initiator in an inert solvent; a second step of reacting siloxane with the conjugated diene polymer chain having the active end; and a third step of reacting a compound having a 1,6-dioxa-2-silacyclooctane structure the 8th position of which is substituted with a group having a tertiary amine structure with the conjugated diene polymer chain with which the siloxane has been reacted that is obtained in the second step.

RELATED ART DOCUMENTS

PATENT DOCUMENTS

[0004] Patent Document 1: International Publication No. 2016/0208739

SUMMARY

PROBLEM TO BE SOLVED

[0005] In consideration of a recently increasing demand for the performance of tires for automobiles, newly developed tires hereafter requires a rubber which can provide a cross-linked rubber excellent in low heat buildup, wet grip, and operation stability than those of conventional rubber such as the rubber disclosed in Patent Document 1.

[0006] The present disclosure has been accomplished in view of the above problems, and aims to provide a method for producing a conjugated diene rubber that can provide a cross-linked rubber excellent in low heat buildup, wet grip, and operation stability.

MEANS FOR SOLVING PROBLEMS

[0007] As a result of extensive studies to achieve the above object, the present inventors have found that a cross-linked rubber excellent in low heat buildup, wet grip, and operation stability can be obtained by using a conjugated diene rubber obtained by reacting a conjugated diene polymer chain having an active end, which is obtained by polymerizing a monomer containing a conjugated diene compound and a vinyl compound having

a functional group interactive with silica, and siloxane as a modifier, and then reacting the conjugated diene polymer chain with wihch the siloxane has been reacted and a hydrocarbyloxysilane compound as a modifier, and thereby the present disclosure has been accomplished.

[0007a] In an aspect, there is provided a method for producing a conjugated diene rubber, comprising:

a first step of obtaining a conjugated diene polymer chain having an active end by polymerizing a monomer comprising a conjugated diene compound and a vinyl compound having a functional group interactive with silica using a polymerization initiator in an inert solvent;

a second step of reacting a siloxane compound with the active end of the conjugated diene polymer chain having the active end; and

a third step of reacting a hydrocarbyloxysilane compound with the conjugated diene polymer chain with which the siloxane compound is reacted that is obtained in the second step,

wherein the functional group interactive with silica is at least one selected from a group consisting of a nitrogen atom-containing functional group, a silicon atom-containing functional group, and an oxygen atom-containing functional group.

[0008] That is, the present disclosure provides a method for producing conjugated diene rubber, comprising:

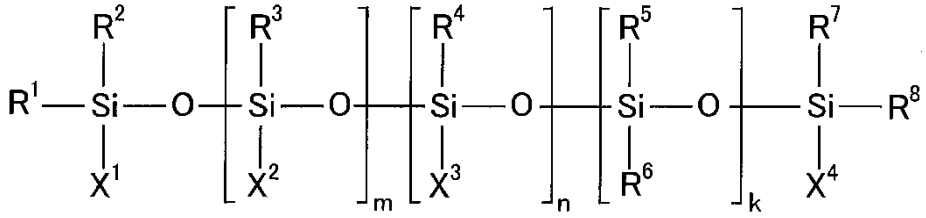
a first step of obtaining a conjugated diene polymer chain having an active end by polymerizing a monomer comprising a conjugated diene compound and a vinyl compound having a functional group interactive with silica using a polymerization initiator in an inert solvent;

a second step of reacting a siloxane compound with the active end of the conjugated diene polymer chain having the active end; and

a third step of reacting a hydrocarbyloxysilane compound with the conjugated diene polymer chain with which the siloxane compound is

reacted that is obtained in the second step.

[0009] In the method of production according to the present disclosure, it is preferable to use polyorganosiloxane represented by the following general formula (1) as the siloxane compound.

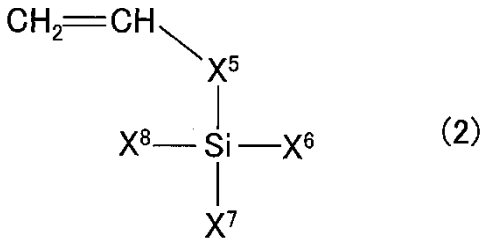


(1)

In the general formula (1) above, R^1 to R^8 are an alkyl group having 1 to 6 carbon atoms, or an aryl group having 6 to 12 carbon atoms, these may be the same or may be different from each other; X^1 and X^4 are any group selected from the group consisting of an alkyl group having 1 to 6 carbon atoms, aryl group having 6 to 12 carbon atoms, alkoxy group having 1 to 5 carbon atoms, and epoxy-group containing group having 4 to 12 carbon atoms, these may be the same or may be different from each other; X^2 is an alkoxy group having 1 to 5 carbon atoms, or an epoxy-group

containing group having 4 to 12 carbon atoms, and when there are a plural number of X^2, they may be the same or may be different from each other; X^3 is a group containing 2 to 20 repeating units of alkylene glycol, and when there are a plural number of X^3, they may be the same or may be different from each other; and "m" is an integer of 1 to 200, "n" is an integer of 0 to 200, "k" is an integer of 0 to 200, and m+n+k is 1 or more.

