Description

Title of Invention:

POLYFUNCTIONAL VINYL AROMATIC COPOLYMER HAVING SYNDIOTACTIC STRUCTURE, CURABLE RESIN COMPOSITION, AND CURED PRODUCT

Technical Field

[0001] This invention relates to a polyfunctional vinyl aromatic copolymer.

Background Art

[0002] With the recent increase in the volume of information and communication, information and communication in the high-frequency band has become widespread. To achieve superior electrical properties, particularly to reduce transmission loss in the high-frequency band, there is a need for an electrical insulating material that has a low dielectric constant and a low dielectric loss tangent, and in particular an electrical insulating material that has a small change in dielectric properties after water absorption. Further, printed circuit boards and electronic components that use these electrical insulating materials are exposed to high-temperature solder reflow during assembly, and so a material having a high heat resistance, that is, a material that exhibits a high glass transition temperature, is desired. In particular, recently, due to environmental concerns, lead-free solder having a high melting point is being used, resulting in an increased demand for electrical insulating materials having even higher heat resistance. To meet these demands, curing resins that use vinyl compounds having various chemical structures have been proposed.

[0003] As such a curing resin, for example, Patent Literature 1 discloses a polyfunctional vinyl aromatic copolymer containing structural units derived from a

divinyl aromatic compound, styrene, and a monovinyl aromatic compound other than styrene, and containing specific terminal groups.

[0004] The polyfunctional vinyl aromatic copolymer disclosed in Patent Literature 1 itself has a polymerizable double bond, and therefore gives a cured product that has a high glass transition temperature by curing.

[0005] However, the advanced dielectric properties required in cutting-edge technology fields, as well as the heat discoloration resistance, and heat resistance for continuous use at high temperatures may not be sufficient.

[0006] Patent Literature 2 discloses a styrene-based copolymer having a syndiotactic structure. However, since styrene is used exclusively as the styrene-based monomer, the resulting copolymer has poor solvent solubility and does not satisfy the required properties as an insulating material in advanced electrical and electronic fields.

Citation List

Patent Literature

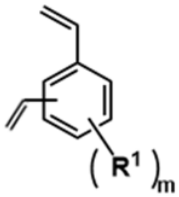
[0007] Patent Literature 1: WO 2018/181842

Patent Literature 2: JPH01-95112 A

Summary of Invention

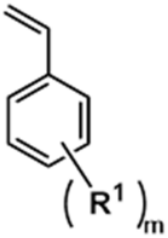
[0008] It is an object of the present invention to provide a novel polyfunctional vinyl aromatic copolymer having a syndiotactic structure that has high dielectric properties, heat resistance, good solvent solubility, and moldability.

[0009] The present invention relates to a polyfunctional vinyl aromatic copolymer including 2 mol% or more and less than 95 mol% of a repeating unit (a) derived from a divinyl aromatic compound (A) represented by the following general formula (1),



(1)

and 5 mol% or more and less than 98 mol% of a repeating unit (b) derived from a monovinyl aromatic compound (B) represented by the following general formula (2),

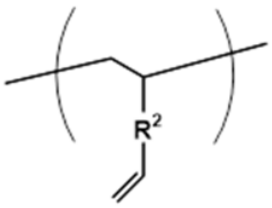


(2)

wherein R1 represents a hydrocarbon group having from 1 to 30 carbon atoms, a halogen atom, or a substituent containing any one or more of an oxygen atom, a nitrogen atom, a sulfur atom, a phosphorus atom, a selenium atom, a silicon atom, and a tin atom; m denotes an integer of from 0 to 5; and when there are a plurality of m, each R1 may be the same or different,

wherein a C^1 carbon of a phenyl group constituting (A) and (B) has a tacticity of 30% or more in a racemic pentad determined by ^{13}C-NMR,

the polyfunctional vinyl aromatic copolymer contains 2 mol% or more and less than 95 mol% of an unsaturated hydrocarbon group represented by the following formula (a1) with respect to the total of (a) and (b),

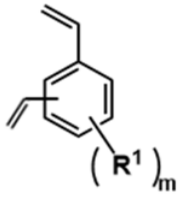


(a1)

wherein R2 represents an aromatic hydrocarbon group having from 6 to 30 carbon atoms,

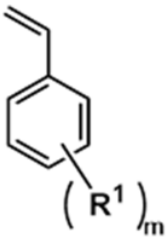
and the polyfunctional vinyl aromatic copolymer has a number average molecular weight (Mn) of from 500 to 30,000, a molecular weight distribution (Mw/Mn) expressed as the ratio of weight average molecular weight to number average molecular weight of 20.0 or less, and is soluble in a solvent.

[0010] The present invention also relates to a method for producing a polyfunctional vinyl aromatic copolymer, the method including polymerizing a divinyl aromatic compound (A) represented by the following general formula (1),



(1)

with a monovinyl aromatic compound (B) represented by the following general formula (2),



(2)

at a temperature of 100°C or lower in the presence of a reaction product of, as a catalytic component (C), at least one transition metal compound selected from compounds represented by the following general formula (3) or (4),

$MR^3aR^4bR^5cX^1_{4-(a+b+c)}$ (3)

$MR^3dR^4eX^1_{3-(d+e)}$ (4)

wherein R3, R4, and R5 each represent a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms, an aryl group having from 6 to 20 carbon atoms, an alkylaryl

group, an arylalkyl group, an acyloxy group having from 1 to 20 carbon atoms, an alkoxy group having from 1 to 20 carbon atoms, a thioalkoxy group having from 1 to 20 carbon atoms, a thioaryloxy group having from 6 to 20 carbon atoms, a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group, or a substituted fluorenyl group; M represents a transition metal selected from the group consisting of titanium (Ti), zirconium (Zr), and hafnium (Hf), and X^1 represents a halogen atom; R3, R4, and R5 may be the same or different; and a, b, and c each represent an integer of from 0 to 4, and d and e each represent an integer of from 0 to 3,

with, as a co-catalytic component (D), at least one compound selected from compounds represented by the following (d) to (g):

(d) an organoaluminum oxy compound;

(e) an ionic compound capable of reacting with the transition metal compound to produce a cationic transition metal compound;

(f) a Lewis acid compound capable of reacting with the transition metal compound to produce a cationic transition metal compound; and

(g) an organometallic compound of a metal element from groups 1, 2, and 13 of the periodic table,

to obtain a polyfunctional vinyl aromatic copolymer in which the C^1 carbon of the phenyl group constituting (A) and (B) has a tacticity of 30% or more in a racemic pentad determined by ^{13}C-NMR.

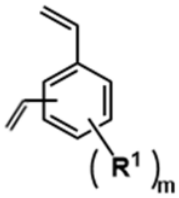
[0011] The present invention relates to a curable resin composition containing a polyfunctional vinyl aromatic copolymer, or a cured product thereof. The present invention relates to a curable composite material including the curable resin composition and a base material, a laminate having a layer of the cured composite material and a metal foil layer, a resin-coated metal foil having a film formed from the curable resin composition on one side of a metal foil, and a varnish for a circuit

board material obtained by dissolving the curable resin composition in an organic solvent.

[0012] The cured product obtained from a material containing the polyfunctional vinyl aromatic copolymer having a syndiotactic structure of the present invention has improved heat resistance, compatibility, dielectric properties, moist heat reliability, and heat resistance. According to the production method of the present invention, a polyfunctional vinyl aromatic copolymer having the above-mentioned syndiotactic structure can be produced with high efficiency.

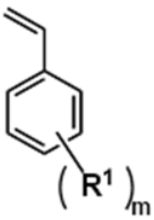
Description of Embodiments

[0013] The polyfunctional vinyl aromatic copolymer of the present invention includes 2 mol% or more and less than 95 mol% of a repeating unit (a) derived from a divinyl aromatic compound (A) represented by the following general formula (1),



(1)

and 5 mol% or more and less than 98 mol% of a repeating unit (b) derived from a monovinyl aromatic compound (B) represented by the following general formula (2).

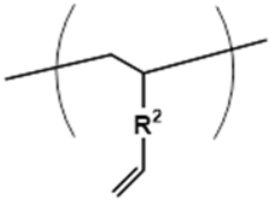


(2)

In formulas (1) and (2), R1 represents a hydrocarbon group having from 1 to 30 carbon atoms, a halogen atom, or a substituent containing any one or more of an oxygen atom, a nitrogen atom, a sulfur atom, a phosphorus atom, a selenium atom, a

silicon atom, and a tin atom; m denotes an integer of from 0 to 5; and when there are a plurality of m, each R1 may be the same or different. In formula (2), m is preferably 1 or more.

[0014] In the polyfunctional vinyl aromatic copolymer of the present invention, the C^1 carbon of the phenyl group has a tacticity of 30% or more in a racemic pentad determined by ^{13}C-NMR. The polyfunctional vinyl aromatic copolymer of the present invention contains an unsaturated hydrocarbon group represented by the following formula (a1),



(a1)

wherein R2 represents an aromatic hydrocarbon group having from 6 to 30 carbon atoms,

and the polyfunctional vinyl aromatic copolymer has a number average molecular weight (Mn) of from 500 to 30,000, a molecular weight distribution (Mw/Mn) expressed as the ratio of weight average molecular weight to number average molecular weight of 20.0 or less, and is soluble in a solvent such as toluene, xylene, or tetrahydrofuran.

[0015] The polyfunctional vinyl aromatic copolymer of the present invention is solvent-soluble even in common hydrocarbon solvents such as toluene and xylene, which are also used in the production process of copper-clad laminates.

As used herein, "structural unit" includes the repeating units present in the main chain of the copolymer and the units or terminal groups present in the terminals or side chains.

[0016] The content of the repeating unit (a) derived from the divinyl aromatic compound (A) represented by general formula (1) is 2 mol% or more and less than

95 mol% of the total of (a) and (b). It is possible for (a) to take on multiple structures, such as one vinyl group reacting with (A), two vinyl groups reacting with (A), and the like, but it is preferred that the repeating unit (a) contain from 2 to 80 mol% of the structure represented by the above formula (a1), in which only one vinyl group has reacted. More preferably, the repeating unit (a) contains from 5 to 70 mol%, further preferably from 10 to 60%, and still further preferably from 15 to 50%. By setting the content of the structure represented by the above formula (a1) to 2 mol% or more and less than 95 mol%, the dielectric loss tangent is low, toughness is high, and heat resistance is excellent.

Further, compatibility with other resins is excellent. Additionally, when used in a resin composition, moist heat resistance, heat resistance, and moldability are excellent. However, when the content is less than 2 mol%, heat resistance tends to decrease, and when the content is 95 mol% or more, the interlayer peel strength when used as a laminate tends to decrease.

[0017] The vinyl group constituting the unsaturated hydrocarbon represented by formula (a1), derived from the divinyl aromatic compound (A) represented by general formula (1), acts as a crosslinking component, contributing to the heat resistance of the polyfunctional vinyl aromatic copolymer.

[0018] On the other hand, it is thought that the repeating unit (b) derived from the monovinyl aromatic compound (B) usually undergoes polymerization by a 1,2-addition reaction of (B), and therefore does not have a vinyl group. In other words, (b) does not act as a crosslinking component. However, despite having a highly syndiotactic structure, the repeating unit (b) contributes to exhibiting good solvent solubility.

