DESCRIPTION

TITLE: MODIFIED CONJUGATED-DIENE-BASED POLYMER, RUBBER COMPOSITION, CROSSLINKED RUBBER, AND METHOD FOR PRODUCING TIRE

TECHNICAL FIELD

[0001] The present invention relates to a modified conjugated diene polymer, a rubber composition, a cross-linked rubber, and a method of production of a tire.

BACKGROUND ART

[0002] Recently, with increasing interest in environmental problems, there is a demand for polymers used for automobile tires achieving excellent low fuel consumption. Compared to tires obtained using a rubber composition containing conventionally used carbon black, a tire obtained using a rubber composition containing silica as a filler in addition to a conjugated diene polymer is improved in heat buildup, and thus is more excellent in low fuel consumption.

[0003] As a conjugated diene polymer for producing such a tire, Patent Document 1 proposes a modified conjugated diene polymer produced by modification of a conjugated diene polymer chain with a polyorganosiloxane. The technique disclosed in Patent Document 1 can improve the affinity of the polymer with silica due to the modified structure introduced by the polyorganosiloxane, and thus improve low fuel consumption.

RELATED ART DOCUMENT

PATENT DOCUMENT

[0004] Patent Document 1: WO 2003/102053

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0005] On the other hand, from the viewpoint of addressing the recent environmental problems or the like, there is a demand for higher productivity in the production of the modified conjugated diene polymer modified by a polyorganosiloxane, or the like.

[0006] The present invention has been made in consideration of such circumstances, and an object of the present invention is to provide a method of production of a modified conjugated diene polymer which can produce a modified conjugated diene polymer achieving excellent low fuel consumption with high productivity.

MEANS FOR SOLVING THE PROBLEMS

[0007] The present inventors, who have conducted research to achieve the above object, have found that a modified conjugated diene polymer achieving excellent low fuel consumption can be produced with high productivity by reacting a conjugated diene polymer chain having an active end with a specific polyorganosiloxane by adding the polyorganosiloxane continuously over 2 to 60 minutes or in portions, and thus have completed the present invention.

[0008] Specifically, the present invention provides [1] to [8] below.

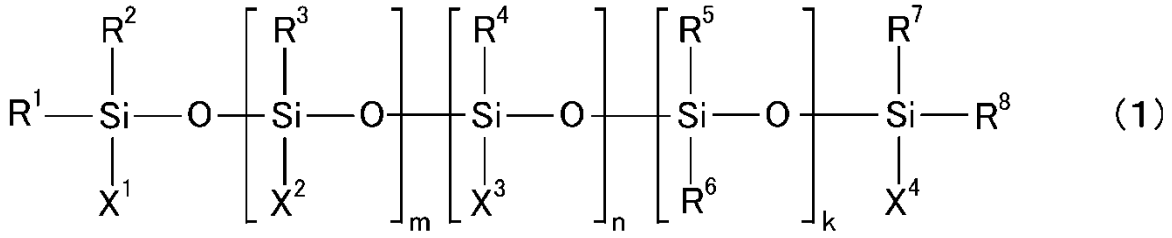
[1] A method of production of a modified conjugated diene polymer, comprising:

a first step of polymerizing a monomer containing a conjugated diene compound using a polymerization initiator in an inert solvent to obtain a conjugated diene polymer chain having an active end; and

a second step of reacting the conjugated diene polymer chain having an active end with a polyorganosiloxane represented by the following general formula (1) by adding the polyorganosiloxane to the conjugated diene polymer chain having an active end continuously over 2 to 60

minutes or in portions:

[Chem. 1]



(1)

wherein in the general formula (1), R^1 to R^8 may be the same or different from each other and are each a hydrocarbon group having 1 to 20 carbon atoms, X^1 and X^4 may be the same or different from each other and are each a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms, a polar functional group having an atom of Group 15 or Group 16 of the periodic table, a halogen atom, or a hydrocarbon group having 1 to 20 carbon atoms and optionally having a polar functional group having an atom of Group 15 or Group 16 of the periodic table or a halogen atom; X^2 is a polar functional group having an atom of Group 15 or Group 16 of the periodic table, a halogen atom, or a hydrocarbon group having 1 to 20 carbon atoms and optionally having a polar functional group having an atom of Group 15 or Group 16 of the periodic table or a halogen atom, and when a plurality of X^2s are present, they may be the same or different from each other; X^3 is a group containing 2 to 20 repeating units of an alkylene glycol, a part of X^3 may be a group derived from a group containing 2 to 20 repeating units of an alkylene glycol, and when a plurality of X^3s are present, they may be the same or different from each other; "m" is an integer of 1 to 200; "n" is an integer of 0 to 200; and "k" is an integer of 0 to 200.

[2] The method of production of a modified conjugated diene polymer according to [1], wherein the polar functional group having an atom of Group 16 of the periodic table is a polar functional group having an oxygen atom.

[3] The method of production of a modified conjugated diene polymer according to [1] or [2], wherein X^1 and X^4 are each a hydrocarbon group having 1 to 20 carbon atoms, and X^2 is a hydrocarbon group having 1 to 20 carbon atoms and optionally having an alkoxy group or an epoxy group.

[4] The method of production of a modified conjugated diene polymer according to any one of [1] to [3], wherein the modified conjugated diene polymer contains an isoprene-containing block containing 80 to 100 wt% of an isoprene unit.

[5] The method of production of a modified conjugated diene polymer according to any one of [1] to [4], wherein a polar compound is added in an amount of 0.5 to 5.0 moles in total with respect to 1 mole of the polymerization initiator before the second step.

[6] A method of production of a rubber composition comprising: obtaining a modified conjugated diene polymer by the method of production according to any one of [1] to [5], and adding silica to the modified conjugated diene polymer.

[7] The method of production of a rubber composition according to [6], further comprising: adding a cross-linking agent.

[8] A method of production of a cross-linked rubber, comprising: obtaining a rubber composition by the method of production according to [6] or [7], and cross-linking the rubber composition.

[9] A method of production of a tire, comprising: obtaining a rubber composition by the method of production according to [6] or [7], and cross-linking the rubber composition to produce a tire containing a cross-linked rubber of the rubber composition.

EFFECT OF THE INVENTION

[0009] The present invention provides a method of production of a modified conjugated diene polymer which can produce a modified conjugated diene polymer achieving excellent low fuel consumption with

high productivity.

DESCRIPTION OF EMBODIMENTS

[0010] <Method of production of modified conjugated diene polymer>

The method of production of a modified conjugated diene polymer according to the present invention comprises:

a first step of polymerizing a monomer containing a conjugated diene compound using a polymerization initiator in an inert solvent to obtain a conjugated diene polymer chain having an active end; and

a second step of reacting the conjugated diene polymer chain having an active end with a polyorganosiloxane represented by the following general formula (1) by adding the polyorganosiloxane to the conjugated diene polymer chain having an active end continuously over 2 to 60 minutes or in portions (i.e., in a plurality of installments).

[0011] <First Step>

The first step of the method of production according to the present invention is a step of polymerizing a monomer containing a conjugated diene compound using a polymerization initiator in an inert solvent to obtain a conjugated diene polymer chain having an active end.

[0012] In the first step of the method of production according to the present invention, the conjugated diene compound used as the monomer to obtain the conjugated diene polymer chain having an active end is not particularly limited, but examples thereof include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 2-phenyl-1,3-butadiene, 1,3-pentadiene, 2-methyl-1,3-pentadiene, 1,3-hexadiene, 4,5-diethyl-1,3-octadiene, 3-butyl-1,3-octadiene, and the like. Among these, 1,3-butadiene and isoprene are preferred, and 1,3-butadiene is more preferred. These conjugated diene compounds may be used alone or in combination.

[0013] Further, in the first step of the method of production

according to the present invention, an aromatic vinyl compound may be used together with the conjugated diene compound as the monomer used for the polymerization. Examples of the aromatic vinyl compound used as the monomer include styrene, methylstyrene, ethylstyrene, t-butylstyrene, α-methylstyrene, α-methyl-p-methylstyrene, chlorostyrene, bromostyrene, methoxystyrene, dimethylamino methylstyrene, dimethylamino ethylstyrene, diethylamino methylstyrene, diethylamino ethylstyrene, cyano ethylstyrene, vinylnaphthalene, and the like. Among these, styrene is preferred. The conjugated diene polymer chain having an active end obtained in the first step of the method of production according to the present invention contains preferably 50 to 100 wt%, more preferably 52 to 98 wt%, particularly preferably 55 to 84 wt% of a conjugated diene monomer unit, and further contains preferably 0 to 50 wt%, more preferably 2 to 48 wt%, particularly preferably 16 to 45 wt%, of an aromatic vinyl monomer unit.

[0014] Further, in the first step of the method of production according to the present invention, a compound that can copolymerize with the conjugated diene compound and is different from the aromatic vinyl compound may be used together with the conjugated diene compound. Examples of such a compound that can copolymerize with the conjugated diene compound include chain olefin compounds such as ethylene, propylene and 1-butene; cyclic olefin compounds such as cyclopentene and 2-norbornene; nonconjugated diene compounds such as 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, dicyclopentadiene, and 5-ethylidene-2-norbornene; (meth)acrylic acid esters such as methyl (meth)acrylate, ethyl (meth)acrylate, and butyl (meth)acrylate; other (meth)acrylic acid derivatives such as (meth)acrylonitrile and (meth)acrylamide; and the like. These compounds that can copolymerize with the conjugated diene compound are preferably contained, as the monomer unit, in an amount of 10 wt% or less, more preferably 5 wt% or less in the conjugated diene

polymer chain having an active end obtained in the first step of the method of production according to the present invention.

[0015] The inert solvent used for the polymerization is not particularly limited so long as the solvent is usually used in solution polymerization and does not obstruct the polymerization reaction. Specific examples of the inert solvent include chain aliphatic hydrocarbons such as butane, pentane, hexane, and heptane; alicyclic hydrocarbons such as cyclopentane and cyclohexane; aromatic hydrocarbons such as benzene, toluene, xylene, and ethylbenzene; ether compounds such as tetrahydrofuran and diethyl ether; and the like. These inert solvents may be used alone or in combination. The amount of the inert solvent used is not particularly limited, but it is used in such an amount that the monomer concentration becomes, for example, 1 to 50 wt%, preferably 10 to 40 wt%.

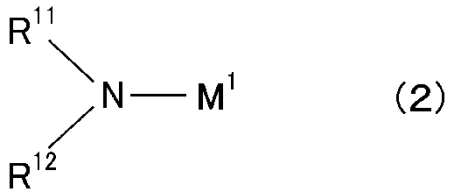
[0016] The polymerization initiator used for polymerization is not particularly limited so long as it can cause a monomer containing a conjugated diene compound to polymerize to give the conjugated diene polymer chain having an active end. Specific examples thereof include polymerization initiators containing an organic alkali metal compound, an organic alkali earth metal compound, or a lanthanide-series metal compound as a primary catalyst. Examples of the organic alkali metal compound include organic monolithium compounds such as n-butyllithium, sec-butyllithium, t-butyllithium, hexyllithium, phenyllithium, and stilbenelithium; organic polyvalent lithium compounds such as dilithiomethane, 1,4-dilithiobutane, 1,4-dilithio-2-ethylcyclohexane, 1,3,5-trilithiobenzene, and 1,3,5-tris(lithiomethyl)benzene; organic sodium compounds such as sodium naphthalene; organic potassium compounds such as potassium naphthalene; and the like. Further, examples of the organic alkali earth metal compound include di-n-butylmagnesium, di-n-hexylmagnesium, diethoxycalcium, calcium distearate, di-t-

butoxystrontium, diethoxybarium, diisopropoxybarium, diethylmercaptobarium, di-t-butoxybarium, diphenoxybarium, diethylaminobarium, barium distearate, diketylbarium, and the like. Examples of the polymerization initiator containing a lanthanide-series metal compound as a primary catalyst include polymerization initiators containing a lanthanide-series metal salt of a lanthanide-series metal, such as lanthanum, cerium, praseodymium, neodymium, samarium, or gadolinium, and a carboxylic acid, phosphorus-containing organic acid, or the like as a primary catalyst and a co-catalyst such as an alkylaluminum compound, an organic aluminum hydride compound, an organic aluminum halide compound, or the like. Among these polymerization initiators, organic monolithium compounds and organic polyvalent lithium compounds are preferably used, organic monolithium compounds are more preferably used, and n-butyllithium is particularly preferably used.

Note that, the organic alkali metal compound may be reacted in advance with a secondary amine compound such as dibutylamine, dihexylamine, dibenzylamine, pyrrolidine, piperidine, hexamethyleneimine, or heptamethyleneimine, and may be used as an organic alkali metal amide compound. By using an organic alkali metal amide compound as the polymerization initiator, a cross-linked rubber having more excellent wet grip and wear resistance can be obtained. These polymerization initiators may be used alone or in combination.

[0017] Examples of the organic alkali metal amide compound include compounds obtained by reacting a secondary amine compound with an organic alkali metal compound. Among these, in the method of production according to the present invention, the compound represented by the following general formula (2) can be preferably used.

[Chem. 2]



(2)

[0018] In the general formula (2), M^1 represents an alkali metal atom, R^{11} and R^{12} each independently represent an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group, a protecting group for an amino group, or a group which can be hydrolyzed to produce a hydroxyl group, R^{11} and R^{12} may be bonded to each other to form a ring structure together with the nitrogen atom to which they are bonded, and when they form a ring structure, they may form the ring structure together with a heteroatom other than the nitrogen atom to which they are bonded in addition to the nitrogen atom to which they are bonded.

[0019] The alkyl group is not particularly limited, but is preferably an alkyl group having 1 to 20 carbon atoms, more preferably an alkyl group having 1 to 10 carbon atoms. Examples of the alkyl group include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, an n-octyl group, an n-decyl group, and the like.

[0020] The cycloalkyl group is not particularly limited, but is preferably a cycloalkyl group having 3 to 20 carbon atoms, more preferably a cycloalkyl group having 3 to 12 carbon atoms. Examples of the cycloalkyl group include a cyclopropyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a cyclooctyl group, a cyclododecyl group, and the like.

[0021] The aryl group is not particularly limited, but is preferably an aryl group having 6 to 12 carbon atoms, more preferably an aryl group having 6 to 10 carbon atoms. Examples of the aryl group include a phenyl group, a 1-naphthyl group, a 2-naphthyl group, and the like.

[0022] The aralkyl group is not particularly limited, but is preferably an aralkyl group having 7 to 13 carbon atoms, more preferably an aralkyl group having 7 to 9 carbon atoms. Examples of the aralkyl group include a benzyl group, a phenethyl group, and the like.

[0023] The protecting group for an amino group is not particularly limited and can be any group as long as it can act as a protecting group for an amino group, and examples thereof include alkylsilyl groups, and the like. Examples of the alkylsilyl groups include a trimethylsilyl group, a triethylsilyl group, a triphenylsilyl group, a methyldiphenylsilyl group, an ethylmethylphenylsilyl group, a tert-butyldimethylsilyl group, and the like.

Note that when R^{11} and/or R^{12} is a protecting group for an amino group, by removal of the protecting group for an amino group, the structure where R^{13} and/or R^{14} in the general formula (4) to be described later is a hydrogen atom can be introduced to one end of the polymer chain forming the obtained conjugated diene rubber.

[0024] The group which can be hydrolyzed to produce a hydroxyl group is not particularly limited, and can be any group as long as it can be hydrolyzed in the presence of an acid to produce a hydroxyl group, and examples thereof include alkoxyalkyl groups, epoxy-group containing groups, and the like.

Examples of the alkoxyalkyl groups include a methoxymethyl group, an ethoxymethyl group, an ethoxyethyl group, a propoxymethyl group, a butoxymethyl group, a butoxyethyl group, and a propoxyethyl group

Further, examples of the epoxy-group containing group include a group represented by the following general formula (3):

$$-Z^1-Z^2-E^1 \qquad (3)$$

wherein in the general formula (3), Z^1 represents an alkylene group or an alkylarylene group having 1 to 10 carbon atoms, Z^2 represents a methylene group, a sulfur atom, or an oxygen atom, and E^1 represents a glycidyl

group.

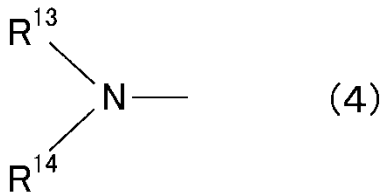
[0025] Further, R^{11} and R^{12} may be bonded to each other to form a ring structure together with the nitrogen atom to which they are bonded, and in such a case, specific examples of the structure formed by R^{11} and R^{12} together with the nitrogen atom to which they are bonded include an azetidine ring (where R^{11} and R^{12} form a propylene moiety), a pyrrolidine ring (where R^{11} and R^{12} form a butylene moiety), a piperidine ring (where R^{11} and R^{12} form a pentylene moiety), a hexamethyleneimine ring (where R^{11} and R^{12} form a hexylene moiety), and the like.

When R^{11} and R^{12} are bonded to each other to form a ring structure together with the nitrogen atom to which they are bonded, the ring structure is preferably a 4- to 8-membered ring structure.

[0026] Further, in the general formula (2), M^1 is an alkali metal atom, and examples of the alkali metal atom include a lithium atom, a sodium atom, a potassium atom, and the like. Among these, a lithium atom is preferred from the viewpoint of polymerization activity.

