrogen atom-containing group.

[0086]

Examples of the isocyanate compound used as the coupling agent having a nitrogen atom-containing group include, but are not limited to, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, diphenylmethane diisocyanate, polymeric type diphenylmethane diisocyanate (C-MDI), phenyl isocyanate, isophorone diisocyanate, hexamethylene diisocyanate, butyl isocyanate, and 1,3,5-benzene triisocyanate.

[0087]

Examples of the isocyanuric acid derivative used as the coupling agent having a nitrogen atom-containing group include, but are not limited to, 1,3,5-tris(3-trimethoxysilylpropyl)isocyanurate, 1,3,5-tris(3-triethoxysilylpropyl)isocyanurate, 1,3,5-tris(oxysilan-2-yl)-1,3,5-triazinane-2,4,6-trione, 1,3,5-tris(isocyanatomethyl)-1,3,5-triazinane-2,4,6-trione, and 1,3,5-trivinyl-1,3,5-triazinane-2,4,6-trione.

[0088]

Examples of the carbonyl compound used as the coupling agent having a nitrogen atom-containing group include, but are not limited to, 1,3-dimethyl-2-imidazolidinone, 1-methyl-3-ethyl-2-imidazolidinone, 1-methyl-3-(2-methoxyethyl)-2-imidazolidinone, N-methyl-2-pyrrolidone, N-methyl-2-piperidone, N-methyl-2-quinolone, 4,4'-bis(diethylamino)benzophenone, 4,4'-bis(dimethylamino)benzophenone, methyl-2-pyridylketone, methyl-4-pyridylketone, propyl-2-pyridylketone, di-4-pyridylketone, 2-benzoylpyridine, N,N,N',N'-tetramethylurea, N,N-dimethyl-N',N'-diphenylurea, methyl N,N-diethylcarbamate, N,N-diethylacetamide, N,N-dimethyl-N',N'-dimethylaminoacetamide, N,N-dimethylpicolinamide, and N,N-dimethylisonicotinamide.

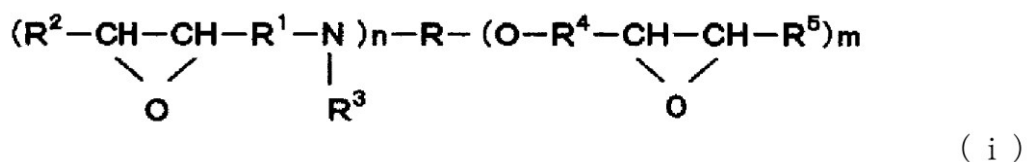
[0089]

Examples of the vinyl compound used as the coupling agent having a nitrogen atom-containing group include, but are not limited to, N,N-dimethylacrylamide, N,N-dimethylmethacrylamide, N-methylmaleimide, N-methylphthalimide, N,N-bis(trimethylsilyl)acrylamide, morpholinoacrylamide, 3-(2-dimethylaminoethyl)styrene, (dimethylamino)dimethyl-4-vinylphenylsilane, 4,4'-vinylidenebis(N,N-dimethylaniline), 4,4'-vinylidenebis(N,N-diethylaniline), 1,1-bis(4-morpholinophenyl)ethylene, and 1-phenyl-1-(4-N,N-dimethylaminophenyl)ethylene.

[0090]

Examples of the epoxy compound used as the coupling agent having a nitrogen atom-containing group include, but are not limited to, an epoxy group-containing hydrocarbon compound bonded to an amino group, and an epoxy group-containing hydrocarbon compound bonded to an ether group. An example of such an epoxy compound includes, but is not limited to, an epoxy compound represented by the following general formula (i):

[0091]



[0092]

In the formula (i), R represents a di- or higher valent hydrocarbon group, or a di- or higher valent organic group having at least one polar group selected from the group consisting of a polar group having oxygen such as ether, epoxy, or ketone, a polar group having sulfur such as thioether or thioketone, and a polar group having nitrogen such as a tertiary amino group or an imino group.

[0093]

The di- or higher valent hydrocarbon group is a saturated or unsaturated and optionally straight-chain, branched or cyclic hydrocarbon group, and includes an alkylene group, an alkenylene group, a phenylene group or the like. It is preferably a hydrocarbon group having 1

to 20 carbon atoms. Examples include methylene, ethylene, butylene, cyclohexylene, 1,3-bis(methylene) - cyclohexane, 1,3-bis(ethylene)-cyclohexane, o-, m- or p-phenylene, m- or p-xylene, and bis(phenylene)-methane.

[0094]

In the formula (i), R^1 and R^4 represent a hydrocarbon group having 1 to 10 carbon atoms, and R^1 and R^4 may be the same as or different from each other.

In the formula (i), R^2 and R^5 represent hydrogen or a hydrocarbon group having 1 to 10 carbon atoms, and R^2 and R^5 may be the same as or different from each other.

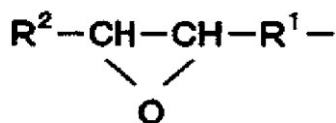
In the formula (i), R^3 represents a hydrocarbon group having 1 to 10 carbon atoms, or a structure represented by the following formula (ii).

R^1 , R^2 and R^3 may have a cyclic structure mutually bonded.

If R^3 is a hydrocarbon group, it may have a cyclic structure bonded to R. When the cyclic structure is formed, N and R bonded to R^3 may be directly bonded to each other.

In the formula (i), n represents an integer of 1 or more, and m represents 0, or an integer of 1 or more.

[0095]



(i i)

[0096]

In the formula (ii), R^1 and R^2 are defined the same as R^1 and R^2 of the formula (i), and R^1 and R^2 may be the same as or different from each other.

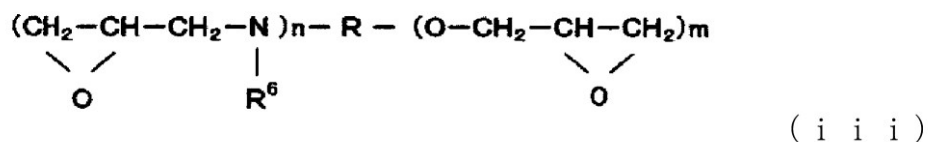
[0097]

The epoxy compound used as the coupling agent having a nitrogen atom-containing group is preferably one having an epoxy group-containing hydrocarbon group, and more preferably one having a glycidyl group-containing hydrocarbon group.

[0098]

The epoxy-group containing hydrocarbon group bonded to an amino group or an ether group is not especially limited, and examples include a glycidylamino group, a diglycidylamino group, and a glycidoxy group. A more preferable molecular structure is an epoxy group-containing compound having a glycidylamino group, a diglycidylamino group, or a glycidoxy group, and an example includes a compound represented by the following general formula (iii):

[0099]



[0100]

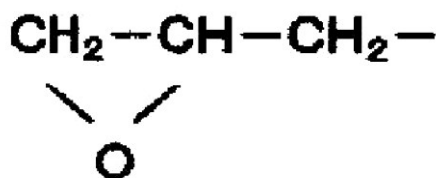
In the formula (iii), R is defined the same as R of the formula (i), and R^6 represents a hydrocarbon group

having 1 to 10 carbon atoms, or a structure represented by the following formula (iv).

If R^6 is a hydrocarbon group, it may be mutually bonded to R to form a ring structure, and in this case, N and R bonded to R^6 may be directly bonded to each other.

In the formula (iii), n represents an integer of 1 or more, and m represents 0, or an integer of 1 or more.

[0101]



(i v)

[0102]

The epoxy compound used as the coupling agent having a nitrogen atom-containing group is particularly preferably a compound having one or more diglycidylamino groups and one or more glycidoxy groups in a molecule.

[0103]

Examples of the epoxy compound used as the coupling agent having a nitrogen atom-containing group include, but are not limited to, N,N-diglycidyl-4-glycidoxyaniline, 1-N,N-diglycidylaminomethyl-4-glycidoxy-cyclohexane, 4-(4-glycidoxyphenyl)-(N,N-diglycidyl)aniline, 4-(4-glycidoxyphenoxy)-(N,N-diglycidyl)aniline, 4-(4-glycidoxybenzyl)-(N,N-diglycidyl)aniline, 4-(N,N'-diglycidyl-2-piperazinyl)-

glycidoxybenzene, 1,3-bis(N,N-diglycidylaminomethyl)cyclohexane, N,N,N',N'-tetraglycidyl-m-xylenediamine, 4,4-methylene-bis(N,N-diglycidylaniline), 1,4-bis(N,N-diglycidylamino)cyclohexane, N,N,N',N'-tetraglycidyl-p-phenylenediamine, 4,4'-bis(diglycidylamino)benzophenone, 4-(4-glycidylpiperaziny)-(N,N-diglycidyl)aniline, 2-[2-(N,N-diglycidylamino)ethyl]-1-glycidylpyrrolidine, N,N-diglycidylaniline, 4,4'-diglycidyl-dibenzylmethylaniline, N,N-diglycidylaniline, N,N-diglycidylortho-toluidine, and N,N-diglycidylaminomethylcyclohexane. Among these, N,N-diglycidyl-4-glycidoxyaniline and 1,3-bis(N,N-diglycidylaminomethyl)cyclohexane are particularly preferred.

[0104]

Examples of the alkoxysilane compound used as the coupling agent having a nitrogen atom-containing group include, but are not limited to, 3-dimethylaminopropyltrimethoxysilane, 3-dimethylaminopropylmethyldimethoxysilane, 3-diethylaminopropyltriethoxysilane, 3-morpholinopropyltrimethoxysilane, 3-piperidinopropyltriethoxysilane, 3-hexamethyleneiminopropylmethyl diethoxysilane, 3-(4-methyl-1-piperazino)propyltriethoxysilane, 1-[3-(triethoxysilyl)-propyl]-3-methylhexahydropyrimidine, 3-(4-trimethylsilyl-1-piperazino)propyltriethoxysilane, 3-

(3-triethylsilyl-1-imidazolidinyl)propylmethyldiethoxysilane, 3-(3-trimethylsilyl-1-hexahydropyrimidinyl)propyltrimethoxysilane, 3-dimethylamino-2-(dimethylaminomethyl)propyltrimethoxysilane, bis(3-dimethoxymethylsilylpropyl)-N-methylamine, bis(3-trimethoxysilylpropyl)-N-methylamine, bis(3-triethoxysilylpropyl)methylamine, tris(trimethoxysilyl)amine, tris(3-trimethoxysilylpropyl)amine, N,N,N',N'-tetra(3-trimethoxysilylpropyl)ethylenediamine, 3-isocyanatopropyltrimethoxysilane, 3-cyanopropyltrimethoxysilane, 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane, 2,2-diethoxy-1-(3-triethoxysilylpropyl)-1-aza-2-silacyclopentane, 2,2-dimethoxy-1-(4-trimethoxysilylbutyl)-1-aza-2-silacyclohexane, 2,2-dimethoxy-1-(3-dimethoxymethylsilylpropyl)-1-aza-2-silacyclopentane, 2,2-dimethoxy-1-phenyl-1-aza-2-silacyclopentane, 2,2-diethoxy-1-butyl-1-aza-2-silacyclopentane, 2,2-dimethoxy-1-methyl-1-aza-2-silacyclopentane, 2,2-dimethoxy-8-(4-methylpiperazinyl)methyl-1,6-dioxa-2-silacyclooctane, and 2,2-dimethoxy-8-(N,N-diethylamino)methyl-1,6-dioxa-2-silacyclooctane.

[0105]

Among protected amine compounds capable of forming a primary or secondary amine used as the coupling agent having a nitrogen atom-containing group, examples of a compound having an unsaturated bond and a protected amine in a molecule include, but are not limited to, 4,4'-vinylidenebis[N,N-bis(trimethylsilyl)aniline], 4,4'-vinylidenebis[N,N-bis(triethylsilyl)aniline], 4,4'-vinylidenebis[N,N-bis(t-butyldimethylsilyl)aniline], 4,4'-vinylidenebis[N-methyl-N-(trimethylsilyl)aniline], 4,4'-vinylidenebis[N-ethyl-N-(trimethylsilyl)aniline], 4,4'-vinylidenebis[N-methyl-N-(triethylsilyl)aniline], 4,4'-vinylidenebis[N-ethyl-N-(triethylsilyl)aniline], 4,4'-vinylidenebis[N-methyl-N-(t-butyldimethylsilyl)aniline], 4,4'-vinylidenebis[N-ethyl-N-(t-butyldimethylsilyl)aniline], 1-[4-N,N-bis(trimethylsilyl)aminophenyl]-1-[4-N-methyl-N-(trimethylsilyl)aminophenyl]ethylene, and 1-[4-N,N-bis(trimethylsilyl)aminophenyl]-1-[4-N,N-dimethylaminophenyl]ethylene.

[0106]

Examples of a protected amine compound, used as the coupling agent having a nitrogen atom-containing group, capable of forming a primary or secondary amine, and containing alkoxysilane and protected amine in a molecule include, but are not limited to, N,N-bis(trimethylsilyl)aminopropyltrimethoxysilane, N,N-bis(trimethylsilyl)aminopropylmethyldimethoxysilane, N,N-

bis(trimethylsilyl)aminopropyltriethoxysilane, N,N-bis(trimethylsilyl)aminopropylmethyldiethoxysilane, N,N-bis(trimethylsilyl)aminoethyltrimethoxysilane, N,N-bis(trimethylsilyl)aminoethylmethyldiethoxysilane, N,N-bis(triethylsilyl)aminopropylmethyldiethoxysilane, 3-(4-trimethylsilyl-1-piperazino)propyltriethoxysilane, 3-(3-triethylsilyl)-1-imidazolidinyl)propylmethyldiethoxysilane, 3-(3-trimethylsilyl-1-hexahydropyrimidinyl)propyltrimethoxysilane, 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane, 2,2-diethoxy-1-(3-triethoxysilylpropyl)-1-aza-2-silacyclopentane, 2,2-dimethoxy-1-(4-trimethoxysilylbutyl)-1-aza-2-silacyclohexane, 2,2-dimethoxy-1-(3-dimethoxymethylsilylpropyl)-1-aza-2-silacyclopentane, 2,2-dimethoxy-1-phenyl-1-aza-2-silacyclopentane, 2,2-diethoxy-1-butyl-1-aza-2-silacyclopentane, 2,2-dimethoxy-1-methyl-1-aza-2-silacyclopentane, N-(1-methylethylidene)-3-(triethoxysilyl)-1-propanamine, N-ethylidene-3-(triethoxysilyl)-1-propanamine, and N-(4-N,N-dimethylaminobenzylidene)-3-(triethoxysilyl)-1-propanamine, and include N-(1-methylpropylidene)-3-(triethoxysilyl)-1-propanamine, N-(1,3-dimethylbutylidene)-3-(triethoxysilyl)-1-propanamine, 3-(benzylideneamino)propyltrimethoxysilane, 3-(benzylideneamino)propyltriethoxysilane, and 3-(benzylideneamino)propyltripropylsilane.

[0107]

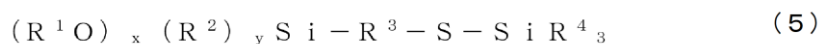
Examples of the alkoxysilane compound particularly preferably used as the coupling agent having a nitrogen atom-containing group include, but are not limited to, tris(3-trimethoxysilylpropyl)amine, tris(3-triethoxysilylpropyl)amine, tris(3-tripropoxysilylpropyl)amine, bis(3-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]amine, tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine, tris(3-trimethoxysilylpropyl)-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, tris(3-trimethoxysilylpropyl)-[3-(1-methoxy-2-methyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, bis(3-triethoxysilylpropyl)-[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-ethoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, tetrakis(3-trimethoxysilylpropyl)-1,3-bisaminomethylcyclohexane, tris(3-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, tetrakis(3-trimethoxysilylpropyl)-1,6-hexamethylenediamine, pentakis(3-trimethoxysilylpropyl)-diethylenetriamine, tris(3-trimethoxysilylpropyl)-methyl-1,3-propanediamine, tetrakis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]silane, bis(3-trimethoxysilylpropyl)-bis[3-(2,2-dimethoxy-1-aza-2-

silacyclopentane)propyl]silane, tris[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-(3-trimethoxysilylpropyl)silane, tris[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]silane, 3-tris[2-(2,2-dimethoxy-1-aza-2-silacyclopentane)ethoxy]silyl-1-trimethoxysilylpropane, 1-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-3,4,5-tris(3-trimethoxysilylpropyl)-cyclohexane, 1-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-3,4,5-tris(3-trimethoxysilylpropyl)-cyclohexane, 3,4,5-tris(3-trimethoxysilylpropyl)-cyclohexyl-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]ether, (3-trimethoxysilylpropyl)phosphate, bis(3-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]phosphate, bis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-(3-trimethoxysilylpropyl)phosphate, and tris[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]phosphate.

[0108]

As the coupling agent used in the reaction step, a silane sulfide compound represented by the following formula (5) is preferably used.

[0109]



[0110]

wherein Si represents a silicon atom, O represents an oxygen atom, and S represents a sulfur atom;

x represents an integer of 1 to 3, y represents 0, or an integer of 1 to 2, and $x + y$ is 3; and

R^1 , R^2 , and R^4 may be the same or different, and represent an alkyl group having 1 to 16 carbon atoms, and R^3 represents an aryl group having 6 to 16 carbon atoms, an alkylene group having 1 to 16 carbon atoms, or an alkyl chain having 1 to 16 carbon atoms.

[0111]

Examples of the coupling agent represented by the formula (5) include, but are not limited to, S-trimethylsilylmercaptopropyltrimethoxysilane, S-trimethylsilylmercaptopropyltriethoxysilane, S-trimethylsilylmercaptopropyltripropoxysilane, S-trimethylsilylmercaptopropyltributoxysilane, S-trimethylsilylmercaptomethyltrimethoxysilane, S-trimethylsilylmercaptomethyltriethoxysilane, S-trimethylsilylmercaptomethyltripropoxysilane, S-trimethylsilylmercaptomethyltributoxysilane, S-trimethylsilylmercaptomethyltrimethoxysilane, S-trimethylsilylmercaptomethyltriethoxysilane, S-trimethylsilylmercaptomethyltripropoxysilane, S-trimethylsilylmercaptomethyltributoxysilane, S-trimethylsilylmercapto-2,2-dimethylpropyltrimethoxysilane, S-trimethylsilylmercapto-

2,2-dimethylpropyltriethoxysilane, S-
trimethylsilylmercapto-2,2-
dimethylpropyltripropoxysilane, S-trimethylsilylmercapto-
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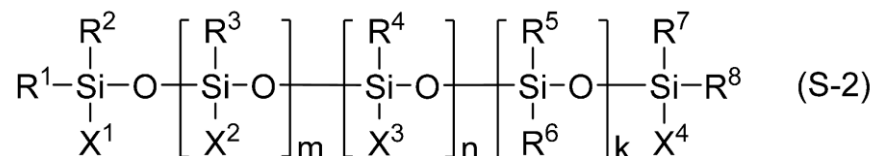
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[0112]

In the production method for a branched conjugated diene-based polymer of the present embodiment, in the reaction step, the active end of the conjugated diene-based polymer resulting from the branching step is preferably reacted with a coupling agent represented by the following formula (S-2):

[0113]



[0114]

In the formula (S-2), R¹ to R⁸ each independently represent any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms and an aryl group having 6 to 20 carbon atoms, and may be the same or different.

X¹ and X⁴ satisfy the following (i) or (ii).

(i): one of a plurality of X¹ and X⁴ represents a group selected from the group consisting of an alkoxysilyl group having 1 to 5 carbon atoms, a 2-pyrrolidonyl group-containing hydrocarbon group, and an

epoxy group-containing group having 4 to 12 carbon atoms, and the other represents a group derived from such a group, or a single bond.

(ii): X^1 and X^4 represent an alkyl group having 1 to 6 carbon atoms or an aryl group having 6 to 12 carbon atoms, X^1 and X^4 may be the same or different.

some of a plurality of X^2 represent a group selected from the group consisting of an alkoxysilyl group having 1 to 5 carbon atoms, a 2-pyrrolidonyl group-containing hydrocarbon group, and an epoxy group-containing group having 4 to 12 carbon atoms, and the others represent a group derived from such a group, or a single bond.

X^3 represents a group containing 2 to 20 alkylene glycol repeating units.

m represents an integer of 3 to 200, n represents an integer of 0 to 200, and k represents an integer of 0 to 200.

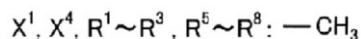
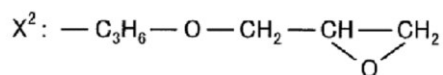
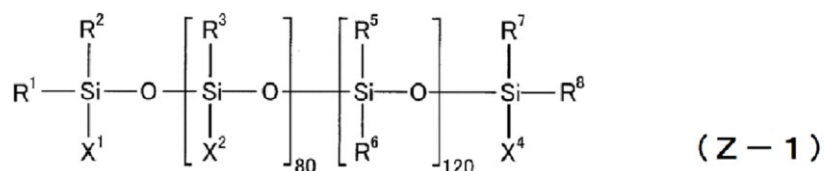
From the viewpoints of ease of synthesis of the coupling agent and ease of use in the coupling reaction, m preferably represents an integer of 60 to 100, n preferably represents an integer of 0 to 40, and k preferably represents an integer of 100 to 150.

[0115]

The coupling agent represented by the formula (S-2) is preferably a compound represented by the following formula (Z-1).

The coupling agent represented by the formula (S-2) is used, and thus, the branch number is further increased and the effect of improving workability is obtained.

[0116]

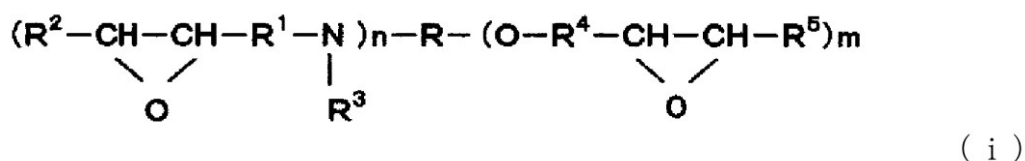


[0117]

<Branched Conjugated Diene-based Polymer obtained through Polymerizing Step, Branching Step, and Reaction Step>

The branched conjugated diene-based polymer obtained through the reaction step, particularly the step of causing a reaction with a coupling agent, in the production method for a branched conjugated diene-based polymer of the present embodiment preferably contains a structure derived from a compound having a nitrogen atom-containing group represented by the following general formula (i) or any one of the general formulas (A) to (C):

[0118]



[0119]

In the formula (i), R represents a di- or higher valent hydrocarbon group, or a di- or higher valent organic group having at least one polar group selected from a polar group having oxygen such as ether, epoxy, or ketone, a polar group having sulfur such as thioether or thioketone, and a polar group having nitrogen such as a tertiary amino group or an imino group.

[0120]

The di- or higher valent hydrocarbon group is a saturated or unsaturated and optionally straight-chain, branched or cyclic hydrocarbon group, and includes an alkylene group, an alkenylene group, a phenylene group or the like. It is preferably a hydrocarbon group having 1 to 20 carbon atoms. Examples include methylene, ethylene, butylene, cyclohexylene, 1,3-bis(methylene)-cyclohexane, 1,3-bis(ethylene)-cyclohexane, o-, m- or p-phenylene, m- or p-xylene, and bis(phenylene)-methane.

[0121]

In the formula (i), R¹ and R⁴ represent a hydrocarbon group having 1 to 10 carbon atoms, and R¹ and R⁴ may be the same as or different from each other.

In the formula (i), R^2 and R^5 represent hydrogen or a hydrocarbon group having 1 to 10 carbon atoms, and R^2 and R^5 may be the same as or different from each other.

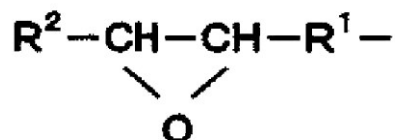
In the formula (i), R^3 represents a hydrocarbon group having 1 to 10 carbon atoms, or a structure represented by the following formula (ii).

R^1 , R^2 and R^3 may have a cyclic structure mutually bonded.

If R^3 is a hydrocarbon group, it may have a cyclic structure bonded to R. When the cyclic structure is formed, N and R bonded to R^3 may be directly bonded to each other.

In the formula (i), n represents an integer of 1 or more, and m represents 0, or an integer of 1 or more.

[0122]

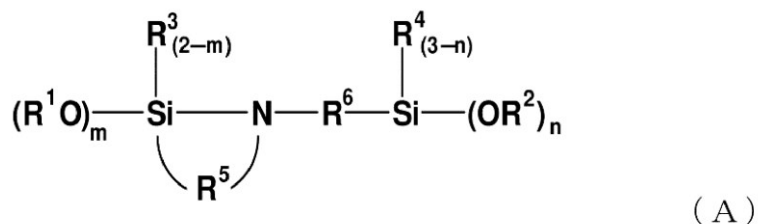


(i i)

[0123]

In the formula (ii), R^1 and R^2 are defined the same as R^1 and R^2 of the formula (i), and R^1 and R^2 may be the same as or different from each other.

[0124]

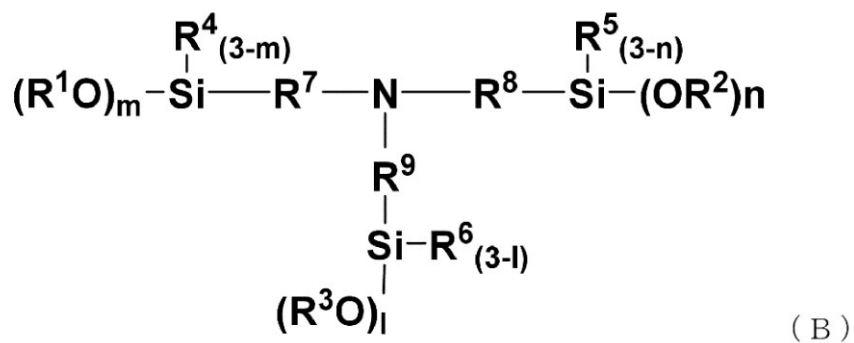


[0125]

In the formula (A), R^1 to R^4 each independently represent an alkyl group having 1 to 20 carbon atoms, or an aryl group having 6 to 20 carbon atoms, R^5 represents an alkylene group having 1 to 10 carbon atoms, and R^6 represents an alkylene group having 1 to 20 carbon atoms.

m represents an integer of 1 or 2, n represents an integer of 2 or 3, $(m + n)$ is an integer of 4 or more. Each of R^1 to R^4 , if present in a plural number, is respectively independent.

[0126]



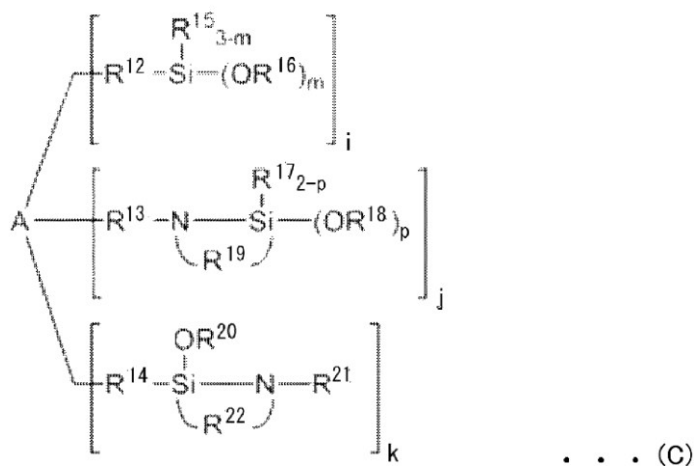
[0127]

In the formula (B), R^1 to R^6 each independently represent an alkyl group having 1 to 20 carbon atoms, or an aryl group having 6 to 20 carbon atoms, and R^7 to R^9

each independently represent an alkylene group having 1 to 20 carbon atoms.

m, n, and l each independently represent an integer of 1 to 3, (m + n + l) is an integer of 4 or more. Each of R¹ to R⁶, if present in a plural number, is respectively independent.

[0128]



[0129]

In the formula (C), R¹² to R¹⁴ each independently represent a single bond, or an alkylene group having 1 to 20 carbon atoms, R¹⁵ to R¹⁸ and R²⁰ each independently represent an alkyl group having 1 to 20 carbon atoms, R¹⁹ and R²² each independently represent an alkylene group having 1 to 20 carbon atoms, and R²¹ represents an alkyl group having 1 to 20 carbon atoms or a trialkylsilyl group.

m represents an integer of 1 to 3, and p represents 1 or 2.

Each of R^{12} to R^{22} , m, and p, if present in a plural number, is respectively independent, and may be the same or different.

i represents an integer of 0 to 6, j represents an integer of 0 to 6, k represents an integer of 0 to 6, and (i + j + k) is an integer of 4 to 10.

A represents a hydrocarbon group having 1 to 20 carbon atoms, or an organic group having at least one atom selected from the group consisting of an oxygen atom, a nitrogen atom, a silicon atom, a sulfur atom, and a phosphorus atom, and not having active hydrogen.

[0130]

Examples of the coupling agent having a nitrogen atom-containing group represented by the formula (A) include, but are not limited to, 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane, 2,2-diethoxy-1-(3-triethoxysilylpropyl)-1-aza-2-silacyclopentane, 2,2-dimethoxy-1-(4-trimethoxysilylbutyl)-1-aza-2-silacyclohexane, 2,2-dimethoxy-1-(5-trimethoxysilylpentyl)-1-aza-2-silacycloheptane, 2,2-dimethoxy-1-(3-dimethoxymethylsilylpropyl)-1-aza-2-silacyclopentane, 2,2-diethoxy-1-(3-diethoxyethylsilylpropyl)-1-aza-2-silacyclopentane, 2-methoxy-2-methyl-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane, 2-ethoxy-2-ethyl-1-(3-triethoxysilylpropyl)-1-aza-2-silacyclopentane, 2-methoxy-2-methyl-1-(3-

dimethoxymethylsilylpropyl)-1-aza-2-silacyclopentane, and 2-ethoxy-2-ethyl-1-(3-diethoxyethylsilylpropyl)-1-aza-2-silacyclopentane.

[0131]

Among these, from the viewpoint of reactivity and interactivity between a functional group of the coupling agent having a nitrogen atom-containing group and the inorganic filler such as silica, and from the viewpoint of workability, one in which m represents 2 and n represents 3 is preferred. Specifically, 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane and 2,2-diethoxy-1-(3-triethoxysilylpropyl)-1-aza-2-silacyclopentane are preferred.

[0132]

The reaction temperature, the reaction time and the like in causing the coupling agent having a nitrogen atom-containing group represented by formula (A) to react with the polymer active end are not especially limited, and it is preferable to perform the reaction at 0°C or more and 120°C or less for 30 seconds or more.

[0133]

A total mole number of an alkoxy group bonded to a silyl group of the compound used as the coupling agent having a nitrogen atom-containing group represented by the formula (A) is preferably 0.6 or more times and 3.0 or less times, more preferably 0.8 or more times and 2.5 or less times, and further preferably 0.8 or more times

and 2.0 or less times of a mole number of an alkali metal compound and/or an alkaline earth metal compound to be added as a polymerization initiator. From the viewpoint that the thus obtained branched conjugated diene-based polymer has sufficient modification ratio and molecular weight and has a branch structure, the total mole number is preferably 0.6 times or more, and a branched conjugated diene-based polymer component is preferably obtained by coupling polymer ends for improving workability, and in addition, from the viewpoint of cost of the coupling agent, the total mole number is preferably 3.0 times or less.

