

## DESCRIPTION

### METHOD FOR MANUFACTURING MODIFIED POLYMER AND HYDROGEN ADDUCT THEREOF

5

#### TECHNICAL FIELD

[0001]

The present invention relates to a method for producing a modified polymer or a hydrogenated product thereof. More specifically, the invention relates to a method for producing a modified polymer or a hydrogenated product thereof that removes a silanol compound that inhibits polymerization by distillation and extraction from a solvent fraction that has been separated from a solid fraction including a polymer or the like using a steam stripping method or the like, and recycles the raffinate as a polymerization solvent.

#### 15 BACKGROUND ART

[0002]

A polymer or a copolymer having different properties or the like can be produced using a conjugated diene and an aromatic vinyl compound by changing the content of the aromatic vinyl compound or the like, and has been used in various applications. Such a polymer or copolymer is normally produced by solution polymerization that uses a hydrocarbon-based solvent or the like and an active organometal catalyst or the like as a polymerization initiator. It is necessary to use a high-purity raw material (monomer) and a high-purity polymerization solvent for solution polymerization since impurities affect the polymerization reaction. However, the solvent recovered after polymerization includes light components such as water, unreacted monomer, an alcohol, and an aldehyde, and heavy components such as a low-molecular-weight polymer (e.g., oligomer) and various additives (e.g., antioxidant). It is undesirable to recycle the recovered solvent directly for polymerization.

[0003]

A functional group may be introduced into the main chain, the side chain, or the molecular end of the above polymer or copolymer during production using the modification method described later in order to provide various properties. A functional group that includes an active proton (e.g., amino group or mercapto group) is useful as the functional group although the desirable functional group differs depending on the properties required for the modified polymer or the copolymer. However, when a compound having an active proton is added to the reaction solution, the polymerization active end may be inactivated due to the active proton. In order to deal with the above problem, a method has been proposed that introduces a functional group into a polymer using a compound in which an active proton is protected with a silyl group, and effects hydrolysis using an appropriate method to obtain a modified polymer or a modified copolymer that includes a functional group having an active proton. In this case, a silanol compound is included in a solvent to be recovered.

A functional group-containing compound used to incorporate a functional group in the main chain, the side chain, or the molecular end of a polymer is referred hereinafter to as “modifier”. Note that three modification methods may be used as described later, and the term “modifier” is used as a generic name for an initiator, a functional group-introducing monomer, or a polymerization terminator having a functional group.

[0004]

When a silanol compound is included in a polymerization solvent, polymerization is inhibited by the silanol compound. When the content of the silanol compound is low, the silanol compound can be made harmless by increasing the amount of the polymerization initiator to produce a metal silanolate, for example. However, since a silanol compound is produced when the reaction solution containing the metal silanolate is brought into contact with water in a solvent removal step using a steam stripping method or the like, the solvent to be recovered includes silanol compounds derived from the modifier and the metal silanolate. Therefore, when the solvent is repeatedly recycled, the silanol compound concentration in the solvent increases, and it becomes difficult to make the silanol compound harmless by

increasing the amount of the polymerization initiator, for example. In this case, the recovered solvent cannot be recycled as a polymerization solvent. Therefore, it is necessary to remove the silanol compound in order to recycle the recovered solvent for polymerization when producing a modified polymer or a hydrogenated product thereof.

5 The hydrogenated product is obtained by hydrogenating the modified polymer or the copolymer using a normal method, and the silanol compound is included in the solvent recovered using a steam stripping method or the like.

[0005]

10 It is necessary to remove a component that inhibits polymerization when recycling the recovered solvent as a polymerization solvent. For example, a method has been known that washes a hydrocarbon-based solvent separated from a polymer with water, followed by dehydration to remove a lower alcohol used as a polymerization terminator, and recycles at least part of the hydrocarbon-based solvent for a polymerization reaction (see Patent Document 1, for example). A method that removes a silanol compound through adsorption  
15 on alumina has also been known (see Patent Document 2, for example).

## PRIOR TECHNICAL DOCUMENT

## PATENT DOCUMENT

[0006]

20 Patent Document 1: JP-A H9-255716

Patent Document 2: WO2010/056694

## SUMMARY OF THE INVENTION

## TECHNICAL PROBLEM

25 [0007]

According to the method disclosed in Patent Document 1 that removes a lower alcohol through washing with water and dehydration, it is possible to remove a silanol compound in addition to a lower alcohol by optimizing the volume of water used for washing.

However, since the method treats the entire solvent, the construction cost of washing equipment increases, and an increase in running cost occurs due to use of a large amount of water. According to the method disclosed in Patent Document 2 that utilizes adsorption on alumina, since the adsorption capacity of alumina is not sufficiently high, it is necessary to provide adsorption equipment having a very large filling capacity, equipment that replaces or regenerates several tons of alumina per hour, and the like in order to remove a silanol compound produced in an amount of several kilograms per hour, for example. Therefore, the method is impractical for industrial applications.

[0008]

The present invention was conceived in view of the above situation. An object of the invention is to provide a method for producing a modified polymer or a hydrogenated product thereof that can remove a silanol compound that inhibits polymerization by distillation and extraction from a solvent fraction that has been separated from a solid fraction including a polymer or the like using a steam stripping method or the like, and recycle the raffinate as a polymerization solvent.

## SOLUTION TO PROBLEM

[0009]

The present invention is as follows.

1. A method for producing a modified polymer or a hydrogenated product thereof comprising polymerizing a monomer comprising at least one of a conjugated diene and an aromatic vinyl compound in a hydrocarbon-based solvent as a polymerization solvent using an active organometal as a polymerization initiator to obtain a modified polymer or a hydrogenated product thereof, the modified polymer including a functional group in at least one of a main chain and a side chain,

the functional group being introduced into the modified polymer using a compound having a functional group protected with a silyl group as a polymerization initiator, a functional group-introducing monomer, or a polymerization terminator,

the method further sequentially comprising:

- (a) a solvent removal step that separates a reaction solution in which the modified polymer or the hydrogenated product is dissolved in the polymerization solvent into a solvent fraction including the hydrocarbon-based solvent, and a solid fraction including the modified polymer or the hydrogenated product;
- (b) a low-boiling fraction separation step that distills the solvent fraction to separate a low-boiling fraction including the hydrocarbon-based solvent and a silanol compound; and
- (c) a silanol removal step that removes at least part of the silanol compound from the low-boiling fraction by liquid-liquid extraction using the low-boiling fraction and an extraction solvent,

at least part of a raffinate from which the silanol compound has been removed by the liquid-liquid extraction being recycled as a polymerization solvent.

2. The method according to 1 above, wherein the silanol compound is at least one compound selected from the group consisting of trimethylsilanol, ethyldimethylsilanol, diethylmethylsilanol, dimethylpropylsilanol, dimethylisopropylsilanol, ethylmethylpropylsilanol, ethylmethylisopropylsilanol, triethylsilanol, n-butyldimethylsilanol, sec-butyldimethylsilanol, and tert-butyldimethylsilanol.

3. The method according to 1 or 2 above, wherein the extraction solvent used for the liquid-liquid extraction is water.

4. The method according to any one of 1 to 3 above, wherein a content of the low-boiling fraction in the solvent fraction is in a range from 0.1% to 20% by mass.