[0027] In the first step of the method of production according to the present invention, when the compound represented by the general formula (2) is used as the polymerization initiator, the amine structure forming an organic alkali metal amide compound remains in the state where it is bonded to the polymerization initiation end of the polymer chain. Accordingly, when the compound represented by the general formula (2) is used as the polymerization initiator, a structure represented by the following general formula (4) is introduced to one end of the polymer chain forming the obtained conjugated diene rubber.

[Chem. 3]



(4)

[0028] In the general formula (4), R^{13} and R^{14} each independently represent a hydrogen atom, an alkyl group, a cycloalkyl group, an aryl group, an aralkyl group, a protecting group for an amino group, or a group which can be hydrolyzed to produce a hydroxyl group, R^{13} and R^{14} may be bonded to each other to form a ring structure together with the nitrogen atom to which they are bonded, and when they form a ring structure, they may form the ring structure together with a heteroatom other than the nitrogen atom to which they are bonded, in addition to the nitrogen atom to which they are bonded.

[0029] Examples of the alkyl group, the cycloalkyl group, the aryl group, the aralkyl group, the protecting group for an amino group, and the group which can be hydrolyzed to produce a hydroxyl group, which can be R^{13} or R^{14}, include those listed in R^{11} and R^{12} in the general formula (2). Further, when R^{13} and R^{14} are bonded to each other to form a ring structure together with the nitrogen atom to which they are bonded, examples thereof include those listed in R^{11} and R^{12} in the general formula (2).

Note that the hydrogen atom, which can be R^{13} or R^{14}, is introduced by the removal of the protecting group for an amino group.

[0030] In the method of production according to the present invention, when an organic alkali metal amide compound is used as the polymerization initiator, the obtained conjugated diene rubber can have an amine structure at one end and a specific structure derived from the modifying agent at the other end. As a result, due to the effect of such an amine structure, the cross-linked rubber obtained by using the modified conjugated diene rubber can be further improved in low fuel consumption.

[0031] The method of adding an organic alkali metal amide compound as the polymerization initiator to the polymerization system is not particularly limited, but a method may be employed where a secondary

amine compound is reacted with an organic alkali metal compound in advance to obtain an organic alkali metal amide compound, which is then mixed with a monomer containing the conjugated diene compound to cause the polymerization reaction to proceed. Alternatively, a method can also be employed, in which an organic alkali metal compound and a secondary amine compound are separately added to the polymerization system, mixed with a monomer containing the conjugated diene compound so as to produce an organic alkali metal amide compound in the polymerization system, thereby causing the polymerization reaction to proceed. The reaction conditions such as a reaction temperature are not particularly limited and can be selected, for example, according to the targeted polymerization reaction conditions.

[0032] The amount of the secondary amine compound used may be determined according to the targeted amount of the polymerization initiator to be added, but is in the range of usually 0.01 to 1.5 mmoles with respect to 1 mmole of the organic alkali metal compound, preferably 0.1 to 1.2 mmoles, more preferably 0.5 to 1.0 mmole.

[0033] The amount of the polymerization initiator used may be determined according to the targeted molecular weight of the conjugated diene polymer chain, but is in the range of usually 1 to 50 mmoles with respect to 1000 g of the monomer, preferably 1.5 to 20 mmoles, more preferably 2 to 15 mmoles.

[0034] The polymerization temperature is in the range of usually -80 to +150°C, preferably 0 to 100°C, more preferably 30 to 90°C. As the polymerization process, a batch process, continuous process, or any other process can be employed, but when copolymerizing a conjugated diene compound and aromatic vinyl compound, the batch process is preferred from the viewpoint of facilitating control of the randomness in bonding between the conjugated diene monomer units and aromatic vinyl monomer units.

[0035] In the first step of the method of production according to the present invention, the polymerization of the monomers including the conjugated diene compound is preferably carried out in the presence of a polar compound. Specifically, a polar compound is used in an amount of preferably 0.01 to 5.0 moles, more preferably 0.1 to 4.0 moles, still more preferably 0.2 to 3.0 moles with respect to 1 mole of the polymerization initiator. Such use of a polar compound in the polymerization enables suitable control of the vinyl bond content of conjugated diene monomer units contained in the conjugated diene polymer chain formed in the first step. Specifically, the vinyl bond content of conjugated diene monomer units contained in the conjugated diene polymer chain can be preferably 70 wt% or less, more preferably 68 wt% or less, still more preferably 65 wt% or less. On the other hand, the lower limit of the vinyl bond content is preferably 5 wt% or more, more preferably 10 wt% or more, still more preferably 20 wt% or more, but not particularly limited thereto. When the vinyl bond content of conjugated diene monomer units contained in the conjugated diene polymer chain is within the above ranges, the vinyl bond content of conjugated diene monomer units contained in the conjugated diene rubber finally obtained can be 70 wt% or less, and thus a cross-linked rubber further improved in low fuel consumption can be obtained.

[0036] The polymerization in the presence of a polar compound may be carried out by any method without limitation, and examples thereof include methods such as performing polymerization in an inert solvent for polymerization containing a polar compound. Specific examples of the polar compound include ethers such as tetrahydrofuran, diethyl ether, dibutyl ether, dioxane, ethylene glycol dimethyl ether, ethylene glycol dibutyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, and 2,2-di(tetrahydrofuryl)propane; tertiary amine compounds such as tetramethylethylenediamine, trimethylamine,

triethylamine, pyridine, and quinuclidine; alkali metal alkoxide compounds such as potassium t-amyloxide and potassium t-butyloxide; phosphine compounds such as triphenylphosphine; and the like. Among these, polar compounds capable of multiple coordination are more preferred, and tetramethylethylenediamine is particularly preferred. These polar compounds may be used alone or in combination.

[0037] The peak top molecular weight (Mp) of a peak with the smallest molecular weight of the conjugated diene polymer chain having an active end obtained in the first step of the method of production according to the present invention is preferably 100,000 to 1,000,000, more preferably 150,000 to 700,000, particularly preferably 150,000 to 500,000 as measured by gel permeation chromatography against polystyrene standards, but not particularly limited thereto.

[0038] Further, the molecular weight distribution represented by the ratio (Mw/Mn) of the weight average molecular weight (Mw) and the number average molecular weight (Mn) of the conjugated diene polymer chain having an active end obtained in the first step of the method of production according to the present invention is also not particularly limited, but is preferably 1.0 to 3.0, more preferably 1.0 to 2.5. By controlling the molecular weight distribution (Mw/Mn) of the conjugated diene polymer chain having an active end within the above ranges, the production of the conjugated diene rubber becomes easy.

[0039] Further, in the method of production according to the present invention, to obtain a cross-linked rubber further improved in low fuel consumption, it is preferred for the first step to be configured as follows.

More specifically, it is preferred that the first step comprise a step of polymerizing a monomer containing isoprene, or isoprene and an aromatic vinyl compound, in an inert solvent using a polymerization initiator to form a polymer block (A) having an active end and

containing 80 to 100 wt% of an isoprene monomer unit, and

a step of mixing the polymer block (A) having an active end and a monomer containing 1,3-butadiene, or 1,3-butadiene and an aromatic vinyl compound, and continuing the polymerization reaction to form a polymer block (B) having an active end and containing 50 to 100 wt% of a 1,3-butadiene monomer unit and 0 to 50 wt% of an aromatic vinyl monomer unit, the polymer block (B) being linked to the polymer block (A), thereby obtaining a conjugated diene polymer chain having an active end.

[0040] When such a process is used, the conjugated diene polymer chain having an active end obtained in the first step and the obtained modified conjugated diene polymer can include the isoprene-containing block (A) containing 80 to 100 wt% of an isoprene unit, and more preferably the obtained modified conjugated diene polymer can include the polymer block (A) containing 80 to 100 wt% of isoprene monomer units and the polymer block (B) containing 50 to 100 wt% of 1,3-butadiene monomer units and 0 to 50 wt% of aromatic vinyl monomer units, the polymer block (A) and the polymer block (B) being linked to each other.

Hereinafter, such an embodiment is described.

[0041] [Polymer Block (A)]

The polymer block (A) in the conjugated diene polymer chain according to an embodiment of the present invention can contain 80 to 100 wt% of isoprene monomer units, but preferably contains 80 to 100 wt% of isoprene monomer units and 0 to 20 wt% of aromatic vinyl monomer units, more preferably contains 85 to 97 wt% of isoprene monomer units and 3 to 15 wt% of aromatic vinyl monomer units, and still more preferably contains 89 to 95 wt% of isoprene monomer units and 5 to 11 wt% of aromatic vinyl monomer units. With a content ratio of isoprene monomer units being within the above range, when silica is added to the modified conjugated diene rubber, the affinity of the modified conjugated diene rubber and silica becomes good and the low fuel

consumption of the cross-linked rubber obtained using this can be further enhanced.

[0042] As the aromatic vinyl compound used for forming the aromatic vinyl monomer unit contained in the polymer block (A), the same aromatic vinyl compounds as those illustrated above can be used. Among these, styrene is preferred. Note that these aromatic vinyl compounds may be used alone or in combination.

[0043] The polymer block (A) is preferably comprised of substantially only isoprene monomer units, or isoprene monomer units and aromatic vinyl monomer units, but if desired other monomer units may be contained in addition to isoprene monomer units, or isoprene monomer units and aromatic vinyl monomer units. Examples of the other compounds used for forming other monomer units include conjugated diene compounds other than isoprene such as 1,3-butadiene, 2,3-dimethyl-1,3-butadiene, 2-chloro-1,3-butadiene, 1,3-pentadiene, and 1,3-hexadiene; α, β-unsaturated nitriles such as acrylonitrile and methacrylonitrile; unsaturated carboxylic acids or acid anhydrides such as acrylic acid, methacrylic acid, and maleic anhydride; unsaturated carboxylic acid esters such as methyl methacrylate, ethyl acrylate, and butyl acrylate; nonconjugated dienes such as 1,5-hexadiene, 1,6-heptadiene, 1,7-octadiene, dicyclopentadiene, and 5-ethylidene-2-norbornene; and the like. Among these, 1,3-butadiene is preferred. These other monomers may be used alone or in combination. In the polymer block (A), the content ratio of other monomer units is preferably 20 wt% or less, more preferably 10 wt% or less, further more preferably 6 wt% or less.

[0044] In the present invention, the polymer block (A) in the conjugated diene polymer chain is formed by polymerizing a monomer containing isoprene, or isoprene and an aromatic vinyl compound, in an inert solvent using a polymerization initiator. As a result, the formed polymer block (A) has an active end.

[0045] For forming the polymer block (A), as the inert solvent used for polymerizing a monomer containing isoprene, or isoprene and an aromatic vinyl compound, the same inert solvents as those illustrated above can be used. The amount of the inert solvent used is such an amount that the monomer concentration becomes preferably 1 to 80 wt%, preferably 10 to 50 wt%.

[0046] The polymerization initiator used for forming the polymer block (A) is not particularly limited so long as it can polymerize a monomer containing isoprene, or isoprene and an aromatic vinyl compound, and give a polymer chain having an active end. As specific examples thereof, the same polymerization initiators as those illustrated above can be used.

[0047] The amount of the polymerization initiator used may be determined according to the targeted molecular weight, but is in the range of preferably 4 to 250 mmoles, more preferably 6 to 200 mmoles, particularly preferably 10 to 70 mmoles with respect to 100 g of the monomer containing isoprene, or isoprene and an aromatic vinyl compound.

[0048] The polymerization temperature during polymerization of a monomer containing isoprene, or isoprene and an aromatic vinyl compound, is in the range of preferably -80 to +150°C, more preferably 0 to 100°C, further more preferably 20 to 90°C. As the polymerization process, a batch process, continuous process, or any other process can be employed. Additionally, the bonding form may, for example, be a variety of bonding forms such as a block form, a taper form, and a random form.

[0049] In the method of production according to an embodiment of the present invention, the polymer block (A) is preferably formed by polymerizing the monomers including isoprene, or isoprene and the aromatic vinyl compound in the presence of a polar compound. Specifically, a polar compound is used in an amount of preferably 0.01 to 30 moles, more preferably 0.03 to 10 moles, still more preferably

0.05 to 5 moles with respect to 1 mole of the polymerization initiator. Such use of a polar compound in the polymerization enables suitable control of the vinyl bond content of isoprene monomer units in the polymer block (A). The vinyl bond content in isoprene monomer units in the polymer block (A) is preferably 25 wt% or less, more preferably 20 wt% or less, still more preferably 15 wt% or less. On the other hand, the lower limit of the vinyl bond content is preferably 1 wt% or more, more preferably 5 wt% or more, but not particularly limited thereto. When the vinyl bond content in isoprene monomer units is within the above ranges, low fuel consumption of the obtained cross-linked rubber can be further enhanced. The vinyl bonds in isoprene monomer units may be either in the 1,2-vinyl form or in the 3,4-vinyl form.

[0050] Examples of methods for polymerizing the monomers including isoprene, or isoprene and the aromatic vinyl compound in the presence of a polar compound include, but are not particularly limited to, methods such as performing polymerization in an inert solvent for polymerization containing the polar compound. Examples of usable polar compounds include the same polar compounds as those listed above.

[0051] The weight average molecular weight (Mw) of the polymer block (A) is preferably 500 to 15,000, more preferably 1,000 to 12,000, particularly preferably 1,500 to 10,000 as measured by gel permeation chromatography against polystyrene standards. When the weight average molecular weight of the polymer block (A) is within the above ranges, low fuel consumption of the obtained cross-linked rubber can be further enhanced.

[0052] Further, the molecular weight distribution represented by the ratio (Mw/Mn) of the weight average molecular weight (Mw) and the number average molecular weight (Mn) of the polymer block (A) is preferably 1.0 to 1.5, more preferably 1.0 to 1.3. When a value (Mw/Mn) of the molecular weight distribution of the polymer block (A) is within the

above ranges, the production of the modified conjugated diene rubber becomes easy.

[0053] [Polymer Block (B)]

The polymer block (B) in the conjugated diene polymer chain according to an embodiment of the present invention can contain 50 to 100 wt% of 1,3-butadiene monomer units and 0 to 50 wt% of aromatic vinyl monomer units, but preferably contains 52 to 98 wt% of 1,3-butadiene monomer units and 2 to 48 wt% of aromatic vinyl monomer units, and particularly preferably contains 55 to 84 wt% of 1,3-butadiene monomer units and 16 to 45 wt% of aromatic vinyl monomer units. With a content ratio of 1,3-butadiene monomer units and aromatic vinyl monomer units being within the above ranges, the production of the modified conjugated diene rubber becomes easy.

[0054] As the aromatic vinyl compound used for forming the aromatic vinyl monomer unit contained in the polymer block (B), the same aromatic vinyl compounds as those illustrated above can be used, and among these, styrene is preferred.

[0055] The polymer block (B) is preferably comprised of substantially only 1,3-butadiene monomer units, or 1,3-butadiene monomer units and aromatic vinyl monomer units, but if desired other monomer units may be contained in addition to 1,3-butadiene monomer units, or 1,3-butadiene monomer units and aromatic vinyl monomer units, within a range not impairing the essential feature of the present invention. As the other monomers used for forming other monomer units, the same compounds as those illustrated above (provided that 1,3-butadiene is excluded) in the polymer block (A) can be used. Further, in the polymer block (B), isoprene can also be used as the other monomers. In the polymer block (B), the content ratio of other monomer units is preferably 50 wt% or less, more preferably 40 wt% or less, further more preferably 35 wt% or less.

[0056] In an embodiment according to the present invention, the polymer block (B) linked to the polymer block (A) in the conjugated diene polymer chain is formed by mixing the polymer block (A) having an active end described above and a monomer containing 1,3-butadiene, or 1,3-butadiene and an aromatic vinyl compound, and continuing the polymerization reaction. The formed polymer block (B) has an active end. On the other hand, the active end disappears from the polymer block (A).

[0057] For forming the polymer block (B), as the inert solvent used for polymerizing the polymer block (A) and a monomer containing 1,3-butadiene, or 1,3-butadiene and an aromatic vinyl compound, is not particularly limited, and the same inert solvents as those illustrated above can be used.

[0058] The amount of the polymer block (A) having an active end used when forming the polymer block (B) may be determined according to the targeted molecular weight, but is in the range of preferably 0.1 to 5 mmoles, more preferably 0.15 to 2 mmoles, further more preferably 0.2 to 1.5 mmoles with respect to 100 g of the monomer containing 1,3-butadiene, or 1,3-butadiene and an aromatic vinyl compound.

[0059] The method of mixing the polymer block (A) and a monomer containing 1,3-butadiene, or 1,3-butadiene and an aromatic vinyl compound, is not particularly limited. The polymer block (A) having an active end may be added to a solution of a monomer containing 1,3-butadiene, or 1,3-butadiene and an aromatic vinyl compound, or a monomer containing 1,3-butadiene, or 1,3-butadiene and an aromatic vinyl compound, may be added to a solution of the polymer block (A) having an active end. In the light of controlling the polymerization, the method of adding the polymer block (A) having an active end to a solution of a monomer containing 1,3-butadiene, or 1,3-butadiene and an aromatic vinyl compound is preferred.

[0060] The polymerization temperature during polymerization of a

monomer containing 1,3-butadiene, or 1,3-butadiene and an aromatic vinyl compound, is in the range of preferably -80 to +150°C, more preferably 0 to 100°C, further more preferably 20 to 90°C. As the polymerization process, a batch process, continuous process, or any other process can be employed, but when the polymer block (B) is formed as a copolymer chain, the batch process is preferred from the viewpoint of facilitating control of the randomness in bonding.