[0019] The tacticity of the C1 carbon of the phenyl group constituting (A) and (B) is 30% or more in a racemic pentad determined by ^{13}C-NMR. As a result, the polyfunctional vinyl aromatic copolymer of the present invention has a highly

syndiotactic structure. Preferably, the tacticity is 60% or more, more preferably 70% or more, and further preferably 85% or more.

[0020] The number average molecular weight (Mn) of the polyfunctional vinyl aromatic copolymer is preferably from 500 to 30,000, more preferably from 700 to 25,000, and further preferably from 1,000 to 20,000. If Mn is less than 500, the amount of monofunctional copolymer components contained in the polyfunctional vinyl aromatic copolymer increases, and as a result the heat resistance of the cured product tends to decrease. On the other hand, if Mn exceeds 30,000, gel formation tends to occur, and the viscosity also increases, which tends to decrease moldability.

[0021] The molecular weight distribution (Mw/Mn), expressed as the ratio of weight average molecular weight (Mw) to number average molecular weight (Mn), is 20.0 or less, preferably 15.0 or less, more preferably from 1.5 to 10.0, and further preferably from 2.0 to 7.0. When Mw/Mn exceeds 20.0, the processability of the solvent-soluble curable aromatic vinyl copolymer having a syndiotactic structure deteriorates, and a gel tends to form.

[0022] The polyfunctional vinyl aromatic polymer of the present invention is soluble in common hydrocarbon solvents such as toluene and xylene, which are also used in the production process of copper-clad laminates. For a copolymer to be soluble in solvents and polyfunctional, it is necessary to leave some of the vinyl groups of divinylbenzene uncrosslinked and maintain an appropriate degree of branching. "Solvent-soluble" means that 5 g or more of the soluble polyfunctional vinyl aromatic copolymer dissolves in 100 g of solvent.

[0023] Next, a method for producing the polyfunctional vinyl aromatic copolymer having a syndiotactic structure of the present invention will be described.

[0024] In the production method of the present invention, as the main catalytic component, a reaction product of (C) at least one transition metal compound selected from compounds represented by the following general formulas (3) and (4),

$MR^3aR^4bR^5cX^1_{4-(a+b+c)}$ (3)

$MR^3dR^4eX^1_{3-(d+e)}$ (4)

and (D) at least one compound selected from the compounds represented by the following (d) to (g):

(d) an organoaluminum oxy compound;

(e) an ionic compound capable of reacting with the transition metal compound to produce a cationic transition metal compound;

(f) a Lewis acid compound capable of reacting with the transition metal compound to produce a cationic transition metal compound; and

(g) an organometallic compound of a metal element from groups 1, 2, and 13 of the periodic table,

is used, and in the presence of the catalytic component thus obtained, the divinyl aromatic compound (A) and the monovinyl aromatic compound (B) are polymerized at a temperature of 100°C or lower.

The transition metal compound (C) acts as a catalyst, and compounds (d) to (g) (D) act as co-catalysts.

In the transition metal compound (C) represented by general formulas (3) or (4), R3, R4, and R5 each represent a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms, an aryl group having from 6 to 20 carbon atoms, an alkylaryl group, an arylalkyl group, an acyloxy group having from 1 to 20 carbon atoms, an alkoxy group having from 1 to 20 carbon atoms, a thioalkoxy group having from 1 to 20 carbon atoms, a thioaryloxy group having from 6 to 20 carbon atoms, a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group, or a substituted fluorenyl group; M represents a transition metal selected from the group consisting of titanium (Ti), zirconium (Zr), and hafnium (Hf), and X^1 represents a halogen atom; R^3, R^4, and R^5

may be the same or different; and a, b, and c each represent an integer of from 0 to 4, and d and e each represent an integer of from 0 to 3.

[0025] The divinyl aromatic compound (A) represented by general formula (1) plays a role in forming a branched structure and adding functional groups, and also plays a role as a crosslinking component to exert heat resistance when the obtained polyfunctional vinyl aromatic copolymer is thermoset.

[0026] Examples of the divinyl aromatic compound (A) represented by general formula (1) are not limited as long as the compound is an aromatic compound having two vinyl groups, but divinylbenzene (including each positional isomer or mixtures thereof), divinylnaphthalene (including each positional isomer or mixtures thereof), and divinylbiphenyl (including each positional isomer or mixtures thereof) are preferably used. These compounds may be any of the positional isomers or mixtures thereof.

These can be used alone or in combination of two or more. From the viewpoint of moldability, divinylbenzene (m-isomer, p-isomer, or mixture of those positional isomers) is more preferred.

[0027] The monovinyl aromatic compound (B) represented by general formula (2) plays a role as a monomer component in imparting low dielectric properties, solvent solubility, and heat resistance to the polyfunctional vinyl aromatic copolymer.

[0028] Examples of the monovinyl aromatic compounds (B) are not limited to monovinyl aromatic compounds represented by general formula (2), and include nuclear alkyl-substituted vinyl aromatic compounds such as styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, o,p-dimethylstyrene, o-ethylvinylbenzene, m-ethylvinylbenzene, and p-ethylvinylbenzene, and monovinyl aromatic compounds having a substituent containing one or more of a halogen atom, an oxygen atom, a nitrogen atom, a sulfur atom, a phosphorus atom, a selenium atom, a silicon atom, or a tin atom.

Styrene, methylstyrene, ethyl vinylbenzene, ethyl vinyl biphenyl, or ethyl vinyl naphthalene is preferred. A positional isomer or mixture thereof may also be used. From the viewpoint of dielectric properties and cost, more preferred are styrene, methylstyrene, or ethyl vinylbenzene (m-isomer, p-isomer, or mixtures of these positional isomers).

[0029] Another monomer component (E) such as a trivinyl aromatic compound, a trivinyl aliphatic compound, a divinyl aliphatic compound, and a monovinyl aliphatic compound can be, to the extent that the effects of the present invention are not impaired, used in addition to the divinyl aromatic compound (A) and the monovinyl aromatic compound (B). A structural unit (e) derived from (E) can be introduced into the soluble polyfunctional vinyl aromatic copolymer.

[0030] The other monomer component (E) is not limited, but is preferably 1,3,5-trivinylbenzene, 1,3,5-trivinylnaphthalene, 1,2,4-trivinylcyclohexane, ethylene glycol diacrylate, butadiene, 1,4-butanediol divinyl ether, cyclohexanedimethanol divinyl ether, diethylene glycol divinyl ether, triallyl isocyanurate, and the like. These can be used alone or in combination of two or more.

The other monomer component (E) preferably has a mole fraction of less than 30 mol% of the total monomer components, that is, the sum of (A), (B), and (E). In other words, the mole fraction of the repeating unit (e) derived from (E) is preferably less than 30 mol% of the total repeating units in the polyfunctional vinyl aromatic copolymer, that is, the sum of (a), (b), and (e).

[0031] Another vinyl compound (F) containing a hydroxyl group other than (A), (B), and (E), such as hydroxyethyl (meth)acrylate or hydroxypropyl (meth)acrylate, can optionally be used to introduce a structural unit (f) derived from (F) into the polyfunctional vinyl aromatic copolymer.

The vinyl compound (F) containing a hydroxyl group preferably has a mole fraction of less than 10 mol% of the total monomer components, that is, the total of

(A), (B), (E), and (F). It is particularly preferable that the mole fraction is less than 5 mol%. In other words, the mole fraction of the repeating unit (e) derived from (E) is preferably less than 10 mol% of the total repeating units in the polyfunctional vinyl aromatic copolymer, that is, the total of (a), (b), (e), and (f).

[0032] The proportion in which the main monomer components are used is such that (A) is used in an amount of 2 mol% or more and less than 95 mol% of the total of (A) and (B), and (B) is used in an amount of 5 mol% or more and less than 98 mol%. (A) and (B) are polymerized at a temperature of 100°C or lower.

(A) is preferably from 5 to 80 mol%, more preferably from 7 to 70 mol%, and further preferably from 10 to 60 mol%.

(B) is preferably from 95 to 20 mol%, more preferably from 93 to 30 mol%, and particularly preferably from 90 to 40 mol%.

[0033] The catalyst component (C) used is at least one transition metal compound selected from the compounds represented by the following general formulas (3) and (4).

$$MR^3aR^4bR^5cX^1_{4-(a+b+c)} \quad (3)$$

$$MR^3dR^4eX^1_{3-(d+e)} \quad (4)$$

Among these transition metal compounds, it is most preferred to use a titanium compound in terms of polymerization activity. More preferable titanium compounds include mono(cyclopentadiel) titanium compounds, mono(indenyl) titanium compounds, and mono(fluorenyl) titanium compounds represented by general formula (5).

$$TiR^4XYZ \quad (5)$$

In the formula, R4 represents a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group, and the like, and X, Y, and Z each independently represent a hydrogen atom, an alkyl group having from 1 to 12 carbon atoms, an alkoxy group having from 1 to

12 carbon atoms, a thioalkoxy group having from 1 to 20 carbon atoms, an aryl group having from 6 to 20 carbon atoms, an aryloxy group having from 6 to 20 carbon atoms, a thioaryloxy group having from 6 to 20 carbon atoms, an arylalkyl group having from 6 to 20 carbon atoms, or a halogen atom.

[0034] The substituted cyclopentadienyl group represented by R4 is, for example, a cyclopentadienyl group substituted with one or more alkyl groups having from 1 to 6 carbon atoms, specifically a methylcyclopentadienyl group; a 1,3-dimethylcyclopentadienyl group; a 1,2,4-trimethylcyclopentadienyl group; a 1,2,3,4-tetramethylcyclopentadienyl group; a trimethylsilylcyclopentadienyl group; a 1,3-di(trimethylsilyl)cyclopentadienyl group; a tert-butylcyclopentadienyl group; a 1,3-di(tert-butyl)cyclopentadienyl group; a pentamethylcyclopentadienyl group, and the like.

[0035] X, Y, and Z are, each independently, a hydrogen atom, an alkyl group having from 1 to 12 carbon atoms (specifically, a methyl group, an ethyl group, a propyl group, an n-butyl group, an isobutyl group, an amyl group, an isoamyl group, an octyl group, a 2-ethylhexyl group, and the like), an alkoxy group having from 1 to 12 carbon atoms (specifically, a methoxy group, an ethoxy group, a propoxy group, a butoxy group, an amyloxy group, a hexyloxy group, an octyloxy group, a 2-ethylhexyloxy group, and the like), a thioalkoxy group having from 1 to 20 carbon atoms (specifically, a thiomethoxy group and the like), an aryl group having from 6 to 20 carbon atoms (specifically, a phenyl group, a naphthyl group, and the like), an arlyloxy group having from 6 to 20 carbon atoms (specifically, a phenoxy group and the like), a thioaryloxy group having from 6 to 20 carbon atoms (specifically, a thiophenol group and the like), an arylalkyl group having from 6 to 20 carbon atoms (specifically, a benzyl group), or a halogen atom (specifically, chlorine, bromine, iodine, or fluorine).