5. The method according to any one of 1 to 4 above, wherein a content of the silanol compound in the low-boiling fraction is in a range from 200 ppm to 10% by mass.

6. The method according to any one of 1 to 5 above, wherein a weight ratio (Me/Mb) of the extraction solvent (Me) to the low-boiling fraction (Mb) is in a range from 0.5 to 10.

7. The method according to any one of 1 to 6 above, wherein a content of the silanol compound in the at least part of the raffinate that is recycled as the polymerization solvent is 200 ppm or less by mass.

8. The method according to any one of 1 to 7 above, further comprising a step that separates a randomizer between the low-boiling fraction separation step and the silanol removal step, or after the silanol removal step, when the randomizer is used for the polymerization, and at least part of the randomizer is included in the low-boiling fraction.

5

## ADVANTAGEOUS EFFECTS OF THE INVENTION

[0010]

The method for producing a modified polymer or a hydrogenated product thereof according to the invention is designed so that a modified polymer or a hydrogenated product is produced, the solvent fraction obtained by separating the modified polymer or the like from the reaction solution is distilled to separate the low-boiling fraction containing the hydrocarbon-based solvent and the silanol compound, the silanol compound is removed from the low-boiling fraction by liquid-liquid extraction, and the raffinate is recycled as the polymerization solvent. Since only the low-boiling fraction is subjected to liquid-liquid extraction to remove the silanol compound, the silanol compound can be efficiently and sufficiently removed. Since only a small amount of solvent is treated, the construction cost of liquid-liquid extraction equipment can be reduced while reducing the running cost of the extraction solvent. The silanol compound can also be removed by disposing of and incinerating the low-boiling fraction. However, the method for producing a modified polymer or a hydrogenated product thereof according to one aspect of the invention can recycle the hydrocarbon-based solvent included in the low-boiling fraction with reduced running cost.

In the case where the silanol compound is at least one compound among trimethylsilanol, ethyldimethylsilanol, diethylmethylsilanol, dimethylpropylsilanol, dimethylisopropylsilanol, ethylmethylpropylsilanol, ethylmethylisopropylsilanol, triethylsilanol, n-butyldimethylsilanol, sec-butyldimethylsilanol, and tert-butyldimethylsilanol, the silanol compound can be separated and removed from the solvent fraction separated from the polymer or the like by distillation together with the

hydrocarbon-based solvent as the low-boiling fraction.

In the case where the extraction solvent used for liquid-liquid extraction is water, the apparatus and the operation can be simplified as compared with a case of using an organic solvent. It is also advantageous from the environmental point of view.

5 In the case where a content of the low-boiling fraction in the solvent fraction is in a range from 0.1% to 20% by mass, the silanol compound can be sufficiently distilled, and the construction cost of liquid-liquid extraction equipment can be reduced while reducing the running cost.

10 In the case where a content of the silanol compound in the low-boiling fraction is in a range from 200 ppm to 10% by mass, the hydrocarbon-based solvent and the silanol compound included in the low-boiling fraction can be easily and sufficiently separated by liquid-liquid extraction.

15 In the case where a weight ratio (Me/Mb) of the extraction solvent (Me) to the low-boiling fraction (Mb) is in a range from 0.5 to 10, almost the entire silanol compound included in the low-boiling fraction can be separated and removed from the hydrocarbon-based solvent while reducing the amount of extract including the silanol compound.

20 In the case where a content of the silanol compound in at least part of the raffinate that is recycled as the polymerization solvent is 200 ppm or less by mass, the raffinate can be advantageously recycled as the polymerization solvent.

25 In the case where the method further includes a step that separates a randomizer between the low-boiling fraction separation step and the silanol removal step, or after the silanol removal step, when the randomizer is used for the polymerization, and at least part of the randomizer is included in the low-boiling fraction, a fraction containing the randomizer at a high concentration can be recovered, and the randomizer can be recycled by optionally combining an appropriate purification step.

## BRIEF DESCRIPTION OF DRAWINGS

[0011]

FIG. 1 is a schematic view illustrating a process implemented using an example of a solvent purification apparatus according to the present invention.

FIG. 2 is a schematic view illustrating a process implemented using another example  
5 of a solvent purification apparatus according to the present invention.

#### REFERENCE SIGNS LIST

[0012]

1: distillation column, 2: heater, 3: condenser, 4: reflux drum, 5, 6: pump, 7: raw material  
10 solvent feed pipe, 8: drawing pipe, 9: distillation pipe, 10: extraction column, 11: extraction  
solvent feed pipe, 12: extraction solvent phase drawing pipe, 13: solvent phase drawing pipe,  
14: gas drawing pipe, 15: distillation column, 16: heater, 17: condenser, 18: reflux drum, 19,  
20: pump, 21: raw material solvent feed pipe, 22: drawing pipe, 23: distillation pipe, 24: gas  
drawing pipe, 25: distillation column, 26: heater, 27: condenser, 28: reflux drum, 29, 30:  
15 pump, 31: distillation pipe, 32: drawing pipe, 33: gas drawing pipe, 34: condenser, 35:  
extraction column, 36: extraction solvent feed pipe, 37: extraction solvent phase drawing pipe,  
38: solvent phase drawing pipe, a: solvent fraction, b: bottom product from distillation  
column 1, c: overhead extract from extraction column 10, d: solvent fraction, e: bottom  
product from distillation column 15, f: distillate from distillation column 25, g: overhead  
20 extract from extraction column 35

#### DESCRIPTION OF EMBODIMENTS

[0013]

A method for producing a modified polymer or a hydrogenated product thereof of the  
25 present invention includes polymerizing at least one of a conjugated diene and an aromatic  
vinyl compound as a monomer in a hydrocarbon-based solvent used as a polymerization  
solvent using an active organometal as a polymerization initiator to obtain a modified  
polymer or a hydrogenated product thereof, the modified polymer including a functional

group in at least one of a main chain and a side chain, the functional group being introduced into the modified polymer using a compound having a functional group protected with a silyl group as a polymerization initiator, a functional group-introducing monomer, or a polymerization terminator, the method further sequentially including the following steps (a)

5 to (c).

(a) A solvent removal step that separates a reaction solution in which the modified polymer or the hydrogenated product is dissolved in the polymerization solvent into a solvent fraction including the hydrocarbon-based solvent, and a solid fraction including the modified polymer or the hydrogenated product.

10 (b) A low-boiling fraction separation step that distills the solvent fraction to separate a low-boiling fraction including the hydrocarbon-based solvent and a silanol compound.

(c) A silanol removal step that removes at least part of the silanol compound from the low-boiling fraction by liquid-liquid extraction using the low-boiling fraction and an extraction solvent.

15 At least part of the raffinate from which the silanol compound has been removed by liquid-liquid extraction is recycled as a polymerization solvent.

The hydrogenated product may be obtained by hydrogenating the modified polymer using a known method. It is thus possible to obtain a modified polymer that shows excellent weatherability and the like.

20 [0014]

#### 1. Polymerization solvent

The hydrocarbon-based solvent used as the polymerization solvent is not particularly limited. It is preferable to use a hydrocarbon-based solvent having 4 to 8 carbon atoms.