[0134]

A mole number of the polymerization initiator is preferably 3.0-fold moles or more, and more preferably 4.0-fold moles or more relative to the mole number of the coupling agent having a nitrogen atom-containing group represented by the formula (A).

[0135]

Examples of the coupling agent having a nitrogen atom-containing group represented by the formula (B) include, but are not limited to, tris(3-trimethoxysilylpropyl)amine, tris(3-methyldimethoxysilylpropyl)amine, tris(3-triethoxysilylpropyl)amine, tris(3-methyldiethoxysilylpropyl)amine, tris(trimethoxysilylmethyl)amine, tris(2-

trimethoxysilylethyl)amine, and tris(4-trimethoxysilylbutyl)amine.

[0136]

Among these, from the viewpoint of reactivity and interactivity between a functional group of the coupling agent and the inorganic filler such as silica, and from the viewpoint of workability, one in which n, m and l in the formula (B) are all 3 is preferred. Preferable specific examples include tris(3-trimethoxysilylpropyl)amine, and tris(3-triethoxysilylpropyl)amine.

[0137]

The reaction temperature, the reaction time and the like in causing the coupling agent having a nitrogen atom-containing group represented by formula (B) to react with the active end of the branched conjugated diene-based polymer obtained in the branching step are not especially limited, and it is preferable to perform the reaction at 0°C or more and 120°C or less for 30 seconds or more.

[0138]

A total mole number of an alkoxy group bonded to a silyl group of the compound used as the coupling agent represented by the formula (B) is preferably 0.6 or more times and 3.0 or less times, more preferably 0.8 or more times and 2.5 or less times, and further preferably 0.8 or more times and 2.0 or less times of a mole number of

lithium contained in the polymerization initiator. From the viewpoint that the branched conjugated diene-based polymer obtained by the production method of the present embodiment has sufficient modification ratio and molecular weight and has a branch structure, the total mole number is preferably 0.6 times or more, and a branched conjugated diene-based polymer component is preferably obtained by coupling polymer ends for improving workability, and in addition, from the viewpoint of cost of the coupling agent, the total mole number is preferably 3.0 times or less.

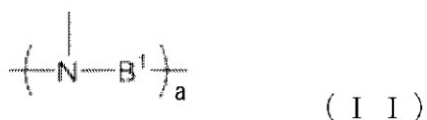
[0139]

A mole number of the polymerization initiator is preferably 4.0-fold moles or more, and more preferably 5.0-fold moles or more relative to the mole number of the coupling agent having a nitrogen atom-containing group represented by the formula (B).

[0140]

In the formula (C), A is preferably represented by any one of the following general formulas (II) to (V).

[0141]

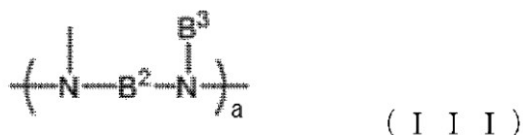


[0142]

In the formula (II), B¹ represents a single bond, or a hydrocarbon group having 1 to 20 carbon atoms, and a

represents an integer of 1 to 10. B¹, if present in plural, is respectively independent.

[0143]



[0144]

In the formula (III), B² represents a single bond, or a hydrocarbon group having 1 to 20 carbon atoms, B³ represents an alkyl group having 1 to 20 carbon atoms, and a represents an integer of 1 to 10. Each of B² and B³, if present in plural, is respectively independent.

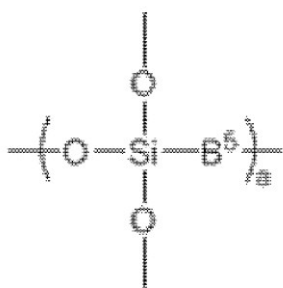
[0145]



[0146]

In the formula (IV), B⁴ represents a single bond, or a hydrocarbon group having 1 to 20 carbon atoms, and a represents an integer of 1 to 10. B⁴, if present in a plural number, is respectively independent.

[0147]



(V)

[0148]

In the formula (V), B⁵ represents a single bond, or a hydrocarbon group having 1 to 20 carbon atoms, and a represents an integer of 1 to 10. B⁵, if present in a plural number, are respectively independent.

[0149]

Examples of the coupling agent having a nitrogen atom-containing group in which A is represented by the formula (II) in the formula (C) include, but are not limited to, tris(3-trimethoxysilylpropyl)amine, bis(3-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]amine, bis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-(3-trimethoxysilylpropyl)amine, tris[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]amine, tris(3-ethoxysilylpropyl)amine, bis(3-triethoxysilylpropyl)-[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]amine, bis[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-(3-triethoxysilylpropyl)amine, tris[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]amine, tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine, tris(3-

trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-1,3-propanediamine, bis(3-trimethoxysilylpropyl)-bis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-1,3-propanediamine, tris[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-(3-trimethoxysilylpropyl)-1,3-propanediamine, tetrakis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-1,3-propanediamine, tris(3-trimethoxysilylpropyl)-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, bis(3-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, bis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-(3-trimethoxysilylpropyl)-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, tris[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, tetrakis(3-triethoxysilylpropyl)-1,3-propanediamine, tris(3-triethoxysilylpropyl)-[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-1,3-propanediamine, bis(3-triethoxysilylpropyl)-bis[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-1,3-propanediamine, tris[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-(3-triethoxysilylpropyl)-1,3-propanediamine, tetrakis[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-1,3-

propanediamine, tris(3-triethoxysilylpropyl)-[3-(1-ethoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, bis(3-triethoxysilylpropyl)-[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-ethoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, bis[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-(3-triethoxysilylpropyl)-[3-(1-ethoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, tris[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-ethoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-propanediamine, tetrakis(3-trimethoxysilylpropyl)-1,3-bisaminomethylcyclohexane, tris(3-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, bis(3-trimethoxysilylpropyl)-bis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, tris[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-(3-trimethoxysilylpropyl)-1,3-bisaminomethylcyclohexane, tetrakis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-1,3-propanediamine, tris(3-trimethoxysilylpropyl)-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, bis(3-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, bis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-(3-

trimethoxysilylpropyl)-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, tris[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, tetrakis(3-triethoxysilylpropyl)-1,3-propanediamine, tris(3-triethoxysilylpropyl)-[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, bis(3-triethoxysilylpropyl)-bis[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, tris[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-(3-triethoxysilylpropyl)-1,3-propanediamine, tetrakis[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-1,3-propanediamine, tris(3-triethoxysilylpropyl)-[3-(1-ethoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, bis(3-triethoxysilylpropyl)-[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-ethoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, bis[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-(3-triethoxysilylpropyl)-[3-(1-ethoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, tris[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-ethoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-1,3-bisaminomethylcyclohexane, tetrakis(3-

trimethoxysilylpropyl)-1,6-hexamethylenediamine, and pentakis(3-trimethoxysilylpropyl)-diethylenetriamine. [0150]

Examples of the coupling agent having a nitrogen atom-containing group in which A is represented by the formula (III) in the formula (C) include, but are not limited to, tris(3-trimethoxysilylpropyl)-methyl-1,3-propanediamine, bis(2-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-methyl-1,3-propanediamine, bis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-(3-trimethoxysilylpropyl)-methyl-1,3-propanediamine, tris(3-triethoxysilylpropyl)-methyl-1,3-propanediamine, bis(2-triethoxysilylpropyl)-[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-methyl-1,3-propanediamine, bis[3-(2,2-diethoxy-1-aza-2-silacyclopentane)propyl]-(3-triethoxysilylpropyl)-methyl-1,3-propanediamine, N1,N1'-(propane-1,3-diyl)bis(N1-methyl-N3,N3-bis(3-(trimethoxysilyl)propyl)-1,3-propanediamine), and N1-(3-(bis(3-(trimethoxysilyl)propyl)amino)propyl)-N1-methyl-N3-(3-(methyl(3-(trimethoxysilyl)propyl)amino)propyl)-N3-(3-(trimethoxysilyl)propyl)-1,3-propanediamine. [0151]

Examples of the coupling agent having a nitrogen atom-containing group in which A is represented by the formula (IV) in the formula (C) include, but are not limited to, tetrakis[3-(2,2-dimethoxy-1-aza-2-

silacyclopentane)propyl]silane, tris[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-(3-trimethoxysilylpropyl)silane, tris[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]silane, bis(3-trimethoxysilylpropyl)-bis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]silane, (3-trimethoxysilyl)-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)-bis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]silane, bis[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)-bis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]silane, tris(3-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]silane, bis(3-trimethoxysilylpropyl)-[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]silane, bis[3-(1-methoxy-2-trimethylsilyl-1-sila-2-azacyclopentane)propyl]-bis(3-trimethoxysilylpropyl)silane, and bis(3-trimethoxysilylpropyl)-bis[3-(1-methoxy-2-methyl-1-sila-2-azacyclopentane)propyl]silane.

[0152]

Examples of the coupling agent having a nitrogen atom-containing group in which A is represented by the formula (V) in the formula (C) include, but are not limited to, 3-tris[2-(2,2-dimethoxy-1-aza-2-silacyclopentane)ethoxy]silyl-1-(2,2-dimethoxy-1-aza-2-

silacyclopentane)propane, and 3-tris[2-(2,2-dimethoxy-1-aza-2-silacyclopentane)ethoxy]silyl-1-trimethoxysilylpropane.

[0153]

It is preferable that A is represented by the formula (II) or (III), and k represents 0 in the formula (C).

[0154]

Such a coupling agent having a nitrogen atom-containing group tends to be easily available, and tends to make the branched conjugated diene-based polymer obtained by the production method of the present embodiment more excellent in abrasion resistance and a low hysteresis loss property when in the form of a vulcanizate. Examples of such a coupling agent having a nitrogen atom-containing group include, but are not limited to, bis(3-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]amine, tris(3-trimethoxysilylpropyl)amine, tris(3-triethoxysilylpropyl)amine, tris(3-trimethoxysilylpropyl)-[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-1,3-propanediamine, tetrakis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-1,3-propanediamine, tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine, tetrakis(3-trimethoxysilylpropyl)-1,3-bisaminomethylcyclohexane, tris(3-trimethoxysilylpropyl)-methyl-1,3-propanediamine, and bis[3-(2,2-dimethoxy-1-

aza-2-silacyclopentane)propyl]-(3-trimethoxysilylpropyl)-methyl-1,3-propanediamine.
[0155]

In the formula (C), A is more preferably represented by formula (II) or formula (III), k represents 0, and a in the formula (II) or formula (III) represents an integer of 2 to 10.

Thus, abrasion resistance and a low hysteresis loss property obtained when in the form of a vulcanizate tend to be more excellent.

Examples of such a coupling agent having a nitrogen atom-containing group include, but are not limited to, tetrakis[3-(2,2-dimethoxy-1-aza-2-silacyclopentane)propyl]-1,3-propanediamine, tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine, tetrakis(3-trimethoxysilylpropyl)-1,3-bisaminomethylcyclohexane, and N₁-(3-(bis(3-trimethoxysilyl)propyl)amino)propyl)-N₁-methyl-N₃-(3-(methyl(3-(trimethoxysilyl)propyl)amino)propyl)-N₃-(3-(trimethoxysilyl)propyl)-1,3-propanediamine.
[0156]

The amount of the compound represented by the formula (C) to be added as the coupling agent having a nitrogen atom-containing group can be adjusted for causing the coupling agent to react with the branched conjugated diene-based polymer in such a manner that a mole number of the coupling agent relative to a mole

number of the branched conjugated diene-based polymer can be in a desired stoichiometric ratio, and thus, a desired star highly branched structure tends to be attained.

[0157]

The mole number of the polymerization initiator is preferably 5.0-fold moles or more, and more preferably 6.0-fold moles or more relative to the mole number of the coupling agent having a nitrogen atom-containing group represented by the formula (C).

[0158]

In this case, in the formula (C), the number of functional groups of the coupling agent $((m - 1) \times i + p \times j + k)$ is preferably an integer of 5 to 10, and more preferably an integer of 6 to 10.

[0159]

In the branched conjugated diene-based polymer obtained by the production method of the present embodiment, a ratio of a polymer having a nitrogen atom-containing group in the polymer is expressed as a modification ratio.

The modification ratio is preferably 60% by mass or more, more preferably 65% by mass or more, further preferably 70% by mass or more, still further preferably 75% by mass or more, still further preferably 80% by mass or more, and particularly preferably 82% by mass or more.

If the modification ratio is 60% by mass or more, there is a tendency that workability obtained when used

for obtaining a vulcanizate is excellent, and that abrasion resistance and a low hysteresis loss property when in the form of a vulcanizate are more excellent.

[0160]

<Polymerization Termination Step>

In the production method for a branched conjugated diene-based polymer of the present embodiment, a reaction step of reacting the active end of the conjugated diene-based polymer obtained through the polymerizing step and the branching step with the coupling agent or the polymerization terminator can be performed.

A polymerization termination step is preferably, for example, a polymerization termination step performed on the active end of the conjugated diene-based polymer with a difunctional reactive compound, or a polymerization termination step performed with a polymerization terminator having a nitrogen atom-containing group (hereinafter both sometimes referred to as the "polymerization terminator").

[0161]

In the polymerization termination step, a polymerization termination reaction is caused on, for example, the polymer active end obtained in the branching step with a difunctional reactive compound or a polymerization terminator having a nitrogen atom-containing group, and thus, a target branched conjugated diene-based polymer can be obtained.

[0162]

[Difunctional Reactive Compound]

The difunctional reactive compound used in the polymerization termination step in the production method for a branched conjugated diene-based polymer of the present embodiment may have any structure, and is preferably a difunctional reactive compound having a silicon atom.

[0163]

[Polymerization Terminator having Nitrogen Atom-containing Group]

The structure of the polymerization terminator having a nitrogen atom-containing group, used in the polymerization termination step in the production method for a branched conjugated diene-based polymer of the present embodiment, is not especially limited, and preferably has a functional group reactive with the conjugated diene-based polymer.

[0164]

From the viewpoint of improvement of low fuel consumption performance, the polymerization terminator having a nitrogen atom-containing group is preferably an alkoxy compound having a nitrogen atom-containing group.

Examples of the polymerization terminator having a nitrogen atom-containing group include 3-(N,N-dimethylaminopropyl)dimethoxymethylsilane, 3-(N,N-diethylaminopropyl)dimethoxymethylsilane, 3-(N,N-

dipropylaminopropyl)dimethoxymethylsilane, 3-(N,N-dimethylaminopropyl)diethoxymethylsilane, 3-(N,N-diethylaminopropyl)diethoxymethylsilane, 3-(N,N-dipropylaminopropyl)diethoxymethylsilane, 3-(N,N-dimethylaminopropyl)dimethoxyethylsilane, 3-(N,N-diethylaminopropyl)dimethoxyethylsilane, 3-(N,N-dipropylaminopropyl)dimethoxyethylsilane, 3-(N,N-dimethylaminopropyl)diethoxyethylsilane, 3-(N,N-diethylaminopropyl)diethoxyethylsilane, and 3-(N,N-dipropylaminopropyl)diethoxyethylsilane.

[0165]

(Branched Conjugated Diene-based Polymer)

The branched conjugated diene-based polymer obtained through the polymerizing step, the branching step and the reaction step according to the production method of the present embodiment is a polymer of the conjugated diene compound, or a copolymer obtained by polymerization of the conjugated diene compound and the aromatic vinyl compound, and preferably further the nitrogen atom-containing vinyl compound, and has a main chain branch structure derived from the styrene derivative as the branching agent, in a polymer main chain.

The branch structure of the branched conjugated diene-based polymer of the present embodiment has preferably 8 branches or more and 36 branches or less, more preferably 10 branches or more and 24 branches or

less, and further preferably 12 branches or more and 20 branches or less.

A total number of branch points in the branched conjugated diene-based polymer obtained by the production method of the present embodiment is preferably 2 or more, more preferably 3 or more, further preferably 4 or more, and much further preferably 5 or more.

If the branch structure and the total number of branch points fall in the above-described ranges, workability, low fuel consumption performance and abrasion resistance tend to be excellent.

In order to construct a branched conjugated diene-based polymer having a branch structure of 8 branches or more and 36 branches or less, and if it is a modified polymer, having a total number of branch points of 2 or more and 15 or less, it is necessary to use a branching agent having a molar ratio to the polymerization initiator of $1/2$ or less and $1/100$ or more, and a coupling agent having three or more functional groups. If it is a polymer not requiring modification, the number of branch points may be 1 or more.

If the branch structure has 8 branches or more and 36 branches or less, in order to construct one having a total number of branch points of 3 or more and 12 or less, it is preferable to set the molar ratio of the branching agent to $1/3$ or less and $1/50$ or more of that

of the polymerization initiator and to use a coupling agent having 4 or more functional groups.

If the branch structure has 10 branches or more and 24 branches or less, in order to construct one having a total number of branch points of 4 or more and 10 or less, it is preferable to set the molar ratio of the branching agent to $1/6$ or less and $1/25$ or more of that of the polymerization initiator and to use a coupling agent having 5 or more functional groups.

If the branch structure has 12 branches or more and 20 branches or less, in order to construct one having a total number of branch points of 5 or more and 9 or less, it is preferable to set the molar ratio of the branching agent to $1/8$ or less and $1/12$ or more of that of the polymerization initiator and to use a coupling agent having 6 or more functional groups.

[0166]

(Condensation Reaction Step)

In the production method for a branched conjugated diene-based polymer of the present embodiment, a condensation reaction step of performing a condensation reaction in the presence of a condensation accelerator may be performed after the coupling step, or before the coupling step.

[0167]

(Hydrogenating Step)

In the production method for a branched conjugated diene-based polymer of the present embodiment, a hydrogenating step of hydrogenating a conjugated diene portion may be performed.

A method for hydrogenating the conjugated diene portion of the conjugated diene-based polymer of the present embodiment is not especially limited, and any of known methods can be employed.

As a suitable hydrogenation method, a method in which the hydrogenation is performed by blowing gaseous hydrogen into the polymer solution in the presence of a catalyst can be employed. Examples of the catalyst include, but are not limited to, heterogeneous catalysts such as a catalyst containing a noble metal supported on a porous inorganic substance; and homogenous catalysts such as a catalyst obtained by reacting a solubilized salt of nickel, cobalt or the like with organic aluminum or the like, and a catalyst using metallocene such as titanocene. Among these catalysts, from the viewpoint that a mild hydrogenation condition can be selected, a titanocene catalyst is preferably used. In addition, hydrogenation of an aromatic group can be performed by using a noble metal-supported catalyst.

[0168]

Examples of the hydrogenation catalyst include, but are not limited to, (1) a supported heterogeneous hydrogenation catalyst obtained by supporting a metal

such as Ni, Pt, Pd or Ru on carbon, silica, alumina or diatomite, (2) what is called a ziegler catalyst using an organic acid salt of Ni, Co, Fe, Cr or the like, or a transition metal salt such as acetylacetonate salt, and a reducing agent such as organic aluminum, and (3) what is called an organic metal complex such as an organic metal compound of Ti, Ru, Rh or Zr. Furthermore, examples of the hydrogenation catalyst include, but are not especially limited to, known hydrogenation catalysts described in, for example, Japanese Patent Publication No. 42-8704, Japanese Patent Publication No. 43-6636, Japanese Patent Publication No. 63-4841, Japanese Patent Publication No. 1-37970, Japanese Patent Publication No. 1-53851, Japanese Patent Publication No. 2-9041 and Japanese Patent Laid-Open No. 8-109219. A preferable hydrogenation catalyst is a reaction mixture of a titanocene compound and a reducing organic metal compound.

[0169]

(Step of Adding Deactivator and Neutralizer)

In the production method for a branched conjugated diene-based polymer of the present embodiment, a deactivator, a neutralizer or the like may be added, if necessary, to the polymer solution after the coupling step described above.

Examples of the deactivator include, but are not limited to, water; and alcohols such as methanol, ethanol and isopropanol.

Examples of the neutralizer include, but are not limited to, carboxylic acids such as stearic acid, oleic acid and versatic acid (a mixture of highly branched carboxylic acids having 9 to 11 carbon atoms, mainly 10 carbon atoms); and an aqueous solution of an inorganic acid, and a carbon dioxide gas.

[0170]

(Step of Adding Stabilizer for Rubber)

In the production method for a branched conjugated diene-based polymer of the present embodiment, from the viewpoints of preventing gel formation after the polymerization and of improving stability in the processing, a stabilizer for rubber is preferably added.

As the stabilizer for rubber, any of known stabilizers, not limited to the following, can be used, and preferable examples include antioxidants such as 2,6-di-tert-butyl-4-hydroxytoluene (hereinafter also referred to as BHT), n-octadecyl-3-(4'-hydroxy-3',5'-di-tert-butylphenol)propionate, and 2-methyl-4,6-bis[(octylthio)methyl]phenol.

[0171]

(Step of Adding Rubber Softener)

In the production method for a branched conjugated diene-based polymer of the present embodiment, a rubber

softener may be added if necessary from the viewpoint of further improving productivity of the branched conjugated diene-based polymer and workability in obtaining a resin composition by blending a filler or the like.

The rubber softener is not especially limited, and for example, an extender oil, a liquid rubber, a resin or the like can be used.

A preferable example of a method for adding the rubber softener to the branched conjugated diene-based polymer includes, but is not limited to, a method in which the rubber softener is added to a solution of the branched conjugated diene-based polymer, the resultant is mixed to obtain a polymer solution containing the rubber softener, and the resultant solution is desolvated.

[0172]

Examples of the preferable extender oil include an aroma oil, a naphthenic oil and a paraffin oil. Among these oils, from the viewpoint of environmental safety, oil bleeding prevention and wet grip characteristics, an aroma-alternative oil containing 3% by mass or less of a polycyclic aromatic (PCA) component according to the IP 346 is preferred. Examples of the aroma-alternative oil include TDAE (Threated Distillate Aromatic Extracts), MES (Mild Extraction Solvate) and the like mentioned in Kautschuk Gummi Kunststoffe 52 (12) 799 (1999), and RAE (Residual Aromatic Extracts).

Examples of the preferable liquid rubber include, but are not limited to, liquid polybutadiene and liquid styrene-butadiene rubber.

As effects obtained by adding the liquid rubber, not only workability in forming a resin composition by blending the branched conjugated diene-based polymer and a filler or the like can be improved but also there is a tendency that abrasion resistance, a low hysteresis loss property and a low temperature characteristic obtained when in the form of a vulcanizate can be improved because a glass transition temperature of the resin composition can be shifted to a lower temperature.

Examples of a resin used as the rubber softener include, but are not limited to, an aromatic petroleum resin, a coumarone-indene resin, a terpene-based resin, a rosin derivative (including a wood oil resin), tall oil, a derivative of tall oil, a rosin ester resin, a natural or synthetic terpene resin, an aliphatic hydrocarbon resin, an aromatic hydrocarbon resin, a mixed aliphatic/aromatic hydrocarbon resin, a coumarin-indene resin, a phenol resin, a p-tert-butylphenol-acetylene resin, a phenol-formaldehyde resin, a xylene-formaldehyde resin, a monoolefin oligomer, a diolefin oligomer, a hydrogenated aromatic hydrocarbon resin, a cyclic aliphatic hydrocarbon resin, a hydrogenated hydrocarbon resin, a hydrocarbon resin, a hydrogenated wood oil resin, a hydrogenated oil resin, an ester of a

hydrogenated oil resin and a monofunctional or polyfunctional alcohol. One of these resins may be singly used, or two or more of these may be used together. When hydrogenated, all unsaturated groups may be hydrogenated, or some may be left not hydrogenated.

As effects obtained by adding the resin as the rubber softener, not only workability in forming a resin composition by blending the branched conjugated diene-based polymer and a filler or the like can be improved but also there is a tendency that fracture strength obtained when in the form of a vulcanizate can be improved, and in addition, there is a tendency that wet skid resistance can be improved because a glass transition temperature of the resin composition can be shifted to a higher temperature.

[0173]

An amount of the extender oil, the liquid rubber, the resin or the like to be added as the rubber softener is not especially limited, and is preferably 1 part by mass or more and 60 parts by mass or less, more preferably 5 parts by mass or more and 50 parts by mass or less, and further preferably 10 parts by mass or more and 37.5 parts by mass or less with respect to 100 parts by mass of the branched conjugated diene-based polymer obtained by the production method of the present embodiment.

If the rubber softener is added in an amount falling in this range, there is a tendency that workability obtained in the form of a resin composition by blending the branched conjugated diene-based polymer obtained by the production method of the present embodiment and a filler or the like is good, and that fracture strength and abrasion resistance when in the form of a vulcanizate are good.

[0174]

(Desolvating Step)

In the production method for a branched conjugated diene-based polymer of the present embodiment, any of known methods can be employed as a method for obtaining the resultant branched conjugated diene-based polymer from the polymer solution. Examples of the method include, but are not especially limited to, a method in which the polymer is filtered after separating the solvent by steam stripping or the like, and the resultant is dehydrated and dried to obtain the polymer, a method in which the solution is concentrated in a flushing tank, and the resultant is devolatilized by using a bent extruder or the like, and a method in which the solution is directly devolatilized by using a drum dryer or the like.

[0175]

[Rubber Composition and Production Method for Rubber Composition]

A rubber composition of the present embodiment contains a rubber component containing 10% by mass or more of the branched conjugated diene-based polymer produced by the production method of the present embodiment described above, and 5.0 parts by mass or more and 150 parts by mass or less of a filler with respect to 100 parts by mass of the rubber component.

A production method for the rubber composition of the present embodiment includes a step of obtaining the branched conjugated diene-based polymer by the above-described production method, a step of obtaining a rubber component containing 10% by mass or more of the branched conjugated diene-based polymer, and a step of causing 5.0 parts by mass or more and 150 parts by mass or less of a filler to be contained with respect to 100 parts by mass of the rubber component.

If the branched conjugated diene-based polymer obtained by the production method of the present embodiment is contained in the rubber component in an amount of 10% by mass, low fuel consumption performance, workability, and abrasion resistance can be improved.

[0176]

The filler preferably contains a silica-based inorganic filler.

If a silica-based inorganic filler is dispersed as the filler in the rubber composition, the rubber composition tends to be more excellent in workability

obtained when used for obtaining a vulcanizate and tends to be more excellent in abrasion resistance and fracture strength, and balance between a low hysteresis loss property and wet skid resistance when in the form of a vulcanizate.

Also when the rubber composition is to be used in application to a vulcanized rubber such as a tire, a vehicle component such as an anti-vibration rubber, or shoes, a silica-based inorganic filler is preferably contained.

[0177]

The rubber composition of the present embodiment is obtained by mixing the rubber component containing 10% by mass or more of the branched conjugated diene-based polymer obtained by the above-described production method with the filler.

The rubber component may contain a rubber-like polymer different from the branched conjugated diene-based polymer described above (hereinafter simply referred to as the "rubber-like polymer").

Examples of such a rubber-like polymer include, but are not limited to, a conjugated diene-based polymer or a hydrogenated product thereof, a random copolymer of a conjugated diene-based compound and a vinyl aromatic compound, or a hydrogenated product thereof, a block copolymer of a conjugated diene-based compound and a vinyl aromatic compound, or a hydrogenated product

thereof as well as a non-diene-based polymer and a natural rubber.

[0178]

Examples of the rubber-like polymer include, but are not limited to, a butadiene rubber or a hydrogenated product thereof, an isoprene rubber or a hydrogenated product thereof, styrene-based elastomers such as a styrene-butadiene rubber or a hydrogenated product thereof, and a styrene-butadiene block copolymer or a hydrogenated product thereof, a styrene-isoprene block copolymer or a hydrogenated product thereof, and an acrylonitrile-butadiene rubber or a hydrogenated product thereof.

[0179]

Examples of the non-diene-based polymer include, but are not limited to, olefin-based elastomers such as an ethylene-propylene rubber, an ethylene-propylene-diene rubber, an ethylene-butene-diene rubber, an ethylene-butene rubber, an ethylene-hexene rubber and an ethylene-octene rubber, a butyl rubber, a brominated butyl rubber, an acrylic rubber, a fluorine rubber, a silicone rubber, a chlorinated polyethylene rubber, an epichlorohydrin rubber, an α,β -unsaturated nitrile-acrylic acid ester-conjugated diene copolymer rubber, a urethane rubber and a polysulfide rubber.

[0180]

Examples of the natural rubber include, but are not limited to, smoked sheets of RSS Nos. 3 to 5, SMR and epoxidized natural rubber.

[0181]

The above-described various rubber-like polymers may be in the form of a modified rubber imparted with a functional group having polarity such as a hydroxyl group or an amino group. When used for a tire, a butadiene rubber, an isoprene rubber, a styrene-butadiene rubber, a natural rubber and a butyl rubber are preferably used.

[0182]

The weight average molecular weight of the rubber-like polymer is, from the viewpoint of balance between various performances of the resin composition and processing characteristics, preferably 2,000 or more and 2,000,000 or less, and more preferably 5,000 or more and 1,500,000 or less. Besides, a rubber-like polymer having a low molecular weight, namely, what is called a liquid rubber, can be used.

One of these rubber-like polymers may be singly used, or two or more of these may be used together.

[0183]

In obtaining the rubber composition using the branched conjugated diene-based polymer obtained by the production method of the present embodiment as the rubber composition containing the rubber-like polymer, a content ratio (in a mass ratio) of the branched conjugated diene-

based polymer described above to the rubber-like polymer is, in terms of (the branched conjugated diene-based polymer/the rubber-like polymer), preferably 10/90 or more and 100/0 or less, more preferably 20/80 or more and 90/10 or less, and further preferably 50/50 or more and 80/20 or less.

Accordingly, the rubber component contains, with respect to the total amount (100% by mass) of the rubber component, preferably 10% by mass or more and 100% by mass or less, more preferably 20% by mass or more and 90% by mass or less, and further preferably 50% by mass or more and 80% by mass or less of the branched conjugated diene-based polymer.

[0184]

If the content ratio of (the branched conjugated diene-based polymer/the rubber-like polymer) falls in the above-described range, there is a tendency that abrasion resistance and fracture strength when in the form of a vulcanizate are excellent, and that balance between a low hysteresis loss property and wet skid resistance is good.

[0185]

Examples of the filler contained in the rubber composition include, but are not limited to, the silica-based inorganic filler as well as carbon black, a metal oxide, and a metal hydroxide. Among these, the silica-based inorganic filler is preferred.

One of these fillers may be singly used, or two or more of these may be used together.

A content of the filler in the rubber composition is 5.0 parts by mass or more and 150 parts by mass or less, preferably 20 parts by mass or more and 100 parts by mass or less, and further preferably 30 parts by mass or more and 90 parts by mass or less with respect to 100 parts by mass of the rubber component containing the branched conjugated diene-based polymer.

From the viewpoint of exhibiting the effect of the filler addition, the content of the filler in the rubber composition is 5.0 parts by mass or more with respect to 100 parts by mass of the rubber component, and from the viewpoint that the filler is sufficiently dispersed to attain practically sufficient workability and mechanical strength of the rubber composition, the content is 150 parts by mass or less with respect to 100 parts by mass of the rubber component.

[0186]

The silica-based inorganic filler is not especially limited, any of known fillers can be used, a solid particle containing SiO_2 or Si_3Al as a constituent unit is preferred, and a solid particle containing SiO_2 or Si_3Al as a principal component of a constituent unit is more preferred. Here, the principal component refers to a component contained in the silica-based inorganic filler in an amount of 50% by mass or more, preferably

70% by mass or more, and more preferably 80% by mass or more.

