

Description

Title of Invention:

METHOD FOR PRODUCING BRANCHED CONJUGATED DIENE-BASED
POLYMER

Technical Field

[0001]

The present invention relates to a method for producing a branched conjugated diene-based polymer.

Background Art

[0002]

A method for producing a branched polymer or copolymer has conventionally been proposed, in which a conjugated diene compound is polymerized or a conjugated diene compound and a vinyl aromatic compound are copolymerized in a hydrocarbon solvent using an alkali metal-based initiator, and the polymer or the copolymer is further reacted with a polyfunctional low molecular compound to perform a coupling reaction (for example, see Patent Document 1).

[0003]

As a method for obtaining a branched copolymer, a technique of continuously performing polymerization in at least two reaction zones is disclosed, in which a polyfunctional low molecular compound is added to the

first reaction zone to perform a coupling reaction (for example, see Patent Document 2).

[0004]

A technique of continuously performing polymerization using two polymerization vessels is disclosed, in which a polyfunctional low molecular compound is added to the second polymerization vessel to perform a coupling reaction (for example, see Patent Document 3).

[0005]

Furthermore, there is disclosed a technique in which continuation polymerization is performed using two polymerization vessels, and a polyfunctional low molecular compound is then added using a static mixer to perform a coupling reaction (for example, see Patent Document 4).

Citation List

Patent Document

[0006]

Patent Document 1: Japanese Patent Publication No. 49-36957

Patent Document 2: Japanese Patent Publication No. 54-6274

Patent Document 3: Japanese Patent Laid-Open No. 61-255917

Patent Document 4: International Publication No.
WO2006/104215

Summary of Invention

Problems to be Solved by the Invention

[0007]

However, in the method for producing the branched conjugated diene-based polymer by continuously polymerizing the conjugated diene polymer followed by the coupling reaction continuously performed, a slight change in a process greatly influences a quality of a final product. It is thus an important subject to produce a branched conjugated diene-based polymer industrially stably.

Then, it is an object of the present invention to provide a method capable of industrially, stably and efficiently providing a branched conjugated diene-based polymer, that is, a branched conjugated diene polymer rubber or a branched random copolymer rubber composed of a conjugated diene compound and a vinyl aromatic compound and producing the above-described high-quality polymer rubber or copolymer rubber.

Means for Solving the Problems

[0008]

The present inventors have investigated, for solving the above-described problems, a method for producing a

branched conjugated diene-based polymer, in which a conjugated diene compound is polymerized or a conjugated diene compound is polymerized with a vinyl aromatic compound in a hydrocarbon solvent using an alkali metal-based initiator continuously to obtain a living polymer or copolymer and the obtained living polymer or copolymer is reacted with a polyfunctional compound to perform a coupling reaction. As a result, it has been found that the object can be achieved by controlling a time until the coupling reaction is performed after the polymerization and controlling a pressure of a product removing outlet of a polymerization vessel in which the polymerization is performed, leading to the completion of the present invention.

That is, the present invention will be described later.

[0009]

[1]

A method for producing a branched conjugated diene-based polymer comprises:

a polymerization step of continuously polymerizing a conjugated diene compound or copolymerizing a conjugated diene compound and a vinyl aromatic compound in a hydrocarbon solvent using an alkali metal-based initiator in a polymerization vessel to obtain a living polymer or copolymer;

a coupling step of performing a coupling reaction by reacting the living polymer or copolymer with a polyfunctional compound in a coupling reactor that is connected to the polymerization vessel via a pipe provided at an outlet of the polymerization vessel from which the living polymer or copolymer is discharged, and that is connected to a discharging pipe having an opening-degree adjusting unit; and

a solvent removal step,

wherein the living polymer or copolymer is reacted with the polyfunctional compound within 5 minutes after the polymerization step, and

a pressure at the outlet of the polymerization vessel is controlled to 0.5 to 2 MPaG by the opening-degree adjusting unit.

[0010]

[2]

The method for producing the branched conjugated diene-based polymer according to the above item [1], wherein the coupling reactor is equipped with a rotary stirrer and is a tank reactor having a volume of 0.5 to 50% based on the volume of the polymerization vessel.

[0011]

[3]

The method for producing the branched conjugated diene-based polymer according to the above item [1] or [2], wherein the polymerization vessel is a tank reactor

equipped with a stirrer; and the conjugated diene compound and the vinyl aromatic compound are randomly copolymerized in the presence of a polar compound in the polymerization step.

[0012]

[4]

The method for producing the branched conjugated diene-based polymer according to any one of the above items [1] to [3], further comprises a step of sampling the living polymer or copolymer between the polymerization step and the coupling step and measuring a Mooney viscosity thereof, and

a step of sampling the branched conjugated diene-based polymer when a residence time from the outlet of the polymerization vessel is less than 15 minutes after the coupling step and measuring a Mooney viscosity thereof.

[0013]

[5]

The method for producing the branched conjugated diene-based polymer according to any one of the above items [1] to [4], wherein one tank reactor equipped with a stirrer is used as the polymerization vessel.

[0014]

[6]

The method for producing the branched conjugated diene-based polymer according to any one of the above

items [1] to [5], wherein a polyepoxy compound having a tertiary amino group in a molecule is used as the polyfunctional compound.

[0015]

[7]

The method for producing the branched conjugated diene-based polymer according to any one of the above items [1] to [6], wherein the polyfunctional compound comprises a glycidylamino group-containing low molecular compound having 2 or more tertiary amino groups and 3 or more glycidyl groups bonded to the tertiary amino groups in a molecule, and an oligomer component of a dimer or higher oligomer of the glycidylamino group-containing low molecular compound; and the polyfunctional compound comprises 75 to 95% by mass of the low molecular compound and 25 to 5% by mass of the oligomer based on a total amount of the polyfunctional compound.

[0016]

[8]

The method for producing the branched conjugated diene-based polymer according to any one of the above items [1] to [7], wherein a coupling reaction ratio of the living polymer or copolymer and the polyfunctional compound is 10 to 80% by mass.

[0017]

[9]

The method for producing the branched conjugated diene-based polymer according to any one of the above items [1] to [8], wherein the branched conjugated diene-based polymer has one peak in a molecular weight distribution measured by gel permeation chromatography (GPC) one peak, and has a weight-average molecular weight of 500,000 to 2,000,000 with respect to a polystyrene-equivalent molecular weight.

[0018]

[10]

The method for producing the branched conjugated diene-based polymer according to any one of the above items [1] to [9], wherein the branched conjugated diene-based polymer is a copolymer of a conjugated diene compound and a vinyl aromatic compound; an amount of a single chain of the vinyl aromatic compound by decomposition with ozone is 40% or more based on a total amount of the vinyl aromatic compound; and an amount of 8 or more chains of the vinyl aromatic compound is 5% or less.

Advantages of the Invention

[0019]

The producing method of the present invention can stably and efficiently produce a high-quality branched conjugated diene-based polymer.

That is, the producing method can continuously produce a branched conjugated diene-based polymer having little fluctuation in viscosity and a branching degree, in a short residence time, and a high conversion rate and a high branching degree, in energy saving with less gel generation.

Mode for Carrying Out the Invention

[0020]

Hereinafter, a mode for carrying out the present invention (hereinafter, referred to as "the present embodiment") will be described in detail.

The present invention is not limited to the following description. The present invention can be implemented by appropriately modifying it within the scope thereof.

[0021]

[Method for Producing Branched Conjugated Diene-based Polymer]

A method for producing a branched conjugated diene-based polymer of the present embodiment comprises:

a polymerization step of continuously polymerizing a conjugated diene compound or copolymerizing a conjugated diene compound and a vinyl aromatic compound in a hydrocarbon solvent using an alkali metal-based initiator in a polymerization vessel to obtain a living polymer or copolymer;

a coupling step of performing a coupling reaction by reacting the living polymer or copolymer with a polyfunctional compound in a coupling reactor that is connected to the polymerization vessel via a pipe provided at an outlet of the polymerization vessel from which the living polymer or copolymer is discharged, and that is connected to a discharging pipe having an opening-degree adjusting unit; and

a solvent removal step,

wherein the living polymer or copolymer is reacted with the polyfunctional compound within 5 minutes after the polymerization step, and

a pressure at the outlet of the polymerization vessel is controlled to 0.5 to 2 MPaG by the opening-degree adjusting unit.

[0022]

(Production Apparatus Carrying out Producing Method of Branched Conjugated Diene-based Polymer)

First, a production apparatus (hereinafter, may be merely referred to as a production apparatus) carrying out the producing method of the branched conjugated diene-based polymer of the present embodiment will be described.

The production apparatus is equipped with a polymerization vessel and a coupling reactor.

<Polymerization Vessel>

The polymerization vessel is preferably a tank reactor having a stirrer, and more preferably a vertical polymerization vessel in view of the ease of start and stop.

The term "vertical" means a structure disposed so that the central axis of the tank reactor is perpendicular.

The use of the tank reactor is preferable for copolymerization having a high random property in a polymerization step as described later, particularly in a polymerization step randomly copolymerizing a conjugated diene compound and a vinyl aromatic compound. An ozone decomposition-based method is used as a method for valuating the random property.

Examples of the structure of the polymerization vessel include a structure using a tank reactor having a stirrer and a structure in which a plurality of polymerization vessels are connected in series. The structure using a polymerization vessel is preferable because of a higher living ratio.

[0023]

<Coupling Reactor>

The coupling reactor is connected via a pipe provided at the polymerization vessel outlet discharging a polymer obtained in the above-described polymerization vessel.

An opening-degree adjusting unit is provided in a discharging pipe from the coupling reactor which is connected to the coupling reactor.

A pressure at the outlet of the polymerization vessel can be controlled by adjusting this opening-degree adjusting function.