[0061] The bonding form of the monomers when the polymer block (B) is formed as a copolymer chain may be, for example, a variety of bonding forms such as a block form, a taper form, and a random form, but a random form is preferred. When a random form is selected, wet grip and wear resistance of the obtained cross-linked rubber can be further enhanced. Note that, when the bonding form of 1,3-butadiene and an aromatic vinyl compound is a random form, it is preferred to carry out polymerization while supplying 1,3-butadiene, or 1,3-butadiene and an aromatic vinyl compound continuously or intermittently to the polymerization system such that the ratio of the aromatic vinyl compound to the total amount of 1,3-butadiene and an aromatic vinyl compound does not become too high in the polymerization system.

[0062] In one embodiment according to the present invention, the polymer block (B) is preferably formed in the same manner as in the polymer block (A) by polymerizing the monomers including 1,3-butadiene, or 1,3-butadiene and the aromatic vinyl compound in the presence of a polar compound. Specifically, a polar compound is used in an amount of preferably 0.01 to 5.0 moles, more preferably 0.1 to 4.0 moles, still more preferably 0.2 to 3.0 moles with respect to 1 mole of the polymerization initiator. Such use of a polar compound in the polymerization enables suitable control of the vinyl bond content of 1,3-butadiene monomer units in the polymer block (B). As a result, the vinyl bond content of conjugated diene monomer units in the conjugated

diene rubber finally obtained can be suitably controlled. The vinyl bond content of 1,3-butadiene monomer units in the polymer block (B) is preferably 70 wt% or less, more preferably 68 wt% or less, still more preferably 65 wt% or less. On the other hand, the lower limit of the vinyl bond content is preferably 5 wt% or more, more preferably 10 wt% or more, still more preferably 20 wt% or more, but not particularly limited thereto.

[0063] The polymerization of the monomers including 1,3-butadiene, or 1,3-butadiene and the aromatic vinyl compound in the presence of a polar compound may be carried out by any method without limitation. Examples thereof include methods such as performing polymerization in an inert solution containing the poler compound. In this method, the polar compound is added such that the total of the amount of the polar compound added to form the polymer block (A) and the amount of the polar compound additionally added falls within the ranges described above. For this reason, when the polymer block (A) is formed in the presence of an amount of the polar compound sufficient to control the vinyl bond content of 1,3-butadiene monomer units in the polymer block (B), further addition of the polar compound is not needed. The polar compound may be any of the same polar compounds as those listed above.

[0064] In this way, the conjugated diene polymer chain having an active end and containing a polymer block (A) and a polymer block (B) can be obtained. In an embodiment according to the present invention, the conjugated polymer chain having an active end is preferably formed by the polymer block (A)-polymer block (B) and has an active end at the end of the polymer block (B) in view of productivity, but may have a plurality of the polymer blocks (A), or may further have other polymer blocks. Examples thereof include a conjugated diene polymer chain having an active end such as the polymer block (A)-polymer block (B)-polymer block (A), or the like. In this case, an active end is formed at the end

of a polymer block (A) formed subsequently to the polymer block (B). When the polymer block (A) is formed at the active end side of the conjugated diene polymer chain, the amount of isoprene used is preferably 10 to 100 moles, more preferably 20 to 90 moles, particularly preferably 30 to 70 moles with respect to 1 mole of the polymerization initiator used for the first polymerization reaction (polymerization reaction for forming the first polymer block (A)).

[0065] In the conjugated diene polymer chain having an active end obtained in an embodiment according to the present invention, the weight ratio of the polymer block (A) to the polymer block (B) (when a plurality of the polymer blocks (A) and polymer blocks (B) are present, the weight ratio is based on the total weight of the polymer blocks (A) and that of the polymer blocks (B)) is preferably 0.001 to 0.2, more preferably 0.005 to 0.1, particularly preferably 0.008 to 0.05 in terms of (weight of polymer block (A))/(weight of polymer block (B)). When the weight ratio of the polymer block (A) to the polymer block (B) is within the above ranges, a cross-linked rubber further improved in low fuel consumption can be obtained.

[0066] The content ratio of the total monomer units of isoprene monomer units and 1,3-butadiene monomer units and the content ratio of aromatic vinyl monomer units in the conjugated diene polymer chain having an active end and containing a polymer block (A) and a polymer block (B) are, in the conjugated diene polymer chain having an active end, preferably 50 to 100 wt% of the total monomer units of isoprene monomer units and 1,3-butadiene monomer units and 0 to 50 wt% of aromatic vinyl monomer units, more preferably 52 to 98 wt% of the total monomer units of isoprene monomer units and 1,3-butadiene monomer units and 2 to 48 wt% of aromatic vinyl monomer units, particularly preferably 55 to 84 wt% of the total monomer units of isoprene monomer units and 1,3-butadiene monomer units and 16 to 45 wt% of aromatic vinyl monomer

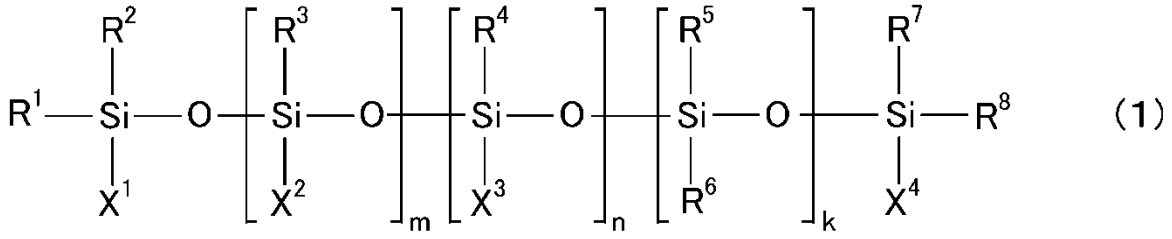
units. Further, the vinyl bond content in isoprene monomer units and 1,3-butadiene monomer units in the conjugated diene polymer chain having an active end and containing a polymer block (A) and a polymer block (B) is preferably within the same range as the vinyl bond content in 1,3-butadiene monomer units in the polymer block (B) described above.

[0067] Before the second step according to the present invention, the polar compound described above may be added. Specifically, the state of association of the conjugated diene polymer chain having an active end can be suitably controlled when the amount of the polar compound added before the second step, more specifically, the amount of the polar compound added in the first step in total is preferably 0.5 to 5.0 moles, more preferably 0.6 to 4.0 moles, particularly preferably 0.9 to 3.0 moles with respect to 1 mole of the polymerization initiator, and, as a result, the maximum dynamic load imposed on a stirrer in the second step can be suitably controlled.

[0068] <Second step>

The second step of the method of production according to the present invention is a step of reacting the conjugated diene polymer chain having an active end obtained in the first step with a polyorganosiloxane represented by the following general formula (1) by adding the polyorganosiloxane to the conjugated diene polymer chain having an active end continuously over 2 to 60 minutes or in portions:

[Chem. 4]



(1)

wherein in the general formula (1), R^1 to R^8 may be the same or different from each other and are each a hydrocarbon group having 1 to 20 carbon

atoms, X^1 and X^4 may be the same or different from each other and are each a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms, a polar functional group having an atom of Group 15 or Group 16 of the periodic table, a halogen atom, or a hydrocarbon group having 1 to 20 carbon atoms and optionally having a polar functional group having an atom of Group 15 or Group 16 of the periodic table or a halogen atom; X^2 is a polar functional group having an atom of Group 15 or Group 16 of the periodic table, a halogen atom, or a hydrocarbon group having 1 to 20 carbon atoms and optionally having a polar functional group having an atom of Group 15 or Group 16 of the periodic table or a halogen atom, and when a plurality of X^2s are present, they may be the same or different from each other; X^3 is a group containing 2 to 20 repeating units of an alkylene glycol, a part of X^3 may be a group derived from a group containing 2 to 20 repeating units of an alkylene glycol, and when a plurality of X^3s are present, they may be the same or different from each other; "m" is an integer of 1 to 200; "n" is an integer of 0 to 200; "k" is an integer of 0 to 200.

[0069] R^1 to R^8 in the general formula (1) may be the same or different from each other and are each a hydrocarbon group having 1 to 20 carbon atoms, preferably an alkyl group having 1 to 20 carbon atoms or an aryl group having 6 to 20 carbon atoms, more preferably an alkyl group having 1 to 6 carbon atoms or an aryl group having 6 to 12 carbon atoms. Examples of the alkyl group having 1 to 6 carbon atoms include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, a butyl group, a pentyl group, a hexyl group, a cyclohexyl group, and the like. Examples of the aryl group having 6 to 12 carbon atoms include a phenyl group, a methylphenyl group, and the like. Among these, a methyl group and an ethyl group are preferred, and a methyl group is more preferred because of ease in production of the polyorganosiloxane itself.

[0070] X^1 and X^4 in the general formula (1) may be the same or different from each other and are each a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms, a polar functional group having an atom of Group 15 or Group 16 of the periodic table, a halogen atom, or a hydrocarbon group having 1 to 20 carbon atoms and optionally having a polar functional group having an atom of Group 15 or Group 16 of the periodic table or a halogen atom. X^1 and X^4 are each preferably any group selected from the group consisting of an alkyl group having 1 to 6 carbon atoms, an aryl group having 6 to 12 carbon atoms, a hydrocarbon group having an alkoxy group and having 1 to 5 carbon atoms (a hydrocarbon group having 1 to 5 carbon atoms in total, including the carbon atoms contained in the alkoxy group), and a hydrocarbon group having an epoxy group and having 4 to 12 carbon atoms (a hydrocarbon group having 4 to 12 carbon atoms in total, including the carbon atoms contained in the epoxy group), more preferably a hydrocarbon group having an epoxy group and having 4 to 12 carbon atoms or an alkyl group having 1 to 6 carbon atoms, still more preferably an alkyl group having 1 to 6 carbon atoms. Examples of the alkyl group having 1 to 6 carbon atoms include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, a butyl group, a pentyl group, a hexyl group, a cyclohexyl group, and the like. Among these, a methyl group and an ethyl group are preferred, and a methyl group is more preferred because of ease in production of the polyorganosiloxane itself.

[0071] X^2 in the general formula (1) is a polar functional group having an atom of Group 15 or Group 16 of the periodic table, a halogen atom, or a hydrocarbon group having 1 to 20 carbon atoms and optionally having a polar functional group having an atom of Group 15 or Group 16 of the periodic table or a halogen atom, and when a plurality of X^2s are present, they may be the same or different from each other. X^2 is preferably a hydrocarbon group having 1 to 20 carbon atoms and

optionally having a polar functional group having an oxygen atom, more preferably a hydrocarbon group having 1 to 20 carbon atoms and optionally having an alkoxy group or an epoxy group, still more preferably a hydrocarbon group having an alkoxy group and having 1 to 5 carbon atoms and a hydrocarbon group having an epoxy group and having 4 to 12 carbon atoms, even more preferably a hydrocarbon group having an epoxy group and having 4 to 12 carbon atoms. In this context, the hydrocarbon group having an alkoxy group and the hydrocarbon group having an epoxy group each preferably have carbon atoms including the carbon atoms contained in the alkoxy group or the epoxy group within the ranges above, and the alkoxy group and the epoxy group are preferably located at an end of a group contained in X^2. In addition, the hydrocarbon group contained in the hydrocarbon group having an alkoxy group or contained in the hydrocarbon group having an epoxy group may contain an ether linkage or a thioether linkage in addition to the alkoxy group and the epoxy group, respectively.

[0072] Examples of the hydrocarbon group having an alkoxy group and having 1 to 5 carbon atoms include a methoxy group, an ethoxy group, a propoxy group, an isopropoxy group, a butoxy group, and the like. Among these, a methoxy group and an ethoxy group are preferred because of ease in production of the polyorganosiloxane itself.

[0073] Examples of epoxy group-containing hydrocarbon groups having 4 to 12 carbon atoms include groups represented by the general formula (5):

$$-Z^3-Z^4-E^2 \quad (5)$$

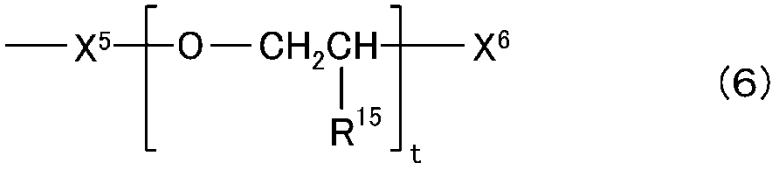
wherein in the general formula (5), Z^3 is an alkylene or an alkylarylene group having 1 to 10 carbon atoms, Z^4 is a methylene group, a sulfur atom, or an oxygen atom, and E^2 is an epoxy group-containing hydrocarbon group having 2 to 10 carbon atoms(a hydrocarbon group having 2 to 10 carbon atoms in total, including the carbon atoms contained in the epoxy

group).

[0074] Preferred groups represented by general formula (5) are those where Z^4 is an oxygen atom, more preferred are those where Z^4 is an oxygen atom and E^2 is a glycidyl group, and particularly preferred are those where Z^3 is an alkylene group having 1 to 10 carbon atoms (preferably an alkylene group having 1 to 3 carbon atoms), Z^4 is an oxygen atom, and E^2 is a glycidyl group.

[0075] X^3 is a group containing 2 to 20 repeating units of an alkylene glycol, a part of X^3 may be a group derived from a group containing 2 to 20 repeating units of an alkylene glycol, and when a plurality of X^3s are present, they may be the same or different from each other. The group containing 2 to 20 repeating units of an alkylene glycol is preferably a group represented by the following general formula (6):

[Chem. 5]



(6)

wherein in the general formula (6), "t" is an integer of 2 to 20, X^5 is an alkylene group or an alkylarylene group having 2 to 10 carbon atoms, R^{15} is a hydrogen atom or a methyl group, and X^6 is an alkoxy group or an aryloxy group having 1 to 10 carbon atoms. Among these, preferred is a group where "t" is an integer of 2 to 8, X^5 is an alkylene group having 3 carbon atoms, R^{15} is hydrogen atom, and X^6 is a methoxy group.

[0076] In the polyorganosiloxane represented by the general formula (1), "m" is an integer of 1 to 200, preferably an integer of 20 to 150, more preferably an integer of 30 to 120. When "m" is 1 or more, the obtained cross-linked rubber can be further improved in low fuel consumption. Further, when "m" is 200 or less, the polyorganosiloxane

itself represented by the general formula (1) is more easily produced and the viscosity thereof does not become too high, resulting in ease in handling.

[0077] Further, in the polyorganosiloxane represented by the general formula (1), "n" is an integer of 0 to 200, preferably an integer of 0 to 150, more preferably an integer of 0 to 120. "k" is an integer of 0 to 200, preferably an integer of 0 to 150, more preferably an integer of 0 to 130. The total of "m", "n" and "k" is 1 or more, preferably 3 to 400, more preferably 20 to 300, particularly preferably 30 to 250. When the total of "m", "n" and "k" is 1 or more, the reaction of the polyorganosiloxane represented by the general formula (1) and the conjugated diene polymer chain having an active end easily proceeds, and further the total of "m", "n" and "k" is 400 or less, the polyorganosiloxane itself represented by the general formula (1) is easily produced and the viscosity thereof does not become too high, resulting in ease in handling.

[0078] The amount of the polyorganosiloxane represented by the general formula (1) used in the second step of the method of production according to the present invention is, as the amount of polar functional groups such as epoxy groups or halogen atoms in polyorganosiloxane, preferably 0.1 moles or more, more preferably 0.15 moles or more, still more preferably 0.2 moles or more, particularly preferably 0.3 moles or more, and preferably 2 moles or less, more preferably 1.5 moles or less, still more preferably 1 mole or less, particularly preferably 0.8 moles or less, with respect to 1 mole of the polymerization initiator used for the polymerization in the first step described above. When the amount of the polyorganosiloxane used is within the ranges above, a cross-linked rubber further improved in low fuel consumption can be obtained.

[0079] Furthermore, in the second step of the method of production according to the present invention, the conjugated diene polymer chain

having an active end obtained in the first step is preferably reacted with a polyorganosiloxane represented by the general formula (1) by adding polyorganosiloxane represented by the general formula (1) to the conjugated diene polymer chain having an active end continuously over 2 to 60 minutes or in portions.

[0080] In this case, usually used is a method including dissolving the conjugated diene polymer chain having an active end in an inert solvent that can dissolve the conjugated diene polymer chain to prepare a polymer solution, and adding the polyorganosiloxane represented by the general formula (1) to the polymer solution continuously over 2 to 60 minutes or in portions with stirring using a stirrer or the like. The inert solvent used in this method is preferably an inert solvent that can dissolve both the conjugated diene polymer chain having an active end and the polyorganosiloxane represented by the general formula (1), and the inert solvents previously described and the like can be used. Furthermore, in this case, a convenient and preferred method includes adding the polyorganosiloxane represented by the general formula (1) to a polymerization solution used for obtaining the conjugated diene polymer chain having an active end continuously or in portions.