[0187]

Examples of the silica-based inorganic filler include, but are not limited to, silica, clay, talc, mica, diatomite, wollastonite, montmorillonite, zeolite and inorganic fibrous substances such as glass fiber. Besides, examples include a silica-based inorganic filler having a hydrophobized surface, and a mixture of a silica-based inorganic filler and an inorganic filler excluding silica.

Among these, from the viewpoint of strength and abrasion resistance, silica and glass fiber are preferred, and silica is more preferred.

Examples of the silica include dry silica, wet silica and synthetic silicate silica. Among these silica, wet silica is preferred from the viewpoint that it is excellent in the effect of improving fracture strength and balance in wet skid resistance.

[0188]

From the viewpoint of obtaining practically good abrasion resistance and fracture strength of the rubber composition, a nitrogen adsorption specific surface area, obtained by the BET adsorption method, of the silica-based inorganic filler is preferably 100 m²/g or more and 300 m²/g or less, and more preferably 170 m²/g or more and 250 m²/g or less.

Besides, a silica-based inorganic filler having a comparatively small specific surface area (for example, a specific surface area of $200 \text{ m}^2/\text{g}$ or less) and a silica-based inorganic filler having a comparatively large specific surface area (for example, $200 \text{ m}^2/\text{g}$ or more) can be used in combination if necessary.

If a silica-based inorganic filler having a comparatively large specific surface area (of, for example, $200 \text{ m}^2/\text{g}$ or more) is used in particular, the rubber composition containing the branched conjugated diene-based polymer described above tends to be improved in dispersibility of silica, and be effective particularly in improvement of abrasion resistance, and be capable of well-balanced in good fracture strength and a low hysteresis loss property.

[0189]

A content of the silica-based inorganic filler in the rubber composition is preferably 5.0 parts by mass or more and 150 parts by mass, more preferably 20 parts by mass or more and 100 parts by mass or less with respect to 100 parts by mass of the rubber component containing the branched conjugated diene-based polymer obtained by the production method of the present embodiment. From the viewpoint of exhibiting the effect of the addition of the silica-based inorganic filler, the content of the silica-based inorganic filler in the rubber composition is 5.0 parts by mass or more with respect to 100 parts by

mass of the rubber component, and from the viewpoint that the silica-based inorganic filler is sufficiently dispersed to attain practically sufficient workability and mechanical strength of the rubber composition, the content is preferably 150 parts by mass or less with respect to 100 parts by mass of the rubber component.

[0190]

Examples of the carbon black include, but are not limited to, carbon blacks of SRF, FEF, HAF, ISAF and SAF classes. Among these, a carbon black having a nitrogen adsorption specific surface area of 50 m²/g or more and dibutyl phthalate (DBP) oil absorption of 80 mL/100 g or less is preferred.

[0191]

A content of the carbon black in the rubber composition is preferably 0.5 parts by mass or more and 100 parts by mass or less, more preferably 3.0 parts by mass or more and 100 parts by mass or less, and further preferably 5.0 parts by mass or more and 50 parts by mass or less with respect to 100 parts by mass of the rubber component containing the branched conjugated diene-based polymer obtained by the production method of the present embodiment. From the viewpoint of exhibiting performances required in use as a tire or the like such as dry grip performance and conductivity, the content of the carbon black in the rubber composition is preferably 0.5 parts by mass or more with respect to 100 parts by

mass of the rubber component, and from the viewpoint of dispersibility, the content is preferably 100 parts by mass or less with respect to 100 parts by mass of the rubber component.

[0192]

The metal oxide refers to a solid particle containing a principal component of a constituent unit represented by chemical formula M_xO_y (wherein M represents a metal atom, and x and y each independently represent an integer of 1 to 6).

[0193]

Examples of the metal oxide include, but are not limited to, alumina, titanium oxide, magnesium oxide and zinc oxide.

[0194]

Examples of the metal hydroxide include, but are not limited to, aluminum hydroxide, magnesium hydroxide and zirconium hydroxide.

[0195]

In a production method for a rubber composition of the present embodiment, a step of causing a silane coupling agent to be contained may be performed.

The silane coupling agent has a function to make the interaction between the rubber component and the inorganic filler close. Specifically, it is preferably a compound having a group having affinity with or a binding property to both of the rubber component and the silica-

based inorganic filler, and containing, in one molecule, a sulfur bond portion and an alkoxysilyl group or silanol group portion.

Examples of such a compound include, but are not especially limited to, bis-[3-(triethoxysilyl)-propyl]-tetrasulfide, bis-[3-(triethoxysilyl)-propyl]-disulfide and bis-[2-(triethoxysilyl)-ethyl]-tetrasulfide.

[0196]

In the rubber composition, a content of the silane coupling agent is preferably 0.1 parts by mass or more and 30 parts by mass or less, more preferably 0.5 parts by mass or more and 20 parts by mass or less, and further preferably 1.0 part by mass or more and 15 parts by mass or less with respect to 100 parts by mass of the filler. If the content of the silane coupling agent falls in this range, there is a tendency that the effect of the addition of the silane coupling agent can be more conspicuous.

[0197]

The rubber composition may contain a rubber softener from the viewpoint of improvement of the workability.

An amount of the rubber softener to be added is expressed, with respect to 100 parts by mass of the rubber component containing the branched conjugated diene-based polymer obtained by the production method of the present embodiment, as a total amount of the rubber softener precedently contained in the branched conjugated

diene-based polymer or another rubber-like polymer, and the rubber softener added in producing the rubber composition.

As the rubber softener, a mineral oil or a liquid or low molecular weight synthetic softer is suitably used.

A mineral oil-based rubber softener, which is used for softening, expanding and improving workability of a rubber and is designated as a process oil or an extender oil, is a mixture of an aromatic ring, a naphthene ring and a paraffin chain, and one in which the number of carbon atoms of the paraffin chain is 50% or more of all the carbon atoms is designated as a paraffin-based softener, one in which the number of carbon atoms of the naphthene ring is 30% or more and 45% or less of all the carbon atoms is designated as a naphthene-based softener, and one in which the number of aromatic carbon atoms exceeds 30% of all the carbon atoms is designated as an aromatic-based softener. When the branched conjugated diene-based polymer of the present embodiment is a copolymer of a conjugated diene compound and a vinyl aromatic compound, a rubber softener to be used is preferably one having an appropriate aromatic content because such a softener tends to fit with the branched conjugated diene-based polymer.

In the rubber composition, the content of the rubber softener is, with respect to 100 parts by mass of the rubber component, preferably 0 part by mass or more and

100 parts by mass or less, more preferably 10 parts by mass or more and 90 parts by mass or less, and further preferably 30 parts by mass or more and 90 parts by mass or less. Since the content of the rubber softener is 100 parts by mass or less with respect to 100 parts by mass of the rubber component, there is a tendency that bleeding out is suppressed and stickiness of the surface of the rubber composition is suppressed.

[0198]

Examples of a method for mixing the branched conjugated diene-based polymer obtained by the production method of the present embodiment with another rubber-like polymer, a silica-based inorganic filler, carbon black or another filler, a silane coupling agent, and additives such as a rubber softener include, but are not limited to, a melt-kneading method using a general mixer such as an open roll, a banbury mixer, a kneader, a single shaft screw extruder, a twin shaft screw extruder or a multi-shaft screw extruder, and a method in which the respective components are melted and mixed followed by removal of a solvent by heating.

Among these methods, the melt-kneading method using a roll, a banbury mixer, a kneader or an extruder is preferred from the viewpoint of productivity and high kneadability. Besides, either of a method in which the rubber component, another filler, a silane coupling agent and additives are kneaded all together or a method in

which these are mixed dividedly in plural times is applicable.

[0199]

The rubber composition may be a vulcanized composition having been vulcanized with a vulcanizing agent. Examples of the vulcanizing agent include, but are not limited to, radical generators such as organic peroxides and azo compounds, oxime compounds, nitroso compounds, polyamine compounds, sulfur and sulfur compounds.

In the rubber composition, a content of the vulcanizing agent is preferably 0.01 parts by mass or more and 20 parts by mass or less, and more preferably 0.1 parts by mass or more and 15 parts by mass or less with respect to 100 parts by mass of the rubber component. As a vulcanizing method, any of known methods is applicable, and a vulcanization temperature is preferably 120°C or more and 200°C or less, and more preferably 140°C or more and 180°C or less.

[0200]

For the vulcanization, a vulcanization accelerator may be used if necessary.

As the vulcanization accelerator, any of known materials can be used, and examples include, but are not limited to, sulphenamide-based, guanidine-based, thiuram-based, aldehyde-amine-based, aldehyde-ammonia-based,

thiazole-based, thiourea-based and dithiocarbamate-based vulcanization accelerators.

Besides, examples of the vulcanization aid include, but are not limited to, zinc oxide and stearic acid.

A content of the vulcanization accelerator is preferably 0.01 parts by mass or more and 20 parts by mass or less, and more preferably 0.1 parts by mass or more and 15 parts by mass or less with respect to 100 parts by mass of the rubber component.

[0201]

The rubber composition of the present embodiment may contain, as long as the object of the present embodiment is not impaired, various additives such as another softener excluding those described above, and another filler, a heat resistance stabilizer, an antistatic agent, a weathering stabilizer, an anti-ageing agent, a colorant and a lubricant.

As another softener, any of known softeners can be used.

Examples of another filler include, but are not especially limited to, calcium carbonate, magnesium carbonate, aluminum sulfate and barium sulfate.

As each of the heat resistance stabilizer, the antistatic agent, the weathering stabilizer, the anti-ageing agent, the colorant and the lubricant, any of known materials can be used.

[0202]

[Tire and Production Method for Tire]

A tire of the present embodiment contains the rubber composition of the present embodiment described above.

A production method for a tire of the present embodiment includes a step of obtaining a branched conjugated diene-based polymer by the production method of the present embodiment, a step of obtaining a rubber composition containing the branched conjugated diene-based polymer, and a step of molding the rubber composition.

The rubber composition containing the branched conjugated diene-based polymer obtained by the production method of the present embodiment described above is suitably used as a rubber composition for a tire.

[0203]

The rubber composition for a tire is applicable to, but not limited to, various tires such as a fuel-efficient tire, an all-season tire, a high-performance tire and a studless tire; and various tire portions such as a tread, a carcass, a sidewall and a bead.

Since the rubber composition for a tire containing the branched conjugated diene-based polymer of the present embodiment is excellent in abrasion resistance, fracture strength, and the balance between a low hysteresis loss property and wet skid resistance obtained when in the form of a vulcanizate, it is suitably used as

a tread of a fuel-efficient tire or a high-performance tire.

[Examples]

[0204]

The present embodiment will now be described in more detail with reference to specific examples and comparative examples, and it is noted that the present embodiment is not limited to the following examples and comparative examples at all.

[First Example]

The present embodiment will now be described in detail with reference to specific examples and comparative examples described as a first example.

In the following description, a conjugated diene-based polymer coupled with a nitrogen atom-containing modifier is referred to as a "coupled conjugated diene-based polymer".

A conjugated diene-based polymer in an unmodified state is referred to as an "unmodified conjugated diene-based polymer". In tables, it is shown simply as "Conjugated Diene-based Polymer".

Besides, a conjugated diene-based polymer having a branch structure is referred to as a "branched conjugated diene-based polymer".

Various physical properties described in the examples and comparative examples were measured by the following methods.

[0205]

(Physical Property 1) Mooney Viscosity of Polymer

An unmodified conjugated diene-based polymer or a conjugated diene-based polymer coupled by using a nitrogen atom-containing modifier (hereinafter also referred to as the "coupled conjugated diene-based polymer") was used as a sample to measure a Mooney viscosity by using a Mooney viscometer (trade name "VR1132" manufactured by Ueshima Seisakusho Co., Ltd.) in accordance with ISO 289 with an L-type rotor used.

A measurement temperature was 110°C when an unmodified conjugated diene-based polymer (shown simply as Conjugated Diene-based Polymer in tables) was used as a sample, and was 100°C when a coupled conjugated diene-based polymer was used as a sample.

First, a sample was preheated at the test temperature for 1 minute, the rotor was rotated at 2 rpm, and a torque was measured 4 minutes after as a Mooney viscosity ($ML_{(1+4)}$).

[0206]

(Physical Property 2) Mooney Stress Relaxation Rate

After measuring, by using a coupled conjugated diene-based polymer as a sample, a Mooney viscosity by using a Mooney viscometer (trade name "VR1132"

manufactured by Ueshima Seisakusho Co., Ltd.) in accordance with ISO 289 with an L-type rotor used, the rotation of the rotor was immediately stopped, and the torque in terms of the Mooney unit was recorded every 0.1 seconds from 1.6 seconds to 5 seconds after the stop. The slope of a straight line resulting from double logarithmic plotting of the torque and the time (sec) was obtained, and the absolute value was defined as a Mooney stress relaxation rate (MSR).

[0207]

(Physical Property 3) Branch Number (Bn)

A branch number (Bn) of a coupled conjugated diene-based polymer was measured by a viscosity detector-equipped GPC-light scattering measurement method as follows.

A coupled conjugated diene-based polymer was used as a sample, and a gel permeation chromatography (GPC) measurement apparatus (trade name "GPCmax VE-2001" manufactured by Malvern Panalytical Ltd.) including a series of three columns using a polystyrene-based gel as a filler was used. The measurement was performed by using three detectors, that is, a light scattering detector, an RI detector, and a viscosity detector (trade name "TDA305" manufactured by Malvern Panalytical Ltd.) connected in the stated order. Based on standard polystyrene, an absolute molecular weight was obtained from results obtained by using the light scattering

detector and the RI detector, and an intrinsic viscosity was obtained from results obtained by using the RI detector and the viscosity detector.

A straight-chain polymer was used under assumption of having an intrinsic viscosity $[\eta]$ of $-3.883 M^{0.771}$, and a contracting factor (g') was calculated as a ratio in the intrinsic viscosity corresponding to each molecular weight. It is noted that M herein represents the absolute molecular weight.

Thereafter, the thus obtained contracting factor (g') was used to calculate a branch number (Bn) defined as $g' = 6 Bn / \{ (Bn + 1) (Bn + 2) \}$.

As an eluent, tetrahydrofuran (hereinafter also referred to as "THF") containing 5 mmol/L of triethylamine was used.

As the columns, columns of trade names "TSKgel G4000HXL", "TSKgel G5000HXL" and "TSKgel G6000HXL" manufactured by Tosoh Corporation were connected for use.

Twenty (20) mg of a sample for the measurement was dissolved in 10 mL of THF to obtain a measurement solution, and 100 μ L of the measurement solution was injected into the GPC measurement apparatus for performing the measurement under conditions of an oven temperature of 40°C and a THF flow rate of 1 mL/min.

[0208]

(Physical Property 4) Molecular Weight

<Measurement Conditions 1>

An unmodified conjugated diene-based polymer or a coupled conjugated diene-based polymer used as a sample was measured for a chromatogram using a GPC measurement apparatus (trade name "HLC-8320GPC" manufactured by Tosoh Corporation) including a series of three columns using a polystyrene-based gel as a filler with an RI detector (trade name "HLC8020" manufactured by Tosoh Corporation) used, and on the basis of a calibration curve obtained using standard polystyrene, a weight average molecular weight (M_w), a number average molecular weight (M_n) and a molecular weight distribution (M_w/M_n) were obtained.

As an eluent, THF (tetrahydrofuran) containing 5 mmol/L of triethylamine was used. As the columns, trade name "TSKguardcolumn Super MP(HZ)-H" manufactured by Tosoh Corporation connected, as a guard column at a previous stage, to a series of three columns of trade name "TSKgel Super Multipore HZ-H" manufactured by Tosoh Corporation were used.

Ten (10) mg of a sample for the measurement was dissolved in 10 mL of THF to obtain a measurement solution, and 10 μ L of the measurement solution was injected into the GPC measurement apparatus for performing the measurement under conditions of an oven temperature of 40°C and a THF flow rate of 0.35 mL/min.

Among various samples having been subjected to the measurement under the above-described measurement conditions 1, a sample having a molecular weight

distribution (M_w/M_n) less than 1.6 was subjected again to the measurement under measurement conditions 2 described below. With respect to a sample having been subjected to the measurement under the measurement conditions 1 and found to have a molecular weight distribution value of 1.6 or more, a measured value obtained under the measurement conditions 1 was employed.

<Measurement Conditions 2>:

An unmodified conjugated diene-based polymer or a coupled conjugated diene-based polymer used as a sample was measured for a chromatogram using a GPC measurement apparatus including a series of three columns using a polystyrene-based gel as a filler, and on the basis of a calibration curve obtained using standard polystyrene, a weight average molecular weight (M_w), and a number average molecular weight (M_n) were obtained.

As an eluent, THF containing 5 mmol/L of triethylamine was used. As the columns, a guard column of trade name "TSKguardcolumn Super H-H" manufactured by Tosoh Corporation, and columns of trade names "TSKgel SuperH5000", "TSKgel SuperH6000", and "TSKgel SuperH7000" manufactured by Tosoh Corporation were used.

An RI detector (trade name "HLC8020" manufactured by Tosoh Corporation) was used under conditions of an oven temperature of 40°C and a THF flow rate of 0.6 mL/min. Ten (10) mg of a sample for the measurement was dissolved in 20 mL of THF to obtain a measurement solution, and 20

μL of the measurement solution was injected into the GPC measurement apparatus for performing the measurement.

With respect to a sample having been subjected to the measurement under the measurement conditions 1 and found to have a molecular weight distribution value less than 1.6, the measurement was performed under the measurement conditions 2, and the resultant measured value was employed.

[0209]

(Physical Property 5) Modification Ratio

A modification ratio of a coupled conjugated diene-based polymer was measured by column adsorption GPC as follows.

A coupled conjugated diene-based polymer was used as a sample, and the measurement was performed by applying a characteristic that a modified basic polymer component adsorbs onto a GPC column using a silica-based gel as a filler.

A modification ratio was obtained by measuring an amount of adsorption onto a silica-based column based on a difference between a chromatogram measured by using a polystyrene-based column and a chromatogram measured by using a silica-based column obtained from a sample solution containing a sample and low molecular weight internal standard polystyrene.

Specifically, the measurement was performed as described below.

With respect to a sample having been subjected to the measurement under the measurement conditions 1 of (Physical Property 4) and found to have a molecular weight distribution value of 1.6 or more, the measurement was performed under measurement conditions 3 described below, and the resultant measured value was employed. With respect to a sample having been subjected to the measurement under the measurement conditions 1 of (Physical Property 4) and found to have a molecular weight distribution value less than 1.6, the measurement was performed under measurement conditions 4 described below, and the resultant measured value was employed.

[0210]

<Preparation of Sample Solution>

Ten (10) mg of a sample and 5 mg of standard polystyrene were dissolved in 20 mL of THF to obtain a sample solution.

<Measurement Conditions 3>

GPC measurement conditions using polystyrene-based column:

An apparatus of trade name "HLC-8320GPC" manufactured by Tosoh Corporation was used, THF containing 5 mmol/L of triethylamine was used as an eluent, and 10 μ L of the sample solution was injected into the apparatus to obtain a chromatogram using an RI detector under conditions of a column oven temperature of 40°C and a THF flow rate of 0.35 mL/min.

As the columns, a series of three columns of trade name "TSKgel Super Multipore HZ-H" and a guard column of trade name "TSKguardcolumn SuperMP(HZ)-H" manufactured by Tosoh Corporation connected at a previous stage were used.

[0211]

<Measurement Conditions 4>:

THF containing 5 mmol/L of triethylamine was used as an eluent, and 20 μ L of the sample solution was injected into the apparatus to perform the measurement.

As the columns, a guard column of trade name "TSKguardcolumn Super H-H" manufactured by Tosoh Corporation and columns of trade names "TSKgel Super H5000", "TSKgel Super H6000", and "TSKgel Super H7000" manufactured by Tosoh Corporation were used. A chromatogram was obtained by performing the measurement by using an RI detector (HLC8020, manufactured by Tosoh Corporation) under conditions of a column oven temperature of 40°C and a THF flow rate of 0.6 mL/min.

[0212]

GPC measurement conditions using silica-based column:

An apparatus of trade name "HLC-8320GPC" manufactured by Tosoh Corporation was used, THF was used as an eluent, and 50 μ L of the sample solution was injected into the apparatus to obtain a chromatogram by using an RI detector under conditions of a column oven

temperature of 40°C and a THF flow rate of 0.5 mL/min. A series of columns of trade names "Zorbax PSM-1000S", "PSM-300S" and "PSM-60S", and a guard column of trade name "DIOL 4.6 x 12.5 mm 5 micron" connected at a previous stage were used.

[0213]

Calculation method for modification ratio:

Assuming that the whole peak area of the chromatogram obtained by using the polystyrene-based column was 100, that a peak area of the sample was P1, that a peak area of standard polystyrene was P2, that the whole peak area of the chromatogram obtained by using the silica-based column was 100, that a peak area of the sample was P3, and that a peak area of standard polystyrene was P4, a modification ratio (%) was obtained in accordance with the following expression:

$$\text{Modification ratio (\%)} = [1 - (P2 \times P3) / (P1 \times P4)] \times 100$$

wherein $P1 + P2 = P3 + P4 = 100$.

[0214]

(Physical Property 6) Amount of Bound Styrene

One hundred (100) mg of a coupled conjugated diene-based polymer not containing a rubber softener used as a sample was dissolved in chloroform to be diluted to 100 mL, and the resultant was used as a measurement sample.

Based on the amount of absorption of a phenyl group of styrene at a UV absorption wavelength (about 254 nm),

the amount of bound styrene (% by mass) with respect to 100% by mass of the sample of the coupled conjugated diene-based polymer was measured (measurement apparatus: spectrophotometer "UV-2450" manufactured by Shimadzu Corporation).

[0215]

(Physical Property 7) Microstructure of Butadiene Portion (Amount of 1,2-Vinyl Bond)

Fifty (50) mg of a coupled conjugated diene-based polymer not containing a rubber softener used as a sample was dissolved in 10 mL of carbon disulfide, and the resultant was used as a measurement sample.

A solution cell was used to measure an infrared spectrum in a range of 600 to 1000 cm^{-1} , and in accordance with a calculation formula of the Hampton method (R. R. Hampton, Analytical Chemistry 21, 923 (1949)) based on absorbance at a prescribed wavelength, a microstructure of a butadiene portion, namely, an amount of 1,2-vinyl bond (also referred to as "Amount of 1,2-Vinyl Bond" in the tables) (mol%), was obtained (measurement apparatus: Fourier transform infrared spectrophotometer "FT-IR230" manufactured by JASCO Corporation).

[0216]

(Physical Property 8) Molecular Weight (Absolute Molecular Weight) obtained by GPC-light Scattering Measurement

A coupled conjugated diene-based polymer was used as a sample, and a GPC-light scattering measurement apparatus including a series of three columns using a polystyrene-based gel as a filler was used to measure a chromatogram for obtaining a weight average molecular weight (M_w) (also designated as an "absolute molecular weight") based on a viscosity of a solution and a light scattering method.

As an eluent, a mixed solution of tetrahydrofuran and triethylamine (THF in TEA: prepared by mixing 5 mL of triethylamine in 1 L of tetrahydrofuran) was used.

As the columns, a series of a guard column of trade name "TSKguardcolumn HHR-H" manufactured by Tosoh Corporation, and columns of trade names "TSKgel G6000HHR", "TSKgel G5000HHR", and "TSKgel G4000HHR" were connected and used.

A GPC-light scattering measurement apparatus (trade name "Viscotek TDAmx" manufactured by Malvern Panalytical Ltd.) was used under conditions of an oven temperature of 40°C and a THF flow rate of 1.0 mL/min.

Ten (10) mg of a sample for measurement was dissolved in 20 mL of THF to obtain a measurement solution, and 200 μ L of the measurement solution was injected into the GPC measurement apparatus for the measurement.

[0217]

[Branched Conjugated Diene-based Polymer]

(Example 1-1) Coupled Conjugated Diene-based Polymer
(Sample 1-1)

Two tank pressure vessels, each of which is a stirrer-equipped tank reactor having an internal volume of 10 L and a ratio (L/D) of internal height (L) and diameter (D) of 4.0, having an inlet at a bottom and an outlet at a top, and equipped with a stirrer and a temperature controlling jacket, were connected to each other as polymerization reactors.

1,3-Butadiene, from which a water content had been precedently removed, styrene and n-hexane were mixed under conditions of 18.6 g/min, 10.0 g/min and 175.2 g/min, respectively. In a static mixer provided in the middle of a pipe for supplying the thus obtained mixed solution to the inlet of the reactor, n-butyllithium to be used for residual impurity inactivation was added and mixed in an amount of 0.103 mmol/min, and the resultant was continuously supplied to the bottom of the reactor. Besides, 2,2-bis(2-oxolanyl)propane used as a polar material and n-butyllithium used as a polymerization initiator were supplied, at rates of respectively 0.081 mmol/min and 0.143 mmol/min, to the bottom of the first reactor in which materials were vigorously mixed by the stirrer, and the internal temperature of the reactor was kept at 67°C.

The thus obtained polymer solution was continuously taken out from the top of the first reactor to be

continuously supplied to the bottom of the second reactor for continuing the reaction at 70°C, and the resultant was further supplied to a static mixer from the top of the second reactor. When the polymerization was sufficiently stabilized, while copolymerizing 1,3-butadiene and styrene, trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) used as a branching agent was added at a rate of 0.0190 mmol/min from the bottom of the second reactor to perform a polymerization reaction and a branching reaction for obtaining a conjugated diene-based polymer having a main chain branch structure.

When the polymerization reaction and the branching reaction were stabilized, a small amount of a conjugated diene-based polymer solution prior to addition of a coupling agent was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and a Mooney viscosity at 110°C and various molecular weights were measured. The physical properties are shown in Table 1.

Next, to the polymer solution flowing out of the outlet of the reactor, tetraethoxysilane (shown as "A" in the table) was added, as a coupling agent, continuously at a rate of 0.0480 mmol/min, and the resultant was mixed by using a static mixer for performing a coupling reaction. Here, a time until the addition of the coupling agent to the polymer solution flowing out of the outlet of the reactor was 4.8 min, the temperature was

68°C, and a difference between the temperature in the polymerizing step and the temperature until the addition of the coupling agent was 2°C. After the coupling reaction, a small amount of a conjugated diene-based polymer solution was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and the amount of bound styrene (Physical Property 6) and the microstructure of a butadiene portion (the amount of 1,2-vinyl bond; Physical Property 7) were measured. Measurement results are shown in Table 1.

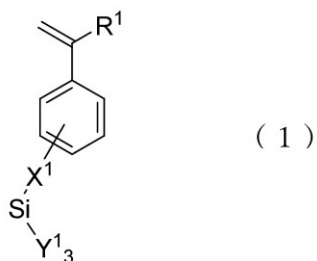
Next, to the polymer solution resulting from the coupling reaction, the antioxidant (BHT) was continuously added in an amount of 0.2 g per 100 g of the polymer at 0.055 g/min (n-hexane solution) to complete the coupling reaction. Simultaneously with the antioxidant, SRAE oil (JOMO Process NC 140, manufactured by JX Nippon Oil & Energy Corporation) was continuously added as a rubber softener in an amount of 25.0 g per 100 g of the polymer, and the resultant was mixed by using a static mixer. The solvent was removed by steam stripping, and thus, a coupled conjugated diene-based polymer (Sample 1-1) having, in a part of a main chain, a 4-branched structure derived from the branching agent corresponding to the compound represented by the formula (1) (hereinafter also referred to as the "branching agent structure (1)") and

having a 3-branched star polymer structure derived from the coupling agent was obtained.

Physical properties of the sample 1-1 are shown in Table 1.

In each of the polymer obtained prior to the addition of the branching agent, the polymer obtained after the addition of the branching agent, and the polymers obtained in the respective steps after the addition of the coupling agent, the structure of the coupled conjugated diene-based polymer was identified based on comparison between a molecular weight measured by GPC and a branch number measured by viscosity detector-equipped GPC. Hereinafter, the structure of each sample was similarly identified.

[0218]



[0219]

In the formula (1), R^1 represents any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms, and may have a branch structure in a part thereof.

X¹ represents a single bond, or an organic group containing any one selected from the group consisting of carbon, hydrogen, nitrogen, sulfur and oxygen.

Y¹ represents any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom. Y¹ is respectively independent, and may be the same or different. [0220]

(Example 1-2) Coupled Conjugated Diene-based Polymer
(Sample 1-2)

A coupled conjugated diene-based polymer (sample 1-2) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to 1,2-bis(triethoxysilyl)ethane (shown as "B" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-2 are shown in Table 1.

[0221]

(Example 1-3) Coupled Conjugated Diene-based Polymer
(Sample 1-3)

A coupled conjugated diene-based polymer (sample 1-3) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1)

and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to 1,3-bis(N,N-diglycidylaminomethyl)cyclohexane (shown as "C" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-3 are shown in Table 1.

[0222]

(Example 1-4) Coupled Conjugated Diene-based Polymer
(Sample 1-4)

A coupled conjugated diene-based polymer (sample 1-4) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-4 are shown in Table 1.

[0223]

(Example 1-5) Coupled Conjugated Diene-based Polymer
(Sample 1-5)

A coupled conjugated diene-based polymer (sample 1-5) having, in a part of a main chain, a 4-branched

structure derived from the branching agent structure (1) and having a 6-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to tris(3-trimethoxysilylpropyl)amine (shown as "E" in the table), and that the amount thereof to be added was changed to 0.0250 mmol/min. Physical properties of the sample 1-5 are shown in Table 1.

[0224]

(Example 1-6) Coupled Conjugated Diene-based Polymer
(Sample 1-6)

A coupled conjugated diene-based polymer (sample 1-6) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0190 mmol/min. Physical properties of the sample 1-6 are shown in Table 1.

[0225]

(Example 1-7) Coupled Conjugated Diene-based Polymer
(Sample 1-7)

A coupled conjugated diene-based polymer (sample 1-7) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 1-7 are shown in Table 1.

[0226]

(Example 1-8) Coupled Conjugated Diene-based Polymer
(Sample 1-8)

A coupled conjugated diene-based polymer (sample 1-8) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the rate of adding 1,3-butadiene was changed from 18.6 g/min to 24.3 g/min, that the rate of adding styrene was changed from 10.0 g/min to 4.3 g/min, that the rate of adding 2,2-bis(2-oxolanyl)propane used as a polar material was changed from 0.081 mmol/min to 0.044 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F"

in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 1-8 are shown in Table 1.

[0227]

(Example 1-9) Coupled Conjugated Diene-based Polymer
(Sample 1-9)

A coupled conjugated diene-based polymer (sample 1-9) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the rate of adding 1,3-butadiene was changed from 18.6 g/min to 17.1 g/min, that the rate of adding styrene was changed from 10.0 g/min to 11.5 g/min, that the rate of adding 2,2-bis(2-oxolanyl)propane used as a polar material was changed from 0.081 mmol/min to 0.089 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 1-9 are shown in Table 2.