[0024]

As described later, in the coupling reactor, a coupling reaction is performed by mixing a polyfunctional compound with a solution of a living polymer or copolymer obtained in a polymerization reaction in the polymerization vessel.

The coupling reactor is equipped with a rotary stirrer. The coupling reactor is preferably a tank reactor having a volume of 0.5 to 50% of that of the polymerization vessel, and more preferably a tank reactor having a volume of 1 to 20% thereof.

The tank reactor provides an advantage that a problem of blockage caused by a gel generated in the polymerization vessel is hard to occur.

The coupling reaction can be stably performed to correspond to variation in the flow rates of the polymer and the polyfunctional compound. Furthermore, the coupling reaction can be more stably performed by the volume of the above-described range.

The excessive volume of the coupling reactor lengthens a residence time, and increases the fluctuation

range of viscosity and a branching degree or the like of a branched polymer after coupling to make it difficult to control the viscosity and the branching degree. The volume is a volume of a liquid phase. When a gaseous phase exists, or when a stirrer and another device exist, the volume does not contain a portion thereof.

[0025]

In the coupling reactor, the relationship d/D between an inner diameter D (m) and a blade diameter d (m) of the stirrer is preferably 0.5 or more, and more preferably 0.6 or more.

When the inner diameter and the blade diameter of the stirrer satisfy the above-described relationship, the fluctuation in the viscosity and the branching degree of a coupling polymer generated is decreased even if the volume is comparatively small, to enable a stable coupling reaction.

A product nd of a rotation number n (s^{-1}) of the rotary stirrer of the coupling reactor and the blade diameter d (m) is preferably 0.1 or more, and more preferably 0.2 to 5 in light of economical efficiency.

In this case, the variation in the viscosity and the branching degree of the generated polymer can be further decreased. In addition, the volume of the coupling reactor can also be decreased.

[0026]

(Polymerization Step)

The polymerization step is a step of continuously polymerizing a conjugated diene compound or copolymerizing a conjugated diene compound and a vinyl aromatic compound in a hydrocarbon solvent using an alkali metal-based initiator in a polymerization vessel to obtain a living polymer or copolymer, in the above-described polymerization vessel.

First, materials used in the polymerization step will be described. Then, the specific polymerization step will be described.

[0027]

<Conjugated Diene Compound>

Examples of the conjugated diene compound include, but are not limited to, 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 3-methyl-1,3-pentadiene, 1,3-heptadiene and 1,3-hexadiene. 1,3-Butadiene and isoprene are particularly preferable. These may be used either singly or in combination of 2 or more thereof.

[0028]

<Vinyl Aromatic Compound>

Examples of the aromatic vinyl compound include, but are not limited to, styrene, p-methylstyrene, α -methylstyrene, vinylethylbenzene, vinylxylene, vinylnaphthalene and diphenylethylene. Styrene is particularly preferable.

These may be used either singly or in combination of 2 or more thereof.

[0029]

<Hydrocarbon Solvent>

Saturated hydrocarbons and aromatic hydrocarbons or the like are used as the hydrocarbon solvent. Examples thereof include aliphatic hydrocarbons such as butane, pentane, hexane, pentane and heptane; alicyclic hydrocarbons such as cyclopentane, cyclohexane, methylcyclopentane and methylcyclohexane; aromatic hydrocarbons such as benzene, toluene and xylene, and hydrocarbons made of mixtures thereof.

[0030]

Before a polymerization reaction described later of each or mixture of the above-described conjugated diene compound, aromatic vinyl compound and hydrocarbon solvent, removal of impurities such as moisture, allenes, acetylenes and carbonyls enables preparation of a polymer having an active end in a high concentration and achievement of a high deformation ratio.

It is preferable that as an amount of these impurities, amounts of the moisture, allenes and acetylenes are respectively less than 20 ppm, less than 200 ppm and less than 200 ppm based on the total mass of monomers presented for the polymerization reaction.

A chain transfer agent of a slight amount for preventing gel generation during the polymerization, for

example, the allenes, specifically, 1,2-butadiene and propadiene may preferably exist within a range of less than 200 ppm.

[0031]

<Alkali metal-based initiator>

As the alkali metal-based initiator, any alkali metal component having a function of initiating polymerization is usable.

Organolithium compounds are particularly preferable.

The organolithium compounds include those having a low-molecular weight, organolithium compounds of a solubilized oligomer, those having, in a molecule thereof, single lithium, those having, in a molecule thereof, a plurality of lithiums, and those in which an organic group and lithium are bound via a carbon-lithium bond, a nitrogen-lithium bond or a tin-lithium bond.

Specific examples of the organolithium compound which is the alkali metal-based initiator including an organomonolithium compound, a polyfunctional organolithium compound and a compound having a nitrogen-lithium bond are shown below.

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

Examples of the polyfunctional organolithium compound include, but are not limited to, 1,4-

dilithiobutane, reaction products between sec-butyllithium and diisopropenylbenzene, 1,3,5-trilithiobenzene, reaction products among n-butyllithium, 1,3-butadiene and divinylbenzene, and reaction products between n-butyllithium and a polyacetylene compound.

Examples of the compounds having the nitrogen-lithium bond include, but are not limited to, dimethylaminolithium, dihexylaminolithium, diisopropylaminolithium and hexamethyleneiminolithium.

In addition, organoalkali metal compounds disclosed in U.S. Patent No. 5,708,092, British Patent No. 2,241,239 and U.S. Patent No. 5,527,753 or the like are also usable.

[0032]

As the organolithium compound, n-butyllithium and sec-butyllithium are more preferable.

These organolithium compounds may be used either singly or in combination of 2 or more thereof.

[0033]

Examples of an organoalkali metal compound other than the organolithium compound include organosodium compounds, organopotassium compounds, organorubidium compounds and organocesium compounds.

Examples of the organoalkali metal compound other than the organolithium compound include, but are not limited to, sodium naphthalene and potassium naphthalene.

In addition, alkoxides, sulfonates, carbonates and amides of lithium, sodium or potassium are usable.

[0034]

The alkali metal-based initiator may be used in combination with another organometal compound.

Examples of the organometal compound include organomagnesium compounds and organoaluminum compounds. Specific examples thereof include dibutyl magnesium and triethyl aluminum.

[0035]

<Polar Compound>

The use of the polar compound together with the above-described alkali metal-based initiator can increase a polymerization initiation rate, control the microstructure of a conjugated diene unit in the polymer, and control a monomer reactivity ratio in the copolymerization.

The polar compound is not limited to the following compounds. However, for example, ether compounds, tertiary amine compounds, metal alkoxide compounds, phosphine compounds and organosulfonic acid metal compounds or the like are used.

The polar compound has an effective randomizing effect in a copolymerization between a conjugated diene compound and an aromatic vinyl compound as described later so that it can be used as a regulating agent of a

distribution of the aromatic vinyl compound or a regulating agent of a styrene block content.

Examples of the polar compound include ethers such as tetrahydrofuran, diethyl ether, dioxane, ethylene glycol dimethyl ether, ethylene glycol dibutyl ether, diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, dimethoxybenzene and 2,2-bis(2-oxolanyl)propane; tertiary amine compounds such as tetramethylethylenediamine, dipiperidinoethane, trimethylamine, triethylamine, pyridine and quinuclidine; alkali metal alkoxide compounds such as potassium-t-amylate, potassium-t-butylate, sodium-t-butylate and sodium-t-amylate; phosphine compounds such as triphenylphosphine; and alkyl or arylsulfonic acid compounds such as potassium dodecylbenzene sulphonate and sodium dodecylbenzene sulphonate.

These polar compounds may be used either singly or in combination of 2 or more thereof.

[0036]

An amount of the polar compound to be used can be suitably selected, depending on the using purpose and degree of effect. It is usually from 0.01 to 100 moles based on 1 mole of the above-described alkali metal-based initiator.

Such a polar compound can be used in an adequate amount as a regulating agent of the microstructure of the polymer diene moiety, depending on a desired vinyl bond

content, in addition to the adjustment of a copolymerization reactivity ratio.

The polar compound is preferably an ether group-containing hydrocarbon compound having 2 or more ether groups at least one of which forms a ring, in a molecule.

The use thereof provides effects of a high monomer conversion rate, small deactivation on the way and a high living polymer rate of the copolymer.

The ether group-containing hydrocarbon compound having 2 or more ether groups at least one of which forms a ring, in a molecule includes 2,2-bis(2-oxolanyl)propane and alkyl ether of tetrahydropyranyl methanol. 2,2-Bis(2-oxolanyl)propane is preferable.

[0037]

<Polymerization Step>

In the above-described polymerization vessel, a living polymer or copolymer is obtained by continuously polymerizing a conjugated diene compound or copolymerizing a conjugated diene compound and a vinyl aromatic compound in the above-described hydrocarbon solvent using the above-described alkali metal-based initiator.

A monomer concentration in a polymerization solution is preferably 5 to 30% by mass, and more preferably 10 to 20% by mass.

In this polymerization step, required raw materials such as a monomer, a hydrocarbon solvent and an alkali

metal-based initiator are continuously fed from one or more predetermined nozzles provided in the polymerization vessel. After the contents are polymerized, the contents are continuously extracted from a predetermined nozzle corresponding to the polymerization vessel outlet discharging a polymer solution and being different from the nozzle.

[0038]

The polymerization step is preferably performed with the temperature of the outlet of the polymerization vessel set to 70°C to 110°C, more preferably 90°C to 110°C and still more preferably 95°C to 107°C.

A living ratio is increased by setting a polymerization temperature to 110°C or less to obtain a high coupling yield.

On the other hand, a high conversion rate is obtained by setting the polymerization temperature to 70°C or more.

A higher conversion rate of the monomer in the outlet of the polymerization vessel is good. The conversion rate is preferably 95% or more, more preferably 98% or more and still more preferably 99% or more.