[0010] In the method of production according to the present disclosure, it is preferable that the vinyl compound having the functional group interactive with the silica is a compound represented by the following general formula (2).



(2)

In the general formula (2) above, X^5 represents a chemical single bond or a hydrocarbylene group, and X^6, X^7 and X^8 each independently represent a substituted amino group, a hydrocarbyloxy group, or a substituted or unsubstituted hydrocarbyl group.

In the method of production according to the present disclosure, it is preferable that the hydrocarbyloxysilane compound is a hydrocarbyloxysilane compound having a group containing a nitrogen atom.

In the method of production according to the present disclosure, it is preferable that the group containing the nitrogen atom is a group containing a primary amino group having an active hydrogen atom and/or a secondary amino group having an active hydrogen atom.

[0011] In the method of production according to the present disclosure, it is preferable that the first step comprises:

a step of polymerizing a monomer (a) containing isoprene using the polymerization initiator in the inert solvent to form a polymer block (A) having an active end; and

a step of mixing the polymer block (A) having the active end and a monomer (b) containing 1,3-butadiene to continue polymerization reaction, so as to obtain the conjugated diene polymer chain that has an active end and comprises the polymer block (A) and the polymer block (B), and

the vinyl compound having the functional group interactive with the silica is contained in at least one of the monomer (a) and the monomer (b).

[0012] In the method of production according to the present disclosure, it is preferable that the second step further comprises a step of reacting a modifier containing a nitrogen atom with a part of the active end of the conjugated diene polymer chain having the active end before reacting the siloxane compound with the conjugated diene polymer chain having the active end.

In the method of production according to the present disclosure, it is preferable that the modifier containing the nitrogen atom is a modifier containing the nitrogen atom and not containing a silicon atom.

In the method of production according to the present disclosure, it is preferable that the modifier containing the nitrogen atom and not containing the silicon atom is N-substituted cyclic amides.

[0013] Further, the present disclosure provides a conjugated diene rubber obtained by the above-mentioned methods of production.

Furthermore, the present disclosure provides a rubber composition comprising a rubber ingredient and silica, the rubber ingredient containing the conjugated diene rubber.

It is preferable that the rubber composition according to the present disclosure further comprises a cross-linking agent.

[0014] Further, the present disclosure provides a cross-linked rubber obtained by cross-linking the rubber composition, and a tire comprising the cross-linked rubber.

EFFECTS OF DISCLOSURE

[0015] According to the present disclosure, it is possible to provide a conjugated diene rubber that can provide a cross-linked rubber excellent in low heat buildup, wet grip, and operation stability; a rubber composition containing the conjugated diene rubber; a cross-linked rubber excellent in the low heat buildup, wet grip, and operation stability that is obtained by cross-linking the rubber composition; and tires comprising the cross-linked rubber.

DESCRIPTION OF EMBODIMENTS

[0016] <Method of Production of Conjugated Diene Rubber>

The method for producing conjugated diene rubber according to the present invention comprises:

a first step of obtaining a conjugated diene polymer chain having an active end by polymerizing a monomer containing a conjugated diene compound and a vinyl compound having a functional group interactive with silica using a polymerization initiator in an inert solvent;

a second step of reacting a siloxane compound with the active end of the conjugated diene polymer chain having the active end; and

a third step of reacting a hydrocarbyloxysilane compound with the conjugated diene polymer chain with which the siloxane compound has been reacted that is obtained in the second step.

[0017] <First Step>

The first step of the method of production according to the present invention is a step of obtaining a conjugated diene polymer chain having an active end by polymerizing a monomer containing a conjugated diene compound and a vinyl compound having a functional group interactive with silica using a polymerization initiator in an inert solvent.

[0018] In the first step of the method of production according to the

CLAIMS

1. A method for producing a conjugated diene rubber, comprising:

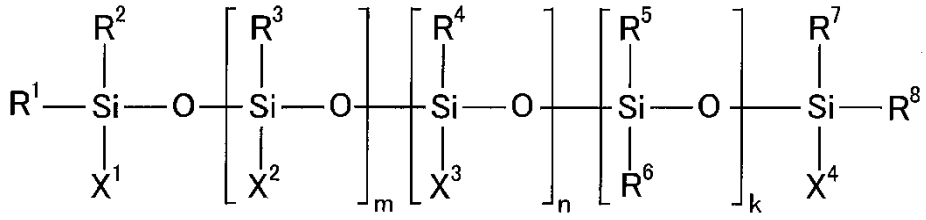
a first step of obtaining a conjugated diene polymer chain having an active end by polymerizing a monomer comprising a conjugated diene compound and a vinyl compound having a functional group interactive with silica using a polymerization initiator in an inert solvent;

a second step of reacting a siloxane compound with the active end of the conjugated diene polymer chain having the active end; and

a third step of reacting a hydrocarbyloxysilane compound with the conjugated diene polymer chain with which the siloxane compound is reacted that is obtained in the second step,

wherein the functional group interactive with silica is at least one selected from a group consisting of a nitrogen atom-containing functional group, a silicon atom-containing functional group, and an oxygen atom-containing functional group.