[0228]

(Example 1-10) Coupled Conjugated Diene-based
Polymer (Sample 1-10)

A coupled conjugated diene-based polymer (sample 1-10) having, in a part of a main chain, a 4-branched

structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the rate of adding 2,2-bis(2-oxolanyl)propane used as a polar material was changed from 0.081 mmol/min to 0.200 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 1-10 are shown in Table 2.

[0229]

(Example 1-11) Coupled Conjugated Diene-based Polymer (Sample 1-11)

A coupled conjugated diene-based polymer (sample 1-11) having, in a part of a main chain, a 2-branched structure derived from the branching agent structure (1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to dimethylmethoxy(4-vinylphenyl)silane (shown as "BS-2" in the table), that the amount thereof to be added was changed to 0.0350 mmol/min, that the coupling agent was changed from tetraethoxysilane to 1,2-bis(triethoxysilyl)ethane (shown as "B" in the table), and that the amount thereof to be added was changed to

0.0360 mmol/min. Physical properties of the sample 1-11 are shown in Table 2.

[0230]

(Example 1-12) Coupled Conjugated Diene-based Polymer (Sample 1-12)

A coupled conjugated diene-based polymer (sample 1-12) having, in a part of a main chain, a 2-branched structure derived from the branching agent structure (1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to dimethylmethoxy(4-vinylphenyl)silane (shown as "BS-2" in the table), that the amount thereof to be added was changed to 0.0350 mmol/min, that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-12 are shown in Table 2.

[0231]

(Example 1-13) Coupled Conjugated Diene-based Polymer (Sample 1-13)

A coupled conjugated diene-based polymer (sample 1-13) having, in a part of a main chain, a 2-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived

from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to dimethylmethoxy(4-vinylphenyl)silane (shown as "BS-2" in the table), that the amount thereof to be added was changed to 0.0350 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 1-13 are shown in Table 2.

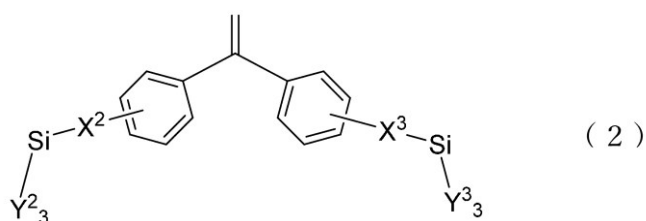
[0232]

(Example 1-14) Coupled Conjugated Diene-based Polymer (Sample 1-14)

A coupled conjugated diene-based polymer (sample 1-14) having, in a part of a main chain, a 3-branched structure derived from the branching agent corresponding to the compound represented by the following formula (2) (hereinafter also referred to as the "branching agent structure (2)") and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-(dimethylmethoxysilyl)phenyl)ethylene (shown as "BS-3" in the table), that the amount thereof to be added was changed to 0.0120 mmol/min, that the coupling agent was

changed from tetraethoxysilane to 1,2-bis(triethoxysilyl)ethane (shown as "B" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-14 are shown in Table 2.

[0233]



[0234]

In the formula (2), X^2 and X^3 represent a single bond, or an organic group containing any one selected from the group consisting of carbon, hydrogen, nitrogen, sulfur, and oxygen.

Y^2 and Y^3 represent any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom. Y^2 and Y^3 are respectively independent, and may be the same or different.

[0235]

(Example 1-15) Coupled Conjugated Diene-based Polymer (Sample 1-15)

A coupled conjugated diene-based polymer (sample 1-15) having, in a part of a main chain, a 3-branched structure derived from the branching agent structure (2)

and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-(dimethylmethoxysilyl)phenyl)ethylene (shown as "BS-3" in the table), that the amount thereof to be added was changed to 0.0120 mmol/min, that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-15 are shown in Table 2.

[0236]

(Example 1-16) Coupled Conjugated Diene-based Polymer (Sample 1-16)

A coupled conjugated diene-based polymer (sample 1-16) having, in a part of a main chain, a 3-branched structure derived from the branching agent structure (2) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-(dimethylmethoxysilyl)phenyl)ethylene (shown as "BS-3" in the table), that the amount thereof to be added was changed to 0.0120 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F"

in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 1-16 are shown in Table 2.

[0237]

(Example 1-17) Coupled Conjugated Diene-based Polymer (Sample 1-17)

A coupled conjugated diene-based polymer (sample 1-17) having, in a part of a main chain, a 7-branched structure derived from the branching agent structure (2) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-trimethoxysilylphenyl)ethylene (shown as "BS-4" in the table), that the amount thereof to be added was changed to 0.0210 mmol/min, that the coupling agent was changed from tetraethoxysilane to 1,2-bis(triethoxysilyl)ethane (shown as "B" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-17 are shown in Table 3.

[0238]

(Example 1-18) Coupled Conjugated Diene-based Polymer (Sample 1-18)

A coupled conjugated diene-based polymer (sample 1-18) having, in a part of a main chain, a 7-branched structure derived from the branching agent structure (2)

and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-trimethoxysilylphenyl)ethylene (shown as "BS-4" in the table), that the amount thereof to be added was changed to 0.0210 mmol/min, that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-18 are shown in Table 3.

[0239]

(Example 1-19) Coupled Conjugated Diene-based Polymer (Sample 1-19)

A coupled conjugated diene-based polymer (sample 1-19) having, in a part of a main chain, a 7-branched structure derived from the branching agent structure (2) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-trimethoxysilylphenyl)ethylene (shown as "BS-4" in the table), that the amount thereof to be added was changed to 0.0210 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F"

in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 1-19 are shown in Table 3.

[0240]

(Example 1-20) Coupled Conjugated Diene-based Polymer (Sample 1-20)

A coupled conjugated diene-based polymer (sample 1-20) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to trichloro(4-vinylphenyl)silane (shown as "BS-5" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, that the coupling agent was changed from tetraethoxysilane to 1,2-bis(triethoxysilyl)ethane (shown as "B" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-20 are shown in Table 3.

[0241]

(Example 1-21) Coupled Conjugated Diene-based Polymer (Sample 1-21)

A coupled conjugated diene-based polymer (sample 1-21) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived

from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to trichloro(4-vinylphenyl)silane (shown as "BS-5" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-21 are shown in Table 3.

[0242]

(Example 1-22) Coupled Conjugated Diene-based Polymer (Sample 1-22)

A coupled conjugated diene-based polymer (sample 1-22) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to trichloro(4-vinylphenyl)silane (shown as "BS-5" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added

was changed to 0.0160 mmol/min. Physical properties of the sample 1-22 are shown in Table 3.

[0243]

(Example 1-23) Coupled Conjugated Diene-based Polymer (Sample 1-23)

A coupled conjugated diene-based polymer (sample 1-23) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the amount of the branching agent trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) to be added was changed from 0.0190 mmol/min to 0.0100 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in a table), and that the amount thereof to be added was changed to 0.0190 mmol/min. Physical properties of the sample 1-23 are shown in Table 3.

[0244]

(Example 1-24) Coupled Conjugated Diene-based Polymer (Sample 1-24)

A coupled conjugated diene-based polymer (sample 1-24) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner

as in Example 1-1 except that the amount of the branching agent trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) to be added was changed from 0.0190 mmol/min to 0.0250 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in a table), and that the amount thereof to be added was changed to 0.0190 mmol/min. Physical properties of the sample 1-24 are shown in Table 4.

[0245]

(Example 1-25) Coupled Conjugated Diene-based Polymer (Sample 1-25)

A coupled conjugated diene-based polymer (sample 1-25) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the amount of the branching agent trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) to be added was changed from 0.0190 mmol/min to 0.0350 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in a table), and that the amount thereof to be added was changed to 0.0190 mmol/min. Physical properties of the sample 1-25 are shown in Table 4.

[0246]

(Example 1-26) Coupled Conjugated Diene-based
Polymer (Sample 1-26)

A coupled conjugated diene-based polymer (sample 1-26) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, and that a liquid rubber (liquid polybutadiene LBR-302, manufactured by Kuraray Co., Ltd.) was added instead of SRAE oil added as the rubber softener. Physical properties of the sample 1-26 are shown in Table 4.

[0247]

(Example 1-27) Coupled Conjugated Diene-based
Polymer (Sample 1-27)

A coupled conjugated diene-based polymer (sample 1-27) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F"

in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, and that a resin (terpene resin YS resin PX1250, manufactured by Yasuhara Chemical Co., Ltd.) was added instead of SRAE oil added as the rubber softener. Physical properties of the sample 1-27 are shown in Table 4.

[0248]

(Example 1-28) Coupled Conjugated Diene-based Polymer (Sample 1-28)

A coupled conjugated diene-based polymer (sample 1-28) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, and that a naphthene oil (naphthene oil Nytex810, manufactured by Nynas) was added instead of SRAE oil added as the rubber softener. Physical properties of the sample 1-28 are shown in Table 4.

[0249]

(Example 1-29) Coupled Conjugated Diene-based Polymer (Sample 1-29)

A coupled conjugated diene-based polymer (sample 1-29) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, and that a rubber softener was not added. Physical properties of the sample 1-29 are shown in Table 4.

[0250]

(Example 1-30) Coupled Conjugated Diene-based Polymer (Sample 1-30)

A coupled conjugated diene-based polymer (sample 1-30) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, and that the amount of SRAE oil to be added as the rubber softener was changed from

25.0 g to 37.5 g per 100 g of the polymer. Physical properties of the sample 1-30 are shown in Table 4.

[0251]

(Example 1-31) Conjugated Diene-based Polymer
(Sample 1-31)

A conjugated diene-based polymer (sample 1-31) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) but not having a star coupled structure derived from a coupling agent was obtained in the same manner as in Example 1-1 except that trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) was added as the branching agent at a rate of 0.190 mmol/min from the bottom of the second reactor when polymerization was sufficiently stabilized, and that a coupling agent was not added. Physical properties of the sample 1-31 are shown in Table 5.

[0252]

(Example 1-32) Coupled Conjugated Diene-based Polymer (Sample 1-32)

A coupled conjugated diene-based polymer (sample 1-32) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having a partially 3-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) was added as the branching agent at a rate of 0.190 mmol/min

from the bottom of the second reactor when polymerization was sufficiently stabilized, and that the amount of tetraethoxysilane (shown as "A" in the table) to be added as the coupling agent was changed from 0.0480 mmol/min to 0.0120 mmol/min. Physical properties of the sample 1-32 are shown in Table 5.

[0253]

(Example 1-33) Coupled Conjugated Diene-based Polymer (Sample 1-33)

A coupled conjugated diene-based polymer (sample 1-33) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having a partially 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) was added as the branching agent at a rate of 0.190 mmol/min from the bottom of the second reactor when polymerization was sufficiently stabilized, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0038 mmol/min. Physical properties of the sample 1-33 are shown in Table 5.

[0254]

(Example 1-34) Coupled Conjugated Diene-based Polymer (Sample 1-34)

A coupled conjugated diene-based polymer (sample 1-34) having, in a part of a main chain, a 2-branched structure derived from the branching agent structure (1) and having a partially 3-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that dimethylmethoxy(4-vinylphenyl)silane (shown as "BS-2" in the table) was added as the branching agent at a rate of 0.0350 mmol/min from the bottom of the second reactor when polymerization was sufficiently stabilized, and that the amount of tetraethoxysilane to be added as the coupling agent was changed from 0.0480 mmol/min to 0.0120 mmol/min. Physical properties of the sample 1-34 are shown in Table 5.

[0255]

(Example 1-35) Coupled Conjugated Diene-based Polymer (Sample 1-35)

A coupled conjugated diene-based polymer (sample 1-35) having, in a part of a main chain, a 3-branched structure derived from the branching agent structure (2) and having a partially 3-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that 1,1-bis(4-(dimethylmethoxysilyl)phenyl)ethylene (shown as "BS-3" in the table) was added as the branching agent at a rate of 0.0120 mmol/min from the bottom of the second reactor when polymerization was sufficiently stabilized, and that

the amount of tetraethoxysilane to be added as the coupling agent was changed from 0.0480 mmol/min to 0.0120 mmol/min. Physical properties of the sample 1-35 are shown in Table 5.

[0256]

(Example 1-36) Coupled Conjugated Diene-based Polymer (Sample 1-36)

A coupled conjugated diene-based polymer (sample 1-36) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having a 2-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the coupling agent was changed from tetraethoxysilane to 3-(benzylideneamino)propyltriethoxysilane (shown as "G" in the table), and that the amount thereof to be added was changed to 0.0620 mmol/min. Physical properties of the sample 1-36 are shown in Table 5.

[0257]

(Example 1-37) Coupled Conjugated Diene-based Polymer (Sample 1-37)

A coupled conjugated diene-based polymer (sample 1-37) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 1-1 except that the amount of 1,3-butadiene

to be added to the first reactor was changed from 18.6 g/min to 13.95 g/min, and that 1,3-butadiene was added in an amount of 4.65 g/min from the bottom of the second reactor at the same time as the branching agent. Physical properties of the sample 1-37 are shown in Table 5.

[0258]

(Example A-1) Coupled Conjugated Diene-based Polymer
(Sample A-1)

Two tank pressure vessels, each of which is a stirrer-equipped tank reactor having an internal volume of 10 L and a ratio (L/D) of internal height (L) and diameter (D) of 4.0, having an inlet at a bottom and an outlet at a top, and equipped with a stirrer and a temperature controlling jacket, were connected to each other as polymerization reactors.

1,3-Butadiene, from which a water content had been precedently removed, styrene and n-hexane were mixed under conditions of 14.0 g/min, 10.0 g/min and 175.2 g/min, respectively.

In a static mixer provided in the middle of a pipe for supplying the thus obtained mixed solution to the inlet of the reactor, n-butyllithium to be used for residual impurity inactivation was added and mixed in an amount of 0.103 mmol/min, and the resultant was continuously supplied to the bottom of the reactor. Besides, 2,2-bis(2-oxolanyl)propane used as a polar

material and n-butyllithium used as a polymerization initiator were supplied, at rates of respectively 0.081 mmol/min and 0.143 mmol/min, to the bottom of the first reactor in which materials were vigorously mixed by the stirrer, and the internal temperature of the reactor was kept at 67°C.

The thus obtained polymer solution was continuously taken out from the top of the first reactor to be continuously supplied to the bottom of the second reactor for continuing the reaction at 70°C, and the resultant was further supplied to a static mixer from the top of the second reactor. When the polymerization was sufficiently stabilized, while copolymerizing 1,3-butadiene and styrene, 1-(4-N,N-dimethylaminophenyl)-1-phenylethylene (shown as "N-1" in the table) used as a nitrogen atom-containing vinyl compound was added at a rate of 0.120 mmol/min and trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) used as a branching agent was added at a rate of 0.0190 mmol/min, from the bottom of the second reactor, and 1,3-butadiene was added in parallel at 4.6 g/min, so as to perform a polymerization reaction and a branching reaction for obtaining a conjugated diene-based polymer having a main chain branch structure.

When the polymerization reaction and the branching reaction were stabilized, a small amount of a modified branched conjugated diene-based polymer solution prior to

addition of a coupling agent was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and a Mooney viscosity at 110°C and various molecular weights were measured. The physical properties are shown in Table 6.

Next, to the polymer solution flowing out of the outlet of the reactor, 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table) was added, as a coupling agent, continuously in an amount to be added of 0.0360 mmol/min, and the resultant was mixed by using a static mixer for performing a coupling reaction.

Here, a time until the addition of the coupling agent to the polymer solution flowing out of the outlet of the reactor was 4.8 min, the temperature was 68°C, and a difference between the temperature in the polymerizing step and the temperature until the addition of the coupling agent was 2°C.

After the coupling reaction, a small amount of a coupled conjugated diene-based polymer solution was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and the amount of bound styrene (Physical Property 6) and the microstructure of a butadiene portion (the amount of 1,2-vinyl bond; Physical Property 7) were measured. Measurement results are shown in Table 6.

Next, to the polymer solution resulting from the coupling reaction, an antioxidant (BHT) was continuously added in an amount of 0.2 g per 100 g of the polymer at 0.055 g/min (n-hexane solution) to complete the coupling reaction.

Simultaneously with the antioxidant, SRAE oil (JOMO Process NC 140, manufactured by JX Nippon Oil & Energy Corporation) was continuously added as a rubber softener in an amount of 25.0 g per 100 g of the polymer, and the resultant was mixed by using a static mixer.

The solvent was removed by steam stripping, and thus, a coupled conjugated diene-based polymer (modified conjugated diene-based polymer) (Sample A-1) having, in a part of a main chain, a 4-branched structure derived from the branching agent corresponding to the compound represented by the formula (1) (hereinafter also referred to as the "branching agent structure (1)") and having a 4-branched star polymer structure derived from the coupling agent was obtained.

Physical properties of the sample A-1 are shown in Table 6.

In each of the polymer obtained prior to the addition of the branching agent, the polymer obtained after the addition of the branching agent, and the polymers obtained in the respective steps after the addition of the coupling agent, the structure of the coupled conjugated diene-based polymer was identified

based on comparison between a molecular weight measured by GPC and a branch number measured by viscosity detector-equipped GPC. Hereinafter, the structure of each sample was similarly identified.

[0259]

(Example A-2) Coupled Conjugated Diene-based Polymer
(Sample A-2)

Two tank pressure vessels, each of which was a stirrer-equipped tank reactor having an internal volume of 10 L and a ratio (L/D) of an internal height (L) and a diameter (D) of 4.0, having an inlet at a bottom and an outlet at a top, and equipped with a stirrer and a temperature controlling jacket, were connected to each other as polymerization reactors.

1,3-Butadiene, from which a water content had been precedently removed, styrene and n-hexane were mixed under conditions of 14.0 g/min, 8.0 g/min and 175.2 g/min, respectively.

In a static mixer provided in the middle of a pipe for supplying the thus obtained mixed solution to the inlet of the reactor, n-butyllithium to be used for residual impurity inactivation was added and mixed in an amount of 0.103 mmol/min, and the resultant was continuously supplied to the bottom of the reactor. Besides, 2,2-bis(2-oxolanyl)propane used as a polar material and n-butyllithium used as a polymerization initiator were supplied, at rates of respectively 0.081

mmol/min and 0.143 mmol/min, to the bottom of the first reactor in which materials were vigorously mixed by the stirrer, and the internal temperature of the reactor was kept at 67°C.

The thus obtained polymer solution was continuously taken out from the top of the first reactor to be continuously supplied to the bottom of the second reactor for continuing the reaction at 70°C, and the resultant was further supplied to a static mixer from the top of the second reactor. When the polymerization was sufficiently stabilized, while copolymerizing 1,3-butadiene and styrene, 1-(4-N,N-dimethylaminophenyl)-1-phenylethylene (shown as "N-1" in the table) used as a nitrogen atom-containing vinyl compound was added at a rate of 0.120 mmol/min from the bottom of the second reactor and trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) used as a branching agent was added at a rate of 0.0190 mmol/min from the bottom of the second reactor, and 1,3-butadiene and styrene were added in parallel at 4.6 g/min and 2.0 g/min, respectively, so as to perform a polymerization reaction and a branching reaction for obtaining a conjugated diene-based polymer having a main chain branch structure.

When the polymerization reaction and the branching reaction were stabilized, a small amount of a conjugated diene-based polymer solution prior to addition of a coupling agent was taken out, an antioxidant (BHT) was

added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and a Mooney viscosity at 110°C and various molecular weights were measured. The physical properties are shown in Table 6.

Next, to the polymer solution flowing out of the outlet of the reactor, 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table) was added, as a coupling agent, continuously in an amount to be added of 0.0360 mmol/min, and the resultant was mixed by using a static mixer for performing a coupling reaction.

Here, a time until the addition of the coupling agent to the polymer solution flowing out of the outlet of the reactor was 4.8 min, the temperature was 68°C, and a difference between the temperature in the polymerizing step and the temperature until the addition of the coupling agent was 2°C. A small amount of a conjugated diene-based polymer solution after the coupling reaction was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and the amount of bound styrene (Physical Property 6) and the microstructure of a butadiene portion (the amount of 1,2-vinyl bond; Physical Property 7) were measured. Measurement results are shown in Table 6.

Next, to the polymer solution resulting from the coupling reaction, an antioxidant (BHT) was continuously

added in an amount of 0.2 g per 100 g of the polymer at 0.055 g/min (n-hexane solution) to complete the coupling reaction.

Simultaneously with the antioxidant, SRAE oil (JOMO Process NC 140, manufactured by JX Nippon Oil & Energy Corporation) was continuously added as a rubber softener in an amount of 25.0 g per 100 g of the polymer, and the resultant was mixed by using a static mixer.

The solvent was removed by steam stripping, and thus, a coupled conjugated diene-based polymer (Sample A-2) having, in a part of a main chain, a 4-branched structure derived from the branching agent corresponding to the compound represented by the formula (1) (hereinafter also referred to as the "branching agent structure (1)") and having a 4-branched star polymer structure derived from the coupling agent was obtained.

Physical properties of the sample A-2 are shown in Table 6.

In each of the polymer obtained prior to the addition of the branching agent, the polymer obtained after the addition of the branching agent, and the polymers obtained in the respective steps after the addition of the coupling agent, the structure of the coupled conjugated diene-based polymer was identified based on comparison between a molecular weight measured by GPC and a branch number measured by viscosity detector-equipped GPC.

[0260]

(Example A-3) Coupled Conjugated Diene-based Polymer
(Sample A-3)

Two tank pressure vessels, each of which was a stirrer-equipped tank reactor having an internal volume of 10 L and a ratio (L/D) of an internal height (L) and a diameter (D) of 4.0, having an inlet at a bottom and an outlet at a top, and equipped with a stirrer and a temperature controlling jacket, were connected to each other as polymerization reactors.

1,3-Butadiene, from which a water content had been precedently removed, styrene and n-hexane were mixed under conditions of 18.6 g/min, 10.0 g/min and 175.2 g/min, respectively.

In a static mixer provided in the middle of a pipe for supplying the thus obtained mixed solution to the inlet of the reactor, n-butyllithium to be used for residual impurity inactivation was added and mixed in an amount of 0.103 mmol/min, and the resultant was continuously supplied to the bottom of the reactor. Besides, 2,2-bis(2-oxolanyl)propane used as a polar material and n-butyllithium used as a polymerization initiator were supplied, at rates of respectively 0.081 mmol/min and 0.143 mmol/min, to the bottom of the first reactor in which materials were vigorously mixed by the stirrer, and the internal temperature of the reactor was kept at 67°C.

The thus obtained polymer solution was continuously taken out from the top of the first reactor to be continuously supplied to the bottom of the second reactor for continuing the reaction at 70°C, and the resultant was further supplied to a static mixer from the top of the second reactor. When the polymerization was sufficiently stabilized, while copolymerizing 1,3-butadiene and styrene, trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) as a branching agent was added at a rate of 0.0190 mmol/min from the bottom of the second reactor to perform a polymerization reaction and a branching reaction for obtaining a conjugated diene-based polymer having a main chain branch structure.

When the polymerization reaction and the branching reaction were stabilized, a small amount of a branched conjugated diene-based polymer solution prior to addition of a coupling agent was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and a Mooney viscosity at 110°C and various molecular weights were measured. The physical properties are shown in Table 6.

Next, to the polymer solution flowing out of the outlet of the reactor, a coupling agent (shown as "Z-1" in the table) represented by the following (Z-1) was used, as a coupling agent, in an amount to be added of 0.0360 mmol/min. The resultant was mixed by using a static mixer for performing a coupling reaction. Here, a

time until the addition of the coupling agent to the polymer solution flowing out of the outlet of the reactor was 4.8 min, the temperature was 68°C, and a difference between the temperature in the polymerizing step and the temperature until the addition of the coupling agent was 2°C. A small amount of a conjugated diene-based polymer solution after the coupling reaction was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and the amount of bound styrene (Physical Property 6) and the microstructure of a butadiene portion (the amount of 1,2-vinyl bond; Physical Property 7) were measured. Measurement results are shown in Table 6.

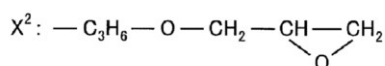
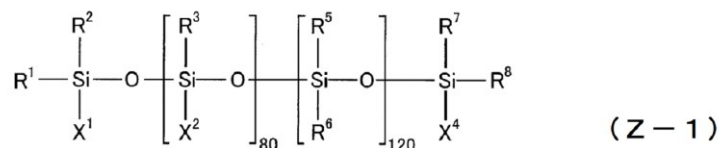
Next, to the polymer solution resulting from the coupling reaction, the antioxidant (BHT) was continuously added in an amount of 0.2 g per 100 g of the polymer at 0.055 g/min (n-hexane solution) to complete the coupling reaction. Simultaneously with the antioxidant, SRAE oil (JOMO Process NC 140, manufactured by JX Nippon Oil & Energy Corporation) was continuously added as a rubber softener in an amount of 25.0 g per 100 g of the polymer, and the resultant was mixed by using a static mixer. The solvent was removed by steam stripping, and thus, a coupled conjugated diene-based polymer (sample A-3) having, in a part of a main chain, a 4-branched structure derived from the branching agent and having a 3-branched

star polymer structure derived from the coupling agent was obtained.

Physical properties of the sample A-3 are shown in Table 6.

In each of the polymer obtained prior to the addition of the branching agent, the polymer obtained after the addition of the branching agent, and the polymers obtained in the respective steps after the addition of the coupling agent, the structure of the coupled conjugated diene-based polymer was identified based on comparison between a molecular weight measured by GPC and a branch number measured by viscosity detector-equipped GPC.

[0261]



[0262]

[Coupled Conjugated Diene-based Polymer]

(Comparative Example 1-1) Coupled Conjugated Diene-based Polymer (Sample 1-38)

Two tank pressure vessels, each of which was a stirrer-equipped tank reactor having an internal volume of 10 L and a ratio (L/D) of an internal height (L) and a

diameter (D) of 4.0, having an inlet at a bottom and an outlet at a top, and equipped with a stirrer and a temperature controlling jacket, were connected to each other as polymerization reactors.

1,3-Butadiene, from which a water content had been precedently removed, styrene and n-hexane were mixed under conditions of 18.6 g/min, 10.0 g/min and 175.2 g/min, respectively. In a static mixer provided in the middle of a pipe for supplying the thus obtained mixed solution to the inlet of the reactor, n-butyllithium to be used for residual impurity inactivation was added and mixed in an amount of 0.103 mmol/min, and the resultant was continuously supplied to the bottom of the reactor. Besides, 2,2-bis(2-oxolanyl)propane used as a polar material and n-butyllithium used as a polymerization initiator were supplied, at rates of respectively 0.081 mmol/min and 0.143 mmol/min, to the bottom of the first reactor in which materials were vigorously mixed by the stirrer, and the internal temperature of the reactor was kept at 67°C.

The thus obtained polymer solution was continuously taken out from the top of the first reactor to be continuously supplied to the bottom of the second reactor for continuing the reaction at 70°C, and the resultant was further supplied to a static mixer from the top of the second reactor. When polymerization was sufficiently stabilized, a small amount of a polymer solution prior to

addition of a coupling agent was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and a Mooney viscosity at 110°C and various molecular weights were measured. The physical properties are shown in Table 7.

Next, to the polymer solution flowing out of the outlet of the reactor, tetraethoxysilane (shown as "A" in the table) was added, as a coupling agent, continuously at a rate of 0.0480 mmol/min, and the resultant was mixed by using a static mixer for performing a coupling reaction. Here, a time until the addition of the coupling agent to the polymer solution flowing out of the outlet of the reactor was 4.8 min, the temperature was 68°C, and a difference between the temperature in the polymerizing step and the temperature until the addition of the coupling agent was 2°C. A small amount of a conjugated diene-based polymer solution after the coupling reaction was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and the amount of bound styrene (Physical Property 6) and the microstructure of a butadiene portion (the amount of 1,2-vinyl bond; Physical Property 7) were measured. Measurement results are shown in Table 7.

Next, to the polymer solution resulting from the coupling reaction, an antioxidant (BHT) was continuously

added in an amount of 0.2 g per 100 g of the polymer at 0.055 g/min (n-hexane solution) to complete the coupling reaction. Simultaneously with the antioxidant, SRAE oil (JOMO Process NC 140, manufactured by JX Nippon Oil & Energy Corporation) was continuously added as a rubber softener in an amount of 25.0 g per 100 g of the polymer, and the resultant was mixed by using a static mixer. The solvent was removed by steam stripping, and thus, a coupled conjugated diene-based polymer (Sample 1-38) not having a main chain branch derived from a branching agent but having a 3-branched star polymer structure derived from the coupling agent was obtained. Physical properties of the sample 1-38 are shown in Table 7.

[0263]

(Comparative Example 1-2) Coupled Conjugated Diene-based Polymer (Sample 1-39)

A coupled conjugated diene-based polymer (sample 1-39) not having a main chain branch derived from a branching agent but having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Comparative Example 1-1 except that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 1-39 are shown in Table 7.

[0264]

(Comparative Example 1-3) Coupled Conjugated Diene-based Polymer (Sample 1-40)

A coupled conjugated diene-based polymer (sample 1-40) not having a main chain branch derived from a branching agent but having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Comparative Example 1-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0190 mmol/min. Physical properties of the sample 40 are shown in Table 7.

[0265]

(Comparative Example B-1) Coupled Conjugated Diene-based Polymer (Sample B-1)

Two tank pressure vessels, each of which was a stirrer-equipped tank reactor having an internal volume of 10 L and a ratio (L/D) of an internal height (L) and a diameter (D) of 4.0, having an inlet at a bottom and an outlet at a top, and equipped with a stirrer and a temperature controlling jacket, were connected to each other as polymerization reactors.

1,3-Butadiene, from which a water content had been precedently removed, styrene and n-hexane were mixed under conditions of 18.6 g/min, 10.0 g/min and 175.2 g/min, respectively.

In a static mixer provided in the middle of a pipe for supplying the thus obtained mixed solution to the inlet of the reactor, n-butyllithium to be used for residual impurity inactivation was added and mixed in an amount of 0.103 mmol/min, and the resultant was continuously supplied to the bottom of the reactor. Besides, 2,2-bis(2-oxolanyl)propane used as a polar material and n-butyllithium used as a polymerization initiator were supplied, at rates of respectively 0.081 mmol/min and 0.143 mmol/min, to the bottom of the first reactor in which materials were vigorously mixed by the stirrer, and the internal temperature of the reactor was kept at 67°C.

The thus obtained polymer solution was continuously taken out from the top of the first reactor to be continuously supplied to the bottom of the second reactor for continuing the reaction at 70°C, and the resultant was further supplied to a static mixer from the top of the second reactor.

When the polymerization was stabilized, a small amount of a polymer solution prior to addition of a coupling agent was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and a Mooney viscosity at 110°C and various molecular weights were measured. The physical properties are shown in Table 8.

Next, to the polymer solution flowing out of the outlet of the reactor, trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) was added at a rate of 0.0190 mmol/min, and simultaneously, tetraethoxysilane (shown as "A" in the table) was continuously added at a rate of 0.0480 mmol/min, and the resultant was mixed by using a static mixer to perform a coupling reaction.

Here, a time until the addition of the coupling agent to the polymer solution flowing out of the outlet of the reactor was 4.8 min, the temperature was 68°C, and a difference between the temperature in the polymerizing step and the temperature until the addition of the coupling agent was 2°C. After the coupling reaction, a small amount of a conjugated diene-based polymer solution was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and the amount of bound styrene (Physical Property 6) and the microstructure of a butadiene portion (the amount of 1,2-vinyl bond; Physical Property 7) were measured. Measurement results are shown in Table 8.