The conversion rate is influenced by the outlet temperature of the polymerization vessel, temperature distribution in the polymerization vessel, a stirring state, the amount of the initiator, the kind and amount

of the polar compound and a mean residence time. The living ratio is desirably increased while the conversion rate is increased. If the conversion rate is sufficiently high as described above, the living ratio of the obtained polymer is higher when the mean residence time in the polymerization vessel is shorter. A coupling yield in a coupling step as described later is higher.

The mean residence time in the polymerization vessel is preferably within 40 minutes. The mean residence time is more preferably within 35 minutes. On the other hand, when the mean residence time is excessively short, the conversion rate is reduced. Thereby, the mean residence time is preferably 15 minutes or longer.

[0039]

(Coupling Step)

The coupling step is a step of performing a coupling reaction by reacting the living polymer or copolymer obtained in the polymerization step with the polyfunctional compound.

First, materials used in the coupling step will be described. Then, the specific coupling step will be described.

[0040]

<Polyfunctional Compound>

A compound having a plurality of functional groups in a molecule is used as the polyfunctional compound.

The functional groups react with the living polymer or copolymer to form a bond.

The polyfunctional compound has 3 or more same or different functional groups in a molecule, and forms at least three branches in a coupling reaction. The polyfunctional compound is preferably a polyfunctional compound which forms four branches to eight branches.

As a result of a bond reaction, a different functional group may be introduced into the end of the polymer or copolymer.

An amount of the polyfunctional compound to be used is preferably 0.05 to 5 equivalent amounts as the functional group of the polyfunctional compound based on 1 mole of the above-described alkali metal-based initiator, and more preferably 0.1 to 2 equivalent amounts.

[0041]

Examples of the functional group reacting with the living polymer or copolymer to form the bond include a halogen group, a carbonyl group, a carboxylic ester group, a carboxylic amide group, a carboxylic halogenide group, a thiocarbonyl group, a thiocarboxylic acid ester group, a thiocarboxylic acid amide group, a thiocarboxylic halogenide group, a isocyanato group, a thioisocyanato group, an epoxy group, a thioepoxy group, an alkoxysilyl group, a vinyl group as a functional double bond and an imino group.

[0042]

A polyfunctional compound which has a functional group having compatibility with a filler without being bonded to a living end or having bond reactivity, in the molecule of the polyfunctional compound is preferably used.

Examples of the functional group include a tertiary amino group, and a primary or secondary amino group protected by a silicon compound.

[0043]

Preferred examples of the polyfunctional compound include tetrahalogenated silicon, bis(trihalogenated silyl)alkane, tetrahalogenated tin, tetraalkoxy silicon, trialkoxyalkyl silicon, hexaalkoxydisilane, bis(trialkoxysilyl)alkane, bis(trialkoxysilylalkyl)alkylamine, bis(trialkoxysilylalkyl)trialkylsilylamine, tris(trialkoxysilylalkyl)amine, 1,4-bis(trialkoxysilylalkyl)piperazine, 1,3-bis(trialkoxysilylalkyl)imidazolidine, 1,3-bis(trialkoxysilylalkyl)hexahydropyrimidine, 1,1-dialkoxy-2(trialkoxysilylalkyl)-1-sila-2-azacyclopentane, 1,1-dialkoxy-2(trialkoxysilylalkyl)-1-sila-2-azacyclohexane, 1,1-dialkoxy-2(trialkoxysilylalkyl)-1-sila-2-azacycloheptane, a dicarboxylic acid diester, a tricarboxylic acid triester, a carbonic acid diester, a compound having 3 or more glycidyl ether groups, a

compound having 3 or more glycidylamino groups, and a compound having 2 or more diglycidylamino groups.

[0044]

Specific examples thereof include silicon tetrachloride, silicon tetrabromide, silicon tetraiodide, stannic chloride, 1,2-bis(trichlorosilyl)ethane, tetramethoxysilicon, tetraethoxysilicon, trimethoxymethylsilicon, hexaethoxydisilane, 1,2-bis(trimethoxysilyl)ethane, 1,1-bis(trimethoxysilyl)ethane, bis(3-triethoxysilylpropyl)methylamine, bis(2-trimethoxysilylethyl)propylamine, bis(3-trimethoxysilylpropyl)trimethylsilylamine, tris(trimethoxysilylmethyl)amine, tris(3-triethoxysilylpropyl)amine, 1,4-bis[3-(trimethoxysilyl)propyl]piperazine, 1,4-bis[3-(triethoxysilyl)propyl]piperazine, 1,3-bis[3-(trimethoxysilyl)propyl]imidazolidine, 1,3-bis[3-(triethoxysilyl)propyl]imidazolidine, 1,3-bis[3-(trimethoxysilyl)propyl]hexahydropyrimidine, 1,3-bis[3-(triethoxysilyl)propyl]hexahydropyrimidine, 1,3-bis[3-(tributoxysilyl)propyl]-1,2,3,4-tetrahydropyrimidine, 1,1-dimethoxy-2(3-trimethoxysilylpropyl)-1-sila-2-azacyclopentane, 1,1-diethoxy-2-(3-triethoxysilylpropyl)-1-sila-2-azacyclopentane, 1,1-dimethoxy-2-(3-dimethoxymethylsilylpropyl)-1-sila-2-azacyclopentane, 1,1-dimethoxy-2(4-trimethoxysilylbutyl)-1-sila-2-

azacyclohexane, 1,1-dimethoxy-2(5-trimethoxysilylpentyl)-1-sila-2-azacycloheptane, dimethyl adipate, trimethyl trimellitate, triethyl trimesinate, dimethyl carbonate, glycerin triglycidylether, pentaerythritol tetraglycidylether, tetraglycidyl-1,3-bisaminomethylcyclohexane, tetraglycidyl-m-xylenediamine, tetraglycidyl-4,4'-diaminodiphenylmethane, N,N-diglycidyl-4-(4-glycidyl-1-piperaziny)aniline and N,N-diglycidyl-4-glycidyloxyaniline.

[0045]

More preferred examples of the polyfunctional compound include a polyepoxy compound having a tertiary amino group in a molecule. 3 or more epoxy groups provide a branched polymer.

In this case, a by-product is not generated. The obtained branched polymer has excellent performance as a rubber.

Specific examples thereof include tetraglycidyl-1,3-bisaminomethylcyclohexane, tetraglycidyl-meta-xylylenediamine, tetraglycidyl-4,4'-diaminodiphenylmethane, N,N-diglycidyl-4-(4-glycidyl-1-piperaziny)aniline and N,N-diglycidyl-4-glycidyloxyaniline.

[0046]

Still more preferred examples of the polyfunctional compound include a polyfunctional compound comprising a glycidylamino group-containing low molecular compound

having 2 or more tertiary amino groups and 3 or more glycidyl groups bonded to the amino groups in a molecule, and an oligomer component of a dimer or higher oligomer of the glycidylamino group-containing low molecular compound; and a polyfunctional compound comprising 75 to 95% by mass of the low molecular compound and 25 to 5% by mass of the oligomer based on a total amount of the polyfunctional compound.

Specific examples thereof include a mixture of tetraglycidyl-1,3-bisaminomethylcyclohexane and an oligomer component thereof.

The use of the above-described polyfunctional compound provides a branched conjugated diene compound having more excellent physical properties as a rubber.

[0047]

<Coupling Step>

In this coupling step, the polyfunctional compound is mixed and reacted with the living polymer or copolymer solution discharged from the outlet of the polymerization vessel.

At this time, the above-described polymerization vessel and coupling reactor are connected in series via the pipe provided at the outlet of the polymerization vessel. The polyfunctional compound needs to be mixed and reacted with the living polymer or copolymer solution discharged from the outlet of the polymerization vessel within 5 minutes as a mean residence time after

discharging from the outlet of the polymerization vessel. The mean residence time is preferably within 3 minutes and more preferably within 2 minutes.

In the present embodiment, as described above, the opening-degree adjusting unit capable of controlling a pressure at the outlet of the above-described polymerization vessel is provided in a discharging pipe connected to the coupling reactor. Thereby, the pressure at the outlet of the polymerization vessel is controlled to 0.5 to 2 MPaG.

The preferred setting value of the pressure may be controlled to such a degree that the solution is not vaporized since the pressure is sufficiently higher than a steam pressure in the polymerization vessel. The setting value of the pressure is preferably within a range of from 0.6 to 1.5 MPaG, and more preferably within a range of from 0.7 to 1.2 MPaG. The fluctuating range of the pressure to the setting value is preferably within ± 0.2 MPa and more preferably less than ± 0.1 MPa. The fluctuating range is preferably smaller.

An automatic or manual pressure control valve, and an orifice plate or the like can be applied as the opening-degree adjusting unit. Particularly, the automatic pressure control valve is preferable. When the automatic pressure control valve is used and the opening-degree of the control valve varies significantly, the

manual pressure control valve is preferably used in combination with the automatic pressure control valve.

The pressure at the outlet of the polymerization vessel is controlled for every step of producing the branched conjugated diene-based polymer which is the object from the above-described polymerization step to the coupling step.

Thus, the branched conjugated diene-based polymer can be stably produced with little variation in the viscosity and branching degree of the produced branched conjugated diene-based polymer by specifying the setting location of the opening-degree adjusting unit to the discharging pipe connected to the coupling reactor and controlling the pressure at the outlet of the polymerization vessel.

[0048]

The setting location of the opening-degree adjusting unit may be any point in the middle to the next step in the discharging pipe corresponding to a downstream of the coupling reactor.

A mixer mixing an additive agent or an extender oil or the like may be provided in the discharging pipe connected to the coupling reactor.

[0049]

In the producing method of the branched conjugated diene-based polymer of the present embodiment, a polymerization apparatus having an opening-degree

adjusting unit provided on the downstream of the coupling reactor is used in order to prevent a sudden pressure drop caused by an operation of the opening-degree adjusting unit, and a vaporization of a solvent resulting therefrom, to maintain a concentration and a flow rate in a uniform state.