[0081] According to the present invention, a modified conjugated diene polymer achieving excellent low fuel consumption can be produced with high productivity by using a method including adding the polyorganosiloxane represented by the general formula (1) to the conjugated diene polymer chain having an active end continuously over 2 to 60 minutes or in portions. Specifically, the polyorganosiloxane represented by the general formula (1) is usually reacted with the conjugated diene polymer chain having an active end using a method including mixing the conjugated diene polymer chain and the polyorganosiloxane in an inert solvent that can dissolve them using a stirrer or the like. This method can reduce the maximum dynamic load

imposed on the stirrer during mixing of the conjugated diene polymer chain and the polyorganosiloxane, and thus the energy required for the production can be reduced. Furthermore, the reaction can be carried out under conditions of relatively high polymer concentration in the inert solvent used while the increase in the maximum dynamic load imposed on the stirrer can be prevented. As a result, the productivity can be improved. Although the reason is not exactly sure, it may be because the proportion of poly-branched polymers having two or more branches produced can be reduced by adding the polyorganosiloxane represented by the general formula (1) to the conjugated diene polymer chain having an active end continuously over 2 to 60 minutes or in portions.

[0082] In the method of adding the polyorganosiloxane represented by the general formula (1) to the conjugated diene polymer chain having an active end continuously over 2 to 60 minutes, the mode of the addition may be adding the polyorganosiloxane represented by the general formula (1) used for the modification substantially continuously, including a mode of adding continuously at a constant rate (at a constant amount), or may be adding a fixed amount of the polyorganosiloxane intermittently and successively, preferably at a short interval of 1 second to less than 2 minutes, more preferably at a short interval of 1 second to 60 seconds. In the mode of adding the polyorganosiloxane continuously, preferred is a mode of adding the polyorganosiloxane continuously at a constant rate (at a constant amount), or a mode of adding a fixed amount of the polyorganosiloxane intermittently. However, a mode of adding the polyorganosiloxane continuously or intermittently and successively while the amount thereof is being varied within ±200%, for example, is also possible.

[0083] When the polyorganosiloxane represented by the general formula (1) is added to the conjugated diene polymer chain having an active end continuously, the period of addition is 2 to 60 minutes, preferably 3 to

50 minutes, more preferably 4 to 40 minutes, still more preferably 5 to 30 minutes. When the period of addition in the continuous addition is too short, the effect of reducing the maximum dynamic load imposed on a stirrer cannot be exerted. On the other hand, when the period of addition in the continuous addition is too long, the production requires more time, resulting in decreased productivity.

[0084] In the method of adding the polyorganosiloxane represented by the general formula (1) to the conjugated diene polymer chain having an active end in portions, the polyorganosiloxane represented by the general formula (1) used for the modification can be added in two or more portions. For example, when the polyorganosiloxane is added in two portions, a specified amount of the polyorganosiloxane can be added in the first addition to drive the modification reaction, then a specified interval can be placed, and the remainder can be added in the second addition. Similarly, when the polyorganosiloxane is added in three portions, a specified amount of the polyorganosiloxane can be added in the first addition to drive the modification reaction, thereafter a specified interval can be placed, then a specified amount of the polyorganosiloxane can be further added in the second addition to further drive the modification reaction, thereafter a specified interval can be placed, and then the reminder can be added in the third addition. When the polyorganosiloxane is added in four or more portions, similar procedures can be used.

[0085] In the addition in portions, the amount added in each time of the addition is not particularly limited. The amounts of the polyorganosiloxane in a plurality of additions can be the same or different from each other. However, preferably, because of a good effect on improving the productivity, the amounts of the polyorganosiloxane in a plurality of additions are the same, or the amount of the polyorganosiloxane added in the first addition is the largest. For

example, when the polyorganosiloxane is added in two portions, the amount in the first addition:the amount in the second addition = 55:45 to 80:20 (weight ratio) is preferred.

[0086] In addition, in the addition in portions, the duration of the addition in each of the additions is preferably less than 2 minutes, more preferably 1 second to less than 1 minute from the viewpoint of improving the productivity. The interval between the additions (i.e., the interval between the addition of the N^{th} portion and the addition of the $(N+1)^{th}$ portion) is preferably 1 to 30 minutes, more preferably 2 to 25 minutes, still more preferably 5 to 20 minutes.

[0087] In the second step of the present invention, it is preferred that all of the polyorganosiloxane represented by the general formula (1) used for the modification be added continuously, or all of the polyorganosiloxane represented by the general formula (1) used for the modification be added in portions. However, a method of adding a part of the polyorganosiloxane represented by the general formula (1) continuously and adding the reminder in portions can be used. In this method, a method of adding continuously first, and adding in portions, or a method of adding in portions, and adding continuously can be used.

[0088] When the polyorganosiloxane represented by the general formula (1) used for the modification is added continuously or in portions, the polyorganosiloxane represented by the general formula (1) may be added directly without being dissolved in an inert solvent or the like, or the polyorganosiloxane represented by the general formula (1) may be dissolved in an inert solvent that can dissolve the polyorganosiloxane, and the solution may be added. In the solution, the concentration is preferably in the range of 1 to 50 wt%.

[0089] In the second step, when the polyorganosiloxane represented by the general formula (1) is added to the conjugated diene polymer chain having an active end continuously or in portions, and thus the

polyorganosiloxane represented by the general formula (1) is reacted with the conjugated diene polymer chain having an active end, the reaction temperature is usually 0 to 120°C, preferably 30 to 90°C. The reaction time in the second step is preferably 2 to 120 minutes, more preferably 5 to 60 minutes, but not particularly limited thereto.

[0090] The timing when the continuous or portionwise addition of the polyorganosiloxane represented by the general formula (1) to the conjugated diene polymer chain having an active end is started is not particularly limited, but is preferably the addition is started when the polymerization reaction is not completed and thus the solution containing the conjugated diene polymer chain having an active end also contains monomers, more specifically, the addition is preferably started when the solution containing the conjugated diene polymer chain having an active end contains 100 ppm or more of monomers, more preferably 300 to 50,000 ppm of monomers.

[0091] After the reaction of the conjugated diene polymer chain having an active end with the polyorganosiloxane represented by the general formula (1), a polymerization terminator, such as an alcohol, such as methanol, ethanol, or isopropanol, or water is preferably added to the polymerization solution to deactivate unreacted active ends.

[0092] The active end of the conjugated diene polymer chain is deactivated, and then an antiaging agent such as a phenol-based stabilizing agent, a phosphorus-based stabilizing agent, or a sulfur-based stabilizing agent, a crumb forming agent, a scale inhibitor, and the like may be added to the reaction solution, if desired, and subsequently the inert solvent is separated from the reaction solution by direct drying or steam stripping to collect the modified conjugated diene rubber. In addition, before the inert solvent is separated from the reaction solution, an oil extender may be mixed with the polymerization solution to collect the modified conjugated diene rubber

as an oil extended rubber.

[0093] Examples of the oil extender used for collecting the modified conjugated diene rubber as an oil extended rubber include paraffin-based, aromatic-based, and naphthene-based oil-based softening agents, plant-based softening agents, softening agents derived from plant-derived resources, and fatty acids. When the oil-based softening agent is used, the content of the polycyclic aromatic compound extracted by the method of IP346 (test method of THE INSTITUTE PETROLEUM of the U.K.) is preferably less than 3%. When an oil extender is used, the amount used is preferably 5 to 100 parts by weight, more preferably 10 to 60 parts by weight, further more preferably 15 to 50 parts by weight with respect to 100 parts by weight of the modified conjugated diene rubber.

[0094] The weight average molecular weight (Mw) of the modified conjugated diene rubber is preferably 50,000 to 5,000,000, more preferably 75,000 to 3,000,000, particularly preferably 100,000 to 1,000,000 as measured by gel permeation chromatography against polystyrene standards.

[0095] Further, the molecular weight distribution represented by the ratio (Mw/Mn) of the weight average molecular weight (Mw) and the number average molecular weight (Mn) of the modified conjugated diene rubber is preferably 1.1 to 3.0, more preferably 1.2 to 2.5, particularly preferably 1.2 to 2.2. When the molecular weight distribution (Mw/Mn) of the modified conjugated diene rubber is within the above range, low fuel consumption of the obtained cross-linked rubber can be further enhanced.

[0096] Further, the Mooney viscosity (ML_{1+4}, 100°C) of the modified conjugated diene rubber is preferably 20 to 150, more preferably 30 to 120, particularly preferably 35 to 90. Note that when the modified conjugated diene rubber is an oil extended rubber, it is preferred that the Mooney viscosity of the oil extended rubber be within the above ranges.

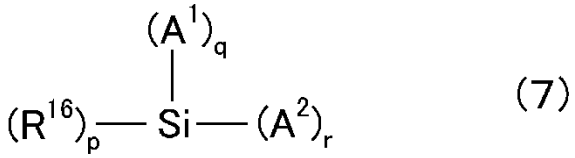
[0097] The glass transition temperature (Tg) of the modified conjugated diene rubber is preferably 20°C to -110°C, more preferably 10°C to -70°C, particularly preferably 0°C to -60°C, most preferably -10°C to -45°C, but not particularly limited thereto. The glass transition temperature of the modified conjugated diene rubber according to the present invention can be suitably controlled, for example, by controlling the content of the aromatic vinyl monomer unit in the modified conjugated diene rubber and the vinyl bond content of the modified conjugated diene monomer unit.

[0098] In the method of production according to the present invention, the conjugated diene polymer chain reacted with the polyorganosiloxane represented by the general formula (1) (i.e., after the second step) may be further reacted with a hydrocarbyloxysilane compound.

[0099] Such a hydrocarbyloxysilane compound is not particularly limited as long as it is a silicon-containing compound having at least one hydrocarbyloxy group excluding the polyorganosiloxane represented by the general formula (1), but is preferably a compound having at least one nitrogen-atom containing group in addition to a hydrocarbyloxy group, more preferably is a compound having a group containing a primary amino group having active hydrogen atoms and/or a secondary amino group having an active hydrogen atom as the nitrogen-atom containing group. The hydrocarbyloxysilane compound acts as a modifier through a reaction of the hydrocarbyloxy group with a conjugated diene polymer chain having an active end or a reaction residue produced by a reaction between a conjugated diene polymer chain having an active end and a polyorganosiloxane represented by the general formula (1).

[0100] Such a hydrocarbyloxysilane compound is not particularly limited, but a compound represented by the general formula (7) can be preferably used:

[Chem. 6]



(7)

wherein in the general formula (7), R^{16} is a hydrocarbyl group, A^1 is a hydrocarbyloxy group, A^2 is a nitrogen atom-containing group, "p" is an integer of 0 to 2, "q" is an integer of 1 to 3, "r" is an integer of 1 to 3, and "p+q+r" is 4.

[0101] In the general formula (7), R^{16} is a hydrocarbyl group. Examples of the hydrocarbyl group include an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group, and an aralkyl group, and an alkyl group having 1 to 6 carbon atoms is preferred. Examples of the alkyl group having 1 to 6 carbon atoms include a methyl group, an ethyl group, an n-propyl group, an isopropyl group, a butyl group, a pentyl group, and a hexyl group. Among these, a methyl group and an ethyl group are more preferred.

[0102] In the general formula (7), A^1 represents a hydrocarbyloxy group. Examples of the hydrocarbyloxy group include alkoxy groups such as a methoxy group, an ethoxy group, an n-propoxy group, an isopropoxy group, an n-butoxy group, an isobutoxy group, a sec-butoxy group, and a tert-butoxy group; alkenyloxy groups such as a vinyloxy group and an allyloxy group; aryloxy groups such as a phenoxy group and a naphthoxy group; aralkyloxy groups such as a benzyloxy group; and the like. Among these, in view of reactivity, alkoxy groups and aryloxy groups are preferred, alkoxy groups are more preferred, and a methoxy group and an ethoxy group are particularly preferred.

[0103] In the general formula (7), A^2 is a nitrogen-atom containing group, and is not particularly limited as long as it contains a nitrogen atom, but an organic group having a nitrogen atom is preferred. Examples

thereof include a 3-aminopropyl group, a 4-aminobutyl group, a 3-(2-aminoethylamino)propyl group, a 2-dimethylaminoethyl group, a 3-diethylaminopropyl group, a 3-diethylaminopropyl group, a 3-dipropylaminopropyl group, a 3-dibutylaminopropyl group, a 3-phenylmethylaminopropyl group, a 3-(4-methylpiperazinyl)propyl group, a N,N-bis(trimethylsilyl)aminopropyl group, a N,N-bis(triethylsilyl)aminopropyl group, a N,N',N'-tris(trimethylsilyl)-N-(2-aminoethyl)-3-aminopropyl group, and the like. Among these, groups containing a primary amino group having active hydrogen atoms and/or a secondary amino group having an active hydrogen atom, such as a 3-aminopropyl group, a 4-aminobutyl group, and a 3-(2-aminoethylamino)propyl group, are preferred in view of further improvement in low fuel consumption of the obtained cross-linked rubber. Note that the "active hydrogen atom" means a hydrogen atom bound to an atom other than a carbon atom, and preferably has binding energy lower than that of the carbon-hydrogen bond of a polymethylene chain.

[0104] In the compound represented by the general formula (7), "p" is an integer of 0 to 2, "q" is an integer of 1 to 3, "r" is an integer of 1 to 3, and "p+q+r" is 4. From the viewpoint of reactivity with the conjugated diene polymer chain reacted with the polyorganosiloxane represented by the general formula (1) (i.e., after the second step), "p", "q", and "r" are preferably an integer of 0 or 1, an integer of 2 or 3 and an integer of 1 or 2, respectively, and "p", "q", and "r" are more preferably 0, 3, and 1, respectively. Note that when "p" is 2, the two groups represented by R^{16} in one molecule of the compound represented by the general formula (7) may be the same or different from each other. Similarly, when "q" is 2 or 3, the multiple groups represented by A^1 in one molecule of the compound represented by the general formula (7) may be the same or different from each other, and when "r" is 2 or 3, the multiple groups represented by A^2 in one molecule of the compound

represented by the general formula (7) may be the same or different from each other.

[0105] Specific examples of the compound represented by the general formula (7) are not particularly limited, but examples of compounds in which A^2 in the general formula (7) is a group containing a primary amino group having active hydrogen atoms and/or a secondary amino group having an active hydrogen atom include compounds having a 3-aminopropyl group as A^2, such as 3-aminopropyldimethylmethoxysilane, 3-aminopropylmethyldimethoxysilane, 3-aminopropyltrimethoxysilane, 3-aminopropyldimethylethoxysilane, 3-aminopropylmethyldiethoxysilane and 3-aminopropyltriethoxysilane; compounds having a 4-aminobutyl group as A^2, such as 4-aminobutyldimethylmethoxysilane, 4-aminobutylmethyldimethoxysilane, 4-aminobutyltrimethoxysilane, 4-aminobutyldimethylethoxysilane, 4-aminobutylmethyldiethoxysilane, and 4-aminobutyltriethoxysilane; and compounds having a 3-(2-aminoethylamino)propyl group as A^2, such as 3-(2-aminoethylamino)propyldimethylmethoxysilane, 3-(2-aminoethylamino)propylmethyldimethoxysilane, 3-(2-aminoethylamino)propyltrimethoxysilane, 3-(2-aminoethylamino)propyldimethylethoxysilane, 3-(2-aminoethylamino)propylmethyldiethoxysilane, and 3-(2-aminoethylamino)propyltriethoxysilane.

[0106] Further, examples of compounds in which A^2 in the general formula (7) is a group other than a group containing a primary amino group having active hydrogen atoms and/or a secondary amino group having an active hydrogen atom include compounds having a 3-dimethylaminopropyl group as A^2, such as 3-dimethylaminopropyltrimethoxysilane, 3-dimethylaminopropylmethyldimethoxysilane, 3-dimethylaminopropyldimethylmethoxysilane, 3-dimethylaminopropyltriethoxysilane, 3-

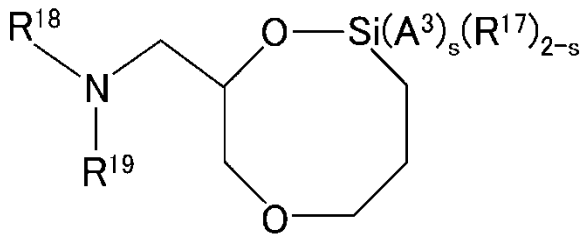
dimethylaminopropylmethyldiethoxysilane and 3-dimethylaminopropyldimethylethoxysilane; compounds having a 3-diethylaminopropyl group as A^2, such as 3-diethylaminopropyltrimethoxysilane, 3-diethylaminopropylmethyldimethoxysilane, 3-diethylaminopropyldimethylmethoxysilane, 3-diethylaminopropyltriethoxysilane, 3-diethylaminopropylmethyldiethoxysilane, and 3-diethylaminopropyldimethylethoxysilane; compounds having a 3-dipropylaminopropyl group as A^2, such as 3-dipropylaminopropyltrimethoxysilane, 3-dipropylaminopropylmethyldimethoxysilane, 3-dipropylaminopropyldimethylmethoxysilane, 3-dipropylaminopropyltriethoxysilane, 3-dipropylaminopropylmethyldiethoxysilane, and 3-dipropylaminopropyldimethylethoxysilane; compounds having a 3-dibutylaminopropyl group as A^2, such as 3-dibutylaminopropyltrimethoxysilane, 3-dibutylaminopropylmethyldimethoxysilane, 3-dibutylaminopropyldimethylmethoxysilane, 3-dibutylaminopropyltriethoxysilane, 3-dibutylaminopropylmethyldiethoxysilane, and 3-dibutylaminopropyldimethylethoxysilane; compounds having 3-phenylmethylaminopropyl group as A^2, such as 3-phenylmethylaminopropyltrimethoxysilane, 3-phenylmethylaminopropylmethyldimethoxysilane, 3-phenylmethylaminopropyldimethylmethoxysilane, 3-phenylmethylaminopropyltriethoxysilane, 3-phenylmethylaminopropylmethyldiethoxysilane, and 3-phenylmethylaminopropyldimethylethoxysilane; compounds having 3-(4-

methylpiperazinyl)propyl group as A^2, such as 3-(4-methylpiperazinyl)propyltrimethoxysilane, 3-(4-methylpiperazinyl)propylmethyldimethoxysilane, 3-(4-methylpiperazinyl)propyldimethylmethoxysilane, 3-(4-methylpiperazinyl)propyltriethoxysilane, 3-(4-methylpiperazinyl)propylmethyldiethoxysilane, and 3-(4-methylpiperazinyl)propyldimethylethoxysilane;

[0107] compounds having a N,N-bis(trimethylsilyl)aminopropyl group as A^2, such as N,N-bis(trimethylsilyl)aminopropyltrimethoxysilane, N,N-bis(trimethylsilyl)aminopropyltriethoxysilane, N,N-bis(trimethylsilyl)aminopropylmethyldimethoxysilane and N,N-bis(trimethylsilyl)aminopropylmethyldiethoxysilane; compounds having N,N-bis(triethylsilyl)aminopropyl group as A^2, such as N,N-bis(triethylsilyl)aminopropyltrimethoxysilane, N,N-bis(trimethylsilyl)aminopropyltriethoxysilane, N,N-bis(triethylsilyl)aminopropylmethyldimethoxysilane, and N,N-bis(triethylsilyl)aminopropylmethyldiethoxysilane; and compounds having a N,N',N'-tris(trimethylsilyl)-N-(2-aminoethyl)-3-aminopropyl group as A^2, such as N,N',N'-tris(trimethylsilyl)-N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N,N',N'-tris(trimethylsilyl)-N-(2-aminoethyl)-3-aminopropyltriethoxysilane, N,N',N'-tris(trimethylsilyl)-N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, and N,N',N'-tris(trimethylsilyl)-N-(2-aminoethyl)-3-aminopropylmethyldiethoxysilane.