Examples of the hydrocarbon-based solvent include n-butane, isobutane, n-pentane,

25 isopentane, n-hexane, cyclohexane, 1-pentene, 2-pentene, 1-hexene, 2-hexene, n-heptane, n-octane, benzene, toluene, xylene, ethylbenzene, and the like. Among these, n-butane, cyclohexane, n-hexane, n-heptane, and the like are normally used. These

hydrocarbon-based solvents may be used singly or in combination of two or more types

thereof.

[0015]

## 2. Polymerization initiator

The active organometal is used as a polymerization initiator required for polymerization. An alkali metal compound or an alkaline-earth metal compound is normally used as the active organometal. In this case, a polymer can be produced by anionic polymerization. The polymerization may be by batch polymerization or continuous polymerization. Examples of the alkali metal included in the active site of the molecule of the resulting polymer include lithium, sodium, and potassium. Examples of the alkaline-earth metal included in the active site of the molecule of the resulting polymer include magnesium, barium, and the like. It is particularly preferable to use a lithium compound as the active organometal.

[0016]

The compound used as the polymerization initiator containing an alkali metal or an alkaline-earth metal is not particularly limited. It is preferable to use an alkyllithium having a hydrocarbon group, a lithium compound having an amide group or an imide group (e.g., lithium alkyleneimide), a derivative thereof, or the like. Examples of other compounds used as the polymerization initiator containing an alkali metal or an alkaline-earth metal include sodium naphthalene, potassium naphthalene, n-butylmagnesium, n-hexylmagnesium, ethoxycalcium, calcium stearate, tert-butoxystrontium, ethoxybarium, isopropoxybarium, ethylmercaptobarium, tert-butoxybarium, phenoxybarium, diethylaminobarium, barium stearate, a barium ketyl, sodium biphenyl, a potassium-tetrahydrofuran complex, a potassium-diethoxyethane complex, a sodium salt of an  $\alpha$ -methylstyrene tetramer, and the like.

[0017]

When a lithium compound having a hydrocarbon group is used as the polymerization initiator, a polymer having a hydrocarbon group at the polymerization initiation end, and a polymerization active site at the other end can be obtained.

[0018]

The lithium compound having a hydrocarbon group preferably is a compound including a hydrocarbon group having 1 to 20 carbon atoms. Examples of the lithium compound include methyllithium, ethyllithium, n-propyllithium, isopropyllithium, n-butyllithium, sec-butyllithium, tert-octyllithium, n-decylolithium, phenyllithium, 2-naphthyllithium, 2-butylphenyllithium, 4-phenylbutyllithium, cyclohexyllithium, tert-butyllithium, n-hexyllithium, benzyllithium, stilbenelithium, 1,4-dilithiobutane, a reaction product of n-butyllithium, 1,3-butadiene, and divinylbenzene, and the like. Among these, n-butyllithium and sec-butyllithium are particularly preferable.

[0019]

When producing a polymer by anionic polymerization using a lithium compound or the like as the polymerization initiator, a conjugated diene and/or an aromatic vinyl compound may be subjected to anionic polymerization in an organic solvent that is inert to the reaction (e.g., hydrocarbon-based solvent such as an aliphatic, alicyclic, and aromatic hydrocarbon compound) using a lithium compound or the like as the polymerization initiator optionally in the presence of a randomizer (described later).

[0020]

### 3. Monomer

Examples of the conjugated diene include 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, 1,3-pentadiene, 1,3-hexadiene, 1,3-heptadiene, 2,3-dimethylbutadiene, 2-phenyl-1,3-butadiene, 3-methyl-1,3-pentadiene, 2-chloro-1,3-butadiene, and the like. These conjugated dienes may be used singly or in combination of two or more types thereof. Among these, 1,3-butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, and the like are normally used. In particular, 1,3-butadiene is widely used.

[0021]

Examples of the aromatic vinyl compound include styrene, 2-methylstyrene, 3-methylstyrene, 4-methylstyrene,  $\alpha$ -methylstyrene, 2,4-dimethylstyrene,

2,4-diisopropylstyrene, 4-tert-butylstyrene, 5-tert-butyl-2-methylstyrene, vinyl ethylbenzene, divinylbenzene, trivinylbenzene, divinyl naphthalene, tert-butoxystyrene, vinylbenzyl dimethylamine, (4-vinylbenzyl) dimethylaminoethyl ether, N,N-dimethylaminomethylstyrene, N,N-dimethylaminoethylstyrene, 2-ethylstyrene, 3-ethylstyrene, 4-ethylstyrene, 2-tert-butylstyrene, 3-tert-butylstyrene, 4-tert-butylstyrene, vinylxylene, vinyl naphthalene, vinyltoluene, vinylpyridine, diphenylethylene, tertiary amino group-containing diphenylethylene, and the like. These aromatic vinyl compounds may be used singly or in combination of two or more types thereof. Among these, styrene is normally used.

10 [0022]

When copolymerizing the conjugated diene and the aromatic vinyl compound, it is preferable to use 1,3-butadiene as the conjugated diene, and use styrene as the aromatic vinyl compound. These monomers show excellent living properties during anionic polymerization, and are easily available. When implementing solution polymerization, the monomer concentration in the solvent is in a range from 5% to 50% by mass, and preferably from 10% to 30% by mass, based on 100% by mass of the total amount of the solvent and the monomer(s), from the viewpoint of productivity and ease of polymerization control.

[0023]

#### 4. Polymerization reaction

20 The modified polymer may be obtained using a polymerization initiator having a functional group protected with a silyl group or a functional group-introducing monomer having a functional group protected with a silyl group, or the modified polymer may be obtained by polymerizing a conjugated diene and/or an aromatic vinyl compound, and then applying a polymerization terminator having a functional group protected with a silyl group.

25 In either case, a polymerization temperature is preferably in a range from -20°C to 150°C, and particularly preferably from 0°C to 120°C. The polymerization reaction may be effected under the developed pressure. It is preferable to effect the polymerization reaction under a pressure sufficient to substantially maintain the conjugated diene and/or the aromatic

vinyl compound in a liquid phase. The pressure during polymerization may be determined depending on a type of monomer subjected to polymerization, a type of solvent, polymerization temperature, and the like, and may optionally be set to be higher than the developed pressure. The pressure may be increased by pressurizing the reactor using a gas that is inert to the polymerization reaction, for example.

[0024]

It is preferable to use each raw material (e.g., a polymerization initiator, solvent, and monomer) used for polymerization after removing a reaction inhibitor substance such as water, oxygen, carbon dioxide, and protonic compound. When the polymer is a hydrogenated product included in a thermoplastic elastomer, the glass transition temperature (T<sub>g</sub>) of the polymer or the copolymer measured by differential thermal analysis is preferably in a range from -90°C to 0°C. It is difficult to produce a polymer having a glass transition temperature of less than -90°C. If the glass transition temperature exceeds 0°C, the viscosity may increase to a large extent at room temperature, and handling may be difficult.