[0050]

It is economically preferable to control the pressure at the outlet of the polymerization vessel to 0.5 to 2 MPaG since a sufficient conversion rate can be secured and the producing method can be carried out by comparatively simple equipment.

It is necessary to substantially set the pressure at the outlet of the polymerization vessel to this range. A setting location of a pressure detector for automatically controlling a pressure is not limited to the outlet of the polymerization vessel. The setting location may be in the polymerization vessel, the pipe in between or the coupling reactor, as long as the setting location is on an upstream of the opening-degree adjusting unit.

[0051]

The opening-degree adjusting unit can be also provided in the outlet pipe of the polymerization vessel and the outlet pipe of the coupling reactor. Even in the case, it is preferable that the outlet pressure of the polymerization vessel is mainly controlled by the opening-degree adjusting unit of the outlet pipe of the

coupling reactor. Pressure control caused by the opening-degree adjusting unit provided in the outlet pipe of the coupling reactor may be aided by the opening-degree adjusting unit provided in the outlet pipe of the polymerization vessel.

[0052]

As described above, a branched conjugated diene-based polymer having little fluctuation in viscosity and a branching degree, and a high conversion rate and an optional branching degree for a short residence time can be continuously produced in energy saving while reducing gel generation, by performing and completing the polymerization step and the coupling step at a comparatively high temperature for a short time.

[0053]

[Viscosity Managing Step]

It is preferable that the producing method of the branched conjugated diene-based polymer of the present embodiment further includes a step of sampling the living polymer or copolymer and measuring a Mooney viscosity thereof between the above-described polymerization step and the above-described coupling step, and a step of sampling the branched conjugated diene-based polymer when the residence time from the outlet of the polymerization vessel is less than 15 minutes and measuring a Mooney viscosity thereof after the coupling step.

Thereby, the viscosity and branching degree of the branched conjugated diene-based polymer can be stabilized. The residence time from the outlet of the polymerization vessel to the sampling is more preferably less than 10 minutes.

As shown in [Examples] as described later, preheating is usually performed at an optional temperature of 100°C to 130°C for 1 minute according to JIS K 6300-1 using a Mooney viscosity meter. The Mooney viscosity meter is then rotated at two rotations per minute. The viscosity of the living polymer or copolymer after 4 minutes is measured.

[0054]

In particular, it is preferable that the Mooney viscosity of the living polymer or copolymer in the previous stage of coupling is measured and managed from a predetermined sampling nozzle at the outlet of the polymerization vessel or at the previous stage adding the polyfunctional compound; and the Mooney viscosity of the branched conjugated diene-based polymer obtained after the coupling step is measured and managed from a predetermined sampling nozzle at the outlet of the coupling reactor or later or in a position in which the residence time from the outlet of the polymerization vessel is less than 15 minutes.

The above-described sampling nozzle has a constitution in which a branching pipe is provided in a

predetermined pipe or the like; a vessel having a volume required for sampling is provided; and a predetermined gate valve is provided on front and rear sides of the vessel. Furthermore, the sampling nozzle preferably has a constitution in which a pipe introducing inactive gas into the vessel is provided if needed.

The residence time is calculated based on the volume of a liquid phase passing through equipment.

When a stirrer and other device exist in the case where a gaseous phase exists, the portion thereof is not included.

[0055]

Before and after the coupling step, the variation in a product during the step can be instantaneously sensed and corresponded by measuring and managing the Mooney viscosity of the living polymer or copolymer, and further comparatively shortening the residence time from the outlet of the polymerization vessel, to finally stabilize the viscosity and branching degree of the branched conjugated diene-based polymer which is the object.

[0056]

In the present embodiment, the living polymer or copolymer before the coupling step preferably has a Mooney viscosity (ML-I) of 50 to 100 at 110°C. The branched conjugated diene-based polymer or copolymer after the coupling step preferably has a Mooney viscosity (ML-C) of 100 to 150 at 110°C.

The Mooney viscosity (ML-C) is preferably 1.2 to 3 times as large as the Mooney viscosity (ML-I).

[0057]

A managing width of the Mooney viscosity before the coupling step is preferably within ± 10 with respect to a desired value and more preferably within ± 5 .

A managing width of the Mooney viscosity after the coupling step is preferably within ± 15 with respect to a desired value and more preferably within ± 8 .

[0058]

The width of the Mooney viscosity before the coupling step is preferably managed to a numerical value range narrower than that of the Mooney viscosity after the coupling step.

For example, the width is managed to the numerical value range by increasing and decreasing the amount of the initiator so that the Mooney viscosity before coupling falls within the managing width, and by increasing and decreasing the amount of the polyfunctional compound so that the Mooney viscosity after coupling falls within the managing width.

The managing can optimize the viscosity, molecular weight and branching degree of the branched conjugated diene-based polymer which is the object, and can secure stabilized quality in a processability of a rubber and a performance of a vulcanized rubber.

[0059]

[Quality Managing Step]

In the producing method of the branched conjugated diene-based polymer of the present embodiment, it is preferable to carrying out a quality managing step once collecting the solution of the branched conjugated diene-based polymer (copolymer) passing through the opening-degree adjusting unit provided in the discharging pipe of the coupling reactor after the above-described coupling step in the reservoir and managing the quality of the solution.

The reservoir is preferably held at a pressure of about 0.05 to 0.3 MPaG.

Before the solution is collected, in the reservoir, or before a solvent removal step after the solution comes out of the reservoir, a stop agent, a neutralizer, an antioxidant, or if needed an processing oil or the like can be further added. In the quality managing step, a Mooney viscosity, a branching degree, an amount of an additive agent, and a composition ratio in the case of a copolymer, or the like as test are measured.

[0060]

[Solvent Removal Step]

After the above-described quality managing step, the branched conjugated diene-based polymer (copolymer) solution or the oil extended conjugated diene polymer (copolymer) solution is fed to a predetermined finisher by a predetermined pump or the like, to remove a solvent.

Thereby, the branched conjugated diene-based polymer which is the object is obtained.

A conventionally known method can be applied as a method for removing the solvent to obtain the branched conjugated diene-based polymer.

For example, a method for separating a solvent by steam stripping or the like, thereafter filtering the solvent, further subjecting the obtained product material to an anhydration and drying treatments to obtain a branched conjugated diene-based polymer, a method for concentrating a solution in a flashing tank and further devolatilizing the solution with a vent extruder or the like, and a method for directly devolatilizing a solution with a drum drier or the like can be applied.

[0061]

[Branched Conjugated Diene-based Polymer]

The branched conjugated diene-based polymer which is the object is obtained by each of the above-described steps.

Hereinafter, the characteristics of the branched conjugated diene-based polymer obtained by carrying out the producing method of the present embodiment will be described.

(Coupling Reaction Ratio to Polyfunctional Compound)

A coupling reaction ratio of the branched conjugated diene-based polymer obtained by the producing method of

the present embodiment to the above-described polyfunctional compound is preferably 10 to 80% by mass.

The coupling reaction ratio to the polyfunctional compound of the above-described range provides a moderate branching degree, good processability, and a vulcanized rubber having excellent physical properties.

[0062]

(Molecular Weight Distribution)

A molecular weight distribution according to gel permeation chromatography (GPC) of the branched conjugated diene-based polymer obtained by the producing method of the present embodiment has one mountain, that is, one peak. The branched conjugated diene-based polymer preferably has a weight-average molecular weight of 500,000 to 2,000,000 with respect to a polystyrene-equivalent molecular weight.

The weight-average molecular weight of the above-described numerical value range provides good processability and a vulcanized rubber having excellent physical properties.

The molecular weight distribution according to GPC is preferably 1.7 to 3.0 as M_w (weight-average molecular weight)/ M_n (number-average molecular weight), and preferably 1.8 to 2.8.

The molecular weight distribution of the above-described range provides good processability and a vulcanized rubber having excellent physical properties.

[0063]

(Preferred Embodiment of Branched Conjugated Diene-based Polymer)

The branched conjugated diene-based polymer obtained by the producing method of the present embodiment is obtained by respectively polymerizing a conjugated diene compound or copolymerizing a conjugated diene compound and a vinyl aromatic compound.

For example, the branched conjugated diene-based polymer is preferably polybutadiene, polyisoprene, a butadiene-isoprene copolymer, a styrene-butadiene copolymer, a styrene-isoprene copolymer or a styrene-butadiene-isoprene copolymer, and more preferably the styrene-butadiene copolymer.

When the branched conjugated diene-based polymer is a branched random copolymer of the conjugated diene compound and the vinyl aromatic compound, it is preferable that a mass ratio of the conjugated diene compound in the branched random copolymer is 50 to 80% by mass, and a mass ratio of the vinyl aromatic compound is 50 to 20% by mass.

An amount of a vinyl structure of a conjugated diene moiety of the copolymer is preferably 30 to 65 mol%.

As described later, the above-described range provides good balance between wet skid resistance and fuel consumption properties when a vulcanized rubber is produced using the branched conjugated diene-based

polymer (copolymer) and the vulcanized rubber is utilized as a tread rubber of a passenger vehicle tire.

[0064]

When the branched conjugated diene-based polymer obtained by the producing method of the present embodiment is a branched random copolymer of a conjugated diene compound and a vinyl aromatic compound, it is preferable that a component having a chain length of aromatic vinyl of 30 or more is in a small amount or does not exist.

Specifically, when the branched conjugated diene-based polymer obtained by the producing method of the present embodiment is a butadiene-styrene copolymer; the branched conjugated diene-based polymer is decomposed by the method of Kolthoff (I. M. KOLTHOFF et al., the method described in J. Polym. Sci. 1, 429 (1946)); and measurement is performed by a known method for analyzing an amount of polystyrene (amount of block styrene) insoluble in methanol, the amount of block styrene based on a total amount of the branched conjugated diene-based polymer is preferably 5% by mass or less and more preferably 3% by mass or less.