[0036] Specific examples of titanium compounds represented by general formula (5) include: cyclopentadienyltrimethyltitanium; cyclopentadienyltriethyltitanium; cyclopentadienyltripropyltitanium; cyclopentadienyltributyltitanium; methylcyclopentadienyltrimethyltitanium; 1,2-dimethylcyclopentadienyltrimethyltitanium; 1,2,4-trimethylcyclopentadienyltrimethyltitanium; 1,2,3,4-tetramethylcyclopentadienyltrimethyltitanium; pentamethylcyclopentadienyltrimethyltitanium; pentamethylcyclopentadienyltriethyltitanium; pentamethylcyclopentadienyltripropyltitanium; pentamethylcyclopentadienyltributyltitanium; cyclopentadienylmethyltitanium dichloride; cyclopentadienylethyltitanium dichloride; pentamethylcyclopentadienylmethyltitanium dichloride; pentamethylcyclopentadienylethyltitanium dichloride; cyclopentadienyldimethyltitanium monochloride; cyclopentadienyldiethyltitanium monochloride; cyclopentadienyltitanium trimethoxide; cyclopentadienyltitanium triethoxide; cyclopentadienyltitanium tripropoxide; cyclopentadienyltitanium triphenoxide; pentamethylcyclopentadienyltitanium trimethoxide; pentamethylcyclopentadienyl titanium triethoxide; pentamethylcyclopentadienyl titanium tripropoxide; pentamethylcyclopentadienyl titanium tributoxide; pentamethylcyclopentadienyl titanium triphenoxide; cyclopentadienyl titanium trichloride; pentamethylcyclopentadienyl titanium trichloride; cyclopentadienyl methoxytitanium dichloride; cyclopentadienyl dimethoxytitanium chloride; pentamethylcyclopentadienyl methoxytitanium dichloride; cyclopentadienyltribenzyl titanium; pentamethylcyclopentadienylmethyldiethoxytitanium; indenyl titanium trichloride; indenyl titanium trimethoxide; indenyl titanium triethoxide; indenyl trimethyl titanium; indenyl tribenzylic titanium; pentamethylcyclopentadienyl

titanium trithiomethoxide; pentamethylcyclopentadienyl titanium trithiophenoxide, and the like.

[0037] As the titanium compound, a condensed titanium compound represented by general formula (6) may be used.



(6)

In the formula, R6 and R7 each represent a halogen atom, an alkoxy group having from 1 to 20 carbon atoms, or an acyloxy group, and k denotes an integer of from 2 to 20.

Examples of the trivalent titanium compound represented by general formula (6) typically include titanium trihalides such as titanium trichloride and cyclopentadienyl titanium compounds such as cyclopentadienyl titanium dichloride. Other examples include a trivalent titanium compound obtained by reducing a tetravalent titanium compound. These trivalent titanium compounds may also be used as a complex with an ester, ether, or the like.

[0038] Examples of a zirconium compound as the transition metal compound include tetrabenzylzirconium, zirconium tetraethoxide, zirconium tetrabutoxide, bisindenylzirconium dichloride, triisopropoxydirconium chloride, zirconium benzyl dichloride, and tributoxydirconium chloride. Examples of a hafnium compound as the transition metal compound include tetrabenzylhafnium, hafnium tetraethoxide, and hafnium tetrabutoxide. Examples of a vanadium compound as the transition metal compound include vanadylbisacetylacetonate, vanadyltriacetylacetonate, triethoxyvanadyl, and tripropoxyvanadyl. Among these transition metal compounds, a titanium compound is particularly preferred.

The titanium compound may be a compound that is formed as a complex with an ester or ether.

[0039] The transition metal compound that is component (A) is a transition metal compound having two ligands having conjugated π electrons, and is, for example, at least one compound selected from the group consisting of the transition metal compounds represented by general formula (7).

$M^1R^8R^9R^{10}R^{11}$ (7)

In the formula, M1 represents titanium, zirconium, or hafnium, R8 and R9 each represent a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, or a fluorenyl group, and R10 and R11 each represent a hydrogen atom, a halogen atom, a hydrocarbon group having from 1 to 20 carbon atoms, an alkoxy group having from 1 to 20 carbon atoms, an amino group, or a thioalkoxy group having from 1 to 20 carbon atoms. However, R8 and R9 may be crosslinked with a hydrocarbon group having from 1 to 5 carbon atoms, an alkylsilyl group having from 1 to 20 carbon atoms and from 1 to 5 silicon atoms, or a germanium-containing hydrocarbon group having from 1 to 20 carbon atoms and from 1 to 5 germanium atoms.

[0040] In general formula (7), R8 and R9 are each a cyclopentadienyl group, a substituted cyclopentadienyl group (specifically, a methylcyclopentadienyl group; a 1,3-dimethylcyclopentadienyl group; a 1,2,4-trimethylcyclopentadienyl group; a 1,2,3,4-tetramethylcyclopentadienyl group; a pentamethylcyclopentadienyl group; trimethylsilylcyclopentadienyl group; a 1,3-di(trimethylsilyl)cyclopentadienyl group; a 1,2,4-tri(trimethylsilyl)cyclopentadienyl group; a tert-butylcyclopentadienyl group; a 1,3-di(tert-butyl)cyclopentadienyl group; a 1,2,4-tri(tert-butyl)cyclopentadienyl group, and the like), an indenyl group, a substituted indenyl group (specifically, a methylindenyl group; a dimethylindenyl group; a trimethylindenyl group, and the like), a fluorenyl group, a substituted fluorenyl group (e.g., a methylfluorenyl group).

R8 and R9 may also be structures that are cross-linked by an alkylidene group having from 1 to 5 carbon atoms (specifically, a methine group, an ethylidene group, a propyridene group, a dimethylcarbyl group, and the like) or an alkyl silyl group having from 1 to 20 carbon atoms and from 1 to 5 silicon atoms (specifically, a dimethylsilyl group, a diethylsilyl group, a dibenzylsilyl group, and the like).

[0041] More specifically, R10 and R11 are, each independently, a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms (a methyl group, an ethyl group, a propyl group, an n-butyl group, an isobutyl group, an amyl group, an isoamyl group, an octyl group, a 2-ethylhexyl group, and the like), an aryl group having from 6 to 20 carbon atoms (specifically, a phenyl group, a naphthyl group, and the like), an arylalkyl group having from 7 to 20 carbon atoms (specifically, a benzyl group and the like), an alkoxy group having from 1 to 20 carbon atoms (specifically, a methoxy group, an ethoxy group, a propoxy group, a butoxy group, an amyloxy group, a hexyloxy group, an octyloxy group, a 2-ethylhexyloxy group, and the like), and an aryloxy group having from 6 to 20 carbon atoms (specifically, a phenoxy group), as well as an amino group or thioalkoxy groups having from 1 to 20 carbon atoms.

[0042] Specific examples of the transition metal compound represented by general formula(7) include biscyclopentadienyl titanium dimethyl; biscyclopentadienyl titanium diethyl; biscyclopentadienyl titanium dipropyl; biscyclopentadienyl titanium dibutyl; bis(methylcyclopentadienyl)titanium dimethyl; bis(tert-butylcyclopentadienyl)titanium dimethyl; bis(1,3-dimethylcyclopentadienyl)titanium dimethyl; bis(1,3-ditert-butylcyclopentadienyl)titanium dimethyl; bis(1,2,4-trimethylcyclopentadienyl)titanium dimethyl; bis(1,2,3,4-tetramethylcyclopentadienyl)titaniumdimethyl; biscyclopentadienyltitaniumdimethyl; bis(trimethylsilylcyclopentadienyl)titaniumdimethyl; bis(1,3-di(trimethylsilyl)cyclopentadienyl)titaniumdimethyl; bis(1,2,4-

tri((trimethylsilyl)cyclopentadienyl)titaniumdimethyl; bisindenyltitaniumdimethyl; bisfluorenyltitaniumdimethyl; methylenebiscyclopentadienyltitaniumdimethyl; ethylidenebiscyclopentadienyltitaniumdimethyl; methylenebis(2,3,4,5-tetramethylcyclopentadienyl)titanium dimethyl; ethylidenebis(2,3,4,5-tetramethylcyclopentadienyl)titanium dimethyl; dimethylsilylbis(2,3,4,5-tetramethylcyclopentadienyl)titanium dimethyl; methylenebisindenyl titanium dimethyl; ethylidenebisindenyl titanium dimethyl; dimethylsilylbisindenyl titanium dimethyl; methylenebisfluorenyl titanium dimethyl; ethylidenebisfluorenyl titanium dimethyl; dimethylsilylbisfluorenyl titanium dimethyl; methylene(tert-butylcyclopentadienyl)(cyclopentadienyl)titanium dimethyl; methylene(cyclopentadienyl)(indenyl)titanium dimethyl; ethylidene(cyclopentadienyl)(indenyl)titanium dimethyl; dimethylsilyl(cyclopentadienyl)(indenyl)titanium dimethyl; methylene(cyclopentadienyl)(fluorenyl)titanium dimethyl; ethylidene(cyclopentadienyl)(fluorenyl)titanium dimethyl; dimethylsilyl(cyclopentadienyl)(fluorenyl)titanium dimethyl; methylene(indenyl)(fluorenyl)titanium dimethyl; ethylidene(indenyl)(fluorenyl)titanium dimethyl; dimethylsilyl(indenyl)(fluorenyl)titanium dimethyl; biscyclopentadienyl titanium dibenzyl; bis(tert-butylcyclopentadienyl)titanium dibenzyl; bis(methylcyclopentadienyl)titanium dibenzyl; bis(1,3-dimethylcyclopentadienyl)titanium dibenzyl; bis(1,2,4-trimethylcyclopentadienyl)titanium dibenzyl; bis(1,2,3,4-tetramethylcyclopentadienyl)titanium dibenzyl; bispentamethylcyclopentadienyltitanium dibenzyl; bis(trimethylsilylcyclopentadienyl)titanium dibenzyl; bis(1,3-di-(trimethylsilyl)cyclopentadienyl)titanium dibenzyl; bis(1,2,4-

tri(trimethylsilyl)cyclopentadienyl)titanium dibenzyl; bisindenyl titanium dibenzyl; bisfluorenyl titanium dibenzyl; methylene biscyclopentadienyl titanium dibenzyl; ethylidene biscyclopentadienyl titanium dibenzyl; methylene bis(2,3,4,5-tetramethylcyclopentadienyl)titanium dibenzyl; ethylidene bis(2,3,4,5-tetramethylcyclopentadienyl)titanium dibenzyl; dimethylsilyl bis(2,3,4,5-tetramethylcyclopentadienyl)titanium dibenzyl; methylene bisindenyl titanium dibenzyl; ethylidene bisindenyl titanium dibenzyl; dimethylsilyl bisindenyl titanium dibenzyl; methylene bisfluorenyl titanium dibenzyl; ethylidene bisfluorenyl titanium dibenzyl; dimethylsilyl bisfluorenyl titanium dibenzyl; methylene(cyclopentadienyl)(indenyl)titanium dibenzyl; ethylidene(cyclopentadienyl)(indenyl)titanium dibenzyl; dimethylsilyl(cyclopentadienyl)(indenyl)titanium dibenzyl; methylene(cyclopentadienyl)(fluorenyl)titanium dibenzyl; ethylidene(cyclopentadienyl)(fluorenyl)titanium dibenzyl; dimethylsilyl(cyclopentadienyl)(fluorenyl)titanium dibenzyl; methylene(indenyl)(fluorenyl)titanium dibenzyl; ethylidene(indenyl)(fluorenyl)titanium dibenzyl; dimethylsilyl(indenyl)(fluorenyl)titanium dibenzyl; biscyclopentadienyl titanium dimethoxide; biscyclopentadienyl titanium diethoxide; biscyclopentadienyl titanium dipropoxide; biscyclopentadienyl titanium dibutoxide; biscyclopentadienyl titanium diphenoxide; bis(methylcyclopentadienyl)titanium dimethoxide; bis(1,3-dimethylcyclopentadienyl)titanium dimethoxide; bis(1,2,4-trimethylcyclopentadienyl)titanium dimethoxide; bis(1,2,3,4-taylaminemethylcyclopentadienyl)titanium dimethoxide; bispentamethylcyclopentadienyl titanium dimethoxide; bis(trimethylsilylcyclopentadienyl)titanium dimethoxide; bis(1,3-di(trimethylsilyl)cyclopentadienyl)titanium dimethoxide; bis(1,2,4-

