DESCRIPTION

TITLE OF THE INVENTION

BLOCK COPOLYMER

Technical Field

[0001]

The present invention relates to a block copolymer that has thermosetting properties and may be used in an insulating layer of a printed wiring board.

The present application claims the priority based on Japanese Patent Application No. 2024-044894 filed on March 21, 2024, the contents of which are incorporated herein.

Background Art

[0002]

Various known thermosetting resins are used for producing printed wiring boards and the like contained in mobile communications equipment such as mobile phones and smartphones, and their base station apparatuses, network-related electronic equipment such as servers and routers, and large computers, for example.

In recent years, the network-related electronic equipment has needed to transmit and process a large volume of information with low loss and at a high speed, and increase in frequencies of electrical signals handled in printed wiring boards in such products has also been underway. Transmission loss in printed wiring boards needs to be further reduced because high-frequency electronical signals easily attenuate. Hence, thermosetting resins with

low dielectric loss tangent are desired as materials for use in insulating layers of printed wiring boards. The thermosetting resins for use in insulating layers of printed wiring board are required to have high glass transition temperatures of their cured products from the viewpoint of heat resistance.

[0003]

Patent document 1 discloses that a resin composition containing a polymer having a repeat unit derived from N,N-bis(4-(1,1,3,3-tetramethylbutyl)phenyl)acrylamide and a repeat unit derived from N,N-[4,4'-bis(α,α-dimethylbenzyl)diphenyl]acrylamide has excellent electrical characteristics.

[0004]

Patent document 2 discloses that a resin composition containing a polymer consisting of a repeat unit derived from N,N-bis(4-(tert-butyl)phenyl)acrylamide has excellent electrical characteristics.

[0005]

Patent document 3 discloses that a resin composition containing a polymer consisting of a repeat unit derived from N,N-bis(4-(1,1,3,3-tetramethylbutyl)phenyl)acrylamide has excellent electrical characteristics.

[0006]

Non-patent document 1 discloses that polybutadiene or the like having a 1,2-vinyl group has excellent electrical characteristics.

Prior Art Documents

Patent Documents

[0007]

Patent Document 1: WO2023/286714

Patent Document 2: WO2023/286713

Patent Document 3: Japanese unexamined Patent Application Publication No. 2024-001513

Non-patent Document

[0008]

Non-patent Document 1: Journal of network polymer, Japan, Vol. 43 (2022), No. 2, p. 74-84

Summary of the Invention

Object to be Solved by the Invention

[0009]

Polymers disclosed in patent documents 1 to 3 lack a cross-linking site such as a vinyl group and therefore have no thermosetting properties. Polybutadiene disclosed in non-patent document 1 has a low glass transition temperature of its cured product and has insufficient moisture resistance, though it is a thermosetting resin excellent in electrical characteristics.

[0010]

An object of the present invention is to provide a block copolymer having excellent electrical characteristics, moisture resistance, and heat resistance and having thermosetting properties.

Means to Solve the Object

[0011]

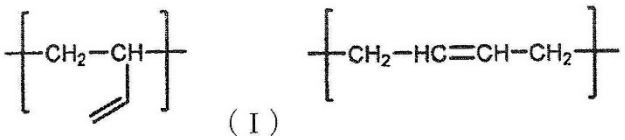
The present inventors have conducted diligent studies and consequently found that the object is attained by a specified polymer.

[0012]

Specifically, the present invention relates to the following invention.

(1) A block copolymer comprising

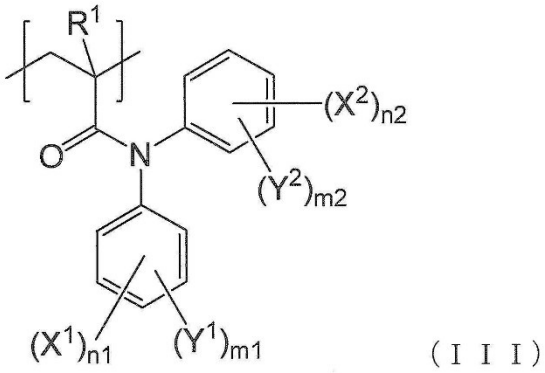
a block chain (A) having (a1) a repeat unit of formula (I), or (a2) a repeat unit of formula (I) and a repeat unit of formula (II):