[0065]

In particular, when the branched conjugated diene-based polymer obtained by the producing method of the present embodiment is decomposed by an ozone decomposition method, and styrene chain distribution is

analyzed by GPC, it is preferable that isolated styrene, that is, styrene having a styrene unit chain of 1 (styrene single chain) amounts to 40% by mass or more based on a total bound styrene, and long chain block styrene, that is, styrene having a chain of styrene units of 8 or more amounts to 5% by mass or less based on the total bound styrene.

The above-described numerical value range is preferably set in common in the vinyl aromatic compound constituting the branched conjugated diene-based polymer without being limited to styrene.

The above-described numerical value range achieves a movement performance of the vulcanized rubber using the branched conjugated diene-based polymer, for example, a reduction in a heating value during a deformation and recovery of a rubber.

[0066]

[Oil-Extended Polymer]

A processing oil may be added to the branched conjugated diene-based polymer obtained by the producing method in the present embodiment if needed before the above-described solvent removal step, thereby producing an oil-extended polymer.

As the above-described processing oil, for example, an aromatic oil, a naphthenic oil, a paraffinic oil and an alternative aromatic oil having a 3% by mass or less

of a polycyclic aromatic component as determined by the method of IP346 are preferable.

Particularly, the alternative aromatic oil having a 3% by mass or less of a polycyclic aromatic component is preferably used in views of an environmental safe, prevention of an oil bleed and wet-grip properties.

Examples of the alternative aromatic oil include TDAE and MES described in Kautschuk Gummi Kunststoffe 52(12), 799 (1999), and RAE.

An amount of the extender oil is not limited, however is usually from 10 to 60 parts by mass based on 100 parts by mass of the branched conjugated diene-based polymer. It is preferable that the amount is typically from 20 to 37.5 parts by mass.

[0067]

[Branched Conjugated Diene-based Polymer Composition]

A vulcanized rubber composition of the branched conjugated diene-based polymer is obtained by adding a predetermined material to the branched conjugated diene-based polymer obtained as described above and mixing the material with the branched conjugated diene-based polymer.

The branched conjugated diene-based polymer is typically processed by a method usually used in the rubber industry and used as a rubber product.

The vulcanized rubber composition using the branched conjugated diene-based polymer is obtained by blending the above-described branched conjugated diene-based

polymer with another predetermined rubber material if needed, mixing a filler thereto, adding a silane coupling agent, a rubber softener, a vulcanizing agent, a vulcanizing aid and another additive agent thereto, and processing the branched conjugated diene-based polymer.

Specifically, another rubber material, filler (silica and/or carbon black), silane coupling agent, rubber softener and antioxidant or the like are added to the branched conjugated diene-based polymer if needed and these are kneaded with a temperature-controllable kneading machine to obtain a rubber composition. In that case, kneading is performed at one or multiple stages. In order to improve the dispersion of the filler, kneading is preferably performed at multiple stages. After the obtained rubber composition is cooled, a vulcanizing agent and a vulcanizing aid or the like are added to the rubber composition, and these are then kneaded. The vulcanized rubber composition using the branched conjugated diene-based polymer which is the object is obtained by molding and vulcanizing the kneaded material.

[0068]

A crude rubber and a synthetic rubber can be applied as the another rubber material. Examples of the synthetic rubber include low-cis polybutadiene, high-cis polybutadiene, VCR (vinyl-cis butadiene rubber) and SBR

(styrene-butadiene rubber), isoprene rubber, butyl rubber and EPDM (ethylene propylene diene rubber).

[0069]

Examples of the filler include carbon black, precipitated silica, fumed silica, clay, talc, mica, diatomaceous earth, wollastonite, montmorillonite, zeolite and inorganic fibrous substances such as a glass fiber.

Particularly, carbon black and precipitated silica are preferably used.

[0070]

The silane coupling agent is a component having a function providing a close interaction between the above-described rubber component and a silica-based inorganic filler and having a group having affinity or bondability to each of the rubber component and the silica-based inorganic filler.

A compound having a sulfur bonding moiety, an alkoxysilyl group and a silanol group moiety in a molecule is typically used as the silane coupling agent.

Examples of the silane coupling agent include, but are not limited to, bis-[3-(triethoxysilyl)-propyl]-tetrasulphido, bis-[3-(triethoxysilyl)-propyl]-disulphido and bis-[2-(triethoxysilyl)-ethyl]-tetrasulphido.

[0071]

A mineral oil, a liquefied softener, a low-molecular weight synthetic softener or a low-molecular weight plant softener is preferably used as the rubber softener.

[0072]

A radical initiator, sulfur and a sulfur compound or the like can be used as the vulcanizing agent.

Zinc oxide and stearic acid or the like can be used as the vulcanizing aid.

A vulcanization accelerator, an antioxidant, wax, a conductive agent and a colorant or the like are used as another additive agent.

Examples

[0073]

Hereinafter, the present invention will be more specifically described with reference to the following examples and comparative examples, though the present invention is not limited these examples.

[0074]

First, a measuring method and an evaluating method of physical properties applied to the examples and the comparative examples will be described later.

[(1) Bound Styrene Content]

A chloroform solution of a measurement sample was obtained, and an amount of absorption of ultraviolet rays (UV) having a wavelength of 254 nm by a phenyl group of styrene was measured using UV-2450 manufactured by

Shimadzu Corporation while using the chloroform solution, and a bound styrene content (% by mass) was measured.

[0075]

[(2) Styrene Chain]

An osmic acid decomposition product of a measurement sample was obtained by Kolthoff method. Insoluble polystyrene corresponding to block polystyrene was deposited in methanol using the osmic acid decomposition product.

The insoluble polystyrene amount was quantitatively determined, and the block styrene amount was calculated in % by mass per polymer.

A content of a styrene single chain having one styrene unit and a styrene long chain having a row of eight or more styrene units was analyzed according to the method of Tanaka, et al. (Polymer, 22, 1721 (1981)) by decomposing a styrene-butadiene copolymer rubber with ozone and then subjecting the decomposed product to gel permeation chromatography (GPC).

[0076]

[(3) Microstructure of Butadiene Moiety (1,2-Vinyl Bond Content)]

A carbon dioxide solution of a measurement sample was obtained, and the microstructure (1,2-vinyl bond content) of a butadiene moiety was determined according to a calculation formula of Hampton method from an absorbance at a predetermined wavenumber by measuring an

infrared spectrum of the carbon dioxide solution within a range of from 600 to 1000 cm^{-1} in "FT-IR230" manufactured by JASCO Corporation by using a solution cell.

[0077]

[(4) Mooney Viscosity]

The viscosity was measured at 4 minute after preheating for 1 minute using an L-type rotor according to JIS K 6300-1.

Measurement temperatures were described with numeric data in the descriptive texts of [example 1], [comparative example 1] and [comparative example 2] as described later.

[0078]

[(5) Average Molecular Weight and Molecular Weight Distribution]

The chromatogram was measured by using gel permeation chromatography (GPC) using three connected columns packed with a polystyrene-based gel as a filler. A frequency of every molecular weight range to the total peak area was calculated according to an ordinary method from the relationship between retention volume and molecular weight obtained based on a calibration curve plotted using standard polystyrene, to calculate a number-average molecular weight, a weight-average molecular weight and molecular weight distribution.

Tetrahydrofuran (THF) was used as an eluting solution.

The measurement was performed by using apparatuses and under conditions: guard column: Tosoh TSK guardcolumn HHR-H, columns: Tosoh TSKgel G6000HHR, TSKgel G5000HHR and TSKgel G4000HHR, oven temperature: 40°C, THF flow rate: 1.0 mL/min, and measuring apparatus: HLC-8020 manufactured by Tosoh Corp. and a detector: IR.

The measurement was performed by injecting 200 μ L of each of measurement samples in which 20 mg of the measurement samples was dissolved in 20 mL of THF.

[0079]

[(6) Coupling Reaction Ratio]

An adsorption property of modified components was applied to a GPC column using a silica-based gel as a filler. A sample solution containing a sample and a low-molecular weight internal standard polystyrene of 5,000 in molecular weight (polystyrene is not adsorbed) was used. There were measured both a chromatogram of GPC (HLC-8020 manufactured by Tosoh Corp.) using the polystyrene-based gel of the above (5) (TSK manufactured by Tosoh Corp.) and a chromatogram of GPC (manufactured by Tosoh Corp., CCP8020 series buildup-type GPC system: AS-8020, SD-8022, CCPS, CO-8020, RI-8021) using a silica-based column (guard column: DIOL 4.6x12.5 mm 5 micron, Columns; Zorbax PSM-1000S, PSM-300S, PSM-60S, oven temperature: 40°C, THF flow rate: 0.5 mL/min). An adsorption amount to the silica column was measured from

their differences based on the internal standard polystyrene peak to determine a coupling reaction ratio.

The measurement was performed in common by injecting 200 μ L of each of measurement samples in which 20 mg of samples to be measured was dissolved with 5 mg of the standard polystyrene in 20 mL of THF.

The specific procedure involves: setting the whole of the peak area of a chromatogram using the polystyrene-based columns to 100, denoting the sample peak area as P1, denoting the peak area of the standard polystyrene as P2, setting the whole of the peak area of a chromatogram using the silica-based columns to 100, denoting the sample peak area as P3, and denoting the peak area of the standard polystyrene as P4. The coupling reaction ratio was calculated from the following formula.

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

[0080]

[(7) Quantitative Determination of Low Molecular Compound of Polyfunctional Compound and Oligomer Component Used for Coupling Reaction]

TSKgel G3000HXL, TSKgel G2000HXL and TSKgel G1000HXL manufactured by Tosoh Corp. were used as GPC columns; THF was used as an eluting solution; and GPC apparatus, HLC-8220 manufactured by Tosoh Corp. was used.