tri(trimethylsilyl)cyclopentadienyl)titanium dimethoxide; bisindenyl titanium dimethoxide; bisfluorenyl titanium dimethoxide; methylene biscyclopentadienyl titanium dimethoxide; ethylidene biscyclopentadienyl titanium dimethoxide; methylene bis(2,3,4,5-tetramethylcyclopentadienyl)titanium dimethoxide; ethylidene bis(2,3,4,5-tetramethylcyclopentadienyl)titanium dimethoxide; dimethylsilyl bis(2,3,4,5-tetramethylcyclopentadienyl)titanium dimethoxide; methylene bisindenyl titanium dimethoxide; methylene bis(methyl-indenyl)titanium dimethoxide; ethylidene bisindenyl titanium dimethoxide; dimethylsilyl bisindenyl titanium dimethoxide; methylene bis-fluorenyl titanium dimethoxide; methylene bis(methyl-fluorenyl)titanium dimethoxide; ethylidene bis-fluorenyl titanium dimethoxide; dimethylsilyl bis-fluorenyl titanium dimethoxide;
methylene(cyclopentadienyl)(indenyl)titanium dimethoxide;
ethylidene(cyclopentadienyl)(indenyl)titanium dimethoxide;
dimethylsilyl(cyclopentadienyl)(indenyl)titanium dimethoxide;
methylene(cyclopentadienyl)(fluorenyl)titanium dimethoxide;
ethylidene(cyclopentadienyl)(fluorenyl)titanium dimethoxide;
dimethylsilyl(cyclopentadienyl)(fluorenyl)titanium dimethoxide;
methylene(indenyl)(fluorenyl)titanium dimethoxide;
ethylidene(indenyl)(fluorenyl)titanium dimethoxide; and
dimethylsilyl(indenyl)(fluorenyl)titanium dimethoxide, and the like.

[0043] Examples of the zirconium compound include ethylidene biscyclopentadienyl zirconium dimethoxide, dimethylsilyl biscyclopentadienyl zirconium dimethoxide, and the like. Further, examples of the hafnium compound include ethylidene biscyclopentadienyl hafnium dimethoxide, dimethylsilyl biscyclopentadienyl hafnium dimethoxide, and the like. Among these, a titanium compound is particularly preferred. In addition to these combinations, bidentate complexes such as 2,2'-thiobis(4-methyl-6-t-butylphenyl)titanium diisopropoxide and 2,2'-thiobis(4-

methyl-6-t-butylphenyl)titanium dimethoxide may be used. Among these transition metal compounds, it is particularly preferred to use a transition metal compound having one π ligand, as shown in general formula (7).

[0044] In the polymerization catalyst used in the present invention, one type of the transition metal compound of the component (C) may be used, or two or more types may be used in combination.

The component (D) contains a compound obtained from at least one co-catalyst selected from the following (a) to (d):

(a) an organoaluminum oxy compound

(b) an ionic compound capable of reacting with the transition metal compound to produce a cationic transition metal compound

(c) a Lewis acid compound capable of reacting with the transition metal compound to produce a cationic transition metal compound

(d) an organometallic compound of a metal element from groups 1, 2, and 13 of the periodic table.

[0045] The organoaluminum oxy compound (a) is preferably a linear or cyclic polymer represented by the following general formula (8), and is a so-called aluminoxane.

$(-Al(R^{12})O-)n$ (8)

In the formula, R12 is a hydrocarbon group having from 1 to 10 carbon atoms, and R12 may be substituted with a halogen atom and/or an $R^{13}O$ group. Specific examples of R12 or R13 include an alkyl group such as methyl, ethyl, propyl, and isobutyl, and of those a methyl group is preferred. n denotes the degree of polymerization, and is preferably 5 or more, more preferably in the range of 10 to 100, and most preferably 10 to 50. If the degree of polymerization n is less than 5, the polymerization activity decreases, which is undesirable, and if it is greater than

100, problems such as decreased polymerization activity and difficulty in demineralization occur, which is also undesirable.

[0046] Examples of the ionic compound (b) that is capable of reacting with the transition metal compound represented by general formula (3) or general formula (4) to form a cationic transition metal compound include non-coordinating anions and cations.

Examples of the non-coordinating anion include tetra(phenyl)borate, tetra(fluorophenyl)borate, tetrakis(difluorophenyl)borate, tetrakis(trifluorophenyl)borate, tetrakis(tetrafluorophenyl)borate, tetrakis(pentafluorophenyl)borate, tetrakis(tetrafluoromethylphenyl)borate, tetra(triyl)borate, tetra(xyl)borate, triphenylpentafluorophenylborate, tris(pentafluorophenyl)phenylborate, and the like.

[0047] Among the non-coordinating anions, tetrakis(pentafluorophenyl)borate is particularly preferred. Specific examples include, for example, triphenylcarbeniumtetrakis(pentafluorophenyl)borate; 4,4',4"-tri(methoxyphenyl)carbeniumtetrakis(pentafluorophenyl)borate; tri(toluyl)carbeniumtetrakis(pentafluorophenyl)borate; 4,4',4"-tri(chlorophenyl)carbeniumtetrakis(pentafluorophenyl)borate; triphenylsilyltetrakis(pentafluorophenyl)borate; trimethoxysilyltetrakis(pentafluorophenyl)borate; tri(thioisopropyl)silyltetrakis(pentafluorophenyl)borate; trimethylsilyltetrakis(pentafluorophenyl)borate; 4,4',4"-tri(methoxyphenyl)silyltetrakis(pentafluorophenyl)borate; tri(toluyl)silyltetrakis(pentafluorophenyl)borate; 4,4',4"-tri(chlorophenyl)silyltetrakis(pentafluorophenyl)borate, and the like

[0048] Examples of the cation include a) carbonium cations, b) oxonium cations, c) ammonium cations, d) phosphonium cations, e) ferrocenium cations having a transition metal, and the like.

Specific examples of the carbonium cation a) include trisubstituted carbonium cations such as a triphenylcarbonium cation and a trisubstituted phenylcarbonium cation. Specific examples of the trisubstituted phenylcarbonium cation include a tri(methylphenyl)carbonium cation and a tri(dimethylphenyl)carbonium cation.

Specific examples of the oxonium cation b) include alkyl oxonium cations such as a hydroxonium cation OH_3^+ and a methyloxonium cation $CH_3OH_2^+$, dialkyloxonium cations such as a dimethyloxonium cation $(CH_3)_2OH^+$, and trialkyloxonium cations such as a trimethyloxonium cation $(CH_3)_3O^+$ and triethyloxonium cation $(C_2H_5)_3O^+$.

Specific examples of the ammonium cation c) include trialkylammonium cations such as a trimethylammonium cation, a triethylammonium cation, a tripropylammonium cation, and a tributylammonium cation; N,N-dialkylanilinium cations such as an N,N-diethylanilinium cation and an N,N-2,4,6-pentamethylanilinium cation; and dialkylammonium cations such as a di(i-propyl)ammonium cation and a dicyclohexylammonium cation.

Specific examples of the phosphonium cation d) include triarylphosphonium cations such as a triphenylphosphonium cation, a tri(methylphenyl)phosphonium cation, and a tri(dimethylphenyl)phosphonium cation.

[0049] The ionic compound (b) can be any combination of the non-coordinating anions and the cation exemplified above. Of these, in particular, it is more preferred to use an ionic compound such as triphenylcarbonium tetra(pentafluorophenyl)borate, N,N-dimethylanilinium tetra(pentafluorophenyl)borate, or 1,1'-dimethylferrocenium tetra(pentafluorophenyl)borate.

[0050] Specific examples of the Lewis acid compound (c) that is capable of reacting with the transition metal compound represented by general formula (3) or general formula (4) to produce a cationic transition metal compound include tris(pentafluorophenyl)boron, tris(monofluorophenyl)boron, tris(difluorophenyl)boron, and triphenylboron.

[0051] The organometallic compound (d) of a metal element from groups 1, 2, and 13 of the periodic table may not only be an organometallic compound in the narrow sense, but may also be an organometallic halogen compound or an organometallic hydride compound of a metal element from groups 1, 2, and 13 of the periodic table.

Here, examples of the metal element from groups 1, 2, and 13 of the periodic table include the following.

Metal element from group 1 of the periodic table: Li and Na

Metal element from group 2 of the periodic table: Mg and Be

Metal element from group 13 of the periodic table: Al and B

Of these, preferred metal elements are Li, Mg, and Al, and particularly preferred is Al.

[0052] Examples of the organometallic compound (d) include methyllithium, butyllithium, phenyllithium, dibutylmagnesium, trimethylaluminum, triethylaluminum, triisobutylaluminum, trihexylaluminum, trioctylaluminum, and the like, and trialkylaluminum is preferred.

Examples of the organometallic halogen compound (d) include ethylmagnesium chloride, butylmagnesium chloride, dimethylaluminum chloride, diethylaluminum chloride, sesquiethylaluminum chloride, ethylaluminum dichloride, and the like.

Examples of the organometallic hydride compound (d) include diethylaluminum hydride, sesquiethylaluminum hydride, and the like.

[0053] In the present invention, the above-described (a) to (d) may be used alone or in combination as the co-catalyst. The preferred co-catalyst is (a) alone, (c) alone, a combination of (a) and (d), a combination of (b) and (d), and a combination of (c) and (d). Particularly preferred is the combination of (c) and (d).

[0054] In the production method of the present invention, a reaction product of the catalyst component (C) and the co-catalyst component (D) is used as the catalyst component, but other catalyst components may be added as long as they do not impair the effects of the present invention.

The blend proportion of the components (C) and (D) in the catalyst of the present invention depends on the monomer components and the polymerization conditions, and is adjusted as appropriate, but it is generally desirable that the molar ratio of the catalyst component (C) to the co-catalyst component (D) be within the following range.

[0055] The molar ratio of aluminum in the organoaluminum oxy compound (d) / transition metal compound (A) is usually from 1 to 1,000,000, preferably from 10 to 50,000, and more preferably from 100 to 5,000.

The molar ratio of the ionic compound (e) / transition metal compound (A) is usually from 0.01 to 100, and preferably from 0.1 to 10.

The molar ratio of the Lewis acid compound (f) / transition metal compound (A) is usually from 0.01 to 100, and preferably from 0.1 to 10. When using a Lewis acid compound as a co-catalyst, it is preferable to use an organometallic compound of a metal element from groups 1, 2, and 13 of the periodic table in combination.

When using the organometallic compound (g), the molar ratio of the organometallic compound (g) / transition metal compound (A) is usually from 0.1 to 10,000, and preferably from 1 to 1,000. Values outside this range are undesirable because polymerization activity is reduced.

[0056] In the present invention, the monomer component may be polymerized by using a metal hydride compound in combination with an organometallic compound of a metal element from groups 1, 2, and 13 of the periodic table, an organometallic halogen compound, or an organometallic hydride compound.