(I) (II)

and

a block chain (B) having a repeat unit of formula (III):



(III)

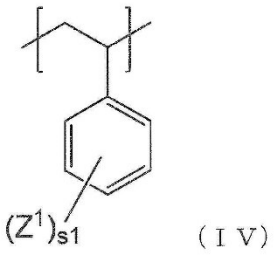
(wherein in formula (III), R^1 represents a hydrogen atom or a methyl group, X^1 and X^2 each independently represent a C1 to C20 alkyl group, a C1 to C20 alkoxy group, a C3 to C6 cyclic alkyl group, a C3 to C6 cyclic alkoxy group, a benzyl group, a 1-phenylethyl group, or a 2-

phenylpropan-2-yl group, n1 and n2 each independently represent 0 or 1, Y^1 and Y^2 each independently represent an organic group or a halogeno group, and m1 and m2 each independently represent any integer of 0 to 4).

(2) The block copolymer according to (1), wherein a molar ratio between the repeat unit of formula (I) and the repeat unit of formula (II) in the block chain (A) is 70:30 to 100:0.

(3) The block copolymer according to (1) or (2), wherein a weight ratio between the block chain (A) and the block chain (B) is 10:90 to 90:10.

(4) The block copolymer according to any one of (1) to (3), further comprising a block chain (C) having a repeat unit of formula (IV):



(IV)

(wherein in formula (IV), Z^1 represents a C1 to C10 alkyl group, a C1 to C10 alkoxy group, a C3 to C6 cyclic alkyl group, a C3 to C6 cyclic alkoxy group, a phenyl group, a halogeno group, an amino group, a dialkylamino group, a C1 to C6 alkylcarbonyl group, a C1 to C6 alkylcarbonyloxy group, a trialkylsilyl group, a trialkoxysilyl group, a cyano group, or a nitro group, and s1 represents any integer of 0 to 5).

(5) The block copolymer according to any one of (1) to (4), wherein a weight-average molecular weight is 1,000 to 100,000.

(6) A resin composition comprising the block copolymer according to any one of (1) to (5).
(7) The resin composition according to (6), further comprising a radical polymerization initiator.
(8) The resin composition according to (6) or (7) for use in an insulating layer of a printed wiring board.
(9) A formed article comprising a cured product of the resin composition according to any one of (6) to (8).

Effect of the Invention

[0013]

The polymer of the present invention has thermosetting properties, has excellent electrical characteristics and moisture resistance, and has a high glass transition temperature of a cured product of the polymer.

Mode of Carrying Out the Invention

[0014]

In the present specification, the "thermosetting properties" refer to characteristics of curing by forming three-dimensional network structure as polymerization reaction progresses by heating.

[0015]

In the present specification, the "excellent electrical characteristics" mean that a cured product of a block copolymer has low dielectric loss tangent. The dielectric loss tangent can be low enough for use in an insulating layer of a printed wiring board.

[0016]

In the present specification, the "moisture resistance" means that an amount of change in dielectric loss tangent of a cured product between before and after moisture absorption operation is small when a block copolymer is subjected to predetermined moisture absorption operation.

[0017]

In the present specification, the "heat resistance" means that a cured product of a block copolymer has a high glass transition temperature. The glass transition temperature of the cured product can be high enough for use in an insulating layer of a printed wiring board.

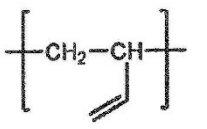
[0018]

The block copolymer of the present invention comprises a block chain (A) and a block chain (B).

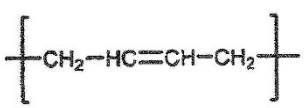
[0019]

The block chain (A) in the block copolymer of the present invention has (a1) a repeat unit of formula (I), or (a2) a repeat unit of formula (I) and a repeat unit of formula (II) (hereinafter, the repeat unit of formula (I) is also referred to as a 1,2-bond structure; and the repeat unit of formula (II) is also referred to as a 1,4-bond structure).

[0020]



(I)



(II)

[0021]

The molar ratio between the repeat unit of formula (I) and the repeat unit of formula (II) in the block chain (A) in the block copolymer of the present invention is preferably 70:30 to 100:0, and more preferably 80:20 to 100:0. A higher proportion of the repeat unit of formula (I) in the block chain (A) increases the amount of a cross-linking vinyl bond and therefore strengthens the