GPC measurement was performed using RI as a detector, and under conditions of an oven temperature of 40°C and

an eluent flow rate of 1.0 mL/minute, and injecting 200 μ L of a THF solution of 1.0 mg/mL of a measurement sample.

The molecular weight was calibrated by the standard polystyrene.

Thereby, there were obtained the contents of "a glycidylamino group-containing low molecular compound having 2 or more tertiary amino groups and 3 or more glycidyl groups bonded to the tertiary amino groups in a molecule" and "an oligomer component of a dimer or higher oligomer of the glycidylamino group-containing low molecular compound" in the polyfunctional compound.

[0081]

[(8) Conversion Rate]

About 20 mL of the polymer solution obtained from the outlet of the polymerization vessel was injected into a bottle of 100 mL in which 0.50 mL of n-propyl benzene and about 20 mL of toluene as internal standards were sealed, to produce a sample.

This sample was measured by gas chromatography provided with a packed column on which Apiezon grease was supported. An amount of a residual monomer in the polymer solution was determined from calibration curves of a butadiene monomer and a styrene monomer preliminarily obtained. The conversion rates of the butadiene monomer and the styrene monomer were determined.

[0082]

[(9) MSR (Mooney Stress Relaxation)]

A Mooney viscosity and a Mooney relaxation rate were measured at a temperature of 120°C using VR1132 manufactured by Ueshima Seisakusho Co., Ltd. as a Mooney viscosity meter by methods specified in ISO289-1 and ISO289-4 (2003).

First, preheating was performed at 120°C for 1 minute, and thereafter, a rotor was rotated at 2 rpm. A torque after 4 minutes was measured to obtain a Mooney viscosity (ML_{1+4}). Then, the rotation of the rotor was immediately stopped, and a torque (T) every 0.1 second for 1.6 to 5 seconds after stopping was recorded in a Mooney unit. An inclination of a straight line in plotting the torque and the time (t (second)) with bilateral logarithm was determined, and the absolute value thereof was denoted as a Mooney relaxation rate (MSR).

Since more branches reduce the Mooney relaxation rate (MSR) when the Mooney viscosity is equal, the Mooney relaxation rate (MSR) can be used as the index of the branching degree.

[0083]

Example 1

A vertical polymerization vessel having an internal volume of 10 liter, having an inlet at the bottom and an outlet at the top, and equipped with a stirrer and a temperature controlling jacket was used. The ratio (L/D)

of an internal height and a diameter of the vertical polymerization vessel was 4.

1,3-Butadiene, styrene, hexane and n-butyllithium whose impurities such as moisture have been removed in advance were mixed at rates of 27.3 g/minute, 12.9 g/minute, 182.9 g/minute, and 0.006 g/minute, respectively in a static mixer immediately before entering the polymerization vessel. The mixed solution was then continuously fed to the bottom of the polymerization vessel at the above-described rate. Further, 2,2-bis(2-oxolanyl)propane as a polar substance and n-butyllithium as a polymerization initiator were fed to the bottom of the polymerization vessel at rates of 0.0402 g/minute and 0.0133 g/minute, respectively. A polymerization reaction was continuously performed so that the inner temperature at the outlet of the polymerization vessel was set to 105°C. At this time, a mean residence time in the polymerization vessel was 30 minutes.

1,3-Butadiene used contained 1,2-butadiene of 70 ppm.
[0084]

After performing the polymerization reaction as described above, a living polymer solution was made to continuously flow out from a pipe connected to the top portion of the polymerization vessel.

A sampling nozzle was provided in the middle of the pipe.

The pipe was led to a bottom of a coupling reactor performing the next step. A polyfunctional compound was fed from a pipe on the near side of the coupling reactor. [0085]

A residence time of the living polymer solution from the outlet of the polymerization vessel to the near side of the coupling reactor was 1 minute.

A mixture made of tetraglycidyl-1,3-bisaminomethylcyclohexane and an oligomer component of a dimer or higher oligomer thereof was used as the polyfunctional compound. The mixture was made of 90% by mass of the tetraglycidyl-1,3-bisaminomethylcyclohexane and 10% by mass of the oligomer based on the total amount of the polyfunctional compound.

The mixture was used as a solution diluted 1,000 times with cyclohexane. The polyfunctional compound was fed at a rate of 0.0095 g/minute, that is, the solution diluted 1,000 times was fed at a rate of 9.5 g/minute to carry out a coupling reaction in the coupling reactor. [0086]

The coupling reactor had an internal volume of 1.5 liter, which was 15% based on the volume of the polymerization vessel.

A mean residence time in the coupling reactor was 4.3 minutes.

The coupling reactor having a cylindrical shape and equipped with a stirring blade was used. The inner

diameter D of the coupling reactor was 0.104 m; the diameter d of the stirring blade thereof was 0.083 m; and the ratio d/D of the stirring blade to the inner diameter was 0.8.

A rotation number n of the stirrer was 10s^{-1} ; and a product nd of the rotation number and the blade diameter was 0.83.

The coupling reactor was kept warm by a steam trace so that the inner temperature thereof was 95°C .

An automatic pressure control valve as an opening-degree adjusting unit was disposed in a discharging pipe from the coupling reactor.

A pressure of the outlet of the top portion of the above-described polymerization vessel was detected, and the opening-degree adjusting unit was controlled so that the pressure was set to 0.9 MPaG.

[0087]

The discharging pipe from the coupling reactor was introduced into a reservoir with a stirrer having a volume of 100 liter.

A sampling nozzle was provided on the downstream of the above-described automatic pressure control valve.

A residence time from the outlet of the above-described polymerization vessel to the sampling nozzle was 6.5 minutes. A residence time immediately before entering the reservoir was 7 minutes.

An antioxidant and an extender oil were continuously added before entering the reservoir.

0.5 Part by mass of BHT (dibutylhydroxytoluene) as the antioxidant per 100 parts by mass of the polymer obtained after the coupling reaction, that is, the polymer in which a solvent was removed from the polymer solution was added. 37.5 Parts by mass of S-RAE oil (NC-140 manufactured by Japan Energy Corporation) per 100 parts by mass of the polymer was added as the extender oil.

The pipe from the outlet of the polymerization vessel to the reservoir was sufficiently kept warm.

A pressure of the reservoir was 0.2 MPa.

The polymer solution of the reservoir was sent to the finisher; the solvent was removed; and the polymer was collected.

A drum drier was used as the finisher.

[0088]

In the state where the polymerization reaction in the above-described polymerization vessel was constant, the polymer solution was extracted in small quantities into a mixed solution of about 1 mL of methanol and about 30 mL of cyclohexane from the sampling nozzle provided in the discharging pipe from the polymerization vessel, while sufficiently taking care so that the polymer solution was not brought into contact with air. After the antioxidant (BHT) was added so that the amount of the

antioxidant was set to 0.2 g per 100 g of the polymer, the solvent was removed by the drum drier to obtain a sample for Mooney viscosity measurement.

The sample was further passed at ten times by a 6-inch roll set to 110°C.

The amount of n-butyllithium which is the polymerization initiator used in the polymerization reaction was increased and decreased so that the Mooney viscosity (ML-I) at 110°C of the sample and the fluctuation range thereof were within a range of 70 ± 3 .

Specifically, the amount of n-butyllithium was controlled so that the amount of n-butyllithium was increased by 1% when the Mooney viscosity approached the upper limit, and the amount of n-butyllithium was decreased by only 1% when the Mooney viscosity approached the lower limit.

With respect to the polymerization conversion rate in a place where the solution was left out of the polymerization vessel, the polymerization conversion rates of butadiene and styrene respectively reached 99.5% and 98.5%.

[0089]

The polymer solution sampled from the sampling nozzle provided in the discharging pipe from the above-described coupling reactor was extracted in small quantities into a mixed solution of about 1 mL of methanol and about 30 mL of cyclohexane while

sufficiently taking care so that the polymer solution was not brought into contact with air. After the antioxidant (BHT) was added so that the amount of the antioxidant was set to 0.2 g per 100 g of the polymer, the solvent was removed by the drum drier to obtain a sample for Mooney viscosity measurement.

The Mooney viscosity (ML-C) at 110°C of the branched conjugated diene-based polymer after the coupling reaction and the fluctuation range thereof were 135 ± 3 .

The molecular weight distribution of the branched conjugated diene-based polymer according to GPC had one peak. The weight-average molecular weight (Mw-C) was 830,000, and the ratio of the weight-average molecular weight and the number-average molecular weight (Mw-C/Mn-C) was 2.5.

A bound styrene content was 32% by mass, and a 1,2-bond content in a butadiene bond unit was 38 mol%.

With respect to the styrene chain, an amount of block styrene by Kolthoff method was 0% by mass; an amount of a styrene single chain by ozone decomposition was 47% by mass based on the total amount of styrene; and a content of a styrene long chain having at least 8 styrene units connected to each other was 1% by mass.

A coupling reaction ratio, that is, a ratio of the branched conjugated diene-based polymer adsorbed into a silica column was 45% by mass.

The Mooney viscosity and the Mooney relaxation rate (MSR) were measured by the method of ISO 289-4: 2003. The Mooney viscosity ML1+4 at 120°C was 125, and the MSR was 0.351.

Furthermore, to this conjugated diene-based polymer solution, 37.5 parts by mass of S-RAE oil (NC-140 manufactured by Japan Energy Corporation) based on 100 parts by mass of the branched conjugated diene-based polymer was added, and the solvent was then removed to obtain an oil-extended branched conjugated diene-based polymer (sample PA).

It was confirmed that generation of a gel was not observed in the obtained branched conjugated diene-based polymer and the equipment.