Next, to the polymer solution resulting from the coupling reaction, the antioxidant (BHT) was continuously added in an amount of 0.2 g per 100 g of the polymer at 0.055 g/min (n-hexane solution) to complete the coupling reaction.

Simultaneously with the antioxidant, SRAE oil (JOMO Process NC 140, manufactured by JX Nippon Oil & Energy Corporation) was continuously added as a rubber softener in an amount of 25.0 g per 100 g of the polymer, and the resultant was mixed by using a static mixer. The solvent was removed by steam stripping, and thus, a coupled conjugated diene-based polymer (modified conjugated diene-based polymer) (sample B-1) was obtained. Physical properties of the sample B-1 are shown in Table 8.

Although "BS-1" is shown in the column of the branching agent of (Comparative Example B-1) in Table 8 below, a main chain branch point could not be formed, and it did not work as the branching agent when the addition method of this example in which "BS-1" and "A" are simultaneously added was employed.

It was supposed with respect to (Comparative Example B-1) that, since the "BS-1" was added after the monomer was consumed, almost no monomer to be polymerized with a vinyl group of the "BS-1" was present after an active end was bound to a methoxy group of the "BS-1". In other words, no "branching step" occurred due to the absence of any monomer even in addition of the "BS-1".

It can be confirmed from the contracting factor of (Sample B-1) that branching is formed only within the number of functional groups of the coupling agent, and it is considered that there is not occurred any increase in

branch number due to one polymer having both a main chain branch structure with the "BS-1" and a coupled structure.

In each of the polymer obtained prior to the addition of "BS-1", the polymer obtained after the addition of "BS-1", and the polymers obtained in the respective steps after the addition of "A", the structure of the coupled conjugated diene-based polymer was identified based on comparison between a molecular weight measured by GPC and a branch number measured by viscosity detector-equipped GPC.

[0266]

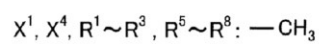
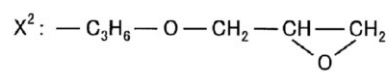
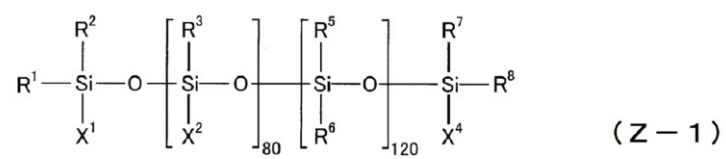
(Comparative Example B-2) Coupled Conjugated Diene-based Polymer (Sample B-2)

A branching agent was not used.

Besides, a coupling agent (shown as "Z-1" in the table) represented by the following formula (Z-1) was used as the coupling agent, and the amount thereof to be added was 0.0360 mmol/min. In the same conditions as in Comparative Example B-1 except for these, a coupled conjugated diene-based polymer (modified conjugated diene-based polymer) (Sample B-2) not having a main chain branch derived from the branching agent but having a 10-branched star polymer structure derived from the coupling agent was obtained.

Physical properties of the sample B-2 are shown in Table 8.

[0267]



[0268]

[Table 1]

		Example 1-1	Example 1-2	Example 1-3	Example 1-4	Example 1-5	Example 1-6	Example 1-7	Example 1-8		
Polymerization Conditions	Branched Conjugated Diene-based Polymer (Sample No.)										
		Butadiene	(g/min)	18.6	18.6	18.6	18.6	18.6	18.6	18.6	18.6
		Styrene	(g/min)	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
		n-Hexane	(g/min)	175.2	175.2	175.2	175.2	175.2	175.2	175.2	175.2
	Polymerization Temperature		(°C)	70	70	70	70	70	70	70	
		n-Butyllithium for Treatment	(mmol/min)	0.103	0.103	0.103	0.103	0.103	0.103	0.103	0.103
		n-Butyllithium as Polymerization Initiator	(mmol/min)	0.143	0.143	0.143	0.143	0.143	0.143	0.143	0.143
		Amount of Polar Material Added	(mmol/min)	0.081	0.081	0.081	0.081	0.081	0.081	0.081	0.081
			Type	BS-1	BS-1	BS-1	BS-1	BS-1	BS-1	BS-1	BS-1
	Branching Agent	Amount Added	(mmol/min)	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190
Physical Property Values	Coupling Agent	Type	A	B	C	D	E	F	F	F	
		Amount Added	(mmol/min)	0.048	0.0360	0.0360	0.0360	0.0250	0.0190	0.0160	0.0160
	Conjugated Diene-based Polymer	(Physical Property 4) Weight Average Molecular Weight	(10 ⁴ g/mol)	63.9	63.9	63.9	63.9	63.9	63.9	63.9	62.3
		(Physical Property 4) Number Average Molecular Weight	(10 ⁴ g/mol)	33.1	33.1	33.1	33.1	33.1	33.1	33.1	32.7
		(Physical Property 4) Mw/Mn		1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93
		(Physical Property 1) Mooney Viscosity (110°C)		92.1	92.1	92.1	92.1	92.1	92.1	92.1	89.4
		Type of Rubber Softener		SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE
	Coupled Conjugated Diene-based Polymer	Amount of Rubber Softener Added	(phm)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
		(Physical Property 1) Mooney Viscosity (100°C)		91	98	99	98	98	97	95	93
		(Physical Property 2) Mooney Relaxation Rate (100°C)		0.264	0.253	0.252	0.253	0.253	0.255	0.258	0.261
(Physical Property 3) Branch Number Bn		per molecule	8.2	8.8	8.8	8.7	12.0	15.8	20.0	19.2	
(Physical Property 4) Weight Average Molecular Weight		(10 ⁴ g/mol)	89.3	92.1	92.3	92.0	96.0	105.3	106.0	105.8	
	(Physical Property 4) Number Average Molecular Weight	(10 ⁴ g/mol)	45.6	46.6	46.8	46.7	48.7	53.4	54.6	54.8	
	(Physical Property 4) Mw/Mn		1.96	1.98	1.97	1.97	1.97	1.97	1.94	1.93	
	(Physical Property 5) Modification Ratio	(%)	-	-	87	88	86	86	82	84	
	(Physical Property 6) Amount of Bound Styrene	(mass%)	35	35	35	35	35	35	35	15	
	(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	(mol%)	40	40	40	40	40	40	40	28	
	(Physical Property 8) Absolute Molecular Weight (Mw-i)	(10 ⁴ Daltons)	132	142	148	144	170	186	281	273	

[0269]

[Table 2]

		Example 1-9	Example 1-10	Example 1-11	Example 1-12	Example 1-13	Example 1-14	Example 1-15	Example 1-16		
Polymerization Conditions	Branched Conjugated Diene-based Polymer (Sample No.)										
	Butadiene	(g/min)	17.1	18.6	18.6	18.6	18.6	18.6	18.6	18.6	
	Styrene	(g/min)	11.5	10.0	10.0	10.0	10.0	10.0	10.0	10.0	
	n-Hexane	(g/min)	175.2	175.2	175.2	175.2	175.2	175.2	175.2	175.2	
	Polymerization Temperature		(°C)	70	70	70	70	70	70	70	
	n-Butyllithium for Treatment		(mmol/min)	0.103	0.103	0.103	0.103	0.103	0.103	0.103	
	n-Butyllithium as Polymerization Initiator		(mmol/min)	0.143	0.143	0.143	0.143	0.143	0.143	0.143	
	Amount of Polar Material Added		(mmol/min)	0.089	0.2	0.081	0.081	0.081	0.081	0.081	
	Branching Agent	Type	BS-1	BS-1	BS-2	BS-2	BS-2	BS-3	BS-3	BS-3	
	Coupling Agent	Amount Added	(mmol/min)	0.0190	0.0190	0.0350	0.0350	0.0350	0.0120	0.0120	
Physical Property Values	Coupling Agent	Type	F	F	B	D	F	B	D	F	
	Conjugated Diene-based Polymer	Amount Added	(mmol/min)	0.0160	0.0160	0.0360	0.0360	0.0160	0.0360	0.0160	
		(Physical Property 4) Weight Average Molecular Weight	(10 ⁴ g/mol)	64.2	64.7	60.3	60.3	60.3	74.5	74.5	74.5
		(Physical Property 4) Number Average Molecular Weight	(10 ⁴ g/mol)	33.5	33.8	32.2	32.2	32.2	37.8	37.8	37.8
		(Physical Property 4) Mw/Mn		1.93	1.93	1.87	1.87	1.87	1.97	1.97	1.97
	Coupled Conjugated Diene-based Polymer	(Physical Property 1) Mooney Viscosity (110°C)		93.8	95.1	88.2	88.2	88.2	99.1	99.1	99.1
		Type of Rubber Softener		SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE
		Amount of Rubber Softener Added	(phm)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
		(Physical Property 1) Mooney Viscosity (100°C)		96	99	93	94	97	94	96	82
		(Physical Property 2) Mooney Relaxation Rate (100°C)		0.256	0.252	0.261	0.260	0.255	0.260	0.256	0.280
(Physical Property 3) Branch Number Bn		per molecule	21.6	22.3	8.2	8.2	13.0	17.4	18.0	30.0	
Coupled Conjugated Diene-based Polymer	(Physical Property 4) Weight Average Molecular Weight	(10 ⁴ g/mol)	107.0	107.4	91.7	#REF!	#REF!	112.6	115.0	135.0	
	(Physical Property 4) Number Average Molecular Weight	(10 ⁴ g/mol)	55.4	54.2	46.5	#REF!	#REF!	56.9	57.2	69.6	
	(Physical Property 4) Mw/Mn		1.93	1.98	1.97	1.98	1.93	1.98	2.01	1.94	
	(Physical Property 5) Modification Ratio	(%)	82	81	-	85	81	-	82	85	
	(Physical Property 6) Amount of Bound Styrene	(mass%)	40	35	35	35	35	35	35	35	
	(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	(mol%)	40	58	40	40	40	40	40	40	
	(Physical Property 8) Absolute Molecular Weight (Mw-i)	(10 ⁴ Daltons)	287	291	133	136	176	153	160	335	

[0270]

[Table 3]

		Example 1-17	Example 1-18	Example 1-19	Example 1-20	Example 1-21	Example 1-22	Example 1-23
Polymerization Conditions	Branched Conjugated Diene-based Polymer (Sample No.)							
		Butadiene	(g/min)	18.6	18.6	18.6	18.6	18.6
		Styrene	(g/min)	10.0	10.0	10.0	10.0	10.0
		n-Hexane	(g/min)	175.2	175.2	175.2	175.2	175.2
		Polymerization Temperature	(°C)	70	70	70	70	70
		n-Butyllithium for Treatment	(mmol/min)	0.103	0.103	0.103	0.103	0.103
		n-Butyllithium as Polymerization Initiator	(mmol/min)	0.143	0.143	0.143	0.143	0.143
		Amount of Polar Material Added	(mmol/min)	0.081	0.081	0.081	0.081	0.081
	Branching Agent	Type	BS-4	BS-4	BS-5	BS-5	BS-5	BS-1
	Coupling Agent	Amount Added	0.0210	0.0210	0.0190	0.0190	0.0190	0.0100
Physical Property Values	Conjugated Diene-based Polymer	Type	B	F	B	D	F	F
		Amount Added	0.0360	0.0360	0.0360	0.0360	0.0160	0.0190
		(Physical Property 4) Weight Average Molecular Weight	61.5	61.5	63.9	63.9	63.9	55.9
		(Physical Property 4) Number Average Molecular Weight	31.1	31.1	33.1	33.1	33.1	28.5
		(Physical Property 4) Mw/Mn	1.98	1.98	1.93	1.93	1.93	1.96
	Coupled Conjugated Diene-based Polymer	(Physical Property 1) Mooney Viscosity (110°C)	90.6	90.6	92.1	92.1	92.1	88.1
		Type of Rubber Softener	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE
		Amount of Rubber Softener Added	25.0	25.0	25.0	25.0	25.0	25.0
		(Physical Property 1) Mooney Viscosity (100°C)	95	97	99	99	101	102
		(Physical Property 2) Mooney Relaxation Rate (100°C)	0.258	0.255	0.252	0.252	0.248	0.247
		(Physical Property 3) Branch Number Bn	8.4	8.5	14.2	8.4	8.7	15.8
		(Physical Property 4) Weight Average Molecular Weight	90.3	91.0	102.3	90.6	92.0	105.3
		(Physical Property 4) Number Average Molecular Weight	45.8	46.0	51.9	45.8	46.7	50.6
		(Physical Property 4) Mw/Mn	1.97	1.98	1.97	1.98	1.97	1.94
		(Physical Property 5) Modification Ratio	-	82	62	-	88	92
		(Physical Property 6) Amount of Bound Styrene	35	35	35	35	35	35
		(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	40	40	40	40	40	40
		(Physical Property 8) Absolute Molecular Weight (Mw-i)	128	135	184	138	144	245

[0271]

[Table 4]

		Example 1-24	Example 1-25	Example 1-26	Example 1-27	Example 1-28	Example 1-29	Example 1-30
Polymerization Conditions	Branched Conjugated Diene-based Polymer (Sample No.)							
		Butadiene	(g/min)	18.6	18.6	18.6	18.6	18.6
		Styrene	(g/min)	10.0	10.0	10.0	10.0	10.0
		n-Hexane	(g/min)	175.2	175.2	175.2	175.2	175.2
		Polymerization Temperature	(°C)	70	70	70	70	70
		n-Butyllithium for Treatment	(mmol/min)	0.103	0.103	0.103	0.103	0.103
		n-Butyllithium as Polymerization Initiator	(mmol/min)	0.143	0.143	0.143	0.143	0.143
		Amount of Polar Material Added	(mmol/min)	0.081	0.081	0.081	0.081	0.081
	Branching Agent	Type	BS-1	BS-1	BS-1	BS-1	BS-1	BS-1
	Coupling Agent	Amount Added	0.0250	0.0350	0.0190	0.0190	0.0190	0.0190
Physical Property Values	Conjugated Diene-based Polymer	Type	F	F	F	F	F	F
		Amount Added	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190
		(Physical Property 4) Weight Average Molecular Weight	78.8	89.3	63.9	63.9	63.9	63.9
		(Physical Property 4) Number Average Molecular Weight	40.1	45.1	33.1	33.1	33.1	33.1
		(Physical Property 4) Mw/Mn	1.97	1.98	1.93	1.93	1.93	1.93
	Coupled Conjugated Diene-based Polymer	(Physical Property 1) Mooney Viscosity (110°C)	98.1	105.3	92.1	92.1	92.1	92.1
		Type of Rubber Softener	SRAE	SRAE	Liquid rubber	Resin	Naphthenic oil	SRAE
		Amount of Rubber Softener Added	25.0	25.0	25.0	25.0	0.0	37.5
		(Physical Property 1) Mooney Viscosity (100°C)	105	107	92	101	103	83
		(Physical Property 2) Mooney Relaxation Rate (100°C)	0.242	0.239	0.263	0.248	0.245	0.296
	Coupled Conjugated Diene-based Polymer	(Physical Property 3) Branch Number Bn	25.3	30.1	15.8	15.8	15.8	15.8
		(Physical Property 4) Weight Average Molecular Weight	117.0	125.0	105.3	105.3	105.3	105.3
		(Physical Property 4) Number Average Molecular Weight	59.7	62.2	53.4	53.4	53.4	53.4
		(Physical Property 4) Mw/Mn	1.96	2.01	1.97	1.97	1.97	1.97
		(Physical Property 5) Modification Ratio	75	68	86	86	86	86
	(Physical Property 6) Amount of Bound Styrene Bond	(mass%)	35	35	35	35	35	35
		(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	40	40	40	40	40	40
		(Physical Property 8) Absolute Molecular Weight (Mw-i)	320	360	186	186	186	186

[0272]

[Table 5]

		Example 1-31	Example 1-32	Example 1-33	Example 1-34	Example 1-35	Example 1-36	Example 1-37
Branched Conjugated Diene-based Polymer (Sample No.)		1-31	1-32	1-33	1-34	1-35	1-36	1-37
Polymerization Conditions	Butadiene	18.6	18.6	18.6	18.6	18.6	18.6	18.6
	Styrene	10.0	10.0	10.0	10.0	10.0	10.0	10.0
	n-Hexane	175.2	175.2	175.2	175.2	175.2	175.2	175.2
	Polymerization Temperature	70	70	70	70	70	70	70
	n-Butyllithium for Treatment	0.103	0.103	0.103	0.103	0.103	0.103	0.103
	n-Butyllithium as Polymerization Initiator	0.143	0.143	0.143	0.143	0.143	0.143	0.143
	Amount of Polar Material Added	0.081	0.081	0.081	0.081	0.081	0.081	0.081
	Type	BS-1	BS-1	BS-1	BS-2	BS-3	BS-1	BS-1
	Amount Added	0.0190	0.0190	0.0190	0.0350	0.0120	0.0190	0.0190
	Type	-	A	F	A	A	G	A
Physical Property Values	Amount Added	-	0.0120	0.0038	0.0120	0.0120	0.0620	0.048
	(Physical Property 4) Weight Average Molecular Weight	63.9	63.9	63.9	63.9	63.9	63.9	63.9
	(Physical Property 4) Number Average Molecular Weight	33.1	33.1	33.1	33.1	33.1	33.1	33.1
	(Physical Property 4) Mw/Mn	1.93	1.93	1.93	1.93	1.93	1.93	1.93
	(Physical Property 1) Mooney Viscosity (110°C)	92.1	92.1	92.1	92.1	92.1	92.1	95.1
	Type of Rubber Softener	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE
	Amount of Rubber Softener Added	25.0	25.0	25.0	25.0	25.0	25.0	25.0
	(Physical Property 1) Mooney Viscosity (100°C)	52	65	74	53	60	91	91
	(Physical Property 2) Mooney Relaxation Rate (100°C)	0.655	0.617	0.591	0.652	0.632	0.264	0.260
	(Physical Property 3) Branch Number Bn	1.7	4.6	7.1	2.7	3.7	8.2	8.6
	(Physical Property 4) Weight Average Molecular Weight	63.9	65.1	71.8	64.7	62.1	89.3	89.3
	(Physical Property 4) Number Average Molecular Weight	31.8	32.4	38.2	34.6	33.0	45.6	45.2
	(Physical Property 4) Mw/Mn	2.01	2.01	1.88	1.87	1.88	1.96	1.98
	(Physical Property 5) Modification Ratio	-	-	24	-	-	-	-
	(Physical Property 6) Amount of Bound Styrene	35	35	35	35	35	35	35
	(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	40	40	40	40	40	40	40
	(Physical Property 8) Absolute Molecular Weight (Mw-i)	38	72	84	71	68	132	140

[0273]

[Table 6]

Coupled Conjugated Diene-based Polymer (Sample No.)		Example A-1	Example A-2	Example A-3
Polymerization Conditions	Butadiene	(g/min)	14.0	18.6
	Styrene	(g/min)	8.0	10.0
	n-Hexane	(g/min)	175.2	175.2
	Nitrogen Atom-containing Vinyl Compound	Type	N-1	-
		Amount Added	0.120	-
	Butadiene Added	(mmol/min)	4.6	-
		(g/min)	2.0	-
	Styrene Added	(°C)	70	70
		(mmol/min)	0.103	0.103
	n-Butyllithium for Treatment	(mmol/min)	0.143	0.143
		(mmol/min)	0.081	0.081
	Amount of Polar Material Added	(mmol/min)	BS-1	BS-1
		(mmol/min)	0.0190	0.0190
	Branching Agent	Type	D	Z-1
Physical Property Values	Coupling Agent	Amount Added	0.0360	0.0360
		(Physical Property 4) Weight Average Molecular Weight	63.9	63.9
	Conjugated Diene-based Polymer	(Physical Property 4) Number Average Molecular Weight	33.1	33.1
		(Physical Property 4) Mw/Mn	1.9	1.9
	(Physical Property 1) Mooney Viscosity (110°C)	(Physical Property 1) Mooney Viscosity (110°C)	92.1	92.1
		(Physical Property 5) Modification Ratio	80	0
	Type of Rubber Softener	(%)	80	0
		(phm)	SRAE	SRAE
	Amount of Rubber Softener Added	(phm)	25.0	25.0
		(Physical Property 1) Mooney Viscosity (100°C)	98	98
	(Physical Property 2) Mooney Stress Relaxation Rate (100°C)	(Physical Property 2) Mooney Stress Relaxation Rate (100°C)	0.253	0.253
		(Physical Property 3) Branch Number Bn	8.7	8.7
	Coupled Conjugated Diene-based Polymer	per molecule	8.7	8.7
		(Physical Property 4) Weight Average Molecular Weight	93.0	92.0
	(Physical Property 4) Number Average Molecular Weight	(10 ⁻⁴ g/mol)	46.7	46.7
		(Physical Property 4) Mw/Mn	1.97	1.97
	(Physical Property 5) Modification Ratio	(%)	89	-
		(mass%)	35	35
	(Physical Property 6) Amount of Bound Styrene	(mol%)	40	40
		(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	144	144
	(Physical Property 8) Absolute Molecular Weight (Mw-i)	(10 ⁴ Daltons)	145	144

[0274]

[Table 7]

		Comparative Example 1-1	Comparative Example 1-2	Comparative Example 1-3
Polymerization Conditions	Coupled Conjugated Diene-based Polymer (Sample No.)	1-38	1-39	1-40
	Butadiene	18.6	18.6	18.6
	Styrene	10.0	10.0	10.0
	n-Hexane	175.2	175.2	175.2
	Polymerization Temperature	70	70	70
	n-Butyllithium for Treatment	0.103	0.103	0.103
	n-Butyllithium as Polymerization Initiator	0.143	0.143	0.143
	Amount of Polar Material Added	0.081	0.081	0.081
	Type	-	-	-
	Amount Added	-	-	-
	Type	A	D	F
	Amount Added	0.0480	0.0360	0.0190
	(Physical Property 4) Weight Average Molecular Weight	48.9	48.9	48.9
Physical Property Values	(Physical Property 4) Number Average Molecular Weight	27.9	27.9	27.9
	(Physical Property 4) Mw/Mn	1.75	1.75	1.75
	(Physical Property 1) Mooney Viscosity (110°C)	72.5	72.5	72.5
	Type of Rubber Softener	SRAE	SRAE	SRAE
	Amount of Rubber Softener Added	25.0	25.0	25.0
	(Physical Property 1) Mooney Viscosity (100°C)	74	84	90
	(Physical Property 2) Mooney Stress Relaxation Rate (100°C)	0.761	0.621	0.422
	(Physical Property 3) Branch Number Bn	1.1	2.9	5.9
	(Physical Property 4) Weight Average Molecular Weight	73.4	82.1	97.3
	(Physical Property 4) Number Average Molecular Weight	39.3	40.8	49.1
	(Physical Property 4) Mw/Mn	1.87	2.01	1.98
	(Physical Property 5) Modification Ratio	-	83	80
	(Physical Property 6) Amount of Bound Styrene	35	35	35
	(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	40	40	40
	(Physical Property 8) Absolute Molecular Weight (Mw-i)	84	96	142

[0275]

[Table 8]

		Coupled Conjugated Diene-based Polymer (Sample No.)		Comparative Example B-1		Comparative Example B-2	
Polymerization Conditions	Coupled Conjugated Diene-based Polymer	Butadiene		(g/min)	B-1	B-2	
		Styrene		(g/min)	18.6	18.6	
		n-Hexane		(g/min)	10.0	10.0	
		Nitrogen Atom-containing Vinyl Compound	Type		175.2	175.2	
			Amount Added		-	-	
				(mmol/min)	-	-	
				(g/min)	-	-	
			Butadiene Added		-	-	
			Styrene Added		-	-	
			Polymerization Temperature	(°C)	70	70	
			n-Butyllithium for Treatment	(mmol/min)	0.103	0.103	
			n-Butyllithium as Polymerization Initiator	(mmol/min)	0.143	0.143	
			Amount of Polar Material Added	(mmol/min)	0.081	0.081	
		Branching Agent	Type		BS-1		
			Amount Added	(mmol/min)	0.0190		
Coupling Agent	Type		A	Z-1			
	Amount Added	(mmol/min)	0.0480	0.0360			
Conjugated Diene-based Polymer	Conjugated Diene-based Polymer	(Physical Property 4) Weight Average Molecular Weight	(10 ⁴ -g/mol)	48.9	48.9		
		(Physical Property 4) Number Average Molecular Weight	(10 ⁴ -g/mol)	27.9	27.9		
		(Physical Property 4) Mw/Mn		1.8	1.8		
		(Physical Property 1) Mooney Viscosity (110°C)		72.5	72.5		
		(Physical Property 5) Modification Ratio	(%)	0	0		
		Type of Rubber Softener		SRAE	SRAE		
		Amount of Rubber Softener Added	(phm)	25.0	25.0		
		(Physical Property 1) Mooney Viscosity (100°C)		90	46		
		(Physical Property 2) Mooney Stress Relaxation Rate (100°C)		0.372	0.379		
		(Physical Property 3) Branch Number Bn	per molecule	7.1	10.2		
Coupled Conjugated Diene-based Polymer	Coupled Conjugated Diene-based Polymer	(Physical Property 4) Weight Average Molecular Weight	(10 ⁴ -g/mol)	97.3	74.8		
		(Physical Property 4) Number Average Molecular Weight	(10 ⁴ -g/mol)	49.1	36.8		
		(Physical Property 4) Mw/Mn		1.98	2.03		
		(Physical Property 5) Modification Ratio	(%)	80	-		
		(Physical Property 6) Amount of Bound Styrene	(mass%)	35	35		
		(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	(mol%)	40	40		
		(Physical Property 8) Absolute Molecular Weight (Mw-i)	(10 ⁴ -Daltons)	86	96.2		

[0276]

(Examples 1-38 to 1-74, Examples a-1 to a-3, Comparative Examples 1-4 to 1-6, and Comparative Examples b-1 to b-2)

The samples 1-1 to 1-40 shown in Tables 1 to 5 and Table 7, the samples (A-1 to 3) shown in Table 6, and the samples (B-1 to 2) shown in Table 8 were respectively used as raw material rubbers to obtain rubber compositions respectively containing the raw material rubbers in accordance with the following composition:

[0277]

(Rubber Component)

- Branched conjugated diene-based polymer or coupled conjugated diene-based polymer (each of the samples 1-1 to 1-40)

: 80 parts by mass (excluding a rubber softener)

- High cis-polybutadiene (trade name "UBEPOL BR150" manufactured by Ube Industries, Ltd.)

: 20 parts by mass

[0278]

(Blending Conditions)

The amount of each blending component to be added was indicated in parts by mass with respect to 100 parts by mass of the rubber component excluding a rubber softener.

- Silica 1 (trade name "Ultrasil 7000GR",
manufactured by Evonik Degussa, nitrogen adsorption
specific surface area: 170 m²/g): 50.0 parts by mass
- Silica 2 (trade name "Zeosil Premium 200MP"
manufactured by Rhodia, nitrogen adsorption specific
surface area: 220 m²/g): 25.0 parts by mass
- Carbon black (trade name "Seast KH (N339)",
manufactured by Tokai Carbon Co., Ltd.): 5.0 parts by
mass
- Silane coupling agent: (trade name "Si75",
manufactured by Evonik Degussa,
bis(triethoxysilylpropyl)disulfide): 6.0 parts by mass
- SRAE oil (trade name "Process NC140", manufactured
by JX Nippon Oil & Energy Corporation): 42.0 parts by mass
(including an amount precedently added as the rubber
softener contained in each of the samples 1-1 to 1-40, A-
1 to A-3, and B-1 to B-2)
- Zinc oxide: 2.5 parts by mass
- Stearic acid: 1.0 part by mass
- Anti-ageing agent (N-(1,3-dimethylbutyl)-N'-
phenyl-p-phenylenediamine): 2.0 parts by mass
- Sulfur: 2.2 parts by mass
- Vulcanization accelerator 1 (N-cyclohexyl-2-
benzothiazylsulfonamide): 1.7 parts by mass
- Vulcanization accelerator 2 (diphenylguanidine):
2.0 parts by mass
- Total: 239.4 parts by mass

[0279]

(Kneading Method)

The above-described materials were kneaded by the following method to obtain a rubber composition. A closed kneader (having an internal volume of 0.3 L) equipped with a temperature controller was used to knead, as a first stage of kneading, the raw material rubber (each of the samples 1-1 to 1-40, the samples A-1 to A-3, and the samples B-1 to B-2), the fillers (silica 1, silica 2 and carbon black), the silane coupling agent, the SRAE oil, zinc oxide and stearic acid under conditions of a filling ratio of 65% and a rotor rotation speed of 30 to 50 rpm. Here, the temperature of the closed kneader was controlled to obtain each rubber composition (compound) at a discharging temperature of 155 to 160°C.

Next, after cooling the compound obtained as described above to room temperature, as a second stage of the kneading, the anti-ageing agent was added thereto, and the resultant was kneaded again to improve dispersibility of the silica. Also in this case, the discharging temperature for the compound was adjusted to 155 to 160°C by the temperature control of the kneader.

After cooling, as a third stage of the kneading, sulfur and the vulcanization accelerators 1 and 2 were added, and the resultant was kneaded by an open roll set to 70°C.

Thereafter, the resultant was molded and vulcanized at 160°C for 20 minutes by a vulcanizing press.

The rubber compositions prior to the vulcanization, and the rubber compositions after the vulcanization were evaluated. Specifically, the evaluations were performed as described below. Results are shown in Tables 9 to 15.

[0280]

(Evaluation of properties)

(Evaluation 1) Mooney Viscosity of Compound

Each compound obtained after the second stage of the kneading and before the third stage of the kneading was used as a sample to measure a viscosity by using a Mooney viscometer in accordance with ISO 289 after preheating the compound at 130°C for 1 minute, and after rotating a rotor for 4 minutes at 2 rpm. The viscosity was shown as an index obtained assuming that a result of Comparative Example 1-4 was 100. A smaller index indicates better workability.

[0281]

(Evaluation 2) Tensile Strength and Tensile Elongation

Tensile strength and tensile elongation were measured in accordance with a tensile test method according to JIS K6251, and were shown as indexes obtained assuming that results of Comparative Example 1-4 were 100. A larger index indicates better tensile strength and tensile elongation (fracture strength).

[0282]

(Evaluation 3) Abrasion Resistance

An Acron abrasion tester (manufactured by Yasuda Seiki Seisakusho, Ltd.) was used to measure an abrasion amount through 1000 rotations at a load of 44.4 N in accordance with JIS K6264-2, and the abrasion amount was shown as an index obtained assuming that a result of Comparative Example 1-4 was 100. A larger index indicates better abrasion resistance.

[0283]

(Evaluation 4) Viscoelasticity Parameter

A viscoelasticity testing machine "ARES" manufactured by Rheometric Scientific, Inc. was used to measure a viscoelasticity parameter in a torsion mode. Each measured value was shown as an index obtained assuming that a result obtained in the rubber composition of Comparative Example 1-4 was 100.

A $\tan \delta$ measured at 0°C at a frequency of 10 Hz and strain of 1% was used as an index of wet skid performance. A larger index indicates better wet skid performance.

Besides, a $\tan \delta$ measured at 50°C at a frequency of 10 Hz and strain of 3% was used as an index of fuel efficiency. A smaller index indicates higher fuel efficiency.