Examples of the metal hydride compound include NaH, LiH, CaH2, LiAlH4, NaBH4, and the like. Examples of the organometallic compound of the main metal element of the metal element from groups 1, 2, and 13 of the periodic table, the organometallic halogen compound, and the organometallic hydride compound include those described above.

[0057] In the present invention, the catalyst component (C) of the transition metal compound represented by general formula (3) or general formula (4) can be used alone, or the catalyst component and at least one co-catalyst component (D) can be supported on a carrier.

Examples of the carrier include inorganic compounds and organic polymer compounds. Preferred inorganic compounds include inorganic oxides, inorganic chlorides, and inorganic hydroxides, which may also contain small amounts of carbonates and sulfates. Preferred examples include inorganic oxides such as silica, alumina, magnesia, titania, zirconia, and calcia, and inorganic chlorides such as magnesium chloride. The inorganic compound is preferably a porous fine particle having an average particle size of from 5 to 150 μm and a specific surface area of from 2 to 800 m^2/g, and can be used after a heat treatment at, for example, from 100 to 800°C.

[0058] The organic polymer compound (g) as the co-catalyst preferably has an aromatic ring, a substituted aromatic ring, or a functional group such as a hydroxy group, a carboxyl group, an ester group, or a halogen atom in a side chain. Specific examples of the organic polymer compound include α-olefin homopolymers and α-olefin copolymers having a functional group obtained by chemically modifying a

polymer having units such as ethylene, propylene, and butene, polymers having units such as acrylic acid, methacrylic acid, vinyl chloride, vinyl alcohol, styrene, and divinylbenzene, and chemically modified products of these.

The organic polymer compound is composed of spherical fine particles having an average particle size of from 5 to 250 μm. By supporting the transition metal compound as a catalyst and the co-catalyst individually, contamination due to the catalyst adhering to the polymerization reactor can be prevented.

[0059] The polyfunctional vinyl aromatic copolymer of the present invention can be obtained by polymerizing using the monomer component, catalyst, and co-catalyst, for example, as follows.

[0060] (I) Polymerization is carried out by first bringing the co-catalyst component (D) into contact with the monomer component, and then further bringing into contact with the catalyst component (C).

(II) Polymerization is carried out by first bringing the catalyst component (C) into contact with the co-catalyst component (D) and a small amount of the monomer component, and then further bringing into contact with the monomer component.

(III) Polymerization is carried out by first bringing the catalyst component (C) into contact with the co-catalyst component (D), and then further bringing into contact with the monomer component.

(IV) Polymerization is carried out by first bringing the catalyst component (C) into contact with the monomer component, and then further bringing into contact with the co-catalyst component (D).

(V) Polymerization is carried out by mixing the catalyst component (C) and the co-catalyst component (D), bringing the mixture into contact with the carrier, and bringing the resulting supported catalyst into contact with the monomer component.

(VI) Polymerization is carried out by bringing the catalyst component (C) into contact with the carrier, then further bringing into contact with the co-catalyst

component (D), and bringing the resulting supported catalyst into contact with the monomer component.

(VII) Polymerization is carried out by bringing the co-catalyst component (D) into contact with the carrier, then further bringing into contact with the catalyst component (C), and bringing the resulting supported catalyst into contact with the monomer component.

[0061] Among methods (I) to (VII), methods (I), (II), (III), and (IV) are preferred because they improve initiator efficiency and polymerization activity, and can further narrow the molecular weight distribution of the resulting polymer. Methods (II) and (III) are even more preferred.

Particularly preferred are methods (II) and (III), in which the catalyst component (C) and co-catalyst component (D) are brought into contact in advance for from 0.001 to 300 minutes before bringing them into contact with the monomer component to carry out polymerization. This method allows for the highly efficient acquisition of polyfunctional vinyl aromatic copolymers having a syndiotactic structure with a narrow molecular weight distribution (Mw/Mn), which is the ratio of weight average molecular weight (Mw) to number average molecular weight (Mn).

[0062] The catalyst component (C) and the co-catalyst component (D) can each be used in either solution or slurry state, but to obtain higher polymerization activity, a solution state is preferred. The solvent used to prepare the solution or slurry is a hydrocarbon solvent such as butane, pentane, hexane, heptane, octane, cyclohexane, mineral oil, benzene, toluene, or xylene, or a halogenated hydrocarbon solvent such as chloroform, methylene chloride, dichloroethane, or chlorobenzene. Preferred solvents are aromatic hydrocarbons such as toluene and benzene. Two or more solvents may be used by mixing them.

[0063] The polymerization temperature is usually 100°C or lower, preferably 80°C or lower, and more preferably 0 to 60°C.

If the polymerization temperature is higher than 100°C, an insoluble gel tends to form. The typical polymerization time is from 10 seconds to 36 hours, preferably from 1 minute to 20 hours, and more preferably from 5 minutes to 10 hours. The optimal time required to produce the desired polymer depends on the temperature, solvent, and polymerization conditions used.

[0064] The polymerization can be carried out at a pressure lower than atmospheric pressure or at a pressure higher than atmospheric pressure. The polymerization can also be carried out under reduced pressure where the lowest component of the polymerization mixture vaporizes. It is preferable to use a pressure near atmospheric pressure.

The polymerization is usually carried out by a solution polymerization method in an inert solvent, a slurry polymerization method, or a bulk polymerization method using the monomer as a diluent. Solution polymerization method or bulk polymerization method is preferred.

[0065] Examples of the inert solvent used for polymerization include aliphatic, cyclic aliphatic, aromatic, and halogenated aromatic hydrocarbons, as well as mixtures thereof. Preferred inert solvents are C4-C26 alkanes, particularly branched alkanes, toluene, ethylbenzene, and mixtures thereof. A solvent suitable for giving a monomer concentration of from 2 to 100% by weight is used.

The polymerization reaction may be carried out by adding a small amount of a polar compound, for example, an ether such as anisole, diphenyl ether, ethyl ether, diglyme, tetrahydrofuran, and dioxane, or an amine such as triethylamine and tetramethylethylenediamine within a range that does not impair the effects of the present invention.

[0066] To adjust the molecular weight of the polymer, a chain transfer agent may be added within a range that does not impair the effects of the present invention. Preferably, an allene such as 1,2-butadiene, a cyclic diene such as cyclooctadiene, or

hydrogen is used as the chain transfer agent. The polymerization reaction is usually terminated by adding a polymerization terminator to the polymerization system when a predetermined conversion rate is reached. For example, an alcohol such as methanol, ethanol, propanol, butanol, or isobutanol can be used as the polymerization terminator. These examples may also contain an acid such as hydrochloric acid. The method for recovering the polymer after terminating the polymerization reaction is not particularly limited, and for example, steam stripping or precipitation with a poor solvent may be used.

[0067] The polyfunctional vinyl aromatic copolymer obtained by this production method contains 2 mol% or more and less than 95 mol% of a repeating unit (a) derived from (A) and 5 mol% or more and less than 98 mol% of a repeating unit (b) derived from the monovinyl aromatic compound (B), and contains an unsaturated hydrocarbon group represented by general formula (a1). Further, the obtained polyfunctional vinyl aromatic copolymer has a Mn of from 500 to 30,000, a molecular weight distribution of 20.0 or less, and is soluble in toluene, xylene, and tetrahydrofuran. The polyfunctional vinyl aromatic copolymer has a syndiotactic structure in which the C1 carbon of the phenyl group constituting the divinyl aromatic compound (A) and the monovinyl aromatic compound (B) has a tacticity of 30% or more in a racemic pentad determined by ^{13}C-NMR.

More preferably, the tacticity of the syndiotactic structure is 60% or more, more preferably 70% or more, further preferably 85% or more, and particularly preferably 95% or more.

[0068] Next, the curable resin composition of the present invention will be described.

The curable resin composition of the present invention contains the polyfunctional vinyl aromatic copolymer and a radical polymerization initiator (radical polymerization catalyst). The radical polymerization initiator causes the curable resin composition of the present invention to cure by, for example,

undergoing a crosslinking reaction by means such as heating, as will be described later. The radical polymerization initiator is included for the purpose of lowering the temperature during the reaction and promoting the crosslinking reaction of unsaturated groups.

[0069] A known substance can be used as the radical polymerization initiator (h). Representative examples include, but are not limited to, peroxides such as benzoyl peroxide, cumene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, 2,5-dimethyl-2,5-di(t-butylperoxy)hexine-3, di-t-butylperoxide, t-butylcumyl peroxide, α,α'-bis(t-butylperoxy-m-isopropyl)benzene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexane, dicumyl peroxide, di-t-butyl peroxyisophthalate, t-butyl peroxybenzoate, 2,2-bis(t-butylperoxy)butane, 2,2-bis(t-butylperoxy)octane, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, di(trimethylsilyl)peroxide, and trimethylsilyltriphenylsilylperoxide, and azo compounds such as 2-phenylazo-4-methoxy-2,4-dimethylvaleronitrile, 1-[(1-cyano-1-methylethyl)azo]formamide, 1,1'-azobis(cyclohexane-1-carbonitrile), 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(2,4-dimethyl-4-methoxyvaleronitrile), 2,2'-azobis(2-methylpropionamidine)dihydrochloride, 2,2'-azobis(2-methyl-N-phenylpropionamidine)dihydrochloride, 2,2'-azobis[N-(4-chlorophenyl)-2-methylpropionamidine]dihydrochloride, 2,2'-azobis[N-(4-hydrophenyl)-2-methylpropionamidine]dihydrochloride, 2,2'-azobis[2-methyl-N-(phenylmethyl)propionamidine]dihydrochloride, 2,2'-azobis[2-methyl-N-(2-propenyl)propionamidine]dihydrochloride, 2,2'-azobis[N-(2-hydroxyethyl)-2-methylpropionamidine]dihydrochloride, 2,2'-azobis[2-(5-methyl-2-imidazolin-2-yl)propane]dihydrochloride, 2,2'-azobis[2-(2-imidazolin-2-yl)propane]dihydrochloride, 2,2'-azobis[2-(4,5,6,7-tetrahydro-1H-1,3-diazepine-2-yl)propane]dihydrochloride, 2,2'-azobis[2-(3,4,5,6-tetrahydropyrimidine-2-

yl)propane]dihydrochloride, 2,2'-azobis[2-(5-hydroxy-3,4,5,6-tetrahydropyrimidine-2-yl)propane]dihydrochloride, 2,2'-azobis{2-[1-(2-hydroxyethyl)-2-imidazolin-2-yl]propane}dihydrochloride, 2,2'-azobis[2-(2-imidazoline-2-yl)propane], 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}, 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide}, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobis(2-methylpropionamide), 2,2'-azobis(2,4,4-trimethylpentane), 2,2'-azobis(2-methylpropane), dimethyl-2,2-azobis(2-methylpropionate), 4,4'-azobis(4-cyanopentanoic acid), 2,2'-azobis[2-(hydroxymethyl)propionitrile], and 2,2'-azobis(tert-butane). Although not a peroxide, 2,3-dimethyl-2,3-diphenylbutane can also be used as (h). These compounds may be used alone or in combination of two or more.

Among these, it is preferred to use α,α'-bis(t-butylperoxy-m-isopropyl)benzene and 2,2'-azobis(2,4,4-trimethylpentane). α,α'-bis(t-butylperoxy-m-isopropyl)benzene and 2,2'-azobis(2,4,4-trimethylpentane) have relatively high reaction initiation temperatures and excellent storage stability.