[0090]

[Comparative Example 1]

An automatic pressure control valve was not provided in "a discharging pipe from a coupling reactor" but provided in a discharging pipe from the above-described polymerization vessel.

Other conditions were the same as those of the example 1.

A Mooney viscosity (ML-I) at 110°C of the copolymer before performing the coupling reaction and the fluctuation range thereof were 70 ± 3 . A Mooney viscosity (ML-C) at 110°C of the branched conjugated diene-based

polymer after the coupling reaction and the fluctuation range thereof were 128 ± 9 .

A weight-average molecular weight (M_w -C) of the branched conjugated diene-based polymer after the coupling reaction was 790,000, and a ratio of the weight-average molecular weight and the number-average molecular weight (M_w -C/ M_n -C) was 2.7.

A bound styrene content was 32% by mass, and a 1,2-bond content in a butadiene bond unit was 38 mol%.

A coupling reaction ratio, that is, a ratio of the branched conjugated diene-based polymer adsorbed into a silica column was 40% by mass.

A Mooney viscosity and a Mooney relaxation rate (MSR) were similarly measured. The Mooney viscosity ML1+4 at 120°C was 117, and the MSR was 0.422.

The branched conjugated diene-based polymer was further oil-extended to obtain an oil-extended branched conjugated diene-based polymer (sample PB).

Slight generation of a gel was observed in the obtained branched conjugated diene-based polymer and the reservoir.

[0091]

[Comparative Example 2]

Butadiene, styrene, hexane and n-butyllithium were mixed at rates of 13.65 g/minute, 6.45 g/minute, 91.45 g/minute, and 0.003 g/minute, respectively in a static mixer immediately before entering a polymerization vessel.

The mixed solution was then continuously fed to the bottom of the polymerization vessel at the above-described rate. Further, 2,2-bis(2-oxolanyl)propane as a polar substance and n-butyllithium as a polymerization initiator were fed to the bottom of the polymerization vessel at rates of 0.0201 g/minute and 0.00665 g/minute, respectively. A polymerization reaction was performed such that the inner temperature at the outlet of the polymerization vessel was 105°C.

At this time, a mean residence time in the polymerization vessel was 60 minutes.

[0092]

A living polymer solution was made to continuously flow out from the top portion of the polymerization vessel. A sampling nozzle was provided in the middle of the discharging pipe in the top portion of the polymerization vessel.

The pipe was led to the bottom of a coupling reactor performing a coupling reaction in the next step. A polyfunctional compound was fed from the pipe on the near side of the coupling reactor.

The pipe from the outlet of the polymerization vessel to the near side of the coupling reactor was three times longer than the apparatus used in the example 1.

A residence time from the outlet of the polymerization vessel to the near side of the coupling reactor was 6 minutes.

[0093]

A mixture made of tetraglycidyl-1,3-bisaminomethylcyclohexane and an oligomer component of a dimer or higher oligomer thereof was used as the polyfunctional compound. The mixture was made of 90% by mass of the tetraglycidyl-1,3-bisaminomethylcyclohexane and 10% by mass of the oligomer based on the total amount of the polyfunctional compound.

The mixture was used as a solution diluted 1,000 times with cyclohexane. The polyfunctional compound was fed at a rate of 0.00475 g/minute, that is, the solution diluted 1,000 times was fed at a rate of 4.75 g/minute to carry out a coupling reaction.

A mean residence time in the coupling reactor was 8.3 minutes.

An automatic pressure control valve as an opening-degree adjusting unit was disposed in a discharging pipe from the coupling reactor.

The pressure of the outlet of the top portion of the above-described polymerization vessel was detected, and the opening-degree adjusting unit was controlled so that the pressure was set to 0.9 MPaG.

A mean residence time from the outlet of the polymerization vessel to the sampling nozzle after the coupling reaction was 18 minutes.

[0094]

A Mooney viscosity (ML-I) at 110°C of the living copolymer before the coupling reaction and a fluctuation range thereof were 70 ± 7 . A Mooney viscosity (ML-C) at 110°C of the branched conjugated diene-based polymer after the coupling reaction and a fluctuation range thereof were 123 ± 9 .

A weight-average molecular weight (Mw-C) of the branched conjugated diene-based polymer after the coupling reaction was 750,000, and a ratio of the weight-average molecular weight and the number-average molecular weight (Mw-C/Mn-C) was 2.8.

A bound styrene content was 32% by mass, and a 1,2-bond content in a butadiene bond unit was 38 mol%.

A coupling reaction ratio, that is, a ratio of the branched conjugated diene-based polymer adsorbed into a silica column was 35% by mass.

A Mooney viscosity and a Mooney relaxation rate (MSR) were similarly measured. The Mooney viscosity ML1+4 at 120°C was 113, and the MSR was 0.473.

The branched conjugated diene-based polymer was further oil-extended to obtain an oil-extended branched conjugated diene-based polymer (sample PC). Slight generation of a gel was observed in the obtained branched conjugated diene-based polymer and the polymerization vessel.

[0095]

In the example 1, the variation in the Mooney viscosity of the obtained branched conjugated diene-based polymer was little, and the coupling reaction ratio was also high.

Since the position of the automatic pressure control valve was provided in not the discharging pipe of the coupling reactor but the discharging pipe from the polymerization vessel in the comparative example 1, the Mooney viscosity of the obtained branched conjugated diene-based polymer was reduced, and the variation in the Mooney viscosity was also great. The branching degree and the coupling reaction ratio were also reduced.

Since the residence time until the polyfunctional compound was added from the outlet of the polymerization vessel was departed from the present invention in the comparative example 2, the Mooney viscosity of the obtained branched conjugated diene-based polymer was reduced, the variation in the Mooney viscosity was also great. The branching degree and the coupling reaction ratio were also reduced.

[0096]

A rubber composition was produced according to a composition shown in the following Table 1 using the (sample PA) to (sample PC) produced as described above, that is, the oil-extended branched conjugated diene-based polymers as raw material rubbers.

[0097]

[Table 1]

Oil-Extended Polymer Sample	137.5 parts by mass
Silica Ultrasil VN3 (1)	63 parts by mass
Carbon Seast KH (2)	7.00 parts by mass
Silang Coupling Agent Si75 (3)	5.04 parts by mass
Zinc Oxide	2.50 parts by mass
Stearic Acid	1.00 parts by mass
Sunnoc N(WAX) (4)	1.50 parts by mass
Antioxidant 810NA (5)	2.00 parts by mass
Sulfur	1.70 parts by mass
Vulcanization Accelerator CZ (6)	1.70 parts by mass
Vulcanization Accelerator D (7)	2.00 parts by mass

[0098]

The raw material shown in the above-described Table 1 will be shown later.

(1) Silica Ultrasil VN3: manufactured by Evonik Degussa Japan Co., Ltd.

(2) Seast KH: manufactured by Cabot Japan Co., Ltd., Showblack N339

(3) Si75: manufactured by Evonik Degussa Japan Co., Ltd.

(4) Sunnoc N(WAX): manufactured by Ouchi Shinko Chemical Industrial Co., Ltd.

(5) Antioxidant 810NA: manufactured by Ouchi Shinko Chemical Industrial Co., Ltd., Nocrac 810-NA

(6) Vulcanization Accelerator CZ: manufactured by Ouchi Shinko Chemical Industrial Co., Ltd., Nocceler CZ-G

(7) Vulcanization Accelerator D: manufactured by Ouchi Shinko Chemical Industrial Co., Ltd., Nocceler D

[0099]

[Producing Method of Rubber Composition]

As a first stage kneading, a raw material rubber, fillers (silica and carbon black), an organic silane coupling agent, an oil, zinc oxide and stearic acid were kneaded using a closed kneading machine (internal volume: 0.3 L) provided with a temperature control device with the filling ratio of 65% and under the condition of rotor frequencies of 50/57 rpm.

At this time, the temperature of the closed kneading machine was controlled, and a crude rubber composition was obtained at the discharging temperature (composition) of 155 to 165°C.

Then, as a second stage kneading, the crude rubber composition obtained in the above was cooled to room temperature, thereafter, added with an antioxidant, and again kneaded in order to improve the dispersion of silica, thereby obtaining a rubber composition. Also in this case, the discharging temperature (compositionn) was controlled at 155 to 160°C by the temperature control of the kneading machine.

After the cooling, as a third stage kneading, sulfur and a vulcanization accelerator were kneaded by open rolls set at 70°C.

The kneaded material was molded, and vulcanized at 160°C for a predetermined time on a vulcanizing press, to obtain a vulcanized rubber composition which is the object.

The physical properties of the above-described rubber composition and vulcanized rubber composition were measured by the following method. The measurement results of the physical properties are shown in Table 2.

[0100]

[Measuring Method of Physical Properties of Rubber composition and Vulcanized Rubber Composition]

<(1) Bound Rubber (% by Mass)>

About 0.2 g of the rubber composition after the above-described second-stage kneading was cut into pieces of about 1-mm square, put in a Harris cage (100-mesh metal screen) and measured for the weight.

Thereafter, the pieces were immersed in toluene for 24 hours, dried, and measured for the weight.

Taking undissolved components into account, the amount of the rubber bonded to the fillers was calculated, and the proportion of the rubber bonded to the fillers based on the rubber amount in the first rubber composition was determined.

[0101]

<(2) Mooney Viscosity of Rubber composition>

The Mooney viscosity of the rubber composition after completion of the above-described second-stage kneading was measured using an L type rotor according to JIS K6300-1 using a Mooney viscosity meter. The rubber composition was preheated at 130°C for 1 minute, and then rotated in two rotations per minute. The viscosity of

the rubber composition at 4 minutes after starting of the rotation was measured.

The Mooney viscosity having a small value was judged to provide small consumption energy during kneading for good processability.