[0108] In addition, as the hydrocarbyloxysilane compound, a compound represented by the general formula (8) can be preferably used:

[Chem. 7]



(8)

wherein in the general formula (8), A^3 is a hydrocarbyloxy group, R^{17} represents an optionally substituted hydrocarbon group, R^{18} and R^{19} each independently represent an optionally substituted hydrocarbon group, R^{18} and R^{19} may be bonded to each other to form a ring structure together with the nitrogen atom to which they are bonded, and when they form a ring structure, they may form the ring structure together with a heteroatom other than the nitrogen atom to which they are bonded, in addition to the nitrogen atom to which they are bonded. "s" is an integer of 0 to 2.

[0109] In the general formula (8), A^3 represents a hydrocarbyloxy group. Examples of the hydrocarbyloxy group include alkoxy groups such as a methoxy group, an ethoxy group, an n-propoxy group, an isopropoxy group, an n-butoxy group, an isobutoxy group, a sec-butoxy group, and a tert-butoxy group; alkenyloxy groups such as a vinyloxy group and an allyloxy group; aryloxy groups such as a phenoxy group and a naphthoxy group; aralkyloxy groups such as a benzyloxy group; and the like. Among these, in view of reactivity, alkoxy groups and aryloxy groups are preferred, alkoxy groups are more preferred, and a methoxy group and an ethoxy group are particularly preferred.

[0110] In the general formula (8), "s" (i.e., the number of groups represented by A^3 in the general formula (8)) is an integer of 0 to 2, and "s" is preferably 2. In the general formula (8), when "s" is 2, the two groups represented by A^3 contained in one molecule of the compound represented by the general formula (8) may be the same or different from each other.

[0111] In the general formula (8), R^{17} represents a substituted or unsubstituted hydrocarbon group. Examples of the hydrocarbon group which can be R^{17} include, but are not particularly limited to, alkyl groups such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, and a tert-butyl group; alkenyl groups such as a vinyl group and an allyl group; alkynyl groups such as an ethynyl group and a propinyl group; aryl groups such as a phenyl group and a naphthyl group; aralkyl groups such as a benzyl group; and the like. Among these, alkyl groups and aryl groups are preferred, alkyl groups are more preferred, and a methyl group and an ethyl group are particularly preferred. Further, the hydrocarbon group represented by R^{17} may have a substituent other than a hydrocarbon group. The substituent is not particularly limited, but examples thereof include carbonyl group-containing groups such as a carboxyl group, an acid anhydride group, a hydrocarbylcarbonyl group, an alkoxycarbonyl group, and an acyloxy group; an epoxy group; an oxy group; a cyano group; an amino group; halogen groups, and the like. Note that when "s" in the general formula (8) is 0, the two groups represented by R^{17} contained in one molecule of the compound represented by the general formula (8) may be the same or different from each other.

[0112] In the general formula (8), R^{18} and R^{19} each independently represent an optionally substituted hydrocarbon group, R^{18} and R^{19} may be bonded to each other to form a ring structure together with the nitrogen atom to which they are bonded. When they form a ring structure, they may form the ring structure together with a heteroatom other than the nitrogen atom to which they are bonded, in addition to the nitrogen atom to which they are bonded. When R^{18} and R^{19} are not bonded to each other, examples of the hydrocarbon group which can be R^{18} and R^{19} include, but are not particularly limited to, alkyl groups such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an

isobutyl group, a sec-butyl group, and a tert-butyl group; alkenyl groups such as a vinyl group and an allyl group; alkynyl groups such as an ethynyl group and a propinyl group; aryl groups such as a phenyl group and a naphthyl group; aralkyl groups such as a benzyl group; and the like. Among these, alkyl groups and aryl groups are preferred, alkyl groups are more preferred, and a methyl group and an ethyl group are particularly preferred. On the other hand, when R^{18} and R^{19} are bonded to each other to form a ring structure together with the nitrogen atom to which they are bonded, examples of the bivalent hydrocarbon group formed by R^{18} and R^{19} bonded to each other include, but are not particularly limited to, alkylene groups such as an n-butylene group (i.e., in the general formula (8), R^{18} and R^{19} form a 1-pyrrolidine group together with the nitrogen atom to which they are bonded) and an n-pentylene group (i.e., R^{18} and R^{19} form a 1-piperidine group therewith), and a butadienylene group (i.e., R^{18} and R^{19} form a 1-pyrrole group therewith).

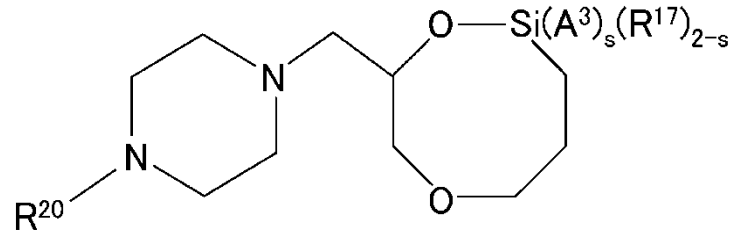
In addition, when R^{18} and R^{19} are bonded to each other to form a ring structure together with the nitrogen atom to which they are bonded, the ring structure is preferably a 4- to 8-membered ring structure.

[0113] Further, the hydrocarbon group represented by R^{18} and R^{19} may have a substituent other than hydrocarbon group regardless of whether R^{18} and R^{19} form a ring structure. The substituent is not particularly limited, but examples thereof include carbonyl-group containing groups such as a carboxyl group, an acid anhydride group, a hydrocarbylcarbonyl group, an alkoxycarbonyl group, and an acyloxy group; an epoxy group; an oxy group; a cyano group; an amino group; halogen groups; and the like. Furthermore, when R^{18} and R^{19} are bonded to each other to form a ring structure together with the nitrogen atom to which they are bonded, the atoms forming the ring structure may include carbon atoms and a heteroatom other than the nitrogen atom to which they are bonded. Examples of such hetero atoms include a nitrogen atom and an oxygen

atom.

[0114] Particularly preferred examples of the compound represented by the general formula (8) include a compound where the hydrocarbon groups represented by R^{18} and R^{19} are bonded to each other to form a piperazine ring structure together with the nitrogen atom to which they are bonded. More specifically, a compound represented by the following general formula (9) is particularly preferred. By using a compound having such a structure as a compound represented by the general formula (8), it is possible to obtain a cross-linked rubber particularly improved in low fuel consumption:

[Chem. 8]



(9)

wherein in the general formula (9), A^3, R^{17}, and "s" are the same as those in the general formula (8), while R^{20} represents a hydrocarbon group.

[0115] In the general formula (9), R^{20} represents a hydrocarbon group. The hydrocarbon group which can be R^{20} is not particularly limited, but examples thereof include alkyl groups such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, and a tert-butyl group; alkenyl groups such as a vinyl group and an allyl group; alkynyl groups such as an ethynyl group and a propinyl group; aryl groups such as a phenyl group and a naphthyl group; aralkyl groups such as a benzyl group; and the like. Among these, alkyl groups and aryl groups are preferred, alkyl groups are more preferred, and a methyl group is particularly preferred.

[0116] Specific examples of the compound represented by the formula

(8) include 2,2-dimethoxy-8-(4-methylpiperazinyl)methyl-1,6-dioxa-2-silacyclooctane, 2,2-diethoxy-8-(4-methylpiperazinyl)methyl-1,6-dioxa-2-silacyclooctane, 2,2-dimethoxy-8-(N,N-diethylamino)methyl-1,6-dioxa-2-silacyclooctane, and 2-methoxy-2-methyl-8-(4-methylpiperazinyl)methyl-1,6-dioxa-2-silacyclooctane. These compounds represented by the general formula (8) may be used alone or in combination.

[0117] The amount of the hydrocarbyloxysilane compound used is preferably 0.1 to 5 moles, more preferably 0.2 to 2 moles, still more preferably 0.4 to 1.5 moles with respect to 1 mole of the active end of the conjugated diene polymer chain having an active end obtained in the first step, but not particularly limited thereto. When the amount of the hydrocarbyloxysilane compound used is within the above ranges, a cross-linked rubber further improved in low fuel consumption can be obtained.

[0118] The method for reacting the hydrocarbyloxysilane compound with the conjugated diene polymer chain reacted with the polyorganosiloxane represented by the general formula (1) (i.e., after the second step) is not particularly limited, but examples of the method include a method of mixing them in an inert solvent capable of dissolving them. Examples of the inert solvent used in this method include the inert solvents described above. In this method, a method of adding the hydrocarbyloxysilane compound to a reaction solution used in the second step for the reaction of the conjugated diene polymer chain having an active end with the polyorganosiloxane compound represented by the general formula (1) is convenient and preferred. Further, in this method, the hydrocarbyloxysilane compound is preferably added to the polymerization system as a solution thereof dissolved in an inert solvent. The concentration of the solution is preferably within a range of 1 to 50 wt%. The reaction temperature is not particularly limited, but is usually 0 to 120°C. The reaction time is also not particularly limited, but is usually 1 minute to 1 hour.

[0119] Similarly, when the hydrocarbyloxysilane compound is reacted, in the same manner as described above, after the reaction of the hydrocarbyloxysilane compound, a polymerization terminator, such as an alcohol, such as methanol, ethanol, or isopropanol, or water is preferably added to deactivate unreacted active ends. Furthermore, in the same manner as described above, an antiaging agent such as a phenol-based stabilizing agent, a phosphorus-based stabilizing agent, or a sulfur-based stabilizing agent, a crumb forming agent, a scale inhibitor, and the like may be added to the reaction solution, and subsequently the inert solvent is separated from the reaction solution by direct drying or steam stripping to collect the modified conjugated diene rubber. In addition, in the same manner as described above, before the inert solvent is separated from the reaction solution, an oil extender may be mixed with the polymerization solution to collect the modified conjugated diene rubber as an oil extended rubber.

[0120] <Rubber composition>

The rubber composition according to the present invention is a composition containing silica added to the rubber ingredients containing the modified conjugated diene rubber obtained by the method of production according to the present invention as described above.

[0121] The rubber composition according to the present invention may contain other rubbers besides the modified conjugated diene rubber obtained by the above-mentioned method of production according to the present invention. Examples of the above-mentioned other rubbers include rubbers other than the modified conjugated diene rubber obtained by the above-mentioned method of production according to the present invention among rubbers such as natural rubber (including reformed natural rubbers such as epoxidized natural rubber (ENR), hydrogenated natural rubber (HNR), deproteinized natural rubber (DPNR), ultra pure natural rubber (UPNR), and grafted natural rubber), polyisoprene rubber, emulsion

polymerized styrene-butadiene copolymer rubber, solution polymerized styrene-butadiene copolymer rubber, polybutadiene rubber (including high cis-BR or low cis BR, further, polybutadiene rubber containing crystal fibers made of 1,2-polybutadiene polymer), styrene-isoprene copolymer rubber, butadiene-isoprene copolymer rubber, styrene-isoprene-butadiene copolymer rubber, acrylonitrile-butadiene copolymer rubber, acrylonitrile-styrene-butadiene copolymer rubber, butyl rubber (IIR), ethylene-propylene copolymer, chloroprene rubber, nitrile chloroprene rubber, and nitrile isoprene rubber. Among these, natural rubber, polyisoprene rubber, polybutadiene rubber, and solution polymerized styrene-butadiene copolymer rubber are preferred. These rubbers can be used alone or in combination of two or more, for example, in a combination of natural rubber and polybutadiene rubber, natural rubber and styrene-butadiene copolymer rubber, and the like.

[0122] In the rubber composition according to the present invention, the modified conjugated diene rubber obtained by the method of production according to the present invention preferably accounts for 10 to 100 wt% of the rubber ingredients in the rubber composition, particularly preferably accounts for 50 to 100 wt%. When the modified conjugated diene rubber obtained by the method of production according to the present invention is included in such a proportion in the rubber ingredients, a cross-linked rubber further improved in low fuel consumption can be obtained.

[0123] Examples of the silica used in the present invention include dry white carbon, wet white carbon, colloidal silica, precipitated silica, calcium silicate, aluminum silicate, and the like. Among these, wet white carbon mainly comprised of hydrous silicic acid is preferred. Further, a carbon-silica dual phase filler comprised of carbon black on the surface of which silica is carried may be used. These silicas may be used alone or in combination. The nitrogen adsorption specific surface

area of the silica which is used (measured by BET method based on ASTM D3037-81) is preferably 20 to 400 m^2/g, more preferably 50 to 220 m^2/g, particularly preferably 80 to 170 m^2/g. Further, the pH of the silica is preferably 5 to 10.

[0124] The silica used in the present invention preferably has a dibutyl phthalate (DBP) absorption in the range of about 100 to about 400, particularly preferably in the range of about 150 to about 300.

[0125] The silica used in the present invention preferably has an average ultimate particle size in the range of 0.01 to 0.05 μm as measured with an electron microscope. However, the average ultimate particle size of the silica is not limited within the ranges, and may be smaller or larger.

[0126] Examples of the silica used in the present invention include various commercially available silicas. Specific examples thereof include Hi-Sil 210, Hi-Sil 233, and Hi-Sil 243LD available from PPG Industries; Zeosil 1115MP, Zeosil 1165MP, Zeosil 165GR, and Zeosil Premium 200MP available from Solvay ; ULTRASIL VN2 and ULTRASIL VN3 available from Evonik; and the like.

[0127] The amount of silica in the rubber composition according to the present invention is preferably 10 to 250 parts by weight, more preferably 15 to 150 parts by weight, still more preferably 20 to 130 parts by weight with respect to 100 parts by weight of the rubber ingredients in the rubber composition. By controlling the amount of the silica within the above ranges, the obtained cross-linked rubber becomes further improved in low fuel consumption.

[0128] The rubber composition according to the present invention may further contain a silane coupling agent from the viewpoint of a further improvement in low fuel consumption. The silane coupling agent in the present invention is not particularly limited, and various silane coupling agents can be used. Examples of the silane coupling agent

suitably used in the invention include sulfide-based, mercapto-based, protected mercapto-based (e.g., those having a carbonylthio group), thiocyanate-based, vinyl-based, amino-based, methacrylate-based, glycidoxy-based, nitro-based, epoxy-based, and chloro-based silane coupling agents. Specific examples of the silane coupling agent include bis(3-(triethoxysilyl)propyl) disulfide, bis(3-(triethoxysilyl)propyl)tetrasulfide, bis(3-triethoxysilylpropyl) tetrasulfide, γ-mercaptopropyltriethoxysilane, 3-[ethoxybis(3,6,9,12,15-pentaoxaoctacosan-1-yloxy)silyl]-1-propanethiol, 3-octanoylthio-1-propyl-triethoxysilane, 3-trimethoxysilylpropyl-N,N-dimethylthiocarbamoyl tetrasulfide, γ-trimethoxysilylpropylbenzothiazyl tetrasulfide, 3-trimethoxysilylpropylbenzothiazole tetrasulfide, 3-thiocyanatopropyltriethoxysilane, vinyltriethoxysilane, N-(β-aminoethyl)-γ-aminopropyltrimethoxysilane, 3-trimethoxysilylpropyl methacrylate monosulfide, γ-glycidoxypropyltriethoxysilane, 3-nitropropyltrimethoxysilane, β-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, 3-chloropropyltrimethoxysilane; and the like. In addition, NXT-Z100, NXT-Z30, NXT-Z45, NXT-Z60, NXT-Z45, and NXT available from Momentive Performance Materials Inc.; Si 69, Si 75, and VP Si 363 available from Evonik; and the like may be used. These silane coupling agents may be used alone or in combination. Alternatively, one of these silane coupling agents or two or more of these silane coupling agents may be oligomerized and used as a oligomer. The amount of the silane coupling agent contained is preferably 0.1 to 30 parts by weight, more preferably 1 to 15 parts by weight with respect to 100 parts by weight of the silica.