2. The method for producing the conjugated diene rubber according to claim 1, wherein the siloxane compound is polyorganosiloxane represented by the following general formula (1),

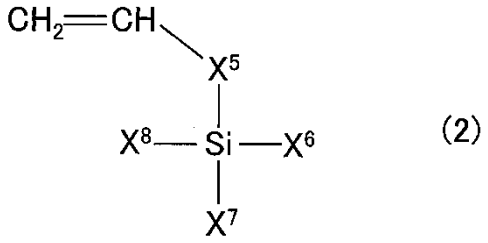


(1)

wherein, in the general formula (1) above, R^1 to R^8 are an alkyl group having 1 to 6 carbon atoms, or an aryl group having 6 to 12 carbon atoms, these may be the same or may be different from each other; X^1 and X^4 are any group selected from the group consisting of an alkyl group having 1 to 6 carbon atoms, aryl group having 6 to 12 carbon atoms, alkoxy group having 1 to 5 carbon atoms, and epoxy-group containing group having 4 to

12 carbon atoms, these may be the same or may be different from each other; X^2 is an alkoxy group having 1 to 5 carbon atoms, or an epoxy-group containing group having 4 to 12 carbon atoms, and when there are a plural number of X^2, they may be the same or may be different from each other; X^3 is a group containing 2 to 20 repeating units of alkylene glycol, and when there are a plural number of X^3, they may be the same or may be different from each other; and "m" is an integer of 1 to 200, "n" is an integer of 0 to 200, "k" is an integer of 0 to 200, and m+n+k is 1 or more.

3. The method for producing the conjugated diene rubber according to claim 1 or 2, wherein the vinyl compound having the functional group interactive with the silica is a compound represented by the following general formula (2),



(2)

wherein, in the general formula (2) above, X^5 represents a chemical single bond or a hydrocarbylene group, and X^6, X^7 and X^8 each independently represent a substituted amino group, a hydrocarbyloxy group, or a substituted or unsubstituted hydrocarbyl group.

4. The method for producing the conjugated diene rubber according to any one of claims 1 to 3, wherein the hydrocarbyloxysilane compound is a hydrocarbyloxysilane compound having a group containing a nitrogen atom.

5. The method for producing the conjugated diene rubber according to claim 4, wherein the group containing the nitrogen atom is a group containing a primary amino group having an active hydrogen atom and/or a secondary amino group having an active hydrogen atom.

6. The method for producing the conjugated diene rubber according to any one of claims 1 to 5, wherein

the first step comprises:

a step of polymerizing a monomer (a) containing isoprene using the polymerization initiator in the inert solvent to form a polymer block (A) having an active end; and

a step of mixing the polymer block (A) having the active end and a monomer (b) containing 1,3-butadiene to continue polymerization reaction, so as to obtain the conjugated diene polymer chain that has an active end and comprises the polymer block (A) and the polymer block (B), and

the vinyl compound having the functional group interactive with the silica is contained in at least one of the monomer (a) and the monomer (b).

7. The method for producing the conjugated diene rubber according to any one of claims 1 to 6, further comprising a step of reacting a modifier containing a nitrogen atom with a part of the active end of the conjugated diene polymer chain having the active end before reacting the siloxane compound with the conjugated diene polymer chain having the active end in the second step.

8. The method for producing the conjugated diene rubber according to claim 7, wherein the modifier containing the nitrogen atom is a modifier containing the nitrogen atom and not containing a silicon atom.

9. The method for producing the conjugated diene rubber according to claim 8, wherein the modifier containing the nitrogen atom and not containing the silicon atom is N-substituted cyclic amides.

10. The method for producing the conjugated diene rubber according to any one of claims 1 to 9, wherein the polymerization initiator is an organic monolithium compound or an organic polyvalent lithium compound.

11. The method for producing the conjugated diene rubber according to any one of claims 1 to 10, wherein the amount of the polymerization initiator to be used is in the range of 1 to 50 mmol with respect to 1000 g of the monomers.

12. The method for producing the conjugated diene rubber according to any one of claims 1 to 11, wherein a polar compound is used in addition to the polymerization initiator in the first step, and the vinyl bond content in the conjugated diene monomer unit of the conjugated diene polymer chain having an active end obtained in the first step is 3 to 90 wt %.

13. The method for producing the conjugated diene rubber according to any one of claims 1 to 12, wherein the amount of the vinyl compound having the functional group interactive with silica to be used is an amount so that the content ratio of a unit of vinyl compound having the functional group interactive with silica in the conjugated diene polymer chain having the active end obtained in the first step becomes 0.01 to 20 wt %.

14. The method for producing the conjugated diene rubber according to claim 3, wherein, in the general formula (2) above, at least one of X^6, X^7, and X^8 is a substituted amino group.

15. The method for producing the conjugated diene rubber according to

claim 3, wherein, in the general formula (2) above, X^5 is a chemical single bond, X^6 and X^7 are each a diethylamino group, and X^8 is a methyl group.