[0025]

## 5. Modification reaction

The functional group protected with a silyl group may be introduced into a main chain, side chain, or molecular end of a polymer or copolymer (modification reaction) by (1) effecting a polymerization reaction using an organometallic compound having a functional group protected with a silyl group (or a derivative thereof) as a polymerization initiator to obtain a modified polymer, (2) copolymerizing a conjugated diene, an aromatic vinyl compound, and a monomer that is copolymerizable with the conjugated diene and/or the aromatic vinyl compound and includes a functional group protected with a silyl group to obtain a modified polymer, or (3) polymerizing a conjugated diene and/or an aromatic vinyl compound to obtain a polymer, and terminating polymerization using a compound having a functional group protected with a silyl group as a polymerization terminator to obtain a modified polymer, for example.

[0026]

Specific examples of the organometallic compound having a functional group protected with a silyl group (see (1)) include

3-[N,N-bis(trimethylsilyl)amino]-1-propyllithium,  
5-[N,N-bis(trimethylsilyl)amino]-1-pentyllithium, and the like.

5 [0027]

Specific examples of the functional group-introducing monomer that is copolymerizable with the conjugated diene and/or the aromatic vinyl compound and includes a functional group protected with a silyl group (see (2)) include

1-[4-N,N-bis(trimethylsilyl)aminophenyl]-1-phenylethylene, and the like.

10 [0028]

Specific examples of the compound that has a functional group protected with a silyl group and is used as the polymerization terminator (see (3)) include

N,N-bis(triethylsilyl)aminopropylmethyldimethoxysilane,

N,N-bis(trimethylsilyl)aminopropylmethyldimethoxysilane,

15 N,N-bis(trimethylsilyl)aminopropylmethyldiethoxysilane,

N,N-bis(trimethylsilyl)aminopropyltriethoxysilane,

N,N',N'-tris(trimethylsilyl)-N-(2-aminoethyl)-3-aminopropyltriethoxysilane,

1-trimethylsilyl-2,2-dimethoxy-1-aza-2-silacyclopentane,

N-[3-(trimethoxysilyl)-propyl]-N,N'-diethyl-N'-trimethylsilyl-ethane-1,2-diamine,

20 N-[3-(triethoxysilyl)-propyl]-N,N'-diethyl-N'-trimethylsilyl-ethane-1,2-diamine,

3-(4-trimethylsilyl-1-piperazino)propyltriethoxysilane,

1-[3-(triethoxysilyl)-propyl]-4-trimethylsilylpiperazine,

1-[3-(trimethoxysilyl)-propyl]-4-trimethylsilylpiperazine,

bis[3-(triethoxysilyl)propyl]trimethylsilylamine,

25 bis[3-(trimethoxysilyl)propyl]trimethylsilylamine,

S-trimethylsilylmercaptopropylmethyldimethoxysilane,

S-trimethylsilylmercaptopropyltrimethoxysilane,

S-trimethylsilylmercaptopropyltriethoxysilane,

S-trimethylsilylmercaptopropylmethyldiethoxysilane, and the like.

[0029]

## 6. Randomizer

A randomizer is optionally used when producing the polymer. The randomizer is a compound that controls the microstructure of a polymer (e.g., increases the number of a vinyl bond (1,2-bonds) of a butadiene moiety of a butadiene-styrene copolymer, or increases the number of a vinyl bond (1,2-bond or 3,4-bond) of an isoprene polymer), or controls the compositional distribution of monomer units in the polymer (e.g., randomizes butadiene unit and styrene unit of a butadiene-styrene copolymer).

[0030]

The randomizer is not particularly limited. Examples of the randomizer include ethers and tertiary amines such as dimethoxybenzene, tetrahydrofuran, dimethoxyethane, diethylene glycol dibutyl ether, diethylene glycol diethyl ether, diethylene glycol dimethyl ether, 2,2-di(tetrahydrofuryl)propane, 2-(2-ethoxyethoxy)-2-methylpropane, triethylamine, pyridine, N-methylmorpholine, N,N,N',N'-tetramethylethylenediamine, 1,2-dipiperidinoethane, ethylene glycol dibutyl ether, ethylene glycol diethyl ether, ethylene glycol dimethyl ether, dioxane, trimethylamine, quinuclidine, potassium tert-amylate, potassium tert-butyrate, triphenylphosphine, tetrahydropyran, dibutyl ether, diphenyl ether, anisole, tripropylamine, tributylamine, N,N-diethylaniline, and quinoline, and the like. The randomizer may be used singly or in combination of two or more types thereof.

[0031]

## 7. Recycling of polymerization solvent

When a conjugated diene and/or an aromatic vinyl compound is polymerized using the above-mentioned hydrocarbon-based solvent and polymerization initiator, a polymer is obtained. When a functional group is introduced into the polymer in the above-mentioned modification reaction, a modified polymer is obtained. Further, a hydrogenated product is obtained by hydrogenating the modified polymer using a known method. The silanol compound is removed from the solvent fraction separated from the solid fraction (i.e.,

modified polymer or hydrogenated product) by performing the solvent removal step (a), the low-boiling fraction separation step (b), and the silanol removal step (c), and at least part of the raffinate is recycled as the polymerization solvent.

[0032]

5           The solvent removal step (a) separates the reaction solution in which the modified polymer or the hydrogenated product is dissolved into a solvent fraction containing the hydrocarbon-based solvent and a solid fraction containing the modified polymer or the hydrogenated product after the polymerization reaction and the modification reaction, or after the hydrogenation reaction. The solvent removal method is not particularly limited. For  
10       example, the reaction solution containing the modified polymer or the like is added to and dispersed in hot water contain in a solvent removal tank to produce an emulsion, and the solvent is separated and removed from the modified polymer or the like using water vapor introduced through the bottom of the solvent removal tank (i.e., steam stripping method).

[0033]

15           The low-boiling fraction separation step (b) distills the solvent fraction to separate the low-boiling fraction containing the hydrocarbon-based solvent and the silanol compound. The low-boiling fraction is a fraction that is produced when distilling the solvent fraction separated from the solid fraction by the solvent removal step. The low-boiling fraction includes part of the hydrocarbon-based solvent used as the polymerization solvent, and the  
20       silanol compound produced from the compound having a silyl group and is used as the modifier. The solvent fraction may be distilled using a normal method that utilizes a distillation column. The low-boiling fraction is a fraction that leaves the top of the distillation column. The silanol compound that leaves the top of the distillation column as the low-boiling fraction together with the polymerization solvent during distillation varies  
25       depending on the type of compound having a silyl group (modifier) and the type of hydrocarbon-based solvent. Examples of the silanol compound include trimethylsilanol, ethyldimethylsilanol, diethylmethylsilanol, dimethylpropylsilanol, dimethylisopropylsilanol, ethylmethylpropylsilanol, ethylmethylisopropylsilanol, triethylsilanol, n-butyldimethylsilanol,

sec-butyldimethylsilanol, tert-butyldimethylsilanol, and the like.

[0034]

The combination of the polymerization solvent and the compound having a silyl group (modifier) is not particularly limited. It is preferable to select the polymerization solvent and the compound having a silyl group so that a larger amount of silanol compound produced from the compound having a silyl group leaves the top of the distillation column as the low-boiling fraction together with the polymerization solvent during distillation. For example, when using cyclohexane or n-hexane (particularly cyclohexane) as the polymerization solvent, it is preferable to use a compound that has a silyl group and produces trimethylsilanol or ethyldimethylsilanol (particularly trimethylsilanol) as the silanol compound.