[0070] The blended amount of the radical polymerization initiator (h) is in the range of 0.01 to 10 parts by weight, and preferably 0.1 to 8 parts by weight, with respect to 100 parts by weight of the polyfunctional vinyl aromatic copolymer. Within this range, the reaction proceeds well without inhibiting the curing reaction.

[0071] The curable resin composition can contain a known curable reactive resin or thermoplastic resin (j).

Examples of the curable reactive resin include thermosetting resins, as well as resins or compounds that provide a curable resin when copolymerized with a soluble polyfunctional vinyl aromatic copolymer. Examples include vinyl ester resins, polyvinyl benzyl resins, unsaturated polyester resins, curable vinyl resins, polyphenylene ether resins, maleimide resins, epoxy resins, polycyanate resins,

phenolic resins, one or more vinyl compounds having one or more polymerizable unsaturated hydrocarbon groups in one molecule, and the like.

Examples of the thermoplastic resin include polystyrene, polyphenylene ether resins, polyetherimide resins, polyethersulfone resins, PPS resins, polycyclopentadiene resins, polycycloolefin resins, and the like, as well as known thermoplastic elastomers such as styrene-ethylene-propylene copolymers, styrene-ethylene-butylene copolymers, styrene-butadiene copolymers, styrene-isoprene copolymers, hydrogenated styrene-butadiene copolymers, hydrogenated styrene-isoprene copolymers, and the like, or rubbers such as polybutadiene and polyisoprene.

The blended amount of the curable reactive resin or thermoplastic resin can be in the range of 10 to 90 parts by weight with respect to 100 parts by weight of the total with the polyfunctional vinyl aromatic copolymer, but is preferably less than 50 parts by weight, more preferably less than 30 parts by weight, and further preferably less than 10 parts by weight.

[0072] The curable resin composition of the present invention may also contain a known flame retardant.

The flame retardant can be selected from among a wide range, including halogen-based flame retardants such as a brominated flame retardant, and halogen-free flame retardants such as a phosphate ester flame retardant, a phosphazene flame retardant, and a phosphinate flame retardant.

[0073] The curable resin composition of the present invention can contain a known filler. Specifically, examples include silica such as spherical silica, metal oxides such as alumina, titanium oxide, and mica, metal hydroxides such as aluminum hydroxide and magnesium hydroxide, talc, aluminum borate, barium sulfate, calcium carbonate, and the like. These may be used as is, or they may be used after being

surface-treated with a silane coupling agent such as an epoxysilane type or aminosilane type.

The filler content is, for example, from 10 to 200 parts by mass with respect to 100 parts by mass of the organic component.

[0074] The curable resin composition of the present invention may further contain other additives. Examples of additives include a defoamer such as a silicone-based defoamer and an acrylic acid ester-based defoamer, a heat stabilizer, an antistatic agent, an ultraviolet absorber, dyes and pigments, a lubricant, and a dispersant such as a wetting dispersant.

[0075] During the production of a prepreg, the curable resin composition of the present invention can be prepared in a varnish-like form to be used as a resin varnish, either for the purpose of impregnation into a base material (fibrous base material) for forming the prepreg, or as a circuit board material for forming a circuit board.

[0076] The resin varnish is prepared by dissolving a polyfunctional vinyl aromatic copolymer in an organic solvent. Examples of the organic solvent include ketones such as acetone, methyl ethyl ketone, and methyl isobutyl ketone; esters such as ethyl acetate, propyl acetate, and butyl acetate; polar solvents such as dimethylacetamide and dimethylformamide; aromatic hydrocarbon solvents such as toluene and xylene, and the like. It is also possible to use one or two more of these in combination. From the viewpoint of dielectric properties, an aromatic hydrocarbon such as benzene, toluene, and xylene is preferred.

When making the resin varnish, the amount of organic solvent used is preferably from 5 to 900% by weight with respect to 100% by weight of the curable resin composition of the present invention.

[0077] The cured product obtained by curing the curable resin composition of the present invention can be used as a molded product, a laminate, a cast product, an adhesive, a coating, or a film. For example, the cured product of a semiconductor

encapsulating material is a cast product or molded product. A cured product for such an application can be obtained by a method in which the curable resin composition is molded using a casting or transfer molding machine, injection molding machine, or the like, and then heated at from 80 to 230°C for 0.5 to 10 hours to obtain the cured product.

The cured product of a circuit board varnish is a laminate. This cured product can be obtained by impregnating a base material such as glass fiber, carbon fiber, polyester fiber, polyamide fiber, alumina fiber, or paper with the circuit board varnish, heating and drying to obtain a prepreg, and then laminating prepregs together or with a metal foil such as a copper foil and heat-pressing.

[0078] By incorporating an inorganic high-dielectric powder such as barium titanate, or an inorganic magnetic material such as ferrite, into the curable resin composition or resin varnish, the material becomes a better electronic component material, particularly as a high-frequency electronic component material.

[0079] The curable composite material of the present invention includes a base material to increase mechanical strength and dimensional stability.

Known materials can be used as the base material. For example, various types of glass cloth such as roving cloth, cloth, chopped mat, and surfacing mat, asbestos cloth, metal fiber cloth and other synthetic or natural inorganic fiber cloths, woven or nonwoven fabrics obtained from liquid crystal fibers such as fully aromatic polyamide fibers, fully aromatic polyester fibers, and polybenzoxazole fibers, woven or nonwoven fabrics obtained from synthetic fibers such as polyvinyl alcohol fibers, polyester fibers, and acrylic fibers, natural fiber fabrics such as cotton fabric, linen fabric, and felt, carbon fiber fabric, fabrics and papers of natural cellulose-based fabrics such as kraft paper, cotton paper, and paper-glass fiber blend paper can be used alone or in combination of two or more.

[0080] The proportion of the base material is from 5 to 90% by weight, preferably from 10 to 80% by weight, and further preferably from 20 to 70% by weight of the curable composite material.

[0081] The curing, or the molding and curing, of the curable resin composition or curable composite material of the present invention can be carried out, for example, in a temperature range of 80 to 300°C, a pressure of from 0.1 to 1000 kg/cm^2, and a time of from 1 minute to 10 hours, and more preferably in a temperature range of 150 to 250°C, a pressure of from 1 to 500 kg/cm^2, and a time of from 1 minute to 5 hours.

[0082] The laminate of the present invention is composed of a layer of the cured composite material of the present invention and a layer of a metal foil. Examples of the metal foil include copper foil, stainless steel foil, titanium foil, aluminum foil, and the like. The thickness is not particularly limited, but is in the range of 3 to 200 μm, and more preferably 3 to 100 μm.

[0083] The curable resin composition of the present invention can also be molded into a film. The film thickness is similarly in the range of, for example, 3 to 200 μm, and more preferably 5 to 100 μm.

[0084] The polyfunctional vinyl aromatic copolymer of the present invention can be processed into a molded material, a sheet, or a film, and can be used in fields such as the electrical industry, aerospace industry, and automotive industry as a low dielectric material, an insulating material, a heat-resistant material, a structural material, and the like, satisfying properties such as low dielectric constant, low water absorption rate, and high heat resistance. In particular, the polyfunctional vinyl aromatic copolymer of the present invention can be used as a single-sided, double-sided, or multilayer printed circuit board, flexible printed circuit board, and build-up boards. Further, the polyfunctional vinyl aromatic copolymer of the present invention can be applied to semiconductor-related materials or optical materials, as well as paints, photosensitive materials, adhesives, wastewater treatment agents,

heavy metal adsorbents, ion exchange resins, antistatic agents, antioxidants, antifogging agents, rust inhibitors, anti-dyeing agents, disinfectants, insecticides, medical materials, flocculants, surfactants, lubricants, binders for solid fuels, conductive treatment agents, resin modifiers, asphalt modifier plasticizers, sintering binders, and the like.

[0085] The curable resin composition of the present invention has high dielectric properties (low dielectric constant and low dielectric loss tangent) even after a harsh thermal history, provides a cured product having high adhesion reliability even under harsh environments, and has excellent resin fluidity, low linear expansion, and excellent flatness for wiring embedding.

Examples

[0086] The present invention will now be described with reference to examples, but the present invention is not limited thereto. The term "parts" in the examples means parts by weight. Measurement of the softening point and the like in the examples was performed by preparing samples and measuring using the methods described below.

[0087] 1) Molecular weight and molecular weight distribution of the polymer

The molecular weight and molecular weight distribution of the soluble polyfunctional aromatic copolymer were measured using a GPC system (HLC-8120GPC, manufactured by Tosoh), with tetrahydrofuran as the solvent, a flow rate of 1.0 ml/min, a column temperature of 38°C, and a calibration curve using monodisperse polystyrene.

2) Polymer structure

The structure was determined by ^{13}C-NMR and ^{1}H-NMR analysis using a JEOL JNM-LA600 nuclear magnetic resonance spectrometer. Chloroform-d_1 was

used as the solvent, and the resonance line of tetramethylsilane was used as an internal standard.

3) Analysis of terminal groups

The number of terminal groups was calculated by determining the amount of specific structural units introduced at the terminals of the copolymer from data on the total amount of each structural unit introduced into the copolymer obtained from ^{13}C-NMR and ^{1}H-NMR measurement results, as well as from GC analysis, and calculating the number of terminal groups of specific structural units contained in one molecule of the polyfunctional vinyl aromatic copolymer from the amount of these specific structural units introduced at the terminals and the number average molecular weight obtained from the GPC measurement described above.

[0088] 4) Glass transition temperature (Tg) of cured product

A solution of the polyfunctional vinyl aromatic copolymer dissolved in toluene was uniformly applied to a glass substrate so that the thickness after drying was 20 μm, and then heated on a hot plate for 90 minutes for 30 minutes to dry. The resin film obtained together with the glass substrate was placed in a thermomechanical analyzer (TMA), and heated to 220°C at a heating rate of 10 °C/min under a nitrogen stream, and then further heated at 220°C for 20 minutes to remove any remaining solvent and to cure the polyfunctional vinyl aromatic copolymer. The glass substrate was allowed to cool to room temperature, then the analytical probe was brought into contact with the sample in the TMA measuring device, scanning measurements were performed from 30°C to 360°C at a heating rate of 10 °C/min under a nitrogen stream, and the softening point was determined by the tangential method.

5) Evaluation of heat resistance and measurement of resistance to heat discoloration

The heat resistance of the soluble polyfunctional vinyl aromatic copolymer was evaluated by setting the sample in a TGA (thermobalance) measuring device,

scanning the sample from 30°C to 400°C under a nitrogen stream at a heating rate of 10 °C/min, and taking the amount of weight loss at 350°C as an indicator of heat resistance.

The resistance to heat discoloration was measured by mixing 6.0 g of soluble polyfunctional vinyl aromatic copolymer, 4.0 g of benzyl methacrylate, and 0.02 g of t-butyl peroxy-2-ethylhexanoate (Perbutyl O, manufactured by NOF Corporation), and heating the resultant mixture at 200°C for 1 hour under a nitrogen stream to obtain a cured product, and evaluated by visually confirming the amount of discoloration in the obtained cured product and classifying as follows: Good (circle): no heat discoloration, Fair (triangle): pale yellow, Poor (cross mark): yellow.