[0129] Further, the rubber composition according to the present invention may further contain carbon black such as furnace black, acetylene black, thermal black, channel black, and graphite. Among these, furnace black is preferred. These carbon blacks may be used alone

or in combination. The amount of the carbon black is usually 120 parts by weight or less with respect to 100 parts by weight of the rubber ingredients in the rubber composition.

[0130] The method of adding silica to the rubber ingredient including the modified conjugated diene rubber obtained by the method of production according to the present invention is not particularly limited, but the method of adding it to and kneading it with the solid rubber ingredient (dry kneading method), the method of adding it to a solution containing the conjugated diene rubber and coagulating and drying them (wet kneading method), and the like may be used.

[0131] Further, the rubber composition according to the present invention preferably further contains a cross-linking agent. Examples of the cross-linking agent include sulfur-containing compounds such as sulfur and halogenated sulfur, organic peroxides, quinone dioximes, organic polyvalent amine compounds, alkylphenol resins having a methylol group, and the like. Among these, sulfur is preferably used. The amount of the cross-linking agent is preferably 0.1 to 15 parts by weight, more preferably 0.5 to 5 parts by weight, particularly preferably 1 to 4 parts by weight with respect to 100 parts by weight of the rubber ingredients in the rubber composition.

[0132] Further, to the rubber composition according to the present invention, in addition to the ingredients described above, required amounts of compounding agents such as a cross-linking accelerator, a cross-linking activator, an antioxidant, a filler (excluding the silica and carbon black as described above), an activating agent, a process oil, a plasticizer, a lubricant, a compatibilizer, and a surfactant may be added by a conventional method. Examples of the process oil include paraffin-based, aromatic-based, and naphthene-based oil-based softening agents; plant-derived softening agents; softening agents derived from plant-derived resources; fatty acids; and the like. When petroleum-based

softening agents are used, the content of polycyclic aromatic compounds as extracted according to the method of IP346 (a method defined by THE INSTITUTE PETROLEUM, U.K.) is preferably less than 3%.

[0133] When sulfur or a sulfur-containing compound is used as a cross-linking agent, use in combination with a cross-linking accelerator and cross-linking activator is preferred. Examples of the cross-linking accelerator include sulfenamide-based cross-linking accelerators; guanidine-based cross-linking accelerators; thiourea-based cross-linking accelerators; thiazole-based cross-linking accelerators; thiuram-based cross-linking accelerators; dithiocarbamic acid-based cross-linking accelerators; xanthic acid-based cross-linking accelerators; and the like. Among these, one including a sulfenamide-based cross-linking accelerator is preferred. These cross-linking accelerators may be used alone or in combination. The amount of cross-linking accelerator is preferably 0.1 to 15 parts by weight, more preferably 0.5 to 5 parts by weight, particularly preferably 1 to 4 parts by weight with respect to 100 parts by weight of the rubber ingredients in the rubber composition.

[0134] Examples of the cross-linking activator include higher fatty acids such as stearic acid; and zinc oxide. These cross-linking activators may be used alone or in combination. The amount of the cross-linking activator is preferably 0.05 to 20 parts by weight, particularly preferably 0.5 to 15 parts by weight with respect to 100 parts by weight of the rubber ingredients in the rubber composition.

[0135] In addition, the rubber composition according to the present invention may contain a resin in addition to the rubber ingredients. Use of the resin imparts tackiness to the rubber composition, and enhances the dispersibility of a filler in the rubber composition. As a result, an improvement in wet grip and wear resistance can be expected. Further, as an effect similar to that of a plasticizer, the processability of the rubber composition can also be improved. Examples of the resin include a

C5 petroleum resin, a C5/C9 petroleum resin, a C9 petroleum resin, a dicyclopentadiene resin, a terpene resin, a terpene phenol resin, an aromatic modified terpene resin, an alkylphenol-acetylene resin, a rosin resin, a rosin ester resin, an indene resin, a C9 resin containing indene, an α-methylstyrene-indene copolymer resin, a coumarone-indene resin, a farnesene resin, a polylimonene resin, and the like. These resins are used alone or in combination. The amount of the resin compounded is preferably 50 parts by weight or less, more preferably 25 parts by weight or less relative to 100 parts by weight of the rubber ingredients in the rubber composition.

[0136] To obtain the rubber composition according to the present invention, it is sufficient to knead the ingredients according to an ordinary method. For example, it is possible to knead the ingredients other than thermally unstable ingredients such as a cross-linking agent and a cross-linking accelerator with the conjugated diene rubber, then mix thermally unstable ingredients such as cross-linking agent and cross-linking accelerator with the kneaded material to obtain the target composition. The kneading temperature for kneading the ingredients other than the thermally unstable ingredients and the conjugated diene rubber is preferably 80 to 200°C, more preferably 120 to 180°C, while the kneading time is preferably 30 seconds to 30 minutes. Further, the kneaded material and thermally unstable ingredients are mixed after the kneaded material is cooled down to usually 100°C or less, preferably 80°C or less.

[0137] <Cross-linked Rubber>

The cross-linked rubber according to the present invention is obtained by cross-linking the above-mentioned rubber composition according to the present invention.

The cross-linked rubber according to the present invention may be produced using the rubber composition according to the present

invention, for example, shaping it by a forming machine corresponding to the desired shape, for example, an extruder, an injection molding machine, a press, rolls, or the like and heating it for a cross-linking reaction to fix the shape as a cross-linked rubber. In this case, the product may be cross-linked after shaping it in advance, or may be cross-linked simultaneously with shaping. The shaping temperature is usually 10 to 200°C, preferably 25 to 120°C. The cross-linking temperature is usually 100 to 200°C, preferably 130 to 190°C, while the cross-linking time is usually 1 minute to 24 hours, preferably 2 minutes to 12 hours, particularly preferably 3 minutes to 6 hours.

[0138] Further, depending on the shape, size, and the like of the cross-linked rubber, sometimes even if the surface thereof is cross-linked, the inside is not sufficiently cross-linked, so the cross-linked rubber may be further heated for secondary cross-linking.

[0139] As the heating method for cross-linking the rubber composition, it is sufficient to suitably select press heating, steam heating, oven heating, hot air heating, and other general methods used to cross-link rubber.

[0140] The thus obtained cross-linked rubber according to the present invention is obtained using the conjugated diene rubber obtained by the above-mentioned method of production according to the present invention, so is excellent in low fuel consumption. Making use of these characteristics, the cross-linked rubber according to the present invention, can for example, be used for materials for parts of tires such as cap treads, base treads, carcasses, sidewalls, and bead parts; materials for industrial products such as hoses, belts, mats, and vibration absorbing rubbers; agents for improving the impact resistance of resins; resin film buffer agents; shoe soles; rubber shoes; golf balls; toys; and other various applications.

EXAMPLES

[0141] Below, the present invention is described in reference to further detailed examples but is not limited thereto. Note that, in below, "parts" is based on weight unless particularly represented otherwise. Additionally, tests and evaluations were performed by the following methods.

[0142] [Peak top molecular weight (Mp), weight average molecular weight (Mw), and molecular weight distribution (Mw/Mn)]

The peak top molecular weight (Mp), the weight average molecular weight (Mw), and the molecular weight distribution (Mw/Mn) of a modified conjugated diene polymer were determined based on a chart of the molecular weight obtained by gel permeation chromatography (GPC) against polystyrene standards. The specific measurement conditions of gel permeation chromatography were as follows:

Measurement device: High performance liquid chromatograph (product name: "HLC-8320", available from Tosoh Corporation)

Columns: Two polystyrene columns (product name: "GMH-HR-H", available from Tosoh Corporation) connected in series

Detector: Differential refractometer

Eluent: tetrahydrofuran

Column temperature: 40°C

[0143] [Styrene unit content and vinyl bond content]

The styrene unit content and the vinyl bond content were measured by ^{1}H-NMR.

[0144] [Mooney viscosity]

The Mooney viscosity was measured according to JIS K6300-1 (2013) using a Mooney viscometer (available from SHIMADZU CORPORATION). When an oil-extended rubber was not made from a rubber, the Mooney viscosity of the rubber was measured as it was (i.e., without making an oil-extended rubber thereof).

[0145] [Maximum dynamic load imposed on stirrer]

In a polymerization reaction and a modification reaction in the production of a modified conjugated diene polymer, the dynamic load imposed on a stirrer used for the polymerization reaction and the modification reaction was continuously recorded, and the maximum dynamic load that is the maximum of the dynamic load was determined to evaluate the production efficiency in the modification reaction. In Examples 1 to 10 and Comparative Example 1, the maximum dynamic load was denoted by an index calculated based on the measured value in Comparative Example 1 as 100. In Examples 11 to 13, and Comparative Example 2, the maximum dynamic load was denoted by an index calculated based on the measured value in Comparative Example 2 as 100. In Examples 14 and 15, and Comparative Example 3, the maximum dynamic load was denoted by an index calculated based on the measured value in Comparative Example 3 as 100. In Reference Examples 1 to 3, the maximum dynamic load was denoted by an index calculated based on the measured value in Reference Example 1 as 100. A smaller index indicates that the modified conjugated diene polymer can be produced under a lighter dynamic load, the energy efficiency is higher, and, moreover, the modified conjugated diene polymer can be produced at a higher polymer concentration with higher energy efficiency. Thus, it can be determined that a high productivity is possible.

[0146] [Proportion of poly-branched polymer]

In the elution curve of the modified conjugated diene polymer obtained by gel permeation chromatography performed under the conditions described above, the proportion of the area of peaks each having a peak top molecular weight at least 1.8 times the peak top molecular weight of a peak with the smallest molecular weight to the total elution area was regarded as the proportion of the area of the peaks derived from poly-branched polymers having two or more branches, and the proportion was

regarded as the proportion of the poly-branched polymers. In Examples 1 to 10, and Comparative Example 1, the proportion of poly-branched polymers was denoted by an index calculated based on the measured value in Comparative Example 1 as 100. In Examples 11 to 13 and Comparative Example 2, the proportion of poly-branched polymers was denoted by an index calculated based on the measured value in Comparative Example 2 as 100. In Examples 14 and 15, and Comparative Example 3, the proportion of poly-branched polymers was denoted by an index calculated based on the measured value in Comparative Example 3 as 100. In Reference Examples 1 to 3, the proportion of poly-branched polymers was denoted by an index calculated based on the measured value in Reference Example 1 as 100. A smaller index indicates that bale shaping is easier, and thus it can be determined that high productivity is possible.

[0147] [Low fuel consumption of cross-linked rubber]

The heat buildup of a cross-linked rubber was evaluated by measuring a test piece with dimensions of 50 mm in length, 12.7 mm in width, and 2 mm in thickness for tanδ at 60°C using an ARES-G2 (available from TA Instruments) at a dynamic strain of 2.0% and a frequency of 10 Hz. In Examples 1 to 10 and Comparative Example 1, the tanδ was denoted by an index calculated based on the measured value in Comparative Example 1 as 100. In Examples 11 to 13 and Comparative Example 2, the tanδ was denoted by an index calculated based on the measured value in Comparative Example 2 as 100. In Examples 14 and 15 and Comparative Example 3, the tanδ was denoted by an index calculated based on the measured value in Comparative Example 3 as 100. In Reference Examples 1 to 3, the tanδ was denoted by an index calculated based on the measured value in Reference Example 1 as 100. A smaller index indicates better low fuel consumption.

[0148] [Example 1]

(Production of polymer block (A))

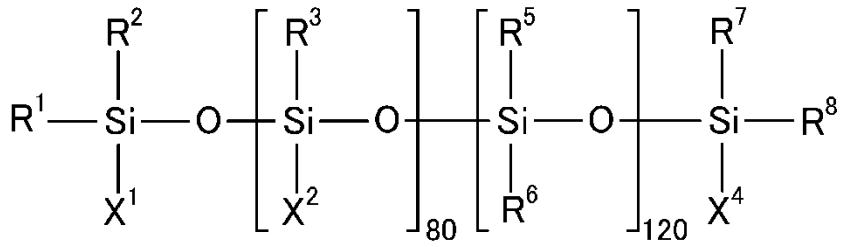
218.1 Parts of cyclohexane, 7.5 parts of styrene, and 0.3 parts of tetramethylethylenediamine were added to a nitrogen-purged vessel, and the temperature in the vessel was controlled to be 50°C. Next, 1.64 parts of n-butyllithium was added to the vessel, and 92.5 parts of isoprene was added over 80 minutes. Thereafter, a reaction was continued for 15 minutes to obtain a solution containing a polymer block (A) having an active end. The polymer block (A) had a weight average molecular weight (Mw) of 6,500, a molecular weight distribution (Mw/Mn) of 1.10, a styrene unit content of 7.5%, an isoprene unit content of 92.5%, and a vinyl bond content of 7.0%.

[0149] (Production of modified conjugated diene polymer)

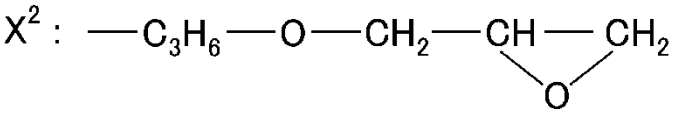
An autoclave equipped with a stirrer was charged with 455.6 parts of cyclohexane, 36.0 parts of styrene, 24.0 parts of 1,3-butadiene, and 0.026 parts of tetramethylethylenediamine under a nitrogen atmosphere. In order to make impurities that inhibit polymerization harmless in advance, n-butyllithium was added to the autoclave as a scavenger, and thereafter 5.3 parts of the obtained solution containing a polymer block (A) having an active end (1.6 parts as the polymer block (A) used) was added to initiate polymerization at 40°C. After 20 minutes following the initiation of the polymerization, 3.8 parts of styrene and 21.3 parts of 1,3-butadiene were added continuously over 20 minutes. Then, 2.3 parts of styrene and 12.8 parts of 1,3-butadiene were added continuously over 30 minutes. The highest temperature during the polymerization reaction was 70°C. After the series of continuous addition, the mixture was stirred for 30 minutes, then the polymerization conversion ratio was confirmed to be within a range of 95% to 100%, and thereafter addition of a polyorganosiloxane represented by the following formula (10) was started. The polyorganosiloxane was used as a 40 wt% solution in xylene, and added continuously at a constant rate over 5 minutes following the beginning of the addition with stirring using a stirrer. The total

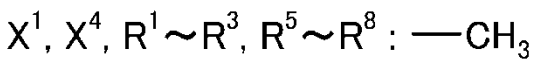
amount of the polyorganosiloxane added was 0.129 parts (i.e., 0.450 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium). Then, a modification reaction was carried out for 30 minutes following the beginning of the addition of the polyorganosiloxane with stirring using a stirrer. Thereafter, methanol as a polymerization terminator was added in an amount equal to twice the amount in moles of the n-butyllithium used, to obtain a solution containing a modified conjugated diene polymer. In Example 1, the concentration of the modified conjugated diene polymer (final polymer concentration) in the solution containing the modified conjugated diene polymer was 18 wt%. Then, 0.20 parts of Irganox 1520L (available from Ciba Specialty Chemicals) with respect to 100 parts of the modified conjugated diene polymer was added as an antioxidant to the solution, then 25 parts of a process oil (product name: Aromax T-DAE, available from ENEOS HOLDINGS, INC.) with respect to 100 parts of the modified conjugated diene polymer was added as an extender oil to the solution and stirred, subsequently the solvent was removed by steam stripping, and the product was dried with hot air to obtain a modified conjugated diene polymer in solid form. The modified conjugated diene polymer obtained was measured for the styrene unit content, the vinyl bond content, the peak top molecular weight (Mp), the weight average molecular weight (Mw), the molecular weight distribution (Mw/Mn), the Mooney viscosity, and the content of poly-branched polymers, as well as the maximum dynamic load imposed on the stirrer during the modification reaction by the polyorganosiloxane. The results are shown in Table 1.

[Chem. 9]



(10)





[0150] (Production of rubber composition and cross-linked rubber)

70 Parts of the modified conjugated diene polymer obtained above (as the amount of polymer except the extender oil) and 30 parts of butadiene rubber (product name: Nipol BR1220, available from Zeon Corporation) were masticated in a 250-ml Brabender type mixer for 30 seconds, then 50 parts of silica (product name: Zeosil 1165MP, available from Solvay), 10 parts of a process oil (product name: AROMAX T-DAE, available from ENEOS HOLDINGS, INC.), and 6.0 parts of a silane coupling agent (product name: Si 69, available from Evonik) were added, kneaded for 1.5 minutes starting at a temperature of 110°C. Then, 25 parts of silica (product name: Zeosil 1165MP, available from Solvay), 3.0 parts of zinc oxide, 2.0 parts of stearic acid, and 2.0 parts of an antioxidant: N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (product name Nocrac 6C, available from OUCHI SHINKO CHEMICAL INDUSTRIAL CO., LTD.) were added and further kneaded for 2.5 minutes, and the kneaded product was discharged from the mixer. The temperature of the kneaded product at the time of completion of the kneading was 150°C. The kneaded product was cooled to room temperature, then kneaded again in a Brabender type mixer for 3 minutes starting at a temperature of 110°C, and the kneaded product was discharged from the mixer. Next, 1.50 parts

of sulfur, 1.8 parts of N-cyclohexyl-2-benzothiazolylsulfenamide (product name: Nocceler CZ-G, available from OUCHI SHINKO CHEMICAL INDUSTRIAL CO., LTD.), and 1.5 parts of 1,3-diphenylguanidine (product name: Nocceler D, available from OUCHI SHINKO CHEMICAL INDUSTRIAL CO., LTD.) were added to the obtained kneaded product, and kneaded using an open roll mill at 50°C to obtain a rubber composition. Then, the obtained rubber composition was shaped into a sheet using an open roll mill at 50°C, and the obtained sheet of the rubber composition was cross-linked by press at 160°C for 20 minutes to obtain a test piece of the cross-linked rubber. The low fuel consumption was evaluated using the resulting cross-linked rubber. The results are shown in Table 1.