[0035]

The ratio of the low-boiling fraction produced by the distilling solvent fraction to the total amount of the solvent fraction is not particularly limited, and varies depending on the types and the amounts of solvent, monomer, additive, and the like used for polymerization, the polymerization conditions, the distillation conditions, and the like. It is preferable that the amount of low-boiling fraction fed to the subsequent silanol removal step be small. The content of the low-boiling fraction in the solvent fraction is normally in a range from 0.1% to 20% by mass, preferably from 0.1% to 10% by mass, and particularly from 0.1% to 5% by mass. The ratio of the silanol compound included in the low-boiling fraction to the total amount of the low-boiling fraction is not particularly limited, and varies depending on the amount of compound having a silyl group, the polymerization conditions, the distillation conditions, and the like. The content of the silanol compound in the low-boiling fraction is normally in a range from 200 ppm to 10% by mass, preferably from 1,000 ppm to 10% by mass, and particularly from 3,000 ppm to 10% by mass.

[0036]

The silanol removal step (c) removes (extracts) at least part of the silanol compound from the low-boiling fraction by liquid-liquid extraction using the low-boiling fraction and

the extraction solvent. Most of the silanol compound is extracted into the extraction solvent by liquid-liquid extraction, while the hydrocarbon-based solvent remains in the low-boiling fraction. Examples of the extraction solvent used for liquid-liquid extraction include water, acetone, methylethylketone, methanol, ethanol, and the like. It is preferable to use water as the extraction solvent when the silanol compound is trimethylsilanol or ethyldimethylsilanol (particularly trimethylsilanol). Since only the low-boiling fraction (i.e., part of the solvent fraction) is subjected to liquid-liquid extraction in the silanol removal step, simple liquid-liquid extraction equipment can be used, and the construction cost can be reduced. Since only a small amount of extraction solvent is used, the liquid-liquid extraction cost can also be reduced.

[0037]

The ratio of the extraction solvent used for liquid-liquid extraction to the total amount of the low-boiling fraction is not particularly limited as long as the silanol compound can be efficiently extracted and removed. The extraction solvent may be used in an appropriate amount depending on the type of extraction solvent, the type of silanol compound, and the like. It is preferable to use the extraction solvent in such an amount that the weight ratio (Me/Mb) of the extraction solvent (Me) to the low-boiling fraction (Mb) is in a range from 0.5 to 10, preferably from 0.5 to 5, and particularly from 0.5 to 2. The weight ratio (Me/Mb) is preferably in a range from 1 to 2 when the silanol compound is trimethylsilanol, and the extraction solvent is water.

[0038]

At least part of the raffinate from which the silanol compound has been removed by liquid-liquid extraction in the silanol removal step can be recycled as a polymerization solvent. When at least part of the raffinate is recycled as the polymerization solvent, it is preferable that the solvent does not include the silanol compound, or a content of the silanol compound in the solvent is preferably 200 ppm or less by mass, and particularly 100 ppm or less by mass. In this case, the silanol compound can be made harmless by increasing the amount of the polymerization initiator, for example. Therefore, polymerization can be

effected successfully. The raffinate may be appropriately recycled to obtain a polymerization solvent having a silanol compound content within the above range. For example, the raffinate may be mixed with the solvent fraction that includes only a small amount of silanol compound and remains after separating the low-boiling fraction in the low-boiling fraction separation step, or the raffinate may be fed back to the distillation column used for distillation for separating the low-boiling fraction from the solvent fraction after polymerization, and the solvent fraction having a silanol compound content within the above range may be obtained from the bottom of the distillation column. In either case, when the solvent fraction obtained by recycling the raffinate includes a heavy component such as an oligomer of the conjugated diene or the aromatic vinyl compound, or an anti-aging agent, it is necessary to perform a heavy component removal step. An amount of the silanol compound included in the solvent (e.g., raffinate) may be quantitatively determined by an internal reference method using gas chromatography.

[0039]

When water is used as the extraction solvent, water remains in the raffinate in an amount of 500 ppm or less by mass (particularly 200 to 300 ppm by mass). Since water inhibits polymerization, it is preferable to remove water before recycling the raffinate as the polymerization solvent. Water may be removed using an arbitrary method, and may be removed using special equipment. It is preferable to feed the raffinate back to the distillation column used for distillation for separating the low-boiling fraction from the solvent fraction after polymerization. In this case, special equipment is unnecessary, and it is advantageous from the viewpoint of the process and cost.

[0040]

When the randomizer is used for polymerization, a step that separates the randomizer (randomizer separation step) may be provided between the low-boiling fraction separation step and the silanol removal step, or after the silanol removal step. When the randomizer is used for polymerization, and has a volatility equal to or higher than that of the silanol compound produced, the low-boiling fraction obtained by distillation includes the randomizer

at a high concentration. If the low-boiling fraction is extracted directly with the extraction solvent, the distribution ratio of the silanol compound may be decreased due to the randomizer, and a large amount of extraction solvent may be required. Moreover, the randomizer may be mixed into the extract together with the silanol compound. The randomizer can be recycled for polymerization by separating and recovering the randomizer in the randomizer separation step, and optionally combining an appropriate purification step. The randomizer separation step is not indispensable when the randomizer is not used for polymerization, or has a volatility lower than that of the silanol compound produced.

[0041]

Each step for recycling the polymerization solvent may be performed using an apparatus illustrated in FIG. 1, for example.

Specifically, a reaction solution is separated into a solvent fraction containing a hydrocarbon-based solvent, and a solid fraction containing a modified polymer or a hydrogenated product using a steam stripping method or the like. A solvent fraction a is fed to a distillation column 1 through a raw material solvent feed pipe 7, and a low-boiling fraction containing the hydrocarbon-based solvent and a silanol compound is extracted from the top of the distillation column 1. The hydrocarbon-based solvent from which most of the silanol compound has been removed is extracted through a drawing pipe 8 at the bottom of the distillation column 1 as a bottom product b. The low-boiling fraction is fed to an extraction column 10 through a distillation pipe 9. An extraction solvent is fed to the extraction column 10 through an extraction solvent feed pipe 11, and the low-boiling fraction is separated into the hydrocarbon-based solvent and the silanol compound by liquid-liquid extraction. The extraction solvent containing the silanol compound is extracted through an extraction solvent phase drawing pipe 12 at the bottom of the extraction column 10, and the hydrocarbon-based solvent containing a small amount of extraction solvent and silanol compound is extracted through a solvent phase drawing pipe 13 at the top of the extraction column 10. A bottom product b containing only a small amount of silanol compound, and an overhead extract c having a low silanol compound concentration can thus be obtained.

[0042]

When a volatile randomizer is used, it is necessary to perform a distillation step for removing the randomizer. In this case, each step for recycling the polymerization solvent may be performed using the apparatus illustrated in FIG. 2, for example.