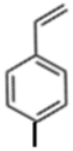
6) Measurement of compatibility

The compatibility of the soluble polyfunctional vinyl aromatic copolymer with an epoxy resin was measured by dissolving 5.0 g of the sample in 3.0 g of epoxy resin (liquid bisphenol A type epoxy resin, Epikote 828, manufactured by Japan Epoxy Resin,) and 2.0 g of phenol resin (melamine skeleton phenol resin, PS-6492, manufactured by Gun Ei Chemical Industry) in 10 g of methyl ethyl ketone (MEK), and evaluated by visually confirming the transparency of the sample after dissolution and classifying as follows: Good (circle): transparent, Fair (triangle): semi-transparent, Poor (cross mark): opaque or not dissolved.

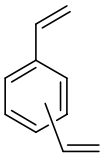
[0089] Example 1

The polymerization reaction was carried out under a nitrogen atmosphere using a dried, nitrogen-purged 500 ml glass three-neck flask. 298.6 ml of toluene and 2.0 mmol of trioctylaluminum were charged into the 500 ml glass three-neck flask and aged at room temperature for 10 minutes. Then, 1.0 mmol of (trimethyl)pentamethylcyclopentadienyltitanium was added, followed by 1.0 mmol of tris(pentafluorophenyl)boron, and the mixture was aged at room temperature for 10 minutes. Next, the temperature was kept constant at 20°C.

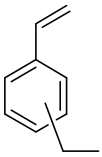
Then, the mixture was charged into a toluene solution containing 0.0303 mol (3.58 g) of p-methylstyrene,



0.0121 mol (1.58 g) of divinylbenzene,



and 0.0005 mol (0.04 g) of ethylvinylbenzene,



and the polymerization reaction was carried out at 20°C for 60 minutes. A small amount of methanol was added to terminate the polymerization reaction, and the polymerization solution was poured into a large amount of acidic methanol to precipitate the polymer. The obtained polymer was washed, filtered, dried, and weighed to obtain 6.35 g of copolymer A (yield: 82.3 wt%).

[0090] The weight average molecular weight (Mw) of the obtained copolymer A was 12900, the number average molecular weight (Mn) was 5460, and the molecular weight distribution (Mw/Mn) was 2.36. The syndiotacticity determined by ^{13}C-NMR measurement was 95% or more in the racemic pentad. ^{13}C-NMR and ^{1}H-NMR analysis showed that, in the copolymer A (including terminal structural units), 28.2 mol% (30.2 wt%) of the structural units derived from divinylbenzene, a total of 1.25 mol% (1.34 wt%) of the structural units derived from ethylvinylbenzene, and 57.4 mol% (52.7 wt%) of the structural units derived from 4-methylstyrene. The

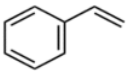
content of structural units derived from divinylbenzene having a residual vinyl group in the copolymer A was 70.5 mol% (68.5 wt%).

TMA measurement of the cured product showed no clear Tg, and the softening point was 300°C or higher. TGA measurement showed a weight loss at 350°C of 1.07 wt%, resistance to heat discoloration was evaluated as being Good (circle), and compatibility with the epoxy resin was evaluated as being Good (circle).

The copolymer A was soluble in toluene, xylene, and THF (100 g or more of the copolymer A dissolved in 100 g of each solvent), and no gel formation was observed.

[0091] Comparative Example 1

A 5.0 L reactor was charged with 3.0 mol (390.6 g) of divinylbenzene, 1.8 mol (229.4 g) of ethylvinylbenzene, and 10.2 mol (1066.3 g) of styrene,



and 15.0 mol (1532.0 g) of n-propyl acetate, 600 mmol of a diethyl ether complex of boron trifluoride was added at 70°C, and the mixture was reacted for 4 hours. The polymerization reaction was terminated with aqueous sodium bicarbonate, then the oil layer was washed three times with pure water, and devolatilized under reduced pressure at 60°C to recover a copolymer. The obtained copolymer was weighed, and it was confirmed that 896.7 g of the copolymer B was obtained.

[0092] The obtained copolymer B had a Mn of 2980, a Mw of 41300, and a Mw/Mn of 13.9. ^{13}C-NMR and ^{1}H-NMR analysis showed that, in the copolymer B (including terminal structural units), 30.4 mol% (33.1 wt%) of the structural units derived from divinylbenzene, a total of 12.2 mol% (14.2 wt%) of the structural units derived from ethylvinylbenzene, and 57.4 mol% (52.7 wt%) of the structural units derived from styrene. The content of structural units derived from divinylbenzene

having a residual vinyl group in the copolymer B was 23.9 mol% (25.9 wt%) (including terminal structural units).

TMA measurement of the cured product showed no clear Tg, and the softening point was 300°C or higher. TGA measurement showed a weight loss at 350°C of 1.83 wt%, resistance to heat discoloration was evaluated as being Good (circle), and compatibility with the epoxy resin was evaluated as being Good (circle).

The copolymer B was soluble in toluene, xylene, and THF (100 g or more of the copolymer B dissolved in 100 g of each solvent), and no gel formation was observed.

[0093] Comparative Example 2

A reaction vessel equipped with a stirrer and having an internal volume of 1.4 L was charged with 180 ml of toluene and 1.5 mmol of methylaluminoxane as aluminum atoms, and then with 0.15 mmol of tetraethoxytitanium. The resultant solution was heated to 50°C, a mixture of 142.5 ml of styrene and 7.5 ml of a mixture of 66.1% by weight of divinylbenzene-containing monomer (a mixture of divinylbenzene (m-,p-) with a mixture of 33.9% by weight of ethyl sterene (m-,p-)) was added, and the reaction was carried out for 2 hours. Then, methanol was added to terminate the reaction. Next, a mixture of hydrochloric acid and methanol was added to break down the catalyst component.

The yield of the obtained styrene-based copolymer C was 42.8 g. Further, when this styrene-based copolymer was washed with methyl ethyl ketone (containing 2% by weight of p-t-butylcatechol) at 50°C for 2 hours, 99% was insoluble. When this methyl ethyl ketone-insoluble styrene-based copolymer C was dissolved in chloroform, it partially dissolved, and a solution of the styrene-based copolymer C in chloroform was obtained from the chloroform-soluble component. The weight average molecular weight of this chloroform-soluble styrene-based copolymer was

360,000, the number average molecular weight was 110,000, and the melting point was 240°C.

The styrene-based copolymer C is a thermoreactive styrene-based copolymer C having a syndiotactic structure. ^{13}C-NMR and ^{1}H-NMR analysis showed that, in the copolymer C (including terminal structural units), 3.95 mol% (4.89 wt%) of the structural units derived from divinylbenzene, a total of 0.18 mol% (0.22 wt%) of the structural units derived from ethylvinylbenzene, and 95.9 mol% (94.9 wt%) of the structural units derived from styrene. The content of structural units derived from divinylbenzene having a residual vinyl group in the copolymer C was 1.38 mol% (1.71 wt%).

TMA measurement of the cured product showed no clear Tg, and the softening point was 300°C or higher. TGA measurement showed a weight loss at 350°C of 2.83 wt% and resistance to heat discoloration was evaluated as being Good (circle). However, compatibility with the epoxy resin was evaluated as being Poor (cross mark).

The copolymer C was insoluble in toluene, xylene, and THF (100 g or more of the copolymer C dissolved in 100 g of each solvent), and due to the high proportion of solvent-insoluble matter, gel formation could not be confirmed.

[0094] Using the copolymers A to C obtained in Example 1 and Comparative Examples 1 to 2, the properties of a varnish and cured product of the curable resin composition using these resins were evaluated in accordance with the following test methods.

[0095] 7) Solution viscosity

The solution viscosity of a varnish of the curable resin composition was measured using an E-type viscometer at a measurement temperature of 25°C.

8) Bending strength and bending elongation at break

For the test specimen to be used in the bending test, a varnish of the curable resin composition was placed on the lower mold of a vacuum press molding machine, and the solvent was devolatilized under heated vacuum. Then, the upper mold was placed thereon, and under vacuum, a heated press was performed. A flat plate having a thickness of 1.0 mm was formed by holding at 200°C for 1 hour.

A test specimen having a width of 5.0 mm, thickness of 1.0 mm, and length of 120 mm was prepared from the formed flat plate, and a bending test was performed. The bending strength and bending elongation at break of the prepared bending test specimen were measured using a universal testing apparatus. The bending strength and bending elongation at fracture were evaluated as follows: Good (circle) for values less than ±10% of the measured value of the standard composition, Excellent (double circle) for values 10% or more, Fair (triangle) for values in the range of -10% to -20%, and Poor (cross mark) for values less than -20%.

9) Coefficient of linear expansion and glass transition temperature

For the test specimen to be used in the test for the coefficient of linear expansion and glass transition temperature, a varnish of the curable resin composition was placed on the lower mold, which had a flat-plate shape, of a vacuum press molding machine, and the solvent was devolatilized under heated vacuum. Then, the upper mold was placed thereon with a 0.2 mm spacer arranged between the upper and lower molds, and under vacuum, a heated press was performed. A flat plate having a thickness of 0.2 mm was formed by holding at 200°C for 1 hour. A test specimen having a width of 3.0 mm, thickness of 0.2 mm, and length of 40 mm was prepared from the formed flat plate. The specimen was placed only in the upper chuck of a thermomechanical analyzer (TMA), and heated to 220°C at a heating rate of 10 °C/min under a nitrogen stream. The specimen was then heated at 220°C for 20 minutes to remove any remaining solvent and to eliminate molding distortion in the test specimen. The TMA was allowed to cool to

room temperature, then the lower part of the test specimen in the TMA measuring device was also placed in the analytical probe. Scanning measurements were performed from 30°C to 360°C at a heating rate of 10 °C/min under a nitrogen stream, and the coefficient of linear expansion was calculated from the dimensional change between 0 and 40°C.

The glass transition temperature was measured by setting the above test specimen in a dynamic viscoelasticity analyzer (DMA) and scanning from 30°C to 320°C under a nitrogen stream at a heating rate of 3 °C/min. The Tg was determined from the peak top of the tanδ curve.

[0096] 10) Dielectric constant and dielectric loss tangent

The dielectric constant and dielectric loss tangent at 18 GHz were measured in accordance with the JIS C2565 standard using a cured product flat test specimen that had been stored for 24 hours in a room at 23°C and 50% humidity after being completely dried, with a cavity resonator dielectric constant measuring device manufactured by AET Inc.

The dielectric constant and dielectric loss tangent were measured after leaving the cured product flat test specimen at 85°C and 85% relative humidity for two weeks, and the dielectric constant and dielectric loss tangent were measured again after the moist heat resistance test.

To confirm the high-temperature heat resistance of the material, the dielectric constant and dielectric loss tangent were measured after leaving the cured product flat test specimen at 140°C in an air atmosphere for 168 hours, and the dielectric constant and dielectric loss tangent were measured again after the high-temperature heat resistance test.

[0097] 11) Copper foil peel strength

A glass cloth (E glass, basis weight 71 g/m^2) was impregnated by dipping it in a varnish of a thermosetting resin composition, and dried in an air oven at 80°C for

10 minutes. At that time, adjustment was carried out so that the obtained prepreg had a resin content (R.C) of 50 wt%.

Using this prepreg, a plurality of layers of the above-described curable composite material were stacked as required to achieve an after-molding thickness of approximately 0.6 mm to 1.0 mm. An 18 μm-thick copper foil (trade name: F2-WS copper foil, Rz: 2.0 μm, Ra: 0.3 μm) was placed on both sides of the stack, and the stack with the copper foil on both sides was molded and cured using a vacuum press molding machine to obtain an evaluation laminate. A laminate cured product was obtained as an evaluation copper-clad laminate by holding at 200°C for 60 minutes while heating at 3 °C/min under a pressure of 3 MPa.