Besides, an elastic modulus (G') measured at 50°C at a frequency of 10 Hz and strain of 3% was used as an

index of steering stability. A larger index indicates better steering stability.

[0284]

[Table 9]

		Example 1-38	Example 1-39	Example 1-40	Example 1-41	Example 1-42	Example 1-43	Example 1-44	Example 1-45	
Branched Conjugated Diene-based Polymer (Sample No.)		1-1	1-2	1-3	1-4	1-5	1-6	1-7	1-8	
(Physical Property 1) Mooney Viscosity of Polymer (100°C)		91	98	99	98	98	97	95	99	
Physical Property Values	(Evaluation 1) Mooney Viscosity of Compound (130°C)	Index	85	88	86	83	85	80	78	83
	(Evaluation 2) Tensile Strength	Index	112	117	121	113	128	134	139	142
	(Evaluation 2) Tensile Elongation	Index	109	108	114	116	120	118	124	125
	(Evaluation 3) Abrasion Resistance	Index	110	113	128	125	130	142	148	152
	(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	Index	111	110	128	125	120	117	126	130
	(Evaluation 4) 50°C tanδ (strain: 3%)	Index	97	96	86	80	75	71	72	69
	(Evaluation 4) 0°C tanδ (strain: 1%)	Index	104	104	113	120	125	131	128	122

[0285]

[Table 10]

	Example 1-46	Example 1-47	Example 1-48	Example 1-49	Example 1-50	Example 1-51	Example 1-52	Example 1-53
Branched Conjugated Diene-based Polymer (Sample No.)	1-9	1-10	1-11	1-12	1-13	1-14	1-15	1-16
(Physical Property 1) Mooney Viscosity of Polymer (100°C)	93	89	93	94	97	94	96	82
(Evaluation 1) Mooney Viscosity of Compound (130°C)	Index	74	88	84	78	86	82	80
(Evaluation 2) Tensile Strength	Index	137	109	112	129	110	138	146
(Evaluation 2) Tensile Elongation	Index	122	120	112	132	113	122	124
(Evaluation 3) Abrasion Resistance	Index	144	137	118	143	128	157	162
(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	Index	121	120	129	125	123	120	118
(Evaluation 4) 50°C tanδ (strain: 3%)	Index	75	78	92	75	91	77	74
(Evaluation 4) 0°C tanδ (strain: 1%)	Index	133	137	107	117	110	120	122

Physical Property Values

[0286]

[Table 11]

	Example 1-54	Example 1-55	Example 1-56	Example 1-57	Example 1-58	Example 1-59	Example 1-60
Branched Conjugated Diene-based Polymer (Sample No.)	1-17	1-18	1-19	1-20	1-21	1-22	1-23
(Physical Property 1) Mooney Viscosity of Polymer (100°C)	95	97	99	97	99	101	102
(Evaluation 1) Mooney Viscosity of Compound (130°C)	Index	89	82	91	86	88	87
(Evaluation 2) Tensile Strength	Index	109	125	107	109	127	109
(Evaluation 2) Tensile Elongation	Index	113	120	118	117	123	118
(Evaluation 3) Abrasion Resistance	Index	113	137	120	126	137	131
(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	Index	118	113	122	123	129	127
(Evaluation 4) 50°C tanδ (strain: 3%)	Index	93	76	92	82	78	83
(Evaluation 4) 0°C tanδ (strain: 1%)	Index	107	123	110	119	126	127

Physical Property Values

[0287]

[Table 12]

	Example 1-61	Example 1-62	Example 1-63	Example 1-64	Example 1-65	Example 1-66	Example 1-67
Branched Conjugated Diene-based Polymer (Sample No.)	1-24	1-25	1-26	1-27	1-28	1-29	1-30
(Physical Property 1) Mooney Viscosity of Polymer (100°C)	105	107	92	101	103	157	83
(Evaluation 1) Mooney Viscosity of Compound (130°C)	Index	92	78	84	81	83	78
(Evaluation 2) Tensile Strength	Index	145	153	143	130	132	135
(Evaluation 2) Tensile Elongation	Index	117	124	128	121	115	120
(Evaluation 3) Abrasion Resistance	Index	152	157	141	137	145	140
(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	Index	131	130	139	124	118	122
(Evaluation 4) 50°C tanδ (strain: 3%)	Index	85	87	88	82	73	71
(Evaluation 4) 0°C tanδ (strain: 1%)	Index	113	110	118	137	128	130

Physical Property Values

[0288]

[Table 13]

	Example 1-68	Example 1-69	Example 1-70	Example 1-71	Example 1-72	Example 1-73	Example 1-74
Branched Conjugated Diene-based Polymer (Sample No.)	1-31	1-32	1-33	1-34	1-35	1-36	1-37
(Physical Property 1) Mooney Viscosity of Polymer (100°C)	52	65	74	53	60	100	91
(Evaluation 1) Mooney Viscosity of Compound (130°C)	74	92	93	90	90	95	87
(Evaluation 2) Tensile Strength	82	98	106	102	104	140	112
(Evaluation 2) Tensile Elongation	89	99	103	100	102	130	109
(Evaluation 3) Abrasion Resistance	71	102	103	106	103	140	114
(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	97	101	100	102	102	116	111
(Evaluation 4) 50°C tanδ (strain: 3%)	102	103	104	98	95	90	97
(Evaluation 4) 0°C tanδ (strain: 1%)	100	102	103	92	92	114	104

Physical Property Values

[0289]

[Table 14]

	Comparative Example 1-4	Comparative Example 1-5	Comparative Example 1-6
Coupled Conjugated Diene-based Polymer (Sample No.)	1-38	1-39	1-40
(Physical Property 1) Mooney Viscosity of Polymer (100°C)	74	84	90
(Evaluation 1) Mooney Viscosity of Compound (130°C)	Index	113	116
(Evaluation 2) Tensile Strength	Index	117	112
(Evaluation 2) Tensile Elongation	Index	102	98
(Evaluation 3) Abrasion Resistance	Index	109	103
(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	Index	98	98
(Evaluation 4) 50°C tanδ (strain: 3%)	Index	112	124
(Evaluation 4) 0°C tanδ (strain: 1%)	Index	107	112

Physical Property Values

[0290]

[Table 15]

	Example a-1	Example a-2	Example a-3	Comparative Example b-1	Comparative Example b-2
Coupled Conjugated Diene-based Polymer (Sample No.)	A-1	A-2	A-3	B-1	B-2
(Physical Property 1) Mooney Viscosity of Polymer (100°C)	98	99	98	78	46
(Evaluation 1) Mooney Viscosity of Compound (130°C)	83	84	83	97	73
Physical Property Values	(Evaluation 2) Tensile Strength	114	110	100	78
	(Evaluation 2) Tensile Elongation	117	110	98	87
	(Evaluation 3) Abrasion Resistance	125	115	105	82
	(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	130	125	100	107
	(Evaluation 4) 50°C tan δ (strain: 3%)	75	90	98	109
	(Evaluation 4) 0°C tan δ (strain: 1%)	125	108	99	102

[0291]

As shown in Tables 9 to 15, it was confirmed that Examples 1-38 to 1-74 have, as compared with Comparative Examples 1-4 to 1-6, a low Mooney viscosity of the compound when used for obtaining a vulcanizate and exhibit good workability, are excellent in abrasion resistance, steering stability and fracture strength when in the form of a vulcanizate, and are excellent in balance between a low hysteresis loss property and wet skid resistance.

As shown in Table 15, it was confirmed that Example a-1 to a-3 has, as compared with Comparative Example b-1 to b-2, a low Mooney viscosity of the compound when used for obtaining a vulcanizate and exhibits good workability, is excellent in abrasion resistance, steering stability and fracture strength when in the form of a vulcanizate, and is excellent in balance between a low hysteresis loss property and wet skid resistance.

[0292]

[Second Example]

The present embodiment will now be described in detail with reference to specific examples and comparative examples described as a second example, and it is noted that the present embodiment is not limited at all to the following examples and comparative examples.

In the following description, a conjugated diene-based polymer coupled with a coupling agent is referred to as "coupled conjugated diene-based polymer".

A conjugated diene-based polymer which is copolymerizable with a nitrogen atom-containing vinyl compound and which has a branch structure derived from a branching agent is referred to as "modified branched conjugated diene-based polymer".

A coupled conjugated diene-based polymer, a conjugated diene-based polymer having a branch structure, and a conjugated diene-based polymer not having a branch structure may be collectively referred to as "conjugated diene-based polymer".

Various physical properties described in the examples and comparative examples were measured by the following methods.

[0293]

(Physical Property 1) Mooney Viscosity of Polymer

A modified branched conjugated diene-based polymer or a conjugated diene-based polymer coupled by using a nitrogen atom-containing modifier (hereinafter also referred to as "coupled conjugated diene-based polymer") was used as a sample to measure a Mooney viscosity by using a Mooney viscometer (trade name "VR1132" manufactured by Ueshima Seisakusho Co., Ltd.) in accordance with ISO 289 with an L-type rotor used.

A measurement temperature was 110°C when a conjugated diene-based polymer prior to a coupling reaction was used as a sample, and was 100°C when a coupled conjugated diene-based polymer was used as a sample.

First, the sample was preheated at the test temperature for 1 minute, a rotor was rotated at 2 rpm, a torque was measured 4 minutes after, and the thus measured value was determined as a Mooney viscosity ($ML_{(1+4)}$).

[0294]

(Physical Property 2) Mooney Stress Relaxation Rate

After measuring, by using a coupled conjugated diene-based polymer as a sample, a Mooney viscosity by using a Mooney viscometer (trade name "VR1132" manufactured by Ueshima Seisakusho Co., Ltd.) in accordance with ISO 289 with an L-type rotor used, the rotation of the rotor was immediately stopped, and the torque in terms of the Mooney unit was recorded every 0.1 seconds from 1.6 seconds to 5 seconds after the stop. The slope of a straight line resulting from double logarithmic plotting of the torque and the time (sec) was obtained, and the absolute value was defined as a Mooney stress relaxation rate (MSR).

[0295]

(Physical Property 3) Branch Number (Bn)

The branch number (Bn) of a coupled conjugated diene-based polymer was measured by viscosity detector-equipped GPC-light scattering measurement as follows.

The coupled conjugated diene-based polymer was used as a sample, and a gel permeation chromatography (GPC) measurement apparatus (trade name "GPCmax VE-2001" manufactured by Malvern Panalytical Ltd.) including a series of three columns using a polystyrene-based gel as a filler was used. The measurement was performed by using three detectors, that is, a light scattering detector, an RI detector, and a viscosity detector (trade name "TDA305" manufactured by Malvern Panalytical Ltd.) connected in the stated order. Based on standard polystyrene, an absolute molecular weight was obtained from results obtained by using the light scattering detector and the RI detector, and an intrinsic viscosity was obtained from results obtained by using the RI detector and the viscosity detector.

A straight-chain polymer was used under assumption of having an intrinsic viscosity $[\eta]$ of $-3.883 M^{0.771}$, and a contracting factor (g') was calculated as a ratio in the intrinsic viscosity to each molecular weight. It is noted that M herein represents the absolute molecular weight.

Thereafter, the thus obtained contracting factor (g') was used to calculate a branch number (Bn) defined as $g' = 6 Bn / \{ (Bn + 1) (Bn + 2) \}$.

As an eluent, tetrahydrofuran (hereinafter also referred to as "THF") containing 5 mmol/L of triethylamine was used.

As the columns, a series of columns of trade names "TSKgel G4000HXL", "TSKgel G5000HXL" and "TSKgel G6000HXL" manufactured by Tosoh Corporation were connected and used.

Twenty (20) mg of a sample for the measurement was dissolved in 10 mL of THF to obtain a measurement solution, and 100 μ L of the measurement solution was injected into the GPC measurement apparatus for performing the measurement under conditions of an oven temperature of 40°C and a THF flow rate of 1 mL/min.

[0296]

(Physical Property 4) Molecular Weight

<Measurement Conditions 1>:

A modified branched conjugated diene-based polymer or a coupled conjugated diene-based polymer used as a sample was measured for a chromatogram using a GPC measurement apparatus (trade name "HLC-8320GPC" manufactured by Tosoh Corporation) including a series of three columns using a polystyrene-based gel as a filler with an RI detector (trade name "HLC8020" manufactured by Tosoh Corporation) used, and on the basis of a calibration curve obtained using standard polystyrene, a weight average molecular weight (M_w), a number average

molecular weight (M_n) and a molecular weight distribution (M_w/M_n) were obtained.

As an eluent, THF (tetrahydrofuran) containing 5 mmol/L of triethylamine was used. As the columns, trade name "TSKguardcolumn Super MP(HZ)-H" manufactured by Tosoh Corporation connected, as a guard column at a previous stage, to a series of three columns of trade name "TSKgel SuperMultipore HZ-H" manufactured by Tosoh Corporation were used.

Ten (10) mg of a sample for the measurement was dissolved in 10 mL of THF to obtain a measurement solution, and 10 μ L of the measurement solution was injected into the GPC measurement apparatus for performing the measurement under conditions of an oven temperature of 40°C and a THF flow rate of 0.35 mL/min.

With respect to a sample out of the various samples having been subjected to the measurement under the measurement conditions 1 and found to have a molecular weight distribution (M_w/M_n) value of less than 1.6, the measurement was performed again under the following measurement conditions 2. With respect to a sample having been subjected to the measurement under the measurement conditions 1 and found to have a molecular weight distribution value of 1.6 or more, a measured value obtained under the measurement conditions 1 was employed.

<Measurement Conditions 2>:

The modified branched conjugated diene-based polymer or the coupled conjugated diene-based polymer used as a sample was measured for a chromatogram using a GPC measurement apparatus including a series of three columns using a polystyrene-based gel as a filler, and on the basis of a calibration curve obtained using standard polystyrene, a weight average molecular weight (Mw), and a number average molecular weight (Mn) were obtained.

As an eluent, THF containing 5 mmol/L of triethylamine was used. As the columns, a guard column of trade name "TSKguardcolumn Super H-H" manufactured by Tosoh Corporation, and columns of trade names "TSKgel SuperH5000", "TSKgel SuperH6000", and "TSKgel SuperH7000" manufactured by Tosoh Corporation were used.

An RI detector (trade name "HLC8020" manufactured by Tosoh Corporation) was used under conditions of an oven temperature of 40°C and a THF flow rate of 0.6 mL/min. Ten (10) mg of a sample for the measurement was dissolved in 20 mL of THF to obtain a measurement solution, and 20 μ L of the measurement solution was injected into the GPC measurement apparatus for performing the measurement.

With respect to a sample having been subjected to the measurement under the measurement conditions 1 and found to have a molecular weight distribution value less than 1.6, the measurement was performed under the measurement conditions 2, and the resultant measured value was employed.

[0297]

(Physical Property 5) Modification Ratio

Each modification ratio of a modified branched conjugated diene-based polymer and a coupled conjugated diene-based polymer was measured by column adsorption GPC as follows.

A modified branched conjugated diene-based polymer and a coupled conjugated diene-based polymer were each used as a sample, and the measurement was performed by applying a characteristic that a modified basic polymer component adsorbs onto a GPC column using a silica-based gel as a filler.

When a nitrogen atom-containing vinyl compound was used as a monomer in a polymerizing step, a conjugated diene-based polymer already modified in the polymerizing step was obtained, and thus, a modification ratio was again measured with respect to a "modified branched conjugated diene-based polymer" at a stage prior to performing of a coupling step.

A modification ratio was obtained by measuring an amount of adsorption onto a silica-based column based on a difference between a chromatogram measured by using a polystyrene-based column and a chromatogram measured by using a silica-based column obtained from a sample solution containing a sample and low molecular weight internal standard polystyrene.

Specifically, the measurement was performed as described below.

With respect to a sample having been subjected to the measurement under the measurement conditions 1 of (Physical Property 4) and found to have a molecular weight distribution value of 1.6 or more, the measurement was performed under measurement conditions 3 described below. With respect to a sample having been subjected to the measurement under the measurement conditions 1 of (Physical Property 4) and found to have a molecular weight distribution value less than 1.6, the measurement was performed under measurement conditions 4 described below.

[0298]

<Preparation of Sample Solution>

Ten (10) mg of a sample and 5 mg of standard polystyrene were dissolved in 20 mL of THF to obtain a sample solution.

<Measurement Conditions 3>

GPC measurement conditions using polystyrene-based column:

An apparatus of trade name "HLC-8320GPC" manufactured by Tosoh Corporation was used, THF containing 5 mmol/L of triethylamine was used as an eluent, and 10 μ L of a sample solution was injected to the apparatus to obtain a chromatogram using an RI

detector under conditions of a column oven temperature of 40°C and a THF flow rate of 0.35 mL/min.

As the columns, a series of three columns of trade name "TSKgel Super Multipore HZ-H" manufactured by Tosoh Corporation and a guard column of trade name "TSKguardcolumn SuperMP(HZ)-H" manufactured by Tosoh Corporation connected at a previous stage were used.

[0299]

<Measurement Conditions 4>

THF containing 5 mmol/L of triethylamine was used as an eluent, and 20 µL of the sample solution was injected into the apparatus to perform the measurement.

As the columns, a guard column of trade name "TSKguardcolumn SuperH-H" manufactured by Tosoh Corporation and columns of trade names "TSKgel SuperH5000", "TSKgel SuperH6000", and "TSKgel SuperH7000" manufactured by Tosoh Corporation were used. A chromatogram was obtained by performing the measurement by using an RI detector (HLC8020 manufactured by Tosoh Corporation) under conditions of a column oven temperature of 40°C and a THF flow rate of 0.6 mL/min.

[0300]

GPC measurement conditions using silica-based column:

An apparatus of trade name "HLC-8320GPC" manufactured by Tosoh Corporation was used, THF was used as an eluent, 50 µL of a sample solution was injected to

the apparatus to obtain a chromatogram using RI detector under conditions of a column oven temperature of 40°C and a THF flow rate of 0.5 ml/min. A series of columns of trade names "Zorbax PSM-1000S", "PSM-300S" and "PSM-60S", and a guard column of trade name "DIOL 4.6 × 12.5 mm 5 micron" connected at a previous stage were used.

[0301]

Calculation method for modification ratio:

Assuming that the whole peak area of the chromatogram obtained by using the polystyrene-based column was 100, that a peak area of the sample was P1, that a peak area of standard polystyrene was P2, that the whole peak area of the chromatogram obtained by using the silica-based column was 100, that a peak area of the sample was P3, and that a peak area of standard polystyrene was P4, a modification ratio (%) was obtained in accordance with the following expression:

$$\text{Modification ratio (\%)} = [1 - (P2 \times P3) / (P1 \times P4)] \times 100$$

wherein $P1 + P2 = P3 + P4 = 100$.

[0302]

(Physical Property 6) Amount of Bound Styrene

One hundred (100) mg of a coupled conjugated diene-based polymer not containing a rubber softener used as a sample was dissolved in chloroform to be diluted to 100 mL, and the resultant was used as a measurement sample.

Based on the amount of absorption of a phenyl group of styrene at a UV absorption wavelength (about 254 nm), the amount of bound styrene (% by mass) with respect to 100% by mass of the sample of the coupled conjugated diene-based polymer was measured (measurement apparatus: spectrophotometer "UV-2450" manufactured by Shimadzu Corporation).

[0303]

(Physical Property 7) Microstructure of Butadiene Portion (Amount of 1,2-Vinyl Bond)

Fifty (50) mg of a coupled conjugated diene-based polymer not containing a rubber softener used as a sample was dissolved in 10 mL of carbon disulfide, and the resultant was used as a measurement sample.

A solution cell was used to measure an infrared spectrum in a range of 600 to 1000 cm^{-1} , and in accordance with a calculation formula of the Hampton method (R. R. Hampton, Analytical Chemistry 21, 923 (1949)) based on absorbance at a prescribed wavelength, a microstructure of a butadiene portion, namely, an amount of 1,2-vinyl bond (referred to as "Amount of Vinyl Bond (Amount of 1,2-Vinyl Bond)" in the tables) (mol%), was obtained (measurement apparatus: Fourier transform infrared spectrophotometer "FT-IR230" manufactured by JASCO Corporation).

[0304]

(Physical Property 8) Molecular Weight (Absolute Molecular Weight) obtained by GPC-light Scattering Measurement

A coupled conjugated diene-based polymer was used as a sample, and a GPC-light scattering measurement apparatus including a series of three columns using a polystyrene-based gel as a filler was used to measure a chromatogram for obtaining a weight average molecular weight (M_w) (also designated as an "absolute molecular weight") based on a viscosity of a solution and a light scattering method.

As an eluent, a mixed solution of tetrahydrofuran and triethylamine (THF in TEA: prepared by mixing 5 mL of triethylamine in 1 L of tetrahydrofuran) was used.

As the columns, a series of a guard column of trade name "TSKguardcolumn HHR-H" manufactured by Tosoh Corporation, and columns of trade names "TSKgel G6000HHR", "TSKgel G5000HHR", and "TSKgel G4000HHR" manufactured by Tosoh Corporation were connected and used.

A GPC-light scattering measurement apparatus (trade name "Viscotek TDAmix" manufactured by Malvern Panalytical Ltd.) was used under conditions of an oven temperature of 40°C and a THF flow rate of 1.0 mL/min.

Ten (10) mg of a sample for measurement was dissolved in 20 mL of THF to obtain a measurement solution, and 200 μ L of the measurement solution was

injected into the GPC measurement apparatus for the measurement.

[0305]

[Conjugated Diene-based Polymer]

(Comparative Example 2-1) Coupled Conjugated Diene-based Polymer (Sample 2-1)

Two tank pressure vessels, each of which was a stirrer-equipped tank reactor having an internal volume of 10 L and a ratio (L/D) of an internal height (L) and a diameter (D) of 4.0, having an inlet at a bottom and an outlet at a top, and equipped with a stirrer and a temperature controlling jacket, were connected to each other as polymerization reactors.

1,3-Butadiene, from which a water content had been precedently removed, styrene and n-hexane were mixed under conditions of 18.6 g/min, 10.0 g/min and 175.2 g/min, respectively. In a static mixer provided in the middle of a pipe for supplying the thus obtained mixed solution to the inlet of the reactor, n-butyllithium to be used for residual impurity inactivation was added and mixed in an amount of 0.103 mmol/min, and the resultant was continuously supplied to the bottom of the reactor. Besides, 2,2-bis(2-oxolanyl)propane used as a polar material and n-butyllithium used as a polymerization initiator were supplied, at rates of respectively 0.081 mmol/min and 0.143 mmol/min, to the bottom of the first reactor in which materials were vigorously mixed by the

stirrer, and the internal temperature of the reactor was kept at 67°C.

The thus obtained polymer solution was continuously taken out from the top of the first reactor to be continuously supplied to the bottom of the second reactor for continuing the reaction at 70°C, and the resultant was further supplied to a static mixer from the top of the second reactor. When the polymerization was sufficiently stabilized, while copolymerizing 1,3-butadiene and styrene, 1-(4-N,N-dimethylaminophenyl)-1-phenylethylene (shown as "N-1" in the table) used as a nitrogen atom-containing vinyl compound was added at a rate of 0.120 mmol/min and trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) used as a branching agent was added at a rate of 0.0190 mmol/min from the bottom of the second reactor, so as to perform a polymerization reaction and a branching reaction for obtaining a conjugated diene-based polymer having a main chain branch structure.

When the polymerization reaction and the branching reaction were stabilized, a small amount of a conjugated diene-based polymer (modified branched conjugated diene-based polymer) solution prior to addition of a coupling agent was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and a Mooney viscosity at

110°C and various molecular weights were measured. The physical properties are shown in Table 16.

Next, to the polymer solution flowing out of the outlet of the reactor, tetraethoxysilane (shown as "A" in the table) was added, as a coupling agent, continuously at a rate of 0.0480 mmol/min, and the resultant was mixed by using a static mixer for performing a coupling reaction. Here, a time until the addition of the coupling agent to the polymer solution flowing out of the outlet of the reactor was 4.8 min, the temperature was 68°C, and a difference between the temperature in the polymerizing step and the temperature until the addition of the coupling agent was 2°C. A small amount of a conjugated diene-based polymer solution after the coupling reaction was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and the amount of bound styrene (Physical Property 6) and the microstructure of a butadiene portion (the amount of 1,2-vinyl bond; Physical Property 7) were measured. Measurement results are shown in Table 16.

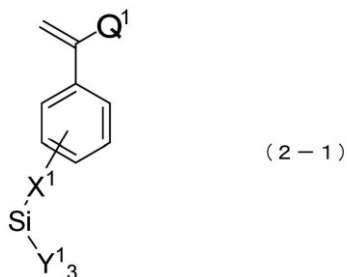
Next, to the polymer solution resulting from the coupling reaction, the antioxidant (BHT) was continuously added in an amount of 0.2 g per 100 g of the polymer at 0.055 g/min (n-hexane solution) to complete the coupling reaction. Simultaneously with the antioxidant, SRAE oil (JOMO Process NC 140, manufactured by JX Nippon Oil &

Energy Corporation) was continuously added as a rubber softener in an amount of 25.0 g per 100 g of the polymer, and the resultant was mixed by using a static mixer. The solvent was removed by steam stripping, and thus, a coupled conjugated diene-based polymer (sample 2-1) having, in a part of a main chain, a 4-branched structure derived from the branching agent corresponding to a compound represented by the following formula (2-1) (hereinafter also referred to as "branching agent structure (2-1)".) and having a 3-branched star polymer structure derived from the coupling agent was obtained.

Physical properties of the sample 2-1 are shown in Table 16.

In each of the polymer obtained prior to the addition of the branching agent, the polymer obtained after the addition of the branching agent, and the polymers obtained in the respective steps after the addition of the coupling agent, the structure of the coupled conjugated diene-based polymer was identified based on comparison between a molecular weight measured by GPC and a branch number measured by viscosity detector-equipped GPC. Hereinafter, the structure of each sample was similarly identified.

[0306]



[0307]

In the formula (2-1), Q^1 represents any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms, and may have a branch structure in a part thereof.

X^1 represents a single bond, or an organic group containing any one selected from the group consisting of carbon, hydrogen, nitrogen, sulfur, and oxygen.

Y^1 represents any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom.

Y^1 is respectively independent and may be the same or different.

[0308]

(Example 2-2) Coupled Conjugated Diene-based Polymer
(Sample 2-2)

A coupled conjugated diene-based polymer (sample 2-2) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-

1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to 1,2-bis(triethoxysilyl)ethane (shown as "B" in the table) and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 2-2 are shown in Table 16.

[0309]

(Example 2-3) Coupled Conjugated Diene-based Polymer (Sample 2-3)

A coupled conjugated diene-based polymer (sample 2-3) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to 1,3-bis(N,N-diglycidylaminomethyl)cyclohexane (shown as "C" in the table) and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 2-3 are shown in Table 16.

[0310]

(Example 2-4) Coupled Conjugated Diene-based Polymer (Sample 2-4)

A coupled conjugated diene-based polymer (sample 2-4) having, in a part of a main chain, a 4-branched

structure derived from the branching agent structure (2-1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table) and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 2-4 are shown in Table 16.

[0311]

(Example 2-5) Coupled Conjugated Diene-based Polymer
(Sample 2-5)

A coupled conjugated diene-based polymer (sample 2-5) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having a 6-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to tris(3-trimethoxysilylpropyl)amine (shown as "E" in the table) and that the amount thereof to be added was changed to 0.0250 mmol/min. Physical properties of the sample 2-5 are shown in Table 16.

[0312]

(Example 2-6) Coupled Conjugated Diene-based Polymer
(Sample 2-6)

A coupled conjugated diene-based polymer (sample 2-6) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table) and that the amount thereof to be added was changed to 0.0190 mmol/min. Physical properties of the sample 2-6 are shown in Table 16.

[0313]

(Example 2-7) Coupled Conjugated Diene-based Polymer
(Sample 2-7)

A coupled conjugated diene-based polymer (sample 2-7) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table) and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 2-7 are shown in Table 16.

[0314]

(Example 2-8) Coupled Conjugated Diene-based Polymer
(Sample 2-8)

A coupled conjugated diene-based polymer (sample 2-8) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the rate of adding 1,3-butadiene was changed from 18.6 g/min to 24.3 g/min, that the rate of adding styrene was changed from 10.0 g/min to 4.3 g/min, that the rate of adding 2,2-bis(2-oxolanyl)propane as a polar material was changed from 0.081 mmol/min to 0.044 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 2-8 are shown in Table 16.

[0315]

(Example 2-9) Coupled Conjugated Diene-based Polymer
(Sample 2-9)

A coupled conjugated diene-based polymer (sample 2-9) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the rate of adding

1,3-butadiene was changed from 18.6 g/min to 17.1 g/min, that the rate of adding styrene was changed from 10.0 g/min to 11.5 g/min, that the rate of adding 2,2-bis(2-oxolanyl)propane as a polar material was changed from 0.081 mmol/min to 0.089 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 2-9 are shown in Table 17.

[0316]

(Example 2-10) Coupled Conjugated Diene-based Polymer (Sample 2-10)

A coupled conjugated diene-based polymer (sample 2-10) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the rate of adding 2,2-bis(2-oxolanyl)propane as a polar material was changed from 0.081 mmol/min to 0.200 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 2-10 are shown in Table 17.

[0317]

(Example 2-11) Coupled Conjugated Diene-based
Polymer (Sample 2-11)

A coupled conjugated diene-based polymer (sample 2-11) having, in a part of a main chain, a 2-branched structure derived from the branching agent structure (2-1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to dimethylmethoxy(4-vinylphenyl)silane (shown as "BS-2" in the table), that the amount thereof to be added was changed to 0.0350 mmol/min, that the coupling agent was changed from tetraethoxysilane to 1,2-bis(triethoxysilyl)ethane (shown as "B" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 2-11 are shown in Table 17.

[0318]

(Example 2-12) Coupled Conjugated Diene-based
Polymer (Sample 2-12)

A coupled conjugated diene-based polymer (sample 2-12) having, in a part of a main chain, a 2-branched structure derived from the branching agent structure (2-1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to

dimethylmethoxy(4-vinylphenyl)silane (shown as "BS-2" in the table), that the amount thereof to be added was changed to 0.0350 mmol/min, that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 2-12 are shown in Table 17.

[0319]

(Example 2-13) Coupled Conjugated Diene-based Polymer (Sample 2-13)

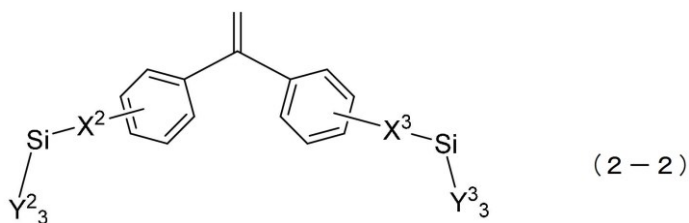
A coupled conjugated diene-based polymer (sample 2-13) having, in a part of a main chain, a 2-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to dimethylmethoxy(4-vinylphenyl)silane (shown as "BS-2" in the table), that the amount thereof to be added was changed to 0.0350 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 2-13 are shown in Table 17.