5 Specifically, a reaction solution separated into a solvent fraction containing a hydrocarbon-based solvent and a solid fraction containing a modified polymer or a hydrogenated product using a steam stripping method or the like. A solvent fraction d is fed to a distillation column 15 through a raw material solvent feed pipe 21, and a low-boiling fraction containing the hydrocarbon-based solvent and a silanol compound is extracted from  
10 the top of the distillation column 15. The hydrocarbon-based solvent from which most of the silanol compound has been removed is extracted through a drawing pipe 22 at the bottom of the distillation column 1 as a bottom product e. The low-boiling fraction is fed to a distillation column 25 through a distillation pipe 23. The randomizer included in the low-boiling fraction is separated, extracted from the top of the distillation column 25 as a  
15 distillate containing a large amount of randomizer, and extracted as a distillate f through a drawing pipe 32. The low-boiling fraction from which most of the randomizer has been removed is fed from the bottom of the distillation column 25 to an extraction column 35 through a distillation pipe 31. An extraction solvent is fed to the extraction column 35 through an extraction solvent feed pipe 36, and the low-boiling fraction is separated into the  
20 hydrocarbon-based solvent and the silanol compound by liquid-liquid extraction. The extraction solvent containing the silanol compound is extracted through an extraction solvent phase drawing pipe 37 at the bottom of the extraction column 35, and the hydrocarbon-based solvent (raffinate) containing a small amount of extraction solvent and silanol compound is extracted as an overhead extract g through a solvent phase drawing pipe 38 at the top of the  
25 extraction column 35. A bottom product e containing only a small amount of silanol compound, and a distillate f and an overhead extract g both having a low silanol compound concentration can thus be obtained.

Since the distillate f includes the randomizer at a high concentration, the randomizer

can be recycled for polymerization by optionally combining an appropriate purification step.

## EXAMPLES

[0043]

5 Hereinafter, the present invention is specifically explained using examples.

### Example 1

Trimethylsilanol was added to cyclohexane at a concentration of 100 ppm to prepare a solvent taking account of a situation in which a small amount of silanol compound is included in a solvent that is recovered and recycled. An autoclave reactor (internal volume:  
10 5 liters) of which the internal atmosphere had been replaced with nitrogen, was charged with 2,750 g of cyclohexane including 100 ppm of trimethylsilanol, 3.25 mmol of 2,2-di(tetrahydrofuryl)propane, 125 g of styrene, and 365 g of 1,3-butadiene. After adjusting the temperature of the mixture contained in the reactor to 10°C, a cyclohexane solution of n-butyllithium (8.80 mmol) was added to the mixture to initiate polymerization.  
15 Note that the amount of n-butyllithium includes an amount necessary for converting trimethylsilanol included in the solvent into lithium trimethylsilanolate (harmless compound) in the reactor. The polymerization successfully proceeded under thermally insulated conditions, and the maximum temperature reached 85°C.

[0044]

20 10 g of 1,3-butadiene was added to the mixture when the polymerization conversion rate reached 99%, and the mixture was subjected to polymerization for a further 5 minutes. A cyclohexane solution of N,N-bis(trimethylsilyl)aminopropyltriethoxysilane (4.96 mmol) was added and reacted for 15 minutes. Subsequently, 2.0 g of 2,6-di-tert-butyl-p-cresol was added to the resulting polymer solution. A solvent was removed by steam stripping using  
25 hot water of which pH had been adjusted to 9 with sodium hydroxide.

[0045]

Mixed vapor of the solvent and water produced by steam stripping was condensed using a condenser, and the solvent phase was separated by static separation to obtain a mixed

solvent (A) having a composition shown in Table 1. A solvent fraction a having the composition shown in Table 1 was prepared based on the composition of the mixed solvent (A). Note that some of the components were omitted when preparing the solvent fraction a. A distillation operation and an extraction operation were performed under the following conditions (raw material solvent: solvent fraction a) using the solvent purification apparatus illustrated in FIG. 1 to obtain a bottom product b and an overhead extract c (see Table 1). The trimethylsilanol concentration in the bottom product b could thus be reduced to a level appropriate for the polymerization solvent. Even when the bottom product b and overhead extract c were mixed, the water concentration and the trimethylsilanol concentration were appropriate for the polymerization solvent. Therefore, the overhead extract c could also be recycled as the polymerization solvent.

Note that it is necessary to perform a heavy component removal step in order to use the bottom product b or a mixture of the bottom product b and overhead extract c as the polymerization solvent when the bottom product b includes a heavy component such as an oligomer of the conjugated diene or the aromatic vinyl compound, or an anti-aging agent.

[0046]

TABLE 1

|                       |                                | Solvent (A) | Solvent fraction a | Bottom product b | Overhead extract c | Mixture of b and c |
|-----------------------|--------------------------------|-------------|--------------------|------------------|--------------------|--------------------|
| Temperature           |                                | -           | 30°C               | 111°C            | 40°C               | -                  |
| Flow rate             |                                | -           | 7500 g/h           | 7480 g/h         | 13.6 g/h           | -                  |
| Component             | Cyclohexane                    | 99.8%       | 99.9%              | 99.9%<           | 84.7%              | 99.9%<             |
|                       | 2,2-Di(tetrahydrofuryl)propane | 218 ppm     | -                  | -                | -                  | -                  |
|                       | Tetrahydrofuran                | -           | -                  | -                | -                  | -                  |
|                       | 1,3-Butadiene                  | 531 ppm     | 550 ppm            | <10 ppm          | 14.1%              | 270 ppm            |
|                       | Styrene                        | 41 ppm      | -                  | -                | -                  | -                  |
|                       | Trimethylsilanol               | 194 ppm     | 200 ppm            | 15 ppm           | 4780 ppm           | 23 ppm             |
|                       | Ethanol                        | 20 ppm      | 20 ppm             | <10 ppm          | <10 ppm            | <10 ppm            |
|                       | Water                          | 261 ppm     | 260 ppm            | <1 ppm           | 349 ppm            | <1 ppm             |
| Other heavy component |                                | 460 ppm     | -                  | -                | -                  | -                  |

[0047]

The distillation operation and the extraction operation using the apparatus illustrated in FIG. 1 may be performed as described below.

A solvent fraction a is fed to a distillation column 1 through a raw material solvent

feed pipe 7, and a low-boiling fraction containing cyclohexane and trimethylsilanol is extracted from the top of the distillation column 1. Cyclohexane from which most of the trimethylsilanol has been removed is extracted through a drawing pipe 8 at the bottom of the distillation column 1 as a bottom product b. The low-boiling fraction is fed to an extraction column 10 through a distillation pipe 9. Water is fed to the extraction column 10 through an extraction solvent feed pipe 11, and the low-boiling fraction is separated into cyclohexane and trimethylsilanol by liquid-liquid extraction. Water containing trimethylsilanol is extracted through an extraction solvent phase drawing pipe 12 at the bottom of the extraction column 10, and cyclohexane containing a small amount of water and trimethylsilanol is extracted through a solvent phase drawing pipe 13 at the top of the extraction column 10. The bottom product b containing only a small amount of trimethylsilanol, and the overhead extract c having a low trimethylsilanol concentration can thus be obtained.

[0048]

Solvent purification apparatus and operation conditions

[1] The solvent purification apparatus illustrated in FIG. 1 was used for solvent purification.