[0151] [Example 2]

A modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 1 except that the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10) was added continuously at a constant rate over 14 minutes following the beginning of the addition with stirring using a stirrer. The results are shown in Table 1.

[0152] [Example 3]

A modified conjugated diene polymer was obtained and evaluated in the same manner as in Example 1 except that the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10) was added continuously at a constant rate over 20 minutes following the beginning of the addition with stirring using a stirrer and the amount of the process oil added was 20 parts with respect to 100 parts the modified conjugated diene polymer, and a cross-linked rubber was obtained and evaluated in the same manner as in Example 1 except that the amount of the process oil added in the production of the rubber composition and the cross-linked rubber was 13.5 parts. The results are shown in Table 1.

[0153] [Example 4]

A modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 1 except that the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10) was added continuously at a constant rate over 33 minutes following the beginning of the addition with stirring using a stirrer and the modification reaction was carried out for 35 minutes following the beginning of the addition of the polyorganosiloxane. The results are shown in Table 1.

[0154] [Example 5]

A modified conjugated diene polymer was obtained in the same manner as in Example 1 except that the amount of tetramethylethylenediamine added and the amount of the solution containing a polymer block (A) having an active end added were changed, and the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10) was added in three portions.

Specifically, a polymerization reaction was carried out in the same manner as in Example 1 except that 0.027 parts of tetramethylethylenediamine and 5.7 parts of the solution containing a polymer block (A) having an active end (1.72 parts as the polymer block (A) used) were added, then the polymerization conversion ratio was confirmed to be within a range of 95% to 100%, and thereafter 0.047 parts (i.e., 0.150 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium) of the polyorganosiloxane (40 wt% solution in xylene) was added within 1 minute with stirring using a stirrer (the first addition), and a modification reaction was carried out for 10 minutes with stirring using a stirrer. Next, after the modification reaction for 10 minutes, 0.047 parts of the polyorganosiloxane (40 wt% solution in xylene) was added within 1 minute with stirring using a stirrer (the second addition), and a modification

reaction was carried out for 10 minutes with stirring using a stirrer. Furthermore, after the modification reaction for 10 minutes, 0.047 parts of the polyorganosiloxane (40 wt% solution in xylene) was added within 1 minute with stirring using a stirrer (the third addition), a modification reaction was carried out with stirring using a stirrer. Then, a modification reaction was carried out for 40 minutes following the beginning of the addition of the polyorganosiloxane with stirring using a stirrer.

Then, a modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 1 except that the amount of tetramethylethylenediamine added and the amount of the solution containing a polymer block (A) having an active end added were changed, and the procedure of the addition of the polyorganosiloxane (40 wt% solution in xylene) was changed as described above. The results are shown in Table 1.

[0155] [Example 6]

A modified conjugated diene polymer was obtained in the same manner as in Example 1 except that the amount of tetramethylethylenediamine added was changed, and the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10) was added in two portions.

Specifically, a polymerization reaction was carried out in the same manner as in Example 1 except that 0.025 parts of tetramethylethylenediamine was added, then the polymerization conversion ratio was confirmed to be within a range of 95% to 100%, and thereafter 0.064 parts (i.e., 0.225 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium) of the polyorganosiloxane (40 wt% solution in xylene) was added within 1 minute with stirring using a stirrer (the first addition), and a modification reaction was carried out for 10 minutes with stirring using a stirrer. Next, after the modification reaction for 10 minutes, 0.064

parts of the polyorganosiloxane (40 wt% solution in xylene) was added within 1 minute with stirring using a stirrer (the second addition), and a modification reaction was carried out with stirring using a stirrer. Then, a modification reaction was carried out for 30 minutes following the beginning of the addition of the polyorganosiloxane with stirring using a stirrer.

Then, a modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 1 except that the amount of tetramethylethylenediamine added was changed, and the procedure of the addition of the polyorganosiloxane (40 wt% solution in xylene) was changed as described above. The results are shown in Table 1.

[0156] [Example 7]

A modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 6 except that the amount of tetramethylethylenediamine added was 0.026 parts, the amount of the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10) added in the first addition was 0.079 parts (i.e., 0.275 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium), and the amount of the polyorganosiloxane (40 wt% solution in xylene) added in the second addition was 0.050 parts (i.e., 0.175 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium). The results are shown in Table 1.

[0157] [Example 8]

A modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 6 except that the amount of tetramethylethylenediamine added was 0.029 parts, the amount of the solution containing a polymer block (A) having an active end added was 6.3 parts (1.9 parts as the polymer block (A) used), and

furthermore, the amount of the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10) added in the first addition was 0.102 parts (i.e., 0.300 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium), and the amount of the polyorganosiloxane (40 wt% solution in xylene) added in the second addition was 0.051 parts (i.e., 0.150 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium). The results are shown in Table 1.

[0158] [Example 9]

A modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 8 except that the amount of cyclohexane as a solvent was 426.3 parts. The results are shown in Table 1. In Example 9, the concentration of the modified conjugated diene polymer (final polymer concentration) in the solution containing the modified conjugated diene polymer was 19 wt%.

[0159] [Example 10]

A modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 8 except that the amount of cyclohexane as a solvent was 400.0 parts. The results are shown in Table 1. In Example 10, the concentration of the modified conjugated diene polymer (final polymer concentration) in the solution containing the modified conjugated diene polymer was 20 wt%.

[0160] [Comparative Example 1]

A modified conjugated diene polymer was obtained in the same manner as in Example 6 except that the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10) was added by one-time addition.

Specifically, a polymerization reaction was carried out in the same manner as in Example 1, then the polymerization conversion ratio was confirmed to be within a range of 95% to 100%, and thereafter the whole quantity of 0.129 parts (i.e., 0.450 moles as the epoxy group equivalent

amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium) of the polyorganosiloxane (40 wt% solution in xylene) was added within 1 minute with stirring using a stirrer, and a modification reaction was carried out for 30 minutes with stirring using a stirrer.

Then, a modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 6 except that the procedure of the addition of the polyorganosiloxane (40 wt% solution in xylene) was changed as described above. The results are shown in Table 1.

[0161] [Example 11]

(Production of modified conjugated diene polymer)

An autoclave equipped with a stirrer was charged with 455.6 parts of cyclohexane, 16.0 parts of styrene, 44.0 parts of 1,3-butadiene, and 0.146 parts of tetramethylethylenediamine under nitrogen atmosphere. In order to make impurities that inhibit polymerization harmless in advance, n-butyllithium was added to the autoclave as a scavenger, and thereafter 9.8 parts of the solution containing a polymer block (A) having an active end obtained in Example 1 above (2.96 parts as the polymer block (A) used) was added to initiate polymerization at 40°C. After 10 minutes following the initiation of the polymerization, 5.0 parts of styrene and 35.0 parts of 1,3-butadiene were added continuously over 40 minutes. The highest temperature during the polymerization reaction was 70°C. After the series of continuous addition, the mixture was stirred for 20 minutes, then the polymerization conversion ratio was confirmed to be within a range of 95% to 100%, and thereafter addition of a polyorganosiloxane represented by the formula (10) was started. Specifically, the polymerization conversion ratio was confirmed to be within a range of 95% to 100%, and thereafter 0.119 parts (i.e., 0.225 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium) of the polyorganosiloxane

as a 40 wt% solution in xylene was added within 1 minute with stirring using a stirrer (the first addition), and a modification reaction was carried out for 10 minutes with stirring using a stirrer. Next, after the modification reaction for 10 minutes, 0.119 parts of the polyorganosiloxane as a 40 wt% solution in xylene was added within 1 minute with stirring using a stirrer (the second addition), and a modification reaction was carried out with stirring using a stirrer. Then, a modification reaction was carried out for 30 minutes following the beginning of the addition of the polyorganosiloxane with stirring using a stirrer. Thereafter, methanol as a polymerization terminator was added in an amount equal to twice the amount in moles of the n-butyllithium used, to obtain a solution containing a modified conjugated diene polymer. In Example 11, the concentration of the modified conjugated diene polymer (final polymer concentration) in the solution containing the modified conjugated diene polymer was 18 wt%. Then, 0.20 parts of Irganox 1520L (available from Ciba Specialty Chemicals) with respect to 100 parts of the modified conjugated diene polymer was added as an antioxidant to the solution. Subsequently, the solvent was removed by steam stripping, and the product was dried with hot air to obtain a modified conjugated diene polymer in solid form. The modified conjugated diene polymer obtained was measured for the styrene unit content, the vinyl bond content, the peak top molecular weight (Mp), the weight average molecular weight (Mw), the molecular weight distribution (Mw/Mn), the Mooney viscosity, and the content of poly-branched polymers, as well as the maximum dynamic load imposed on the stirrer during the modification reaction by the polyorganosiloxane. The results are shown in Table 2.

[0162] (Production of rubber composition and cross-linked rubber)

A rubber composition and a cross-linked rubber were produced in the same manner as in Example 1 except that the modified conjugated diene

polymer obtained above was used, and the amount of the process oil added in the production of the rubber composition and the cross-linked rubber was 25 parts. The low fuel consumption was evaluated using the resulting cross-linked rubber. The results are shown in Table 2.

[0163] [Example 12]

A modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 11 except that after the second addition of the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10), a modification reaction was carried for 30 minutes with stirring using a stirrer, and thereafter, 0.226 parts (i.e., 1.00 mole with respect to 1 mole of the n-butyllithium used) of 2,2-dimethoxy-8-(4-methylpiperazinyl)methyl-1,6-dioxa-2-silacyclooctane (the compound represented by the general formula (9) above) as a hydrocarbyloxirane compound A as a 50 wt% solution in xylene was added within 1 minute with stirring using a stirrer, and a reaction was carried out for 15 minutes. The results are shown in Table 2.

[0164] [Example 13]

A modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 11 except that a modification reaction was carried for 30 minutes with stirring using a stirrer after the second addition of the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10), thereafter 0.165 parts (i.e., 1.00 mole with respect to 1 mole of the n-butyllithium used) of 3-(2-aminoethylamino)propyltrimethoxysilane (the compound represented by the general formula (7) above) as a hydrocarbyloxirane compound B as a 50 wt% solution in xylene was added within 1 minute with stirring using a stirrer. The results are shown in Table 2.

[0165] [Comparative Example 2]

A modified conjugated diene polymer was obtained in the same manner

as in Example 11 except that the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10) was added by one-time addition.

Specifically, a polymerization reaction was carried out in the same manner as in Example 11, then the polymerization conversion ratio was confirmed to be within a range of 95% to 100%, and thereafter the whole quantity of 0.238 parts (i.e., 0.450 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium) of the polyorganosiloxane (40 wt% solution in xylene) was added within 1 minute with stirring using a stirrer, and a modification reaction was carried out for 20 minutes with stirring using a stirrer.

Then, a modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 11 except that the procedure of the addition of the polyorganosiloxane (40 wt% solution in xylene) was changed as described above. The results are shown in Table 2.

[0166] [Example 14]

(Production of modified conjugated diene polymer)

An autoclave equipped with a stirrer was charged with 500.4 parts of cyclohexane, 15.0 parts of styrene, 37.1 parts of 1,3-butadiene, and 0.016 parts of tetramethylethylenediamine under nitrogen atmosphere. In order to make impurities that inhibit polymerization harmless in advance, n-butyllithium was added to the autoclave as a scavenger, and thereafter 8.8 parts of the solution containing a polymer block (A) having an active end obtained in Example 1 above (2.66 parts as the polymer block (A) used) was added to initiate polymerization at 55°C. After 12 minutes following the initiation of the polymerization, 3.3 parts of 1,3-butadiene were added continuously over 4 minutes. One minute after the continuous addition, 17.8 parts of 1,3-butadiene was added continuously over 17 minutes. Further, 13.4 parts of 1,3-butadiene was added continuously over 18 minutes. Thereafter, 13.4 parts of 1,3-

butadiene was added continuously over 35 minutes. The highest temperature during the polymerization reaction was 80°C. After the series of continuous addition, the mixture was stirred for 30 minutes, then the polymerization conversion ratio was confirmed to be within a range of 95% to 100%, and thereafter 0.053 parts of tetramethylethylenediamine was added and stirred for 5 minutes. Thereafter, 0.002 parts of 1,6-bis(trichlorosilyl)hexane was added, and a reaction was carried out for 10 minutes. Thereafter, addition of a polyorganosiloxane represented by the formula (10) was started. Specifically, 0.143 parts (i.e., 0.300 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium) of the polyorganosiloxane as a 40 wt% solution in xylene was added within 1 minute with stirring using a stirrer (the first addition), and a modification reaction was carried out for 10 minutes with stirring using a stirrer. Next, after the modification reaction for 10 minutes, 0.143 parts of the polyorganosiloxane as a 40 wt% solution in xylene was added within 1 minute with stirring using a stirrer (the second addition), and a modification reaction was carried out with stirring using a stirrer. Then, a modification reaction was carried out for 30 minutes following the beginning of the addition of the polyorganosiloxane with stirring using a stirrer. Furthermore, 0.148 parts (i.e., 1.00 mole with respect to 1 mole of the n-butyllithium used) of a hydrocarbyloxirane compound B as a 50 wt% solution in xylene was added within 1 minute with stirring using a stirrer, and a reaction was carried out for 15 minutes. Thereafter, methanol as a polymerization terminator was added in an amount equal to twice the amount in moles of the n-butyllithium used, to obtain a solution containing a modified conjugated diene polymer. In Example 14, the concentration of the modified conjugated diene polymer (final polymer concentration) in the solution containing the modified conjugated diene polymer was 16.7 wt%.

Then, 0.20 parts of Irganox 1520L (available from Ciba Specialty Chemicals) with respect to 100 parts of the modified conjugated diene polymer was added as an antioxidant to the solution, and further, 0.20 parts of Irganox 1076 (available from Ciba Specialty Chemicals) with respect to 100 parts of the modified conjugated diene polymer was added. Subsequently, the solvent was removed by steam stripping, and the product was dried with hot air to obtain a modified conjugated diene polymer in solid form. The modified conjugated diene polymer obtained was measured for the styrene unit content, the vinyl bond content, the peak top molecular weight (Mp), the weight average molecular weight (Mw), the molecular weight distribution (Mw/Mn), the Mooney viscosity, and the content of poly-branched polymers, as well as the maximum dynamic load imposed on the stirrer during the modification reaction by the polyorganosiloxane. The results are shown in Table 3.

[0167] (Production of rubber composition and cross-linked rubber)

50 Parts of natural rubber, 30 parts of the modified conjugated diene polymer obtained above, and 20 parts of butadiene rubber (product name: Nipol BR1220, available from Zeon Corporation) were masticated in a 250-ml Banbury mixer for 30 seconds. Then, 25 parts of silica (product name: Zeosil 1165MP, available from Solvay), 25 parts of carbon black (product name: Seast 9H, available from TOKAI CARBON CO., LTD.), and 2.0 parts of a silane coupling agent: bis(3-(triethoxysilyl)propyl) tetrasulfide (product name: Si 69, available from Evonik) were added, and kneaded for 1.5 minutes starting at a temperature of 110°C. Then, 3 parts of zinc oxide, 2 parts of stearic acid, and 2 parts of an antioxidant: N-phenyl-N'-(1,3-dimethylbutyl)-p-phenylenediamine (product name: Nocrac 6C, available from OUCHI SHINKO CHEMICAL INDUSTRIAL CO., LTD.) were added and further kneaded for 2.5 minutes, and the kneaded product was discharged from the mixer. The temperature of the kneaded product at the time of completion of the kneading was 150°C. The kneaded

product was cooled to room temperature, then kneaded again in a Banbury mixer for 3 minutes starting at a temperature of 110°C, and the kneaded product was discharged from the mixer. Next, 1.75 parts of sulfur, and a mixture of 1.0 part of a cross-linking accelerator: N-(tert-butyl)-2-benzothiazolesulfenamide (product name: Sanceler NS-G, available from SANSHIN CHEMICAL CO., LTD) and 0.53 parts of a cross-linking accelerator: 1,3-diphenylguanidine (product name: Nocceler D, available from OUCHI SHINKO CHEMICAL INDUSTRIAL CO., LTD.) were added to the obtained kneaded product and kneaded in an open roll mill at 50°C, and thereafter a sheet-like rubber composition was discharged. The resulting rubber composition was cross-linked by press at 160°C for 7 minutes to obtain a test piece of the cross-linked rubber, and evaluation of low fuel consumption was carried out. The results are shown in Table 3.

[0168] [Example 15]

A modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 14 except that tetramethylethylenediamine was not added after the polymerization conversion ratio was confirmed to be within a range of 95% to 100%. The results are shown in Table 3.