A test specimen having a width of 20 mm and length of 100 mm was cut out from the obtained laminate-cured product. Parallel cuts 10 mm wide were made on the copper foil surface, and the copper foil was continuously peeled off at a speed of 50 mm/min in a direction 90° to the surface. The stress at this time was measured using a tensile testing machine, and the minimum value of this stress was recorded as the copper foil peel strength (in accordance with JIS C 6481).

The copper foil peel strength test after the moist heat resistance test was performed by leaving the test specimen at 85°C and 85% relative humidity for two weeks, and then measuring in the same manner as above.

[0098] 12) Moldability

A core material was produced by patterning the evaluation copper-clad laminate molded in the previous section with a grid pattern having a line width (L) of 0.5 mm and a line spacing (S) of 1.0 mm (L/S = 0.5/1.0 mm). This core material was blackened, and then a prepreg was further laminated thereon and secondary molding was performed to produce an evaluation laminated substrate having a grid pattern on an inner layer. The produced evaluation laminated substrate was checked for defects such as voids due to insufficient fluidity of the resin varnish, for

example. Then, the evaluation laminated substrate was immersed in boiling water for 4 hours, followed by dipping in a solder bath at 280°C. At that time, if no voids were found and no defects such as swelling, delamination, or measling (white spots) occurred after dipping in the solder bath, the evaluation laminated substrate was evaluated as Good (circle), if no defects were observed but warping occurred, the evaluation laminated substrate was evaluated as Fair (triangle), and if all of the above-described defects occurred, the evaluation laminated substrate was evaluated as Poor (cross mark).

[0099] Example 2

A curable resin composition (varnish A) was obtained by dissolving 20 g of copolymer-A obtained in Example 1, 0.1 g of 2,2'-azobis(2,4,4-trimethylpentane) as a polymerization initiator, and 0.04 g of AO-60 as a curing accelerator and antioxidant in 8.6 g of toluene.

The prepared varnish A was dropped onto a lower mold, the solvent was volatilized under reduced pressure at 130°C, the mold was then assembled, and heat-curing was carried out by vacuum pressing at 200°C and 3 MPa for 1 hour. Various properties, including the dielectric constant and dielectric loss tangent at 18 GHz, were measured for the resulting cured product flat test specimen having a thickness of 0.2 mm. The cured product flat test specimen was left at 85°C and 85% relative humidity for 2 weeks, then the dielectric constant and dielectric loss tangent were measured, and the dielectric constant and dielectric loss tangent after the moist heat resistance test were also measured. The results obtained from these measurements are shown in Table 1.

[0100] Comparative Examples 3 and 4

A curable resin composition (varnish) was obtained in the same manner as in Example 2, except that the formulation shown in Table 1 was used. A cured product flat test specimen was prepared in the same manner as in Example 2, and the

same evaluation items as in Example 2 were tested and evaluated. The results obtained from these tests are shown in Table 1.

[0101] In the table, the solid content in the solution viscosity is 25% in Table 1. For the glass transition temperature, ND means Tg-less. Dielectric constant 85 and dielectric loss tangent 85 are the dielectric constant and dielectric loss tangent after leaving at 85°C × 85 RH × 2 weeks. Dielectric constant 140 and dielectric loss tangent 140 are the dielectric constant and dielectric loss tangent after leaving at 140°C × air × 168 hours. Dielectric loss tangent change rate 1 indicates moist heat resistance, and dielectric loss tangent change rate 2 indicates heat resistance. In Table 1, copper foil peel strength 85 is the measured value after leaving at 85°C × 85 RH × 2 weeks.

[0102]

[Table 1]

	Example 2	Comparative Example 3	Comparative Example 4
Copolymer-A (wt%)	100		
Copolymer-B (wt%)		100	
Copolymer-C (wt%)			100
2,2'-azobis(2,4,4-trimethylpentane) (phr)	0.5	0.5	0.5
ADK Stab AO-60 (phr)	0.2	0.2	0.2
Solution viscosity (mPa·s)	48.6	164.3	13,200
Bending strength (MPa)	○	Δ	○
Bending elongation at break (%)	○	○	○
Coefficient of linear expansion (ppm/°C)	71.3	86.4	91.2
Glass transition temperature (°C)	212	187	134
Dielectric constant	2.357	2.463	2.471
Dielectric loss tangent ($\times 10^{-4}$)	3.12	6.38	4.52
Dielectric constant 85	2.365	2.531	2.581
Dielectric loss tangent 85 ($\times 10^{-4}$)	3.18	6.58	4.91
Dielectric loss tangent change rate 1 (%)	1.9	3.2	8.7
Dielectric constant 140	2.378	2.511	2.498
Dielectric loss tangent 140 ($\times 10^{-4}$)	3.27	6.92	5.26
Dielectric loss tangent change rate 2 (%)	4.81	8.46	7.74
Moldability	○	Δ	×

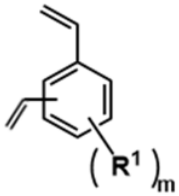
Industrial Applicability

[0103] The polyfunctional vinyl aromatic copolymer of the present invention can be processed into a molded material, a sheet, or a film, and is useful in fields such as the electrical industry, aerospace industry, and automotive industry as a low dielectric material, an insulating material, a heat-resistant material, a structural material, and the like, satisfying properties such as low dielectric constant, low water absorption rate, and high heat resistance.

Claims

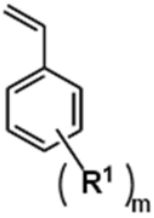
[Claim 1]

A polyfunctional vinyl aromatic copolymer comprising 2 mol% or more and less than 95 mol% of a repeating unit (a) derived from a divinyl aromatic compound (A) represented by the following general formula (1),



(1)

and 5 mol% or more and less than 98 mol% of a repeating unit (b) derived from a monovinyl aromatic compound (B) represented by the following general formula (2),

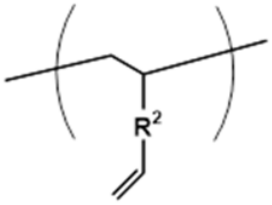


(2)

wherein R1 represents a hydrocarbon group having from 1 to 30 carbon atoms, a halogen atom, or a substituent containing any one or more of an oxygen atom, a nitrogen atom, a sulfur atom, a phosphorus atom, a selenium atom, a silicon atom, and a tin atom; m denotes an integer of from 0 to 5; and when there are a plurality of m, each R1 may be the same or different,

wherein a C^1 carbon of a phenyl group constituting (A) and (B) has a tacticity of 30% or more in a racemic pentad determined by ^{13}C-NMR,

the polyfunctional vinyl aromatic copolymer contains 2 mol% or more and less than 95 mol% of an unsaturated hydrocarbon group represented by the following formula (a1) with respect to the total of (a) and (b),



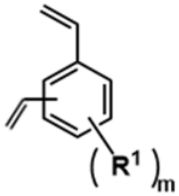
(a1)

wherein R2 represents an aromatic hydrocarbon group having from 6 to 30 carbon atoms,

and the polyfunctional vinyl aromatic copolymer has a number average molecular weight (Mn) of from 500 to 30,000, a molecular weight distribution (Mw/Mn) expressed as the ratio of weight average molecular weight to number average molecular weight of 20.0 or less, and is soluble in a solvent.

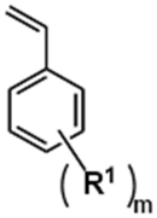
[Claim 2]

A method for producing a polyfunctional vinyl aromatic copolymer, the method comprising polymerizing a divinyl aromatic compound (A) represented by the following general formula (1),



(1)

with a monovinyl aromatic compound (B) represented by the following general formula (2),



(2)

wherein R1 represents a hydrocarbon group having from 1 to 30 carbon atoms, a halogen atom, or a substituent containing any one or more of an oxygen atom, a nitrogen atom, a sulfur atom, a phosphorus atom, a selenium atom, a silicon atom,

and a tin atom, and m denotes an integer of from 0 to 5; and when there are a plurality of m, each R^1 may be the same or different,

at a temperature of 100°C or lower in the presence of a reaction product of, as a catalytic component (C), at least one transition metal compound selected from compounds represented by the following general formula (3) or (4),

$MR^3aR^4bR^5cX^1_{4-(a+b+c)}$ (3)

$MR^3dR^4eX^1_{3-(d+e)}$ (4)

wherein R3, R4, and R5 each represent a hydrogen atom, an alkyl group having from 1 to 20 carbon atoms, an aryl group having from 6 to 20 carbon atoms, an alkylaryl group, an arylalkyl group, an acyloxy group having from 1 to 20 carbon atoms, an alkoxy group having from 1 to 20 carbon atoms, a thioalkoxy group having from 1 to 20 carbon atoms, a thioaryloxy group having from 6 to 20 carbon atoms, a cyclopentadienyl group, a substituted cyclopentadienyl group, an indenyl group, a substituted indenyl group, a fluorenyl group, or a substituted fluorenyl group; M represents a transition metal selected from the group consisting of titanium (Ti), zirconium (Zr), and hafnium (Hf), and X1 represents a halogen atom; R3, R4, and R5 may be the same or different; and a, b, and c each represent an integer of from 0 to 4, and d and e each represent an integer of from 0 to 3,

with, as a co-catalytic component (D), at least one compound selected from compounds represented by the following (d) to (g):

(d) an organoaluminum oxy compound;

(e) an ionic compound capable of reacting with the transition metal compound to produce a cationic transition metal compound;

(f) a Lewis acid compound capable of reacting with the transition metal compound to produce a cationic transition metal compound; and

(g) an organometallic compound of a metal element from groups 1, 2, and 13 of the periodic table,

to obtain a polyfunctional vinyl aromatic copolymer in which a C^1 carbon of a phenyl group constituting (A) and (B) has a tacticity of 30% or more in a racemic pentad determined by ^{13}C-NMR.

[Claim 3]

A curable resin composition comprising the polyfunctional vinyl aromatic copolymer according to claim 1 and a radical polymerization initiator (h).

[Claim 4]

A curable resin composition comprising the polyfunctional vinyl aromatic copolymer according to claim 1 and a curable reactive resin (i) or a thermoplastic resin (j).

[Claim 5]

The curable resin composition according to claim 4, wherein the curable reactive resin (i) is a modified polyphenylene ether compound (ia) in which a terminal is modified by a substituent having a carbon-carbon unsaturated double bond, one or more epoxy resins (ib) selected from the group consisting of epoxy resins having two or more epoxy groups in one molecule, or one or more vinyl compounds (id) having one or more unsaturated hydrocarbon groups in a molecule.

[Claim 6]

A curable resin composition further comprising a flame retardant (k) and/or a filler (l) in the curable resin composition according to claim 3.

[Claim 7]

A cured product obtained by curing the curable resin composition according to any one of claims 3 to 6.

[Claim 8]

A curable composite material consisting of the curable resin composition according to any one of claims 3 to 6 and a base material, wherein a proportion of the base material is from 5 to 90% by weight.

[Claim 9]

A cured composite material obtained by curing the curable composite material according to claim 8.

[Claim 10]

A laminate comprising a layer of the cured composite material according to claim 9 and a metal foil layer.

[Claim 11]

A resin-coated metal foil comprising a film formed from the curable resin composition according to any one of claims 3 to 6 on one side of a metal foil.

[Claim 12]

A varnish for a circuit board material obtained by dissolving the curable resin composition according to any one of claims 3 to 6 in an organic solvent.