[0102]

<(3) Hardness of Vulcanized Rubber Composition>

The hardness was measured by a durometer of type A according to JIS K6253 using a constant pressure loader "CL-150L type" as a digital rubber hardness tester "DD2-A type" manufactured by Kobunshi Keiki Co., Ltd.

[0103]

<(4) Tensile Test for Vulcanized Rubber Composition>

The tensile stress at 100% elongation (100% Mo) (unit: MPa), tensile stress at 300% elongation (300% Mo) (unit: MPa), tensile strength (unit: MPa) and elongation at breaking (unit: %) of a test sample were measured using the test sample of dumbbell shape No. 3 according to the tensile testing method of JIS K6251.

Higher tensile strength and elongation at breaking of the test sample were judged to be good.

[0104]

<(5) Impact Resilience of Vulcanized Rubber Composition (%)>

The impact resilience was measured at 0°C and at 50°C by Rupke type impact resilience testing method according to JIS K6255.

The impact resilience at 0°C was used as an index of wet skid resistance, that is, gripping performance. Lower impact resilience was judged to be good.

The impact resilience at 50°C was used as an index of lower rolling resistance of tires. Higher rolling resistance was judged to be good.

[0105]

<(6) Heat Generation of Vulcanized Rubber Composition (°C)>

The heat generation was tested using a Goodrich Flexometer, at a frequency of 1,800 rpm, at stroke of 0.225 inch, on a load of 55 pounds, with a measurement starting temperature of 50°C, and indicated by a difference between a temperature at 20 minutes after starting of the test and the starting temperature.

The difference having a smaller value was judged to provide excellent heat generation.

[0106]

<(7) Measurement of Viscoelastic Characteristics of Vulcanized Rubber Composition>

A $\tan \delta$ was measured using an ARES viscoelasticity tester, manufactured by Rheometrics Scientific Inc., and varying the strain at a frequency of 10 Hz and at each measurement temperature (0°C and 50°C) by the torsional mode.

A higher $\tan \delta$ (loss tangent) measured at a low temperature (0°C) and at a strain of 1% was judged to

exhibit more excellent wet skid resistance, that is, gripping performance; and a lower $\tan \delta$ (loss tangent) measured at a high temperature (50°C) and at a strain of 3% was judged to exhibit a smaller hysteresis loss, and lower rolling resistance of tires, that is, a lower fuel consumption.

[0107]

<(8) Abrasion Resistance of Vulcanized Rubber Composition (index)>

With respect to the abrasion resistance, the abrasion amount was measured according to JIS K 6264-2 using an Acron rubber abrasion tester manufactured by Yasuda Seiki Seisakusho, Ltd., after 3,000 rotations on a load of 44.1 N in the test method A.

The example 1 was indicated as the index set as 100.

A higher index indicated a smaller abrasion amount, which was judged to be favorable.

[0108]

[Table 2]

Examples/Comparative Examples	Example 1	Comparative Example 1	Comparative Example 2
Polymer Sample	PA	PB	PC
Bound Rubber % by mass	45	38	36
Mooney Viscosity of Rubber Composition	74	65	60
Hardness type A	62	62	60
Tensile Test			
100%Mo MPa	2.1	2	1.9
300%Mo MPa	10.1	9.2	8.9
Tensile Strength MPa	20	19.4	17.6
Elongation at Breaking %	500	480	470

Rupke Impact Resilience	0°C %	10	10	10
Rupke Impact Resilience	50°C %	59	56.5	56
Goodrich Heat Generation	ΔT °C	25	29	33
Viscoelasticity ARES				
$\tan \delta$ (0°C)	1% strain	0.41	0.4	0.395
$\tan \delta$ (50°C)	3% strain	0.185	0.19	0.193
Acron Abrasion	Index	100	95	93

[0109]

As is apparent from the example 1 and the comparative examples 1, 2 in the above-described Table 2, the rubber composition using the branched conjugated diene-based polymer produced by the producing method of the present embodiment had an increased bound rubber amount; and since the vulcanized rubber composition had high impact resilience at the high temperature, and a low $\tan \delta$ (loss tangent) at the high temperature, the vulcanized rubber composition had little hysteresis loss, and low rolling resistance of tires, that is, excellently low fuel consumption.

The balance between the low fuel consumption and the wet skid resistance ($\tan \delta$ at the low temperature) was also excellent. Further, the heat generation was little, and the abrasion resistance was also good.

[0110]

Since the position of automatic pressure control valve was provided in not the discharging pipe of the coupling reactor but the discharging pipe from the polymerization vessel in the comparative example 1, the

Mooney viscosity of the obtained copolymer was reduced; the variation in the Mooney viscosity was also great; and the coupling reaction ratio was also reduced.

Therefore, since the bound rubber amount decreased; the impact resilience at the high temperature was low; and the $\tan \delta$ at the high temperature was high, the hysteresis loss was great, and the low rolling resistance of tires, that is, the low fuel consumption was poor.

The balance between the low fuel consumption and the wet skid resistance (the $\tan \delta$ at the low temperature) was also poor. Further, the heat generation was high, and the abrasion resistance was also poor.

[0111]

Since the residence time until the polyfunctional compound was added from the outlet of the polymerization vessel was departed from the present invention in the comparative example 2, the Mooney viscosity of the obtained branched conjugated diene-based polymer was reduced; the variation in the Mooney viscosity was also great; and the coupling reaction ratio was also reduced.

Therefore, since the bound rubber amount decreased; the rupture strength was poor; the impact resilience at the high temperature was low; and the $\tan \delta$ at the high temperature was high, the hysteresis loss was great, and the low rolling resistance of tires, that is, the low fuel consumption was poor. The balance between the low fuel consumption and the wet skid resistance (the $\tan \delta$

at the low temperature) was also poor. Further, the heat generation was high, and the abrasion resistance was also poor.

[0112]

The present application is based on Japanese Patent application No. 2009-116541, filed to Japan Patent Office on May 13, 2009, the subject of which is incorporated herein by reference.

Industrial Applicability

[0113]

The producing method of the branched conjugated diene-based polymer of the present invention has industrial applicability to the producing technique of the branched conjugated diene-based polymer constituting a rubber composition suitable for tire rubber, vibration absorbing rubber and footwear applications or the like.

Claims

[Claim 1]

A method for producing a branched conjugated diene-based polymer comprising:

a polymerization step of continuously polymerizing a conjugated diene compound or copolymerizing a conjugated diene compound and a vinyl aromatic compound in a hydrocarbon solvent using an alkali metal-based initiator in a polymerization vessel to obtain a living polymer or copolymer;

a coupling step of performing a coupling reaction by reacting the living polymer or copolymer with a polyfunctional compound in a coupling reactor that is connected to the polymerization vessel via a pipe provided at an outlet of the polymerization vessel from which the living polymer or copolymer is discharged, and that is connected to a discharging pipe having an opening-degree adjusting unit; and

a solvent removal step,

wherein the living polymer or copolymer is reacted with the polyfunctional compound within 5 minutes after the polymerization step, and

a pressure at the outlet of the polymerization vessel is controlled to 0.5 to 2 MPaG by the opening-degree adjusting unit.

[Claim 2]

The method for producing the branched conjugated diene-based polymer according to claim 1, wherein the coupling reactor is equipped with a rotary stirrer and is a tank reactor having a volume of 0.5 to 50% based on the volume of the polymerization vessel.

[Claim 3]

The method for producing the branched conjugated diene-based polymer according to claim 1 or 2, wherein the polymerization vessel is a tank reactor equipped with a stirrer; and the conjugated diene compound and the vinyl aromatic compound are randomly copolymerized in the presence of a polar compound in the polymerization step.

[Claim 4]

The method for producing the branched conjugated diene-based polymer according to any one of claims 1 to 3, further comprising a step of sampling the living polymer or copolymer between the polymerization step and the coupling step and measuring a Mooney viscosity thereof, and sampling the branched conjugated diene-based polymer when a residence time from the outlet of the polymerization vessel is less than 15 minutes after the coupling step and measuring a Mooney viscosity thereof.

[Claim 5]

The method for producing the branched conjugated diene-based polymer according to any one of claims 1 to 4, wherein one tank reactor equipped with a stirrer is used as the polymerization vessel.

[Claim 6]

The method for producing the branched conjugated diene-based polymer according to any one of claims 1 to 5, wherein a polyepoxy compound having a tertiary amino group in a molecule is used as the polyfunctional compound.

[Claim 7]

The method for producing the branched conjugated diene-based polymer according to any one of claims 1 to 6, wherein the polyfunctional compound comprises a glycidylamino group-containing low molecular compound having 2 or more tertiary amino groups and 3 or more glycidyl groups bonded to the tertiary amino groups in a molecule, and an oligomer component of a dimer or higher oligomer of the glycidylamino group-containing low molecular compound; and

the polyfunctional compound comprises 75 to 95% by mass of the low molecular compound and 25 to 5% by mass of the oligomer based on a total amount of the polyfunctional compound.

[Claim 8]

The method for producing the branched conjugated diene-based polymer according to any one of claims 1 to 7, wherein a coupling reaction ratio of the living polymer or copolymer and the polyfunctional compound is 10 to 80% by mass.

[Claim 9]

The method for producing the branched conjugated diene-based polymer according to any one of claims 1 to 8, wherein the branched conjugated diene-based polymer has one peak in a molecular weight distribution measured by gel permeation chromatography (GPC), and has a weight-average molecular weight of 500,000 to 2,000,000 with respect to a polystyrene-equivalent molecular weight.

[Claim 10]

The method for producing the branched conjugated diene-based polymer according to any one of claims 1 to 9, wherein the branched conjugated diene-based polymer is a copolymer of a conjugated diene compound and a vinyl aromatic compound; an amount of a single chain of the vinyl aromatic compound by decomposition with ozone is 40% or more based on a total amount of the vinyl aromatic compound; and an amount of 8 or more chains of the vinyl aromatic compound is 5% or less.