(1) Type of distillation column 1 and operation conditions

Type: packed column

Bed height: equivalent to 10 theoretical plates

Operating pressure: 0.12 MPa(G)

Reflux ratio: 4

[0049]

(2) Solvent a fed to distillation column 1

Material: solvent fraction a having the composition shown in Table 1

Feed position: position corresponding to about 1/3rd of the distance from the top of the column to the bed height

Feed rate: 7500 g/h

Feed temperature: 30°C

[0050]

(3) Type of extraction column 2 and operation conditions

Type: packed column

Bed height: equivalent to 5 theoretical plates

5 Operating pressure: 0.10 MPa(G)

[0051]

(4) Solvent fed to extraction column 10

Material: liquid fed through distillation pipe 9

Feed position: channel at the bottom of the extraction column

10 Feed rate: 15 g/h

Feed temperature: 40°C

[0052]

(5) Extraction solvent fed to extraction column 10

Material: water

15 Feed position: channel at the top of the extraction column

Feed rate: 70 g/h

Feed temperature: 40°C

[0053]

Example 2

20 A distillation operation and an extraction operation were performed in the same manner as those in Example 1, except that the overhead extract c extracted through the solvent phase drawing pipe 13 was mixed into the solvent a, and fed to the distillation column 1 through the raw material solvent feed pipe 7. In this case, since trimethylsilanol included in the overhead extract c extracted through the solvent phase drawing pipe 13 is mixed into  
25 the solvent fraction a, the concentration of trimethylsilanol fed to the distillation column 1 increases for a while after the start of purification. However, when the mass flow rate of trimethylsilanol included in the solvent fraction a (raw material solvent) has become equal to the mass flow rate of trimethylsilanol in the extraction solvent phase drawing pipe 12, the

trimethylsilanol concentration in the solvent fed to the distillation column 1, and the trimethylsilanol concentration in the bottom product b extracted through the drawing pipe 8 become constant. Since the water concentration and the trimethylsilanol concentration in the bottom product b extracted through the drawing pipe 8 are appropriate for the polymerization solvent, only the bottom product b extracted through the drawing pipe 8 may be used as the polymerization solvent. Note that it is necessary to perform a heavy component removal step in order to use the bottom product b as the polymerization solvent when the bottom product b includes a heavy component such as an oligomer of the conjugated diene or the aromatic vinyl compound, or an anti-aging agent.

[0054]

### Example 3

A polymerization reaction and a modification reaction were effected in the same manner as those in Example 1, except that 50.0 g of tetrahydrofuran was used instead of 2,2-di(tetrahydrofuryl)propane used in Example 1.

Next, 2.0 g of 2,6-di-tert-butyl-p-cresol was added to the polymer solution. The solvent was removed by steam stripping using hot water of which the pH had been adjusted to 9 with sodium hydroxide.

[0055]

Mixed vapor of the solvent and water produced by steam stripping was condensed using a condenser, and the solvent phase was separated by static separation to obtain a mixed solvent (D) having the composition shown in Table 2. A solvent fraction d having the composition shown in Table 2 was prepared based on the composition of the mixed solvent (D). Note that some of the components were omitted when preparing the solvent fraction d. A distillation operation and an extraction operation were performed under the following conditions (raw material solvent: solvent fraction d) using the solvent purification apparatus illustrated in FIG. 2 to obtain a bottom product e, a distillate f, and an overhead extract g (see Table 2). The trimethylsilanol concentration in the bottom product e could thus be reduced to a level appropriate for the polymerization solvent. Even when the bottom product e and

overhead extract g were mixed, the water concentration and the trimethylsilanol concentration were appropriate for the polymerization solvent.

Note that it is necessary to perform a heavy component removal step in order to use the bottom product e or a mixture of the bottom product e and overhead extract g as the polymerization solvent when the bottom product e includes a heavy component such as an oligomer of the conjugated diene or the aromatic vinyl compound, or an anti-aging agent. Since the distillate f includes tetrahydrofuran at a high concentration, tetrahydrofuran that has been recovered from the distillate f containing 1,3-butadiene, water, and ethanol can be added to the reactor as the randomizer.

[0056]

Since tetrahydrofuran easily volatilizes as compared with trimethylsilanol, the low-boiling fraction fed through the distillation pipe 23 includes tetrahydrofuran at a high concentration. If the low-boiling fraction is extracted directly with water, the distribution ratio (W/O) of trimethylsilanol decreases due to tetrahydrofuran. Specifically, when the low-boiling fraction is fed directly to the extraction column 35, it is necessary to increase the size of the extraction column 35, and a large amount of water is required as the extraction solvent. Therefore, the distillation column 25 was provided to extract the distillate f including tetrahydrofuran at a high concentration, and the low-boiling fraction having a reduced tetrahydrofuran content was fed to the extraction column 35. Since tetrahydrofuran was used as the randomizer in Example 3, the distillation column 25 was provided in addition to the distillation column 15.

[0057]

TABLE 2

|             |                                | Solvent (D) | Solvent fraction d | Bottom product e | Distillate f | Overhead extract g | Mixture of bottom product e and overhead extract g |
|-------------|--------------------------------|-------------|--------------------|------------------|--------------|--------------------|----------------------------------------------------|
| Temperature |                                | -           | 30°C               | 110°C            | 40°C         | 40°C               | -                                                  |
| Flow rate   |                                | -           | 7500 g/h           | 7393 g/h         | 14.4 g/h     | 82.7 g/h           | -                                                  |
| Component   | Cyclohexane                    | 98.1%       | 98.1%              | 98.3%            | 16.6%        | 99.9%              | 98.4%                                              |
|             | 2,2-Di(tetrahydrofuryl)propane | -           | -                  | -                | -            | -                  | -                                                  |
|             | Tetrahydrofuran                | 1.78%       | 1.78%              | 1.65%            | 69.2%        | 836 ppm            | 1.64%                                              |
|             | 1,3-Butadiene                  | 522 ppm     | 550 ppm            | <10 ppm          | 13.1%        | <10 ppm            | <10 ppm                                            |
|             | Styrene                        | 40 ppm      | -                  | -                | -            | -                  | -                                                  |
|             | Trimethylsilanol               | 191 ppm     | 200 ppm            | 34 ppm           | 125 ppm      | 360 ppm            | 37 ppm                                             |
|             | Ethanol                        | 20 ppm      | 20 ppm             | <10 ppm          | 7070 ppm     | <10 ppm            | <10 ppm                                            |
|             | Water                          | 292 ppm     | 300 ppm            | <1 ppm           | 3800 ppm     | 267 ppm            | 3 ppm                                              |
|             | Other heavy component          | 450 ppm     | -                  | -                | -            | -                  | -                                                  |

[0058]

The distillation operation and the extraction operation using the apparatus illustrated in FIG. 2 may be performed as described below.

A solvent fraction d is fed to a distillation column 15 through a raw material solvent feed pipe 21, and a low-boiling fraction containing cyclohexane, tetrahydrofuran, and trimethylsilanol is extracted from the top of the distillation column 15. Cyclohexane from which most of the trimethylsilanol has been removed is extracted through a drawing pipe 22 at the bottom of the distillation column 15 as a bottom product e. The low-boiling fraction is fed to a distillation column 25 through a distillation pipe 23. Tetrahydrofuran included in the low-boiling fraction is separated, extracted from the top of the distillation column 25 as a distillate containing a large amount of tetrahydrofuran, and extracted as a distillate f through a drawing pipe 32. The low-boiling fraction from which most of the tetrahydrofuran has been removed is fed from the bottom of the distillation column 25 to an extraction column 35 through a distillation pipe 31. Water is fed to the extraction column 35 through an extraction solvent feed pipe 36, and the low-boiling fraction is separated into cyclohexane and trimethylsilanol by liquid-liquid extraction. Water containing trimethylsilanol is extracted through an extraction solvent phase drawing pipe 37 at the bottom of the extraction column 35, and cyclohexane containing a small amount of water and trimethylsilanol is extracted through a solvent phase drawing pipe 38 at the top of the extraction column 35. The bottom product e containing only a small amount of trimethylsilanol, and the distillate f and overhead extract g having a low trimethylsilanol concentration can thus be obtained.