[0320]

(Example 2-14) Coupled Conjugated Diene-based
Polymer (Sample 2-14)

A coupled conjugated diene-based polymer (sample 2-14) having, in a part of a main chain, a 3-branched structure derived from a branching agent (hereinafter also referred to as "branching agent structure (2-2)".) as a compound represented by the following formula (2-2) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-(dimethylmethoxysilyl)phenyl)ethylene (shown as "BS-3" in the table), that the amount thereof to be added was changed to 0.0120 mmol/min, that the coupling agent was changed from tetraethoxysilane to 1,2-bis(triethoxysilyl)ethane (shown as "B" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 2-14 are shown in Table 17.

[0321]



[0322]

In the formula (2-2), X^2 and X^3 represent a single bond, or an organic group containing any one selected from the group consisting of carbon, hydrogen, nitrogen, sulfur, and oxygen.

Y^2 and Y^3 represent any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom.

Y^2 and Y^3 are respectively independent, and may be the same or different.

[0323]

(Example 2-15) Coupled Conjugated Diene-based Polymer (Sample 2-15)

A coupled conjugated diene-based polymer (sample 2-15) having, in a part of a main chain, a 3-branched structure derived from the branching agent structure (2-2) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-(dimethylmethoxysilyl)phenyl)ethylene (shown as "BS-3" in the table), that the amount thereof to be added was changed to 0.0120 mmol/min, that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table), and that the amount thereof to be

added was changed to 0.0360 mmol/min. Physical properties of the sample 2-15 are shown in Table 17.

[0324]

(Example 2-16) Coupled Conjugated Diene-based Polymer (Sample 2-16)

A coupled conjugated diene-based polymer (sample 2-16) having, in a part of a main chain, a 3-branched structure derived from the branching agent structure (2-2) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-(dimethylmethoxysilyl)phenyl)ethylene (shown as "BS-3" in the table), that the amount thereof to be added was changed to 0.0120 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 2-16 are shown in Table 17.

[0325]

(Example 2-17) Coupled Conjugated Diene-based Polymer (Sample 2-17)

A coupled conjugated diene-based polymer (sample 2-17) having, in a part of a main chain, a 7-branched structure derived from the branching agent structure (2-2) and having a 4-branched star polymer structure derived

from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-trimethoxysilylphenyl)ethylene (shown as "BS-4" in the table), that the amount thereof to be added was changed to 0.0210 mmol/min, that the coupling agent was changed from tetraethoxysilane to 1,2-bis(triethoxysilyl)ethane (shown as "B" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 2-17 are shown in Table 18.

[0326]

(Example 2-18) Coupled Conjugated Diene-based Polymer (Sample 2-18)

A coupled conjugated diene-based polymer (sample 2-18) having, in a part of a main chain, a 7-branched structure derived from the branching agent structure (2-2) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-trimethoxysilylphenyl)ethylene (shown as "BS-4" in the table), that the amount thereof to be added was changed to 0.0210 mmol/min, that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table), and that the amount thereof to be

added was changed to 0.0360 mmol/min. Physical properties of the sample 2-18 are shown in Table 18.

[0327]

(Example 2-19) Coupled Conjugated Diene-based Polymer (Sample 2-19)

A coupled conjugated diene-based polymer (sample 2-19) having, in a part of a main chain, a 7-branched structure derived from the branching agent structure (2-2) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to 1,1-bis(4-trimethoxysilylphenyl)ethylene (shown as "BS-4" in the table), that the amount thereof to be added was changed to 0.0210 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 2-19 are shown in Table 18.

[0328]

(Example 2-20) Coupled Conjugated Diene-based Polymer (Sample 2-20)

A coupled conjugated diene-based polymer (sample 2-20) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure

derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to trichloro(4-vinylphenyl)silane (shown as "BS-5" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, that the coupling agent was changed from tetraethoxysilane to 1,2-bis(triethoxysilyl)ethane (shown as "B" in the table), and that the amount thereof to be added was changed to 0.0360 mmol/min. Physical properties of the sample 2-20 are shown in Table 18.

[0329]

(Example 2-21) Coupled Conjugated Diene-based Polymer (Sample 2-21)

A coupled conjugated diene-based polymer (sample 2-21) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to trichloro(4-vinylphenyl)silane (shown as "BS-5" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, that the coupling agent was changed from tetraethoxysilane to 2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table), and that the amount thereof to be

added was changed to 0.0360 mmol/min. Physical properties of the sample 2-21 are shown in Table 18.

[0330]

(Example 2-22) Coupled Conjugated Diene-based Polymer (Sample 2-22)

A coupled conjugated diene-based polymer (sample 2-22) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the branching agent was changed from trimethoxy(4-vinylphenyl)silane to trichloro(4-vinylphenyl)silane (shown as "BS-5" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 2-22 are shown in Table 18.

[0331]

(Example 2-23) Coupled Conjugated Diene-based Polymer (Sample 2-23)

A coupled conjugated diene-based polymer (sample 2-23) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure

derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the amount of trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) as a branching agent to be added was changed from 0.0190 mmol/min to 0.0100 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0190 mmol/min. Physical properties of the sample 2-23 are shown in Table 18.

[0332]

(Example 2-24) Coupled Conjugated Diene-based Polymer (Sample 2-24)

A coupled conjugated diene-based polymer (sample 2-24) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the amount of trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) as a branching agent to be added was changed from 0.0190 mmol/min to 0.0250 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0190 mmol/min. Physical properties of the sample 2-24 are shown in Table 19.

[0333]

(Example 2-25) Coupled Conjugated Diene-based
Polymer (Sample 2-25)

A coupled conjugated diene-based polymer (sample 2-25) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the amount of trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) as a branching agent to be added was changed from 0.0190 mmol/min to 0.0350 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0190 mmol/min. Physical properties of the sample 2-25 are shown in Table 19.

[0334]

(Example 2-26) Coupled Conjugated Diene-based
Polymer (Sample 2-26)

A coupled conjugated diene-based polymer (sample 2-26) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-

trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, and that a liquid rubber (liquid polybutadiene LBR-302, manufactured by Kuraray Co., Ltd.) was added instead of SRAE oil added as the rubber softener. Physical properties of the sample 2-26 are shown in Table 19.

[0335]

(Example 2-27) Coupled Conjugated Diene-based Polymer (Sample 2-27)

A coupled conjugated diene-based polymer (sample 2-27) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, and that a resin (terpene resin YS resin PX1250, manufactured by Yasuhara Chemical Co., Ltd.) was added instead of SRAE oil added as the rubber softener. Physical properties of the sample 2-27 are shown in Table 19.

[0336]

(Example 2-28) Coupled Conjugated Diene-based Polymer (Sample 2-28)

A coupled conjugated diene-based polymer (sample 2-28) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, and that a naphthene oil (naphthene oil Nytex810, manufactured by Nynas) was added instead of SRAE oil added as the rubber softener. Physical properties of the sample 2-28 are shown in Table 19.

[0337]

(Example 2-29) Coupled Conjugated Diene-based Polymer (Sample 2-29)

A coupled conjugated diene-based polymer (sample 2-29) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, and that a rubber softener

was not added. Physical properties of the sample 2-29 are shown in Table 19.

[0338]

(Example 2-30) Coupled Conjugated Diene-based Polymer (Sample 2-30)

A coupled conjugated diene-based polymer (sample 2-30) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), that the amount thereof to be added was changed to 0.0190 mmol/min, and that the amount of SRAE oil to be added as the rubber softener was changed from 25.0 g to 37.5 g per 100 g of the polymer. Physical properties of the sample 2-30 are shown in Table 19.

[0339]

(Example 2-31) Conjugated Diene-based Polymer (Sample 2-31)

A conjugated diene-based polymer (sample 2-31) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) but not having a star coupled structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that trimethoxy(4-vinylphenyl)silane (shown as

"BS-1" in the table) was added as the branching agent at a rate of 0.0190 mmol/min from the bottom of the second reactor when polymerization was sufficiently stabilized, and that a coupling agent was not added. Physical properties of the sample 2-31 are shown in Table 20.

Various physical properties of the conjugated diene-based polymer as the sample 2-31 are shown in the column "Coupled Conjugated Diene-based Polymer" in Table 20, for convenience.

[0340]

(Example 2-32) Coupled Conjugated Diene-based Polymer (Sample 2-32)

A coupled conjugated diene-based polymer (sample 2-32) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having a partially 3-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) was added as the branching agent at a rate of 0.0190 mmol/min from the bottom of the second reactor when polymerization was sufficiently stabilized, and that the amount of tetraethoxysilane (shown as "A" in the table) as the coupling agent to be added was changed from 0.0480 mmol/min to 0.0120 mmol/min. Physical properties of the sample 2-32 are shown in Table 20.

[0341]

(Example 2-33) Coupled Conjugated Diene-based
Polymer (Sample 2-33)

A coupled conjugated diene-based polymer (sample 2-33) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having a partially 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) was added as the branching agent at a rate of 0.0190 mmol/min from the bottom of the second reactor when polymerization was sufficiently stabilized, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0038 mmol/min. Physical properties of the sample 2-33 are shown in Table 20.

[0342]

(Example 2-34) Coupled Conjugated Diene-based
Polymer (Sample 2-34)

A coupled conjugated diene-based polymer (sample 2-34) having, in a part of a main chain, a 2-branched structure derived from the branching agent structure (2-1) and having a partially 3-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that dimethylmethoxy(4-vinylphenyl)silane (shown as "BS-2" in

the table) was added as the branching agent at a rate of 0.0350 mmol/min from the bottom of the second reactor when polymerization was sufficiently stabilized, and that the amount of tetraethoxysilane as the coupling agent to be added was changed from 0.0480 mmol/min to 0.0120 mmol/min. Physical properties of the sample 2-34 are shown in Table 20.

[0343]

(Example 2-35) Coupled Conjugated Diene-based
Polymer (Sample 2-35)

A coupled conjugated diene-based polymer (sample 2-35) having, in a part of a main chain, a 3-branched structure derived from the branching agent structure (2-2) and having a partially 3-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that 1,1-bis(4-(dimethylmethoxysilyl)phenyl)ethylene (shown as "BS-3" in the table) was added as the branching agent at a rate of 0.0120 mmol/min from the bottom of the second reactor when polymerization was sufficiently stabilized, and that the amount of tetraethoxysilane as the coupling agent to be added was changed from 0.0480 mmol/min to 0.0120 mmol/min. Physical properties of the sample 2-35 are shown in Table 20.

[0344]

(Example 2-36) Coupled Conjugated Diene-based
Polymer (Sample 2-36)

A coupled conjugated diene-based polymer (sample 2-36) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having a 2-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the coupling agent was changed from tetraethoxysilane to 3-(benzylideneamino)propyltriethoxysilane (shown as "G" in the table), and that the amount thereof to be added was changed to 0.0620 mmol/min. Physical properties of the sample 2-36 are shown in Table 20.

[0345]

(Example 2-37) Coupled Conjugated Diene-based Polymer (Sample 2-37)

A coupled conjugated diene-based polymer (sample 2-37) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the amount of 1,3-butadiene to be added to the first reactor was changed from 18.6 g/min to 13.95 g/min, and that 1,3-butadiene was added in an amount of 4.65 g/min from the bottom of the second reactor at the same time as the branching agent. Physical properties of the sample 2-37 are shown in Table 20.

[0346]

(Example 2-38) Coupled Conjugated Diene-based
Polymer (Sample 2-38)

A coupled conjugated diene-based polymer (sample 2-38) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the nitrogen atom-containing vinyl compound was changed from 1-(4-N,N-dimethylaminophenyl)-1-phenylethylene to N,N-dimethylvinylbenzylamine (shown as "N-2" in the table) and was added at a rate of 0.120 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 2-38 are shown in Table 20.

[0347]

(Example 2-39) Coupled Conjugated Diene-based
Polymer (Sample 2-39)

A coupled conjugated diene-based polymer (sample 2-39) having, in a part of a main chain, a 4-branched structure derived from the branching agent structure (2-1) and having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Example 2-1 except that the nitrogen atom-containing vinyl compound was changed from 1-(4-N,N-

dimethylaminophenyl)-1-phenylethylene to 4-(2-pyrrolidinoethyl)styrene (shown as "N-3" in the table) and added at a rate of 0.120 mmol/min, that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table), and that the amount thereof to be added was changed to 0.0160 mmol/min. Physical properties of the sample 2-39 are shown in Table 20.

[0348]

(Example 2-40) Coupled Conjugated Diene-based Polymer (Sample 2-40)

A temperature controllable autoclave having an internal volume of 5 L (L/D:3.4) and equipped with a stirrer and a jacket was used as a reactor, and the reactor was charged with 1995 g of normal hexane and n-butyllithium for neutralizing an impurity that was present in the reactor and could inhibit a polymerization reaction. The resultant was stirred at 70°C for 5 minutes, and cooled to room temperature, and then the resultant solution was taken out to evacuate the reactor.

Next, the reactor was charged with 1670 g of normal hexane, 83 g of styrene, 236 g of 1,3-butadiene, and 2.73 mmol of 2,2-bis(2-oxolanyl)propane used as a polar material, from which impurities had been precedently removed, and 2.92 mmol of n-butyllithium (referred to as "NBL" in the tables.) was added as a polymerization

initiator at a reactor temperature of 56°C to start polymerization.

Immediately after starting the polymerization, the temperature within the reactor increased, and reached a peak temperature, which was 79°C. When a decrease in temperature was confirmed, both 0.90 mmol of trimethoxy(4-vinylphenyl)silane (shown as "BS-1" in the table) as a branching agent and 0.150 mmol of 1-(4-N,N-dimethylaminophenyl)-1-phenylethylene (shown as "N-1" in the table) as a nitrogen atom-containing vinyl compound were added, and stirred for 5 minutes, and 0.83 mmol of tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table) as a coupling agent was added and stirred for additional 5 minutes. The stirring speed here was 200 rpm. The coupling agent was added at 7 minutes after reaching the peak temperature.

The reaction was stopped by adding 2.92 mmol of ethanol as a polymerization terminator, and thus, a coupled conjugated diene-based polymer-containing polymer solution was obtained.

To the thus obtained polymer solution, 2,6-di-tert-butyl-4-hydroxytoluene as an antioxidant was added in an amount of 0.64 g, then the solvent was removed by steam stripping, vacuum drying was performed, and thus, coupled conjugated diene-based polymer 2-40 was obtained.

Physical properties are shown in Table 22 below.

[0349]

(Comparative Example 2-1) Coupled Conjugated Diene-based Polymer (Sample 2-41)

Two tank pressure vessels, each of which was a stirrer-equipped tank reactor having an internal volume of 10 L and a ratio (L/D) of an internal height (L) and a diameter (D) of 4.0, having an inlet at a bottom and an outlet at a top, and equipped with a stirrer and a temperature controlling jacket, were connected to each other as polymerization reactors.

1,3-Butadiene, from which a water content had been precedently removed, styrene and n-hexane were mixed under conditions of 18.6 g/min, 10.0 g/min and 175.2 g/min, respectively. In a static mixer provided in the middle of a pipe for supplying the thus obtained mixed solution to the inlet of the reactor, n-butyllithium to be used for residual impurity inactivation was added and mixed in an amount of 0.103 mmol/min, and the resultant was continuously supplied to the bottom of the reactor. Furthermore, 2,2-bis(2-oxolanyl)propane used as a polar material and n-butyllithium used as a polymerization initiator were supplied, at rates of respectively 0.081 mmol/min and 0.143 mmol/min, to the bottom of the first reactor in which materials were vigorously mixed by the stirrer, and the internal temperature of the reactor was kept at 67°C.

The thus obtained polymer solution was continuously taken out from the top of the first reactor to be

continuously supplied to the bottom of the second reactor for continuing the reaction at 70°C, and the resultant was further supplied to a static mixer from the top of the second reactor. When the polymerization was sufficiently stabilized, a small amount of a polymer solution prior to addition of a coupling agent was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and a Mooney viscosity at 110°C and various molecular weights were measured. The physical properties are shown in Table 21.

Next, to the polymer solution flowing out of the outlet of the reactor, tetraethoxysilane (shown as "A" in the table) was added, as a coupling agent, continuously at a rate of 0.0480 mmol/min, and the resultant was mixed by using a static mixer for performing a coupling reaction. Here, a time until the addition of the coupling agent to the polymer solution flowing out of the outlet of the reactor was 4.8 min, the temperature was 68°C, and a difference between the temperature in the polymerizing step and the temperature until the addition of the coupling agent was 2°C. A small amount of a conjugated diene-based polymer solution after the coupling reaction was taken out, an antioxidant (BHT) was added thereto in an amount of 0.2 g per 100 g of the polymer, then the solvent was removed, and the amount of bound styrene (Physical Property 6) and the

microstructure of a butadiene portion (the amount of 1,2-vinyl bond; Physical Property 7) were measured.

Measurement results are shown in Table 21.

Next, to the polymer solution resulting from the coupling reaction, the antioxidant (BHT) was continuously added in an amount of 0.2 g per 100 g of the polymer at 0.055 g/min (n-hexane solution) to complete the coupling reaction. Simultaneously with the antioxidant, SRAE oil (JOMO Process NC 140, manufactured by JX Nippon Oil & Energy Corporation) was continuously added as a rubber softener in an amount of 25.0 g per 100 g of the polymer, and the resultant was mixed by using a static mixer. The solvent was removed by steam stripping, and thus, a coupled conjugated diene-based polymer (sample 2-41) not having a main chain branch derived from the branching agent but having a 3-branched star polymer structure derived from the coupling agent was obtained. Physical properties of the sample 2-41 are shown in Table 21.

[0350]

(Comparative Example 2-2) Coupled Conjugated Diene-based Polymer (Sample 2-42)

A coupled conjugated diene-based polymer (sample 2-42) not having a main chain branch derived from the branching agent but having a 4-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Comparative Example 2-1 except that the coupling agent was changed from tetraethoxysilane to

2,2-dimethoxy-1-(3-trimethoxysilylpropyl)-1-aza-2-silacyclopentane (shown as "D" in the table) and that the amount thereof to be added was changed to 0.0360 mmol/min.

Physical properties of the sample 2-42 are shown in Table 21.

[0351]

(Comparative Example 2-3) Coupled Conjugated Diene-based Polymer (Sample 2-43)

A coupled conjugated diene-based polymer (sample 2-43) not having a main chain branch derived from the branching agent but having an 8-branched star polymer structure derived from the coupling agent was obtained in the same manner as in Comparative Example 2-1 except that the coupling agent was changed from tetraethoxysilane to tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table) and that the amount thereof to be added was changed to 0.0190 mmol/min. Physical properties of the sample 2-43 are shown in Table 21.

[0352]

(Comparative Example 2-4) Coupled Conjugated Diene-based Polymer (Sample 2-44)

A temperature controllable autoclave having an internal volume of 5 L and equipped with a stirrer and a jacket was used as a reactor, the reactor was charged with 1670 g of normal hexane, 83 g of styrene, 236 g of 1,3-butadiene, and 1.91 mmol of 2,2-bis(2-

oxolanyl)propane as a polar material, from which impurities had been precedently removed, and 2.55 mmol of n-butyllithium was added as a polymerization initiator at a reactor temperature of 58°C to start polymerization.

Immediately after starting the polymerization, the temperature within the reactor increased, and reached a peak temperature. When a decrease in temperature was confirmed, 0.83 mmol of tetrakis(3-trimethoxysilylpropyl)-1,3-propanediamine (shown as "F" in the table) as a coupling agent was added, and the resultant was stirred for additional 10 minutes. The reaction was stopped by adding 2.55 mmol of ethanol as a polymerization terminator, and thus, a modified conjugated diene-based polymer-containing polymer solution was obtained. To the thus obtained polymer solution, 0.64 g of 2,6-di-tert-butyl-4-hydroxytoluene as a stabilizer was added, then the solvent was removed by steam stripping, vacuum drying was performed, and thus, a modified conjugated diene-based polymer (sample 2-44) was obtained. Physical properties are shown in Table 22 below.

[0353]

[Table 16]

		Example	Example	Example	Example	Example	Example	Example	Example	Example
Polymerization Conditions	Conjugated Diene-based Polymer (Sample No.)		2-1	2-2	2-3	2-4	2-5	2-6	2-7	Example 2-8
		Buladiene	2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8
		Styrene	18.6	18.6	18.6	18.6	18.6	18.6	18.6	24.3
		n-Hexane	10.0	10.0	10.0	10.0	10.0	10.0	10.0	4.3
		Type	175.2	175.2	175.2	175.2	175.2	175.2	175.2	175.2
	Amount Added	Nitrogen Atom-containing Vinyl Compound	N-1	N-1	N-1	N-1	N-1	N-1	N-1	N-1
		Amount Added	0.120	0.120	0.120	0.120	0.120	0.120	0.120	0.120
		Polymerization Temperature	70	70	70	70	70	70	70	70
		n-Butyllithium for Treatment	0.103	0.103	0.103	0.103	0.103	0.103	0.103	0.103
		n-Butyllithium as Polymerization Initiator	0.143	0.143	0.143	0.143	0.143	0.143	0.143	0.143
Physical Property Values	Branching Agent	Amount of Polar Material Added	0.081	0.081	0.081	0.081	0.081	0.081	0.081	0.044
		Type	BS-1	BS-1	BS-1	BS-1	BS-1	BS-1	BS-1	BS-1
		Amount Added	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190
		Type	A	B	C	D	E	F	F	F
		Amount Added	0.048	0.0360	0.0360	0.0360	0.0250	0.0190	0.0160	0.0160
	Coupled Conjugated Diene-based Polymer	(Physical Property 4) Weight Average Molecular Weight	63.9	63.9	63.9	63.9	63.9	63.9	63.9	62.3
		(Physical Property 4) Number Average Molecular Weight	33.1	33.1	33.1	33.1	33.1	33.1	33.1	32.7
		(Physical Property 4) Mw/Mn	1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93
		(Physical Property 1) Mooney Viscosity (110°C)	92.1	92.1	92.1	92.1	92.1	92.1	92.1	89.4
		(Physical Property 5) Modification Ratio	80	80	80	80	80	80	81	82
Coupled Conjugated Diene-based Polymer	Type of Rubber Softener	Amount of Rubber Softener Added	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE
		Amount of Rubber Softener Added	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
		(Physical Property 1) Mooney Viscosity (100°C)	91	98	99	98	98	97	95	93
		(Physical Property 2) Mooney Stress Relaxation Rate (100°C)	0.264	0.253	0.252	0.253	0.253	0.255	0.258	0.261
		(Physical Property 3) Branch Number Bn	8.2	8.8	8.8	8.7	12.0	15.8	20.0	19.2
	Coupled Conjugated Diene-based Polymer	(Physical Property 4) Weight Average Molecular Weight	89.3	92.1	92.3	92.0	96.0	105.3	106.0	105.8
		(Physical Property 4) Number Average Molecular Weight	45.6	46.6	46.8	46.7	48.7	53.4	54.6	54.8
		(Physical Property 4) Mw/Mn	1.96	1.98	1.97	1.97	1.97	1.97	1.94	1.93
		(Physical Property 5) Modification Ratio	80	80	89	89	89	89	89	89
		(Physical Property 6) Amount of Bound Styrene	35	35	35	35	35	35	35	15
Coupled Conjugated Diene-based Polymer	(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	(mol%)	40	40	40	40	40	40	40	28
		(Physical Property 8) Absolute Molecular Weight (Mw-i)	132	142	148	144	170	186	281	273
		(10 ⁴ Daltons)								
		(Physical Property 8) Absolute Molecular Weight (Mw-i)								
		(10 ⁴ Daltons)								
	(Physical Property 8) Absolute Molecular Weight (Mw-i)	(10 ⁴ Daltons)								
		(10 ⁴ Daltons)								
		(10 ⁴ Daltons)								
		(10 ⁴ Daltons)								
		(10 ⁴ Daltons)								
		(10 ⁴ Daltons)								

[0354]

[Table 17]

Conjugated Diene-based Polymer (Sample No.)												
Polymerization Conditions	Butadiene		(g/min)	Example 2-9	Example 2-10	Example 2-11	Example 2-12	Example 2-13	Example 2-14	Example 2-15	Example 2-16	
	Styrene		(g/min)	2-9	2-10	2-11	2-12	2-13	2-14	2-15	2-16	
	n-Hexane		(g/min)	17.1	18.6	18.6	18.6	18.6	18.6	18.6	18.6	
	Nitrogen Atom-containing Vinyl Compound	Type	(g/min)	11.5	10.0	10.0	10.0	10.0	10.0	10.0	10.0	
		Amount Added	(mmol/min)	175.2	175.2	175.2	175.2	175.2	175.2	175.2	175.2	
			(mmol/min)	N-1	N-1	N-1	N-1	N-1	N-1	N-1	N-1	
	Physical Property Values	Modified Branched Conjugated Diene-based Polymer	Amount Added	(mmol/min)	0.1200	0.1200	0.1200	0.1200	0.1200	0.1200	0.1200	0.1200
				(°C)	70	70	70	70	70	70	70	70
				(mmol/min)	0.103	0.103	0.103	0.103	0.103	0.103	0.103	0.103
		Coupling Agent	Amount Added	(mmol/min)	0.143	0.143	0.143	0.143	0.143	0.143	0.143	0.143
(mmol/min)				0.089	0.2	0.081	0.081	0.081	0.081	0.081	0.081	
(mmol/min)				BS-1	BS-1	BS-2	BS-2	BS-2	BS-3	BS-3	BS-3	
Coupled Conjugated Diene-based Polymer		Amount Added	(mmol/min)	BS-1	BS-1	BS-2	BS-2	BS-2	BS-3	BS-3	BS-3	
			(mmol/min)	0.0190	0.0190	0.0350	0.0350	0.0350	0.0350	0.0120	0.0120	
			(%)	F	F	B	D	F	B	D	F	
Physical Property Values		Type of Rubber Softener	Amount of Rubber Softener Added	(mmol/min)	0.0160	0.0160	0.0360	0.0360	0.0160	0.0360	0.0360	0.0160
	(10 ⁶ g/mol)			64.2	64.7	60.3	60.3	60.3	74.5	74.5	74.5	
	(10 ⁶ g/mol)			33.5	33.8	32.2	32.2	32.2	37.8	37.8	37.8	
	Coupled Conjugated Diene-based Polymer	Amount of Rubber Softener Added	(10 ⁶ g/mol)	1.93	1.93	1.87	1.87	1.87	1.97	1.97	1.97	
			(10 ⁶ g/mol)	93.8	95.1	88.2	88.2	88.2	99.1	99.1	99.1	
			(%)	81	81	81	81	81	81	81	81	
	Physical Property Values	Type of Rubber Softener	Amount of Rubber Softener Added	(mmol/min)	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE
				(pHm)	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
				(10 ⁶ g/mol)	93	89	93	94	97	94	96	82
		Coupled Conjugated Diene-based Polymer	Amount of Rubber Softener Added	(10 ⁶ g/mol)	0.256	0.252	0.261	0.260	0.255	0.260	0.256	0.280
(10 ⁶ g/mol)				21.6	22.3	8.2	8.2	13.0	17.4	18.0	30.0	
(10 ⁶ g/mol)				107.0	107.4	91.7	92.0	105.3	112.6	115.0	135.0	
Coupled Conjugated Diene-based Polymer		Amount of Rubber Softener Added	(10 ⁶ g/mol)	55.4	54.2	46.5	46.5	54.6	56.9	57.2	69.6	
			(10 ⁶ g/mol)	1.93	1.98	1.97	1.98	1.93	1.98	2.01	1.94	
			(%)	92	91	81	89	89	81	91	92	
Coupled Conjugated Diene-based Polymer		Amount of Bound Styrene	(mass%)	40	35	35	35	35	35	35	35	
	(mol%)		40	58	40	40	40	40	40	40		
	(10 ⁴ Daltons)		287	291	133	136	176	153	160	335		

[0355]

[Table 18]

		Example 2-17	Example 2-18	Example 2-19	Example 2-20	Example 2-21	Example 2-22	Example 2-23
Polymerization Conditions	Conjugated Diene-based Polymer (Sample No.)							
	Butadiene							
	Styrene							
	n-Hexane							
	Nitrogen Atom-containing Vinyl Compound	Type						
	Amount Added							
	Polymerization Temperature							
	n-Butyllithium for Treatment							
	n-Butyllithium as Polymerization Initiator							
	Amount of Polar Material Added							
Physical Property Values	Branching Agent	Type						
	Amount Added							
	Coupling Agent	Type						
	Amount Added							
	(Physical Property 4) Weight Average Molecular Weight							
	(Physical Property 4) Number Average Molecular Weight							
	(Physical Property 4) Mw/Mn							
	(Physical Property 1) Mooney Viscosity (110°C)							
	(Physical Property 5) Modification Ratio							
	Type of Rubber Softener							
Coupled Conjugated Diene-based Polymer	Amount of Rubber Softener Added							
	(Physical Property 1) Mooney Viscosity (100°C)							
	(Physical Property 2) Mooney Stress Relaxation Rate (100°C)							
	(Physical Property 3) Branch Number Bn							
	(Physical Property 4) Weight Average Molecular Weight							
	(Physical Property 4) Number Average Molecular Weight							
	(Physical Property 4) Mw/Mn							
	(Physical Property 5) Modification Ratio							
	(Physical Property 6) Amount of Bound Styrene							
	(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)							
	(Physical Property 8) Absolute Molecular Weight (Mw-I)							

[0356]

[Table 19]

		Example 2-24	Example 2-25	Example 2-26	Example 2-27	Example 2-28	Example 2-29	Example 2-30
Polymerization Conditions	Conjugated Diene-based Polymer (Sample No.)							
	Butadiene		(g/min)	2-24	2-25	2-26	2-27	2-28
	Styrene		(g/min)	18.6	18.6	18.6	18.6	18.6
	n-Hexane		(g/min)	10.0	10.0	10.0	10.0	10.0
	Type		(g/min)	175.2	175.2	175.2	175.2	175.2
	Nitrogen Atom-containing Vinyl Compound			N-1	N-1	N-1	N-1	N-1
	Amount Added		(mmol/min)	0.1200	0.1200	0.1200	0.1200	0.1200
	Polymerization Temperature		(°C)	70	70	70	70	70
	n-Butyllithium for Treatment		(mmol/min)	0.103	0.103	0.103	0.103	0.103
	n-Butyllithium as Polymerization Initiator		(mmol/min)	0.143	0.143	0.143	0.143	0.143
Physical Property Values	Amount of Polar Material Added		(mmol/min)	0.081	0.081	0.081	0.081	0.081
	Type			BS-1	BS-1	BS-1	BS-1	BS-1
	Branching Agent		(mmol/min)	0.0250	0.0350	0.0190	0.0190	0.0190
	Amount Added			F	F	F	F	F
	Type			0.0190	0.0190	0.0190	0.0190	0.0190
	Coupling Agent		(mmol/min)	78.8	89.3	63.9	63.9	63.9
	Amount Added		(10 ⁴ g/mol)	40.1	45.1	33.1	33.1	33.1
	Modified Branched Conjugated Diene-based Polymer		(10 ⁴ g/mol)	1.97	1.98	1.93	1.93	1.93
	(Physical Property 1) Mooney Viscosity (110°C)			98.1	105.3	92.1	92.1	92.1
	(Physical Property 5) Modification Ratio		(%)	81	81	81	81	81
Coupled Conjugated Diene-based Polymer	Type of Rubber Softener			SRAE	SRAE	Liquid Rubber	Resin	Naphthene Oil
	Amount of Rubber Softener Added		(phm)	25.0	25.0	25.0	25.0	0.0
	(Physical Property 1) Mooney Viscosity (100°C)			105	107	92	101	157
	(Physical Property 2) Mooney Stress Relaxation Rate (100°C)			0.242	0.239	0.263	0.248	0.159
	(Physical Property 3) Branch Number Bn		per molecule	25.3	30.1	15.8	15.8	15.8
	(Physical Property 4) Weight Average Molecular Weight		(10 ⁴ g/mol)	117.0	125.0	105.3	105.3	105.3
	(Physical Property 4) Number Average Molecular Weight		(10 ⁴ g/mol)	59.7	62.2	53.4	53.4	53.4
	(Physical Property 4) Mw/Mn			1.96	2.01	1.97	1.97	1.97
	(Physical Property 5) Modification Ratio		(%)	86	84	91	97	92
	(Physical Property 6) Amount of Bound Styrene		(mass%)	35	35	35	35	35
	(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)		(mol%)	40	40	40	40	40
	(Physical Property 8) Absolute Molecular Weight (Mw-i)		(10 ⁴ Daltons)	320	360	186	186	186