[0169] [Comparative Example 3]

A modified conjugated diene polymer was obtained in the same manner as in Example 15 except that the polyorganosiloxane (40 wt% solution in xylene) represented by the formula (10) was added by one-time addition.

Specifically, a polymerization reaction was carried out in the same manner as in Example 15, then 1,6-bis(trichlorosilyl)hexane was added, and thereafter the whole quantity of 0.286 parts (i.e., 0.600 moles as the epoxy group equivalent amount in the polyorganosiloxane with respect to 1 mole of the n-butyllithium) of the polyorganosiloxane (40 wt% solution in xylene) was added within 1 minute with stirring using a stirrer, and a modification reaction was carried out for 20 minutes with

stirring using a stirrer.

Then, a modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Example 15 except that the procedure of the addition of the polyorganosiloxane (40 wt% solution in xylene) was changed as described above. The results are shown in Table 3.

[0170] [Reference Example 1]

(Production of modified conjugated diene polymer)

An autoclave equipped with a stirrer was charged with 400.0 parts of cyclohexane, 16.0 parts of styrene, 44.0 parts of 1,3-butadiene, and 0.092 parts of tetramethylethylenediamine under nitrogen atmosphere. In order to make impurities that inhibit polymerization harmless in advance, n-butyllithium was added to the autoclave as a scavenger, and thereafter 6.5 parts of the solution containing a polymer block (A) having an active end obtained in Example 1 above (1.96 parts as the polymer block (A) used) was added to initiate polymerization at 40°C. After 10 minutes following the initiation of the polymerization, 5.0 parts of styrene and 35.0 parts of 1,3-butadiene were added continuously over 40 minutes. The highest temperature during the polymerization reaction was 60°C. After the series of continuous addition, the mixture was stirred for 20 minutes, then the polymerization conversion ratio was confirmed to be within a range of 95% to 100%, and thereafter 0.004 parts of 1,6-bis(trichlorosilyl)hexane was added, and a reaction was carried out for 10 minutes. Thereafter, the whole quantity of 0.192 parts (i.e., 1.28 moles with respect to 1 mole of the n-butyllithium) of the hydrocarbyloxirane compound A as a 50 wt% solution in xylene was added within 1 minute with stirring using a stirrer, and a modification reaction was carried out for 25 minutes with stirring using a stirrer. Thereafter, methanol as a polymerization terminator was added in an amount equal to twice the amount in moles of the n-butyllithium used, to

obtain a solution containing a modified conjugated diene polymer. In Reference Example 1, the concentration of the modified conjugated diene polymer (final polymer concentration) in the solution containing the modified conjugated diene polymer was 20 wt%. Then, 0.20 parts of Irganox 1520L (available from Ciba Specialty Chemicals) with respect to 100 parts of the modified conjugated diene polymer was added as an antioxidant to the solution. Subsequently, the solvent was removed by steam stripping, and the product was dried with hot air to obtain a modified conjugated diene polymer in solid form. The modified conjugated diene polymer obtained was measured for the styrene unit content, the vinyl bond content, the peak top molecular weight (Mp), the weight average molecular weight (Mw), the molecular weight distribution (Mw/Mn), the Mooney viscosity, and the content of poly-branched polymers, as well as the maximum dynamic load imposed on the stirrer during the modification reaction by the polyorganosiloxane. The results are shown in Table 4.

[0171] (Production of rubber composition and cross-linked rubber)

A rubber composition and a cross-linked rubber were produced in the same manner as in Example 11 except that the modified conjugated diene polymer obtained above was used. The low fuel consumption was evaluated using the resulting cross-linked rubber. The results are shown in Table 4.

[0172] [Reference Example 2]

A modified conjugated diene polymer was obtained in the same manner as in Reference Example 1 except that the hydrocarbyloxirane compound A was added by continuous addition instead of the one-time addition.

Specifically, a polymerization reaction was carried out in the same manner as in Reference Example 1. After the addition of 1,6-bis(trichlorosilyl)hexane, the hydrocarbyloxirane compound A as a 50 wt% solution in xylene was added continuously at a constant rate over 21

minutes following the beginning of the addition with stirring using a stirrer. The total amount of the hydrocarbyloxirane compound A added was 0.192 parts (1.28 moles with respect to 1 mole of the n-butyllithium). Then, a modification reaction was carried out for 25 minutes following the beginning of the addition of the hydrocarbyloxirane compound A.

Then, a modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Reference Example 1 except that the procedure of the addition of the hydrocarbyloxirane compound A was changed as described above. The results are shown in Table 4.

[0173] [Reference Example 3]

A modified conjugated diene polymer and a cross-linked rubber were obtained and evaluated in the same manner as in Reference Example 2 except that the hydrocarbyloxirane compound A (40 wt% solution in xylene) was added continuously at a constant rate over 4 minutes following the beginning of the addition with stirring using a stirrer. The results are shown in Table 4.

[0174] [Table 1]

[0175] [Table 2]

Table 1

			Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Comp. Ex. 1
Modified conjugated diene polymer													
Styrene unit content		[wt%]	42.9	42.2	42.6	42.6	41.3	42.0	42.0	41.7	42.5	42.1	41.0
Vinyl bond content		[wt%]	26.7	30.7	26.9	26.4	27.1	28.8	28.2	27.2	28.4	28.8	25.4
Peak top molecular weight (Mp)			355,000	498,000	421,000	359,000	362,000	429,000	400,000	391,000	395,000	391,000	417,000
Weight average molecular weight (Mw)			622,000	747,000	638,000	612,000	529,000	682,000	659,000	533,000	549,000	552,000	659,000
Molecular weight distribution (Mw/Mn)			1.51	1.54	1.52	1.50	1.37	1.56	1.48	1.37	1.38	1.37	1.44
Mooney viscosity (ML1+4, 100°C)			50	69	66	48	48	60	57	53	53	55	67
Polymerization conditions													
Final polymer concentration		[wt%]	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	19.0	20.0	18.0
Total amount of polar compound added		[mole]	0.66	0.66	0.66	0.66	0.63	0.63	0.66	0.63	0.63	0.63	0.63
Modification conditions													
First addition of polyorganosiloxane	Amount added	[mole]	0.450	0.450	0.450	0.450	0.150	0.225	0.275	0.300	0.300	0.300	0.450
	Period of addition	[minutes]	5	14	20	33	less than 1	less than 1	less than 1	less than 1	less than 1	less than 1	less than 1
Second addition of polyorganosiloxane	Amount added	[mole]	-	-	-	-	0.150	0.225	0.175	0.150	0.150	0.150	-
	Period of addition	[minutes]	-	-	-	-	less than 1	less than 1	less than 1	less than 1	less than 1	less than 1	-
Third addition of polyorganosiloxane	Amount added	[mole]	-	-	-	-	0.150	-	-	-	-	-	-
	Period of addition	[minutes]	-	-	-	-	less than 1	-	-	-	-	-	-
Evaluations													
Maximum dynamic load imposed on stirrer (index)			88	68	55	54	44	90	60	67	72	87	100
Proportion of poly-branched polymers (index)			96	78	84	97	92	89	94	86	85	95	100
Low fuel consumption (index)			97	98	100	100	95	100	100	98	99	96	100

*) The amount of a polar compound added is an amount with respect to 1 mole of n-butyllithium.

*) The amount of polyorganosiloxane added is an epoxy group equivalent amount with respect to 1 mole of n-butyllithium.

Table 2

			Example 11	Example 12	Example 13	Comp. Ex. 2
Modified conjugated diene polymer						
Styrene unit content		[wt%]	21.5	21.0	21.5	21.4
Vinyl bond content		[wt%]	63.0	62.1	61.2	61.3
Peak top molecular weight (Mp)			248,000	269,000	275,000	223,000
Weight average molecular weight (Mw)			495,000	472,000	456,000	498,000
Molecular weight distribution (Mw/Mn)			1.59	1.49	1.38	1.62
Mooney viscosity (ML1+4, 100°C)			55	61	66	54
Polymerization conditions						
Final polymer concentration		[wt%]	18.0	18.0	18.0	18.0
Total amount of polar compound added		[mole]	1.80	1.80	1.80	1.80
Modification conditions						
First addition of polyorganosiloxane	Amount added	[mole]	0.225	0.225	0.225	0.450
	Period of addition	[minutes]	less than 1	less than 1	less than 1	less than 1
Second addition of polyorganosiloxane	Amount added	[mole]	0.225	0.225	0.225	-
	Period of addition	[minutes]	less than 1	less than 1	less than 1	-
Addition of hydrocarbyloxysilane compound A	Amount added	[mole]	-	1.00	-	-
	Period of addition	[minutes]	-	less than 1	-	-
Addition of hydrocarbyloxysilane compound B	Amount added	[mole]	-	-	1.00	-
	Period of addition	[minutes]	-	-	less than 1	-
Evaluations						
Maximum dynamic load imposed on stirrer (index)			51	93	76	100
Proportion of poly-branched polymers (index)			93	91	83	100
Low fuel consumption (index)			97	95	96	100

*) The amount of a polar compound added is an amount with respect to 1 mole of n-butyllithium.

*) The amount of polyorganosiloxane added is an epoxy group equivalent amount with respect to 1 mole of n-butyllithium, and the amount of hydrocarbyloxysilane compound A or B added is an amount with respect to 1 mole of n-butyllithium.

[0176] [Table 3]

Table 3

			Example 14	Example 15	Comp. Ex. 3
Modified conjugated diene polymer					
Styrene unit content		[wt%]	14.6	14.3	14.5
Vinyl bond content		[wt%]	18.0	18.2	19.5
Peak top molecular weight (Mp)			274,000	276,000	289,000
Weight average molecular weight (Mw)			404,000	415,000	449,000
Molecular weight distribution (Mw/Mn)			1.32	1.34	1.34
Mooney viscosity (ML1+4, 100°C)			48	48	52
Polymerization conditions					
Final polymer concentration		[wt%]	16.7	16.7	16.7
Total amount of polar compound added		[mole]	1.00	0.31	0.31
Modification conditions					
First addition of polyorganosiloxane	Amount added	[mole]	0.300	0.300	0.600
	Period of addition	[minutes]	less than 1	less than 1	less than 1
Second addition of polyorganosiloxane	Amount added	[mole]	0.300	0.300	-
	Period of addition	[minutes]	less than 1	less than 1	-
Addition of hydrocarbyloxysilane compound B	Amount added	[mole]	1.00	1.00	1.00
	Period of addition	[minutes]	less than 1	less than 1	less than 1
Evaluations					
Maximum dynamic load imposed on stirrer (index)			81	93	100
Proportion of poly-branched polymers (index)			89	91	100
Low fuel consumption (index)			97	99	100

*) The amount of a polar compound added is an amount with respect to 1 mole of n-butyllithium.

*) The amount of hydrocarbyloxysilane compound B added is an amount with respect to 1 mole of n-butyllithium.

[0177] [Table 4]

Table 4

			Ref. Ex. 1	Ref. Ex. 2	Ref. Ex. 3
Modified conjugated diene polymer					
	Styrene unit content	[wt%]	20.8	20.5	20.7
	Vinyl bond content	[wt%]	60.4	62.2	60.7
	Peak top molecular weight (Mp)		336,000	367,000	304,000
	Weight average molecular weight (Mw)		525,000	753,000	634,000
	Molecular weight distribution (Mw/Mn)		1.33	1.39	1.32
	Mooney viscosity (ML1+4, 100°C)		73	102	90
Polymerization conditions					
	Final polymer concentration	[wt%]	20.0	20.0	20.0
	Total amount of polar compound added	[mole]	1.70	1.70	1.70
Modification conditions					
	Addition of hydrocarbyloxysilane compound A	Amount added [mole]	1.28	1.28	1.28
		Period of addition [minutes]	less than 1	21	4
Evaluations					
	Maximum dynamic load imposed on stirrer (index)		100	128	109
	Proportion of poly-branched polymers (index)		100	153	160
	Low fuel consumption (index)		100	147	129

*) The amount of a polar compound added is an amount with respect to 1 mole of n-butyllithium.

*) The amount of hydrocarbyloxysilane compound A added is an amount with respect to 1 mole of n-butyllithium.

[0178] As shown in Tables 1, 2, and 3, in each of Examples 1 to 15 in which, in the reaction of a conjugated diene polymer chain having an active end with a polyorganosiloxane represented by the general formula (1), the polyorganosiloxane represented by the general formula (1) was

added to the conjugated diene polymer chain having an active end continuously over 2 to 60 minutes or in portions, the maximum dynamic load imposed on a stirrer during a modification reaction was reduced. Accordingly, a modified conjugated diene polymer was produced under a lighter dynamic load, the energy efficiency was high, and, moreover, the modified conjugated diene polymer was produced at a higher polymer concentration while high energy efficiency was maintained. In addition, the modified conjugated diene polymer obtained was capable of achieving excellent low fuel consumption. In particular, as it is obvious from the results of Examples 9 and 10, even when the polymer concentration was increased, the reduced maximum dynamic load imposed on a stirrer was maintained at a low level.

[0179] On the other hand, the results shown in Table 4 indicate that when other silane modifiers were used (Reference Examples 1 to 3) instead of the polyorganosiloxane represented by the general formula (1), the maximum dynamic load imposed on a stirrer was not reduced by adding continuously or in portions, but rather increased. Accordingly, the effects exerted by adding continuously or in portions can be considered as unique effects exerted by using the polyorganosiloxane represented by the general formula (1).

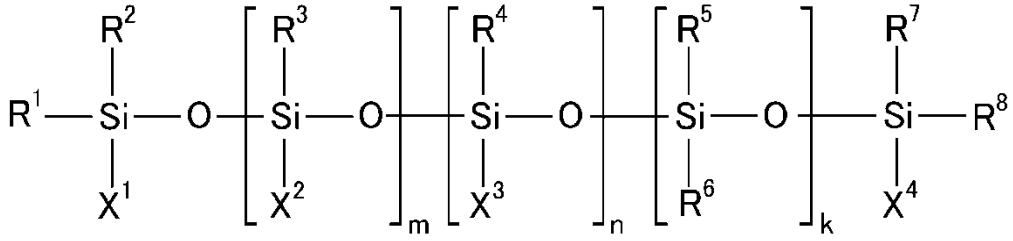
CLAIMS

[Claim 1] A method of production of a modified conjugated diene polymer, comprising:

a first step of polymerizing a monomer containing a conjugated diene compound using a polymerization initiator in an inert solvent to obtain a conjugated diene polymer chain having an active end; and

a second step of reacting the conjugated diene polymer chain having an active end with a polyorganosiloxane represented by the following general formula (1) by adding the polyorganosiloxane to the conjugated diene polymer chain having an active end continuously over 2 to 60 minutes or in portions:

[Chem. 10]



(1)

wherein in the general formula (1), R^1 to R^8 may be the same or different from each other and are each a hydrocarbon group having 1 to 20 carbon atoms, X^1 and X^4 may be the same or different from each other and are each a hydrogen atom, a hydrocarbon group having 1 to 20 carbon atoms, a polar functional group having an atom of Group 15 or Group 16 of the periodic table, a halogen atom, or a hydrocarbon group having 1 to 20 carbon atoms and optionally having a polar functional group having an atom of Group 15 or Group 16 of the periodic table or a halogen atom; X^2 is a polar functional group having an atom of Group 15 or Group 16 of the periodic table, a halogen atom, or a hydrocarbon group having 1 to 20 carbon atoms and optionally having a polar functional group having an atom of Group 15 or Group 16 of the periodic table or a halogen atom,

and when a plurality of X^2s are present, they may be the same or different from each other; X^3 is a group containing 2 to 20 repeating units of an alkylene glycol, a part of X^3 may be a group derived from a group containing 2 to 20 repeating units of an alkylene glycol, and when a plurality of X^3s are present, they may be the same or different from each other; "m" is an integer of 1 to 200; "n" is an integer of 0 to 200; and "k" is an integer of 0 to 200.

[Claim 2] The method of production of a modified conjugated diene polymer according to claim 1, wherein the polar functional group having an atom of Group 16 of the periodic table is a polar functional group having an oxygen atom.

[Claim 3] The method of production of a modified conjugated diene polymer according to claim 1 or 2, wherein X^1 and X^4 are each a hydrocarbon group having 1 to 20 carbon atoms, and X^2 is a hydrocarbon group having 1 to 20 carbon atoms and optionally having an alkoxy group or an epoxy group.

[Claim 4] The method of production of a modified conjugated diene polymer according to any one of claims 1 to 3, wherein the modified conjugated diene polymer contains an isoprene-containing block containing 80 to 100 wt% of an isoprene unit.

[Claim 5] The method of production of a modified conjugated diene polymer according to any one of claims 1 to 4, wherein a polar compound is added in an amount of 0.5 to 5.0 moles in total with respect to 1 mole of the polymerization initiator before the second step.

[Claim 6] A method of production of a rubber composition comprising:

obtaining a modified conjugated diene polymer by the method of production according to any one of claims 1 to 5, and adding silica to the modified conjugated diene polymer.

[Claim 7] The method of production of a rubber composition according to claim 6, further comprising: adding a cross-linking agent.

[Claim 8] A method of production of a cross-linked rubber, comprising: obtaining a rubber composition by the method of production according to claim 6 or 7, and cross-linking the rubber composition.

[Claim 9] A method of production of a tire, comprising: obtaining a rubber composition by the method of production according to claim 6 or 7, and cross-linking the rubber composition to produce a tire containing a cross-linked rubber of the rubber composition.