[0059]

Solvent purification apparatus and operation conditions

[1] The solvent purification apparatus illustrated in FIG. 2 was used for solvent purification.

(1) Type of distillation column 15 and operation conditions

Type: packed column

Bed height: equivalent to 10 theoretical plates

Operating pressure: 0.12 MPa(G)

Reflux ratio: 0.41

[0060]

(2) Solvent d fed to distillation column 15

5 Material: solvent fraction d having the composition shown in Table 1

Feed position: position corresponding to about 1/3rd of the distance from the top of the column to the bed height

Feed rate: 7,500 g/h

Feed temperature: 30°C

10 [0061]

(3) Type of distillation column 25 and operation conditions

Type: packed column

Bed height: equivalent to 45 theoretical plates

Operating pressure: 0.12 MPa(G)

15 Reflux ratio: 20

[0062]

(4) Solvent fed to distillation column 25

Material: liquid fed from distillation column 15

20 Feed position: position corresponding to about 1/4th of the distance from the top of the column to the bed height

Feed rate: 100 g/h

Feed temperature: 40°C

[0063]

(5) Type of extraction column 35 and operation conditions

25 Type: packed column

Bed height: equivalent to 3 theoretical plates

Operating pressure: 0.10 MPa(G)

[0064]

(6) Solvent fed to extraction column 35

Material: bottoms fed from distillation column 25

Feed position: channel at the bottom of the extraction column

Feed rate: 84 g/h

5 Feed temperature: 40°C

[0065]

(7) Extraction solvent fed to extraction column 35

Material: water

Feed position: channel at the top of the extraction column

10 Feed rate: 150 g/h

Feed temperature: 40°C

[0066]

#### Example 4

A distillation operation and an extraction operation were performed in the same  
15 manner as those in Example 3, except that the distillate f and overhead extract g extracted  
through the drawing pipe 32 and the solvent phase drawing pipe 38 were mixed into the  
solvent d, and fed to the distillation column 15 through the raw material solvent feed pipe 21.  
In this case, since trimethylsilanol included in the overhead extract g extracted through the  
solvent phase drawing pipe 38 is mixed into the solvent fraction d, the concentration of  
20 trimethylsilanol fed to the distillation column 15 increases for a while after the start of  
purification. However, when the mass flow rate of trimethylsilanol included in the solvent  
fraction d (raw material solvent) has become equal to the mass flow rate of trimethylsilanol  
included in the liquid that flows through the extraction solvent phase drawing pipe 37, the  
trimethylsilanol concentration in the solvent fed to the distillation column 15, and the  
25 trimethylsilanol concentration in the bottom product e extracted through the drawing pipe 22  
become constant. Since the water concentration and the trimethylsilanol concentration in  
the bottom product e extracted through the drawing pipe 22 are appropriate for the  
polymerization solvent, only the bottom product e extracted through the drawing pipe 22 may

be used as the polymerization solvent. The tetrahydrofuran concentration in the solvent d is almost equal to the tetrahydrofuran concentration in the bottom product e extracted through the drawing pipe 22. Therefore, it suffices to add only a small amount of tetrahydrofuran when recycling the bottom product e extracted through the drawing pipe 22 as the  
5 polymerization solvent. Note that it is necessary to perform a heavy component removal step in order to use the bottom product e as the polymerization solvent when the bottom product e includes a heavy component such as an oligomer of the conjugated diene or the aromatic vinyl compound, or an anti-aging agent.

## 10 INDUSTRIAL APPLICABILITY

[0067]

The invention may be applied to a technical field in which a silanol compound that inhibits polymerization is removed from a solvent fraction separated from a solid fraction containing a polymer or the like, and the residue is recycled as a polymerization solvent when  
15 polymerizing at least one of a conjugated diene and an aromatic vinyl compound using a modifier in a hydrocarbon-based solvent as the polymerization solvent.

## CLAIMS

1. A method for producing a modified polymer or a hydrogenated product thereof comprising polymerizing a monomer comprising at least one of a conjugated diene and an aromatic vinyl compound in a hydrocarbon-based solvent as a polymerization solvent using  
5 an active organometal as a polymerization initiator to obtain a modified polymer or a hydrogenated product thereof, the modified polymer including a functional group in at least one of a main chain and a side chain,

the functional group being introduced into the modified polymer using a compound  
10 having a functional group protected with a silyl group as a polymerization initiator, a functional group-introducing monomer, or a polymerization terminator,

the method further sequentially comprising:

(a) a solvent removal step that separates a reaction solution in which the modified polymer or the hydrogenated product is dissolved in the polymerization solvent into a solvent  
15 fraction including the hydrocarbon-based solvent, and a solid fraction including the modified polymer or the hydrogenated product;

(b) a low-boiling fraction separation step that distills the solvent fraction to separate a low-boiling fraction including the hydrocarbon-based solvent and a silanol compound; and

(c) a silanol removal step that removes at least part of the silanol compound from the  
20 low-boiling fraction by liquid-liquid extraction using the low-boiling fraction and an extraction solvent,

at least part of a raffinate from which the silanol compound has been removed by the liquid-liquid extraction being recycled as a polymerization solvent.

2. The method according to Claim 1, wherein the silanol compound is at least one  
25 compound selected from the group consisting of trimethylsilanol, ethyldimethylsilanol, diethylmethylsilanol, dimethylpropylsilanol, dimethylisopropylsilanol, ethylmethylpropylsilanol, ethylmethylisopropylsilanol, triethylsilanol, n-butyldimethylsilanol, sec-butyldimethylsilanol, and tert-butyldimethylsilanol.

3. The method according to Claim 1 or 2, wherein the extraction solvent used for the liquid-liquid extraction is water.
4. The method according to any one of Claims 1 to 3, wherein a content of the low-boiling fraction in the solvent fraction is in a range from 0.1% to 20% by mass.
- 5 5. The method according to any one of Claims 1 to 4, wherein a content of the silanol compound in the low-boiling fraction is in a range from 200 ppm to 10% by mass.
6. The method according to any one of Claims 1 to 5, wherein a weight ratio (Me/Mb) of the extraction solvent (Me) to the low-boiling fraction (Mb) is in a range from 0.5 to 10.
7. The method according to any one of Claims 1 to 6, wherein a content of the silanol  
10 compound in the at least part of the raffinate that is recycled as the polymerization solvent is 200 ppm or less by mass.
8. The method according to any one of Claims 1 to 7, further comprising a step that separates a randomizer between the low-boiling fraction separation step and the silanol removal step, or after the silanol removal step, when the randomizer is used for the  
15 polymerization, and at least part of the randomizer is included in the low-boiling fraction.