[0357]

[Table 20]

		Example 2-31	Example 2-32	Example 2-33	Example 2-34	Example 2-35	Example 2-36	Example 2-37	Example 2-38	Example 2-39
Conjugated Diene-based Polymer (Sample No.)		2-31	2-32	2-33	2-34	2-35	2-36	2-37	2-38	2-39
Polymerization Conditions	Butadiene	18.6	18.6	18.6	18.6	18.6	18.6	1st reactor: 13.95 2nd reactor: 4.65	18.6	18.6
	Styrene	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
	n-Hexane	175.2	175.2	175.2	175.2	175.2	175.2	175.2	175.2	175.2
	Type	N-1	N-1	N-1	N-1	N-1	N-1	N-1	N-2	N-2
	Amount Added	0.1200	0.1200	0.1200	0.1200	0.1200	0.1200	0.1200	0.120	0.120
	Polymerization Temperature	70	70	70	70	70	70	70	70	70
	n-Butyllithium for Treatment	0.103	0.103	0.103	0.103	0.103	0.103	0.103	0.103	0.103
	n-Butyllithium as Polymerization Initiator	0.143	0.143	0.143	0.143	0.143	0.143	0.143	0.143	0.143
	Amount of Polar Material Added	0.081	0.081	0.081	0.081	0.081	0.081	0.081	0.081	0.081
	Type	BS-1	BS-1	BS-1	BS-2	BS-3	BS-1	BS-1	BS-1	BS-1
Physical Property Values	Amount Added	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190	0.0190
	Type	-	A	F	A	A	G	A	F	F
	Amount Added	-	0.0120	0.0038	0.0120	0.0120	0.0620	0.048	0.0160	0.0160
	(Physical Property 4) Weight Average Molecular Weight	63.9	63.9	63.9	63.9	63.9	63.9	63.9	63.9	63.9
	(Physical Property 4) Number Average Molecular Weight	33.1	33.1	33.1	33.1	33.1	33.1	33.1	33.1	33.1
	(Physical Property 4) Mw/Mn	1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93	1.93
	(Physical Property 1) Mooney Viscosity (110°C)	92.1	92.1	92.1	92.1	92.1	92.1	95.1	92.1	92.1
	(Physical Property 5) Modification Ratio	81	81	81	81	81	81	81	81	81
	Type of Rubber Softener	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE	SRAE
	Amount of Rubber Softener Added	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
Coupled Conjugated Diene-based Polymer	(Physical Property 1) Mooney Viscosity (100°C)	74	84	90	52	65	74	91	95	95
	(Physical Property 2) Mooney Stress Relaxation Rate (100°C)	0.761	0.621	0.422	0.655	0.617	0.591	0.260	0.258	0.258
	(Physical Property 3) Branch Number Bn	1.1	2.9	5.9	1.7	4.6	7.1	8.6	20.0	20.0
	(Physical Property 4) Weight Average Molecular Weight	63.9	82.1	97.3	63.9	65.1	71.8	89.3	106.0	106.0
	(Physical Property 4) Number Average Molecular Weight	33.1	40.8	49.1	31.8	32.4	38.2	45.2	54.6	54.6
	(Physical Property 4) Mw/Mn	1.93	2.01	1.98	2.01	2.01	1.88	1.98	1.94	1.94
	(Physical Property 5) Modification Ratio	81	89	90	81	81	85	-	89	89
	(Physical Property 6) Amount of Bound Styrene	35	35	35	35	35	35	35	35	35
	(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	40	40	40	40	40	40	40	40	40
	(Physical Property 8) Absolute Molecular Weight (Mw-i)	84	96	142	38	72	84	140	281	281

[0358]

[Table 21]

		Conjugated Diene-based Polymer (Sample No.)	Comparative Example 2-1	Comparative Example 2-2	Comparative Example 2-3
Polymerization Conditions		Butadiene	18.6	18.6	18.6
		Styrene	10.0	10.0	10.0
		n-Hexane	175.2	175.2	175.2
		Polymerization Temperature	70	70	70
		n-Butyllithium for Treatment	0.103	0.103	0.103
		n-Butyllithium as Polymerization Initiator	0.143	0.143	0.143
		Amount of Polar Material Added	0.081	0.081	0.081
		Branching Agent	-	-	-
		Amount Added	-	-	-
		Coupling Agent	A	D	F
Physical Property Values	Conjugated Diene-based Polymer	Amount Added	0.0480	0.0360	0.0190
		(Physical Property 4) Weight Average Molecular Weight	48.9	48.9	48.9
		(Physical Property 4) Number Average Molecular Weight	27.9	27.9	27.9
		(Physical Property 4) Mw/Mn	1.75	1.75	1.75
		(Physical Property 1) Mooney Viscosity (110°C)	72.5	72.5	72.5
	Coupled Conjugated Diene-based Polymer	Type of Rubber Softener	SRAE	SRAE	SRAE
		Amount of Rubber Softener Added	25.0	25.0	25.0
		(Physical Property 1) Mooney Viscosity (100°C)	74	84	90
		(Physical Property 2) Mooney Stress Relaxation Rate (100°C)	0.761	0.621	0.422
		(Physical Property 3) Branch Number Bn	1.1	2.9	5.9
		(Physical Property 4) Weight Average Molecular Weight	73.4	82.1	97.3
		(Physical Property 4) Number Average Molecular Weight	39.3	40.8	49.1
		(Physical Property 4) Mw/Mn	1.87	2.01	1.98
		(Physical Property 5) Modification Ratio	0	83	80
		(Physical Property 6) Amount of Bound Styrene	35	35	35
		(Physical Property 7) Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)	40	40	40
		(Physical Property 8) Absolute Molecular Weight (Mw-i)	84	96	142

[0359]

[Table 22]

Conjugated Diene-based Polymer (Sample No.)		Example 2-40	Comparative Example 2-4
Polymerization Conditions		2-40	2-44
	Butadiene	(g)	236
	Styrene	(g)	83
	Normal Hexane	(g)	1670
	Polymerization Initiation Temperature	(°C)	55
	Polymerization Peak Temperature	(°C)	77
	Polymerization Initiator	Type	NBL
		Amount Added	2.92
	Polar Material	Amount Added	2.73
		Type	BS-1
	Branching Agent	Amount Added	0.90
		Type	N-1
	Nitrogen Atom-containing Vinyl Compound	Amount Added	1.50
		Type	F
Analysis Values	Coupling Agent	Amount Added	0.83
		(mmol)	0.83
	Mooney Viscosity of Coupled Conjugated Diene-based Polymer ML ₁₊₄ (100°C)		
	Weight Average Molecular Weight (Mw)		95
			($\times 10^{-4}$)
	Number Average Molecular Weight (Mn)		110.0
			($\times 10^{-4}$)
	Mw/Mn		55.0
	Modification Ratio		2.00
			(%)
	Amount of Bound Styrene		95.0
			(mass%)
	Amount of Bound Vinyl (Amount of 1,2-Vinyl Bond)		27
			(mol%)
	Glass Transition Temperature (Tg)		55
			(°C)
	δ ML Mooney Viscosity		-26
			8
			12

[0360]

(Examples 2-41 to 2-80 and Comparative Examples 5 to 8)

The samples 2-1 to 2-44 shown in Tables 16 to 22 were respectively used as raw material rubbers to obtain rubber compositions respectively containing the raw material rubbers in accordance with the following composition:

[0361]

(Rubber Component)

- Conjugated diene-based polymer and coupled conjugated diene-based polymer (each of the samples 2-1 to 2-44)

: 80 parts by mass (polymer excluding rubber softener (parts by mass))

- High cis-polybutadiene (trade name "UBEPOL BR150" manufactured by Ube Industries, Ltd.)

: 20 parts by mass

[0362]

(Blending Conditions)

The amount of each blending component to be added was indicated in parts by mass with respect to 100 parts by mass of the rubber component excluding a rubber softener.

- Silica 1 (trade name "Ultrasil 7000GR", manufactured by Evonik Degussa, nitrogen adsorption specific surface area: 170 m²/g): 50.0 parts by mass

- Silica 2 (trade name "Zeosil Premium 200MP" manufactured by Rhodia, nitrogen adsorption specific surface area: 220 m²/g): 25.0 parts by mass
- Carbon black (trade name "Seast KH (N339)", manufactured by Tokai Carbon Co., Ltd.)
: 5.0 parts by mass
- Silane coupling agent: (trade name "Si75", manufactured by Evonik Degussa, bis(triethoxysilylpropyl)disulfide): 6.0 parts by mass
- SRAE oil (trade name "Process NC140", manufactured by JX Nippon Oil & Energy Corporation)
: 42.0 parts by mass
(including an amount precedently added as the rubber softener to be contained in each of the samples 2-1 to 2-44)
- Zinc oxide: 2.5 parts by mass
- Stearic acid: 1.0 part by mass
- Anti-ageing agent (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine): 2.0 parts by mass
- Sulfur: 2.2 parts by mass
- Vulcanization accelerator 1 (N-cyclohexyl-2-benzothiazylsulfonamide)
: 1.7 parts by mass
- Vulcanization accelerator 2 (diphenylguanidine):
2.0 parts by mass
- Total: 239.4 parts by mass

[0363]

(Kneading Method)

The above-described materials were kneaded by the following method to obtain a rubber composition.

A closed kneader (having an internal volume of 0.3 L) equipped with a temperature controller was used to knead, as a first stage of kneading, the raw material rubber (each of the samples 2-1 to 2-44), the fillers (silica 1, silica 2 and carbon black), the silane coupling agent, SRAE oil, zinc oxide and stearic acid under conditions of a filling ratio of 65% and a rotor rotation speed of 30 to 50 rpm. Here, the temperature of the closed mixer was controlled to obtain each rubber composition (compound) at a discharging temperature of 155 to 160°C.

Next, after cooling the compound obtained as described above to room temperature, as a second stage of the kneading, the anti-ageing agent was added thereto, and the resultant was kneaded again to improve dispersibility of the silica. Also in this case, the discharging temperature for the compound was adjusted to 155 to 160°C by the temperature controller of the mixer.

After cooling, as a third stage of the kneading, sulfur and the vulcanization accelerators 1 and 2 were added, and the resultant was kneaded by an open roll set to 70°C.

Thereafter, the resultant was molded and vulcanized at 160°C for 20 minutes by a vulcanizing press.

The rubber compositions prior to the vulcanization, and the rubber compositions after the vulcanization were evaluated. Specifically, the evaluations were performed by methods described below. Results thus obtained are shown in Tables 23 to 29.

[0364]

(Evaluation of properties)

(Evaluation 1) Mooney Viscosity of Compound

Each compound obtained after the second stage of the kneading and before the third stage of the kneading was used as a sample to measure a viscosity by using a Mooney viscometer in accordance with ISO 289 after preheating the compound at 130°C for 1 minute, and after rotating a rotor for 4 minutes at 2 rpm. The thus obtained viscosity was shown as an index obtained assuming that the result of Comparative Example 2-5 was 100. A smaller index indicates better workability.

[0365]

(Evaluation 2) Tensile Strength and Tensile Elongation

Tensile strength and tensile elongation were measured in accordance with a tensile test method according to JIS K6251, and were shown as indexes obtained assuming that result of Comparative Example 2-5 was 100. A larger index indicates better tensile strength and tensile elongation (fracture strength).

[0366]

(Evaluation 3) Abrasion Resistance

An Acron abrasion tester (manufactured by Yasuda Seiki Seisakusho, Ltd.) was used to measure an abrasion amount through 1000 rotations at a load of 44.4 N in accordance with JIS K6264-2, and results were shown as indexes obtained assuming that the result of Comparative Example 2-5 was 100. A larger index indicates better abrasion resistance.

[0367]

(Evaluation 4) Viscoelasticity Parameter

A viscoelasticity testing machine "ARES" manufactured by Rheometric Scientific, Inc. was used to measure a viscoelasticity parameter in a torsion mode. Each measured value was shown as an index obtained assuming that a result obtained by the rubber composition of Comparative Example 2-5 was 100.

A $\tan \delta$ measured at 0°C at a frequency of 10 Hz and strain of 1% was used as an index of wet skid performance. A larger index indicates better wet skid performance.

A $\tan \delta$ measured at 50°C at a frequency of 10 Hz and strain of 3% was used as an index of fuel efficiency. A smaller index indicates higher fuel efficiency.

An elastic modulus (G') measured at 50°C at a frequency of 10 Hz and strain of 3% was used as an index of steering stability. A larger index indicates better steering stability.

[0368]

[Table 23]

	Example 2-41	Example 2-42	Example 2-43	Example 2-44	Example 2-45	Example 2-46	Example 2-47	Example 2-48
Conjugated Diene-based Polymer (Sample No.)	2-1	2-2	2-3	2-4	2-5	2-6	2-7	2-8
(Physical Property 1) Mooney Viscosity of Polymer (100°C)	91	98	99	98	98	97	95	99
(Evaluation 1) Mooney Viscosity of Compound (130°C)	Index	88	86	83	85	80	78	83
Physical Property Values	(Evaluation 2) Tensile Strength	Index	117	113	128	134	139	142
	(Evaluation 2) Tensile Elongation	Index	108	114	120	118	124	125
	(Evaluation 3) Abrasion Resistance	Index	113	128	130	142	148	152
	(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	Index	110	128	120	117	126	130
	(Evaluation 4) 50°C tan δ (strain: 3%)	Index	96	86	75	71	72	69
	(Evaluation 4) 0°C tan δ (strain: 1%)	Index	104	113	125	131	128	122

[0369]

[Table 24]

	Example 2-49	Example 2-50	Example 2-51	Example 2-52	Example 2-53	Example 2-54	Example 2-55	Example 2-56
Conjugated Diene-based Polymer (Sample No.)	2-9	2-10	2-11	2-12	2-13	2-14	2-15	2-16
(Physical Property 1) Mooney Viscosity of Polymer (100°C)	93	89	93	94	97	94	96	82
(Evaluation 1) Mooney Viscosity of Compound (130°C)	Index	77	74	88	84	86	82	80
(Evaluation 2) Tensile Strength	Index	137	133	109	112	129	138	146
(Evaluation 2) Tensile Elongation	Index	122	120	112	120	132	122	124
(Evaluation 3) Abrasion Resistance	Index	144	137	118	122	143	157	162
(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	Index	121	120	129	126	125	120	118
(Evaluation 4) 50°C tan δ (strain: 3%)	Index	75	78	92	83	75	77	74
(Evaluation 4) 0°C tan δ (strain: 1%)	Index	133	137	107	117	122	120	122

Physical Property Values

[0370]

[Table 25]

		Example 2-57	Example 2-58	Example 2-59	Example 2-60	Example 2-61	Example 2-62	Example 2-63
Conjugated Diene-based Polymer (Sample No.)		2-17	2-18	2-19	2-20	2-21	2-22	2-23
(Physical Property 1) Mooney Viscosity of Polymer (100°C)		95	97	99	97	99	101	102
(Evaluation 1) Mooney Viscosity of Compound (130°C)		Index	89	82	91	86	88	87
Physical Property Values	(Evaluation 2) Tensile Strength	109	112	125	107	109	127	109
	(Evaluation 2) Tensile Elongation	113	116	120	118	117	123	118
	(Evaluation 3) Abrasion Resistance	113	123	137	120	126	137	131
	(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	118	116	113	122	123	129	127
	(Evaluation 4) 50°C tan δ (strain: 3%)	93	88	76	92	82	78	83
	(Evaluation 4) 0°C tan δ (strain: 1%)	107	114	123	110	119	126	127

[0371]

[Table 26]

		Example 2-64	Example 2-65	Example 2-66	Example 2-67	Example 2-68	Example 2-69	Example 2-70
Conjugated Diene-based Polymer (Sample No.)		2-24	2-25	2-26	2-27	2-28	2-29	2-30
(Physical Property 1) Mooney Viscosity of Polymer (100°C)		105	107	92	101	103	157	83
Physical Property Values	(Evaluation 1) Mooney Viscosity of Compound (130°C)	Index	92	78	84	81	83	78
	(Evaluation 2) Tensile Strength	Index	145	153	120	143	130	135
	(Evaluation 2) Tensile Elongation	Index	117	124	110	128	121	120
	(Evaluation 3) Abrasion Resistance	Index	152	157	132	141	137	140
	(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	Index	131	130	124	139	124	122
	(Evaluation 4) 50°C tan δ (strain: 3%)	Index	85	87	78	88	82	71
	(Evaluation 4) 0°C tan δ (strain: 1%)	Index	113	110	118	137	122	130

[0372]

[Table 27]

		Example 2-71	Example 2-72	Example 2-73	Example 2-74	Example 2-75	Example 2-76	Example 2-77	Example 2-78	Example 2-79
Conjugated Diene-based Polymer (Sample No.)		2-31	2-32	2-33	2-34	2-35	2-36	2-37	2-38	2-39
(Physical Property 1) Mooney Viscosity of Polymer (100°C)		52	65	74	53	60	100	91	95	95
Physical Property Values	(Evaluation 1) Mooney Viscosity of Compound (130°C)	Index	74	92	93	90	95	87	78	78
	(Evaluation 2) Tensile Strength	Index	82	98	106	102	104	112	139	139
	(Evaluation 2) Tensile Elongation	Index	89	99	103	100	102	109	124	124
	(Evaluation 3) Abrasion Resistance	Index	71	102	103	106	103	114	148	148
	(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	Index	97	101	100	102	102	111	126	126
	(Evaluation 4) 50°C tan δ (strain: 3%)	Index	102	103	104	98	95	97	72	72
	(Evaluation 4) 0°C tan δ (strain: 1%)	Index	100	102	103	92	92	104	128	128

[0373]

[Table 28]

		Comparative Example 2-5	Comparative Example 2-6	Comparative Example 2-7
Conjugated Diene-based Polymer (Sample No.)		2-41	2-42	2-43
(Physical Property 1) Mooney Viscosity of Polymer (100°C)		74	84	90
(Evaluation 1) Mooney Viscosity of Compound (130°C)		100	113	116
Physical Property Values	(Evaluation 2) Tensile Strength	Index	100	117
	(Evaluation 2) Tensile Elongation	Index	100	102
	(Evaluation 3) Abrasion Resistance	Index	100	109
	(Evaluation 4) 50°C Elastic Modulus (strain: 3%)	Index	100	98
	(Evaluation 4) 50°C tan δ (strain: 3%)	Index	100	112
	(Evaluation 4) 0°C tan δ (strain: 1%)	Index	100	107

[0374]

[Table 29]

		Example 2-80	Comparative Example 2-8
Conjugated Diene-based Polymer (Sample No.)		2-40	2-44
(Evaluation 1) Mooney Viscosity of Compound (130°C)		78	90
Physical Property Values	(Evaluation 2) Tensile Strength	Index	120
	(Evaluation 2) Tensile Elongation	Index	118
	(Evaluation 3) Abrasion Resistance	Index	120
	(Evaluation 4) 50°C G' (strain: 3%)	Index	122
	(Evaluation 4) 50°C tan δ (strain: 3%)	Index	65
	(Evaluation 4) 0°C tan δ (strain: 1%)	Index	110

[0375]

As shown in Tables 23 to 29, it was confirmed that Examples 2-41 to 2-80 had, as compared with Comparative Examples 2-5 to 2-8, a low Mooney viscosity of the compound when used for obtaining a vulcanizate and

exhibited good workability, were excellent in abrasion resistance, steering stability and fracture strength when in the form of a vulcanizate, and were excellent in balance between a low hysteresis loss property and wet skid resistance.

[Industrial Applicability]

[0376]

A branched conjugated diene-based polymer obtained by a production method according to the present invention is industrially applicable in the fields of tire treads, interiors and exteriors of vehicles, anti-vibration rubbers, belts, shoes, foam bodies, and various industrial products.

[Document Name] Claims

[Claim 1]

A production method for a branched conjugated diene-based polymer, comprising:

a polymerizing step of obtaining a conjugated diene-based polymer having an active end by polymerizing or copolymerizing a conjugated diene compound, or a conjugated diene compound and an aromatic vinyl compound with an alkali metal compound or an alkaline earth metal compound used as a polymerization initiator; and

a branching step of introducing a branch structure by reacting a styrene derivative as a branching agent with the active end of the conjugated diene-based polymer.

[Claim 2]

The production method for a branched conjugated diene-based polymer according to claim 1, further comprising:

a step of adding a conjugated diene compound and/or an aromatic vinyl compound to a reaction system during and/or after the branching step.

[Claim 3]

The production method for a branched conjugated diene-based polymer according to claim 1 or 2, further comprising:

a reaction step of reacting a coupling agent or a polymerization terminator with the active end of the conjugated diene-based polymer resulting from the branching step.

[Claim 4]

The production method for a branched conjugated diene-based polymer according to claim 3, wherein the coupling agent has a nitrogen atom-containing group.

[Claim 5]

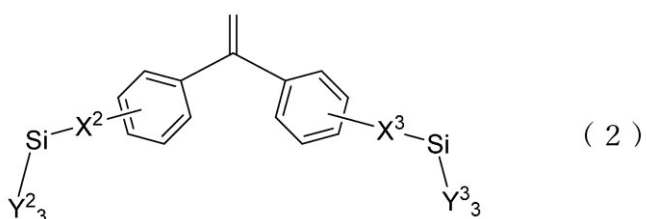
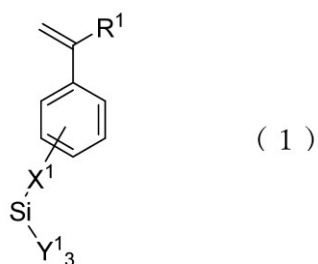
The production method for a branched conjugated diene-based polymer according to claim 3, wherein the polymerization terminator has a nitrogen atom-containing group.

[Claim 6]

The production method for a branched conjugated diene-based polymer according to claim 3 or 5, wherein the polymerization terminator is an alkoxy compound having a nitrogen atom-containing group.

[Claim 7]

The production method for a branched conjugated diene-based polymer according to any one of claims 1 to 6, wherein the styrene derivative is a compound represented by the following formula (1) and/or formula (2):



wherein R^1 represents any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms, and may have a branch structure in a part thereof;

X^1 , X^2 and X^3 represent a single bond, or an organic group containing any one selected from the group consisting of carbon, hydrogen, nitrogen, sulfur, and oxygen; and

Y^1 , Y^2 and Y^3 represent any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom, are respectively independent, and may be the same or different.

[Claim 8]

The production method for a branched conjugated diene-based polymer according to claim 7, wherein, in the

formula (1), R^1 represents a hydrogen atom, and Y^1 represents any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom.

[Claim 9]

The production method for a branched conjugated diene-based polymer according to claim 7, wherein, in the formula (2), X^1 represents a single bond, and Y^2 represents any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms, an alkoxy group having 1 to 20 carbon atoms, and a halogen atom.

[Claim 10]

The production method for a branched conjugated diene-based polymer according to claim 7, wherein, in the formula (1), R^1 represents a hydrogen atom, and Y^1 represents an alkoxy group having 1 to 20 carbon atoms, or a halogen atom.

[Claim 11]

The production method for a branched conjugated diene-based polymer according to claim 7, wherein, in the formula (2), Y^2 represents an alkoxy group having 1 to 20 carbon atoms, or a halogen atom, and Y^3 represents an alkoxy group having 1 to 20 carbon atoms, or a halogen atom.

[Claim 12]

The production method for a branched conjugated diene-based polymer according to claim 7, wherein, in the

formula (1), R^1 represents a hydrogen atom, and Y^1 represents an alkoxy group having 1 to 20 carbon atoms.

[Claim 13]

The production method for a branched conjugated diene-based polymer according to claim 7, wherein, in the formula (1), R^1 represents a hydrogen atom, X^1 represents a single bond, and Y^1 represents an alkoxy group having 1 to 20 carbon atoms.

[Claim 14]

The production method for a branched conjugated diene-based polymer according to claim 7, wherein, in the formula (2), X^2 represents a single bond, Y^2 represents an alkoxy group having 1 to 20 carbon atoms, or a halogen atom, X^3 represents a single bond, and Y^3 represents an alkoxy group having 1 to 20 carbon atoms, or a halogen atom.

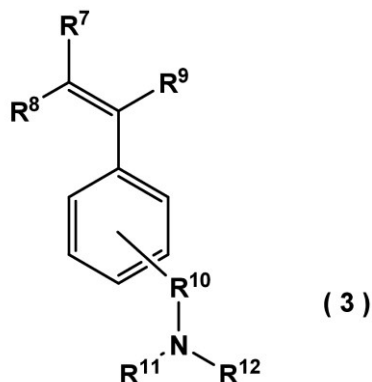
[Claim 15]

The production method for a branched conjugated diene-based polymer according to any one of claims 1 to 14, further comprising:

a step of copolymerizing a nitrogen atom-containing vinyl compound, or copolymerizing a conjugated diene compound and a nitrogen atom-containing vinyl compound, or a conjugated diene compound, a vinyl aromatic compound, and a nitrogen atom-containing vinyl compound, in the polymerizing step.

[Claim 16]

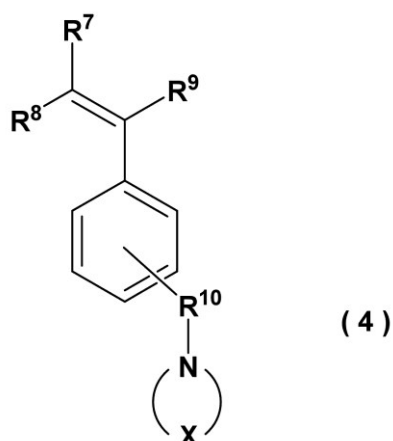
The production method for a branched conjugated diene-based polymer according to claim 15, wherein the nitrogen atom-containing vinyl compound is a compound represented by the following formula (3) or (4):



wherein R⁷ to R⁹ each independently represent any one selected from the group consisting of hydrogen, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms;

R¹⁰ represents a single bond, or a divalent hydrocarbon group having 1 to 6 carbon atoms, in which the chain is optionally interrupted by any of NR¹³, O, and S; and

R¹¹ to R¹³ each independently represent any one selected from the group consisting of an alkyl group having 1 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, and a trisubstituted silyl group having, on silicon, an alkyl group having 1 to 30 carbon atoms and/or an aryl group having 6 to 30 carbon atoms;



wherein R^7 to R^9 each independently represent any one selected from the group consisting of hydrogen, an alkyl group having 1 to 20 carbon atoms, and an aryl group having 6 to 20 carbon atoms;

R^{10} represents a single bond, or a divalent hydrocarbon group having 1 to 6 carbon atoms, in which the chain is optionally interrupted by any of NR^{13} , O, and S;

R^{13} each independently represents any one selected from the group consisting of an alkyl group having 1 to 30 carbon atoms, an aryl group having 6 to 30 carbon atoms, and a trisubstituted silyl group having, on silicon, an alkyl group having 1 to 30 carbon atoms and/or an aryl group having 6 to 30 carbon atoms;

X represents a divalent hydrocarbon group having 3 to 10 carbon atoms, in which the chain is optionally interrupted by any of NR^{14} , O, and S and which corresponds to a saturated ring-forming moiety in which all carbon-carbon bonds are single bonds or an

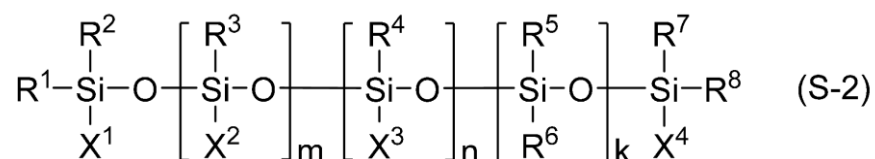
unsaturated ring-forming moiety in which at least some of carbon-carbon bonds are double bonds; and

R¹⁴ represents an alkyl group having 1 to 30 carbon atoms or an aryl group having 6 to 30 carbon atoms.

[Claim 17]

The production method for a branched conjugated diene-based polymer according to any one of claims 3 to 16, wherein, in the reaction step,

the active end of the conjugated diene-based polymer resulting from the branching step is reacted with a coupling agent represented by the following formula (S-2):



wherein R¹ to R⁸ each independently represent any one selected from the group consisting of an alkyl group having 1 to 20 carbon atoms and an aryl group having 6 to 20 carbon atoms, and may be the same or different;

X¹ and X⁴ satisfy the following (i) or (ii):

(i) one of X¹ and X⁴ represents a group selected from the group consisting of an alkoxysilyl group having 1 to 5 carbon atoms, a 2-pyrrolidonyl group-containing hydrocarbon group, and an epoxy group-containing group having 4 to 12 carbon atoms, and the other represents a group derived from such a group, or a single bond; or

(ii) X^1 and X^4 represent an alkyl group having 1 to 6 carbon atoms or an aryl group having 6 to 12 carbon atoms, and X^1 and X^4 may be the same or different;

some of X^2 represent a group selected from the group consisting of an alkoxysilyl group having 1 to 5 carbon atoms, a 2-pyrrolidonyl group-containing hydrocarbon group, and an epoxy group-containing group having 4 to 12 carbon atoms, and the others represent a group derived from such a group, or a single bond;

X^3 represents a group containing 2 to 20 alkylene glycol repeating units; and

m represents an integer of 3 to 200, n represents an integer of 0 to 200, and k represents an integer of 0 to 200.

[Claim 18]

A branched conjugated diene-based polymer which is a copolymer of a conjugated diene compound, or a conjugated diene compound and an aromatic vinyl compound, with a nitrogen atom-containing vinyl compound, and which has a main chain branch structure derived from a styrene derivative, in a polymer main chain.

[Claim 19]

A rubber composition comprising:

a rubber component comprising 10% by mass or more of the branched conjugated diene-based polymer according to claim 18, and

5.0 parts by mass or more and 150 parts by mass or less of a filler with respect to 100 parts by mass of the rubber component.

[Claim 20]

A production method for a rubber composition, comprising:

a step of obtaining a branched conjugated diene-based polymer by the production method according to any one of claims 1 to 17;

a step of obtaining a rubber component containing 10% by mass or more of the branched conjugated diene-based polymer; and

a step of obtaining a rubber composition by causing 5.0 parts by mass or more and 150 parts by mass or less of a filler to be contained with respect to 100 parts by mass of the rubber component.

[Claim 21]

A production method for a tire, comprising:

a step of obtaining a rubber composition by the production method for a rubber composition according to claim 20; and

a step of obtaining a tire by molding the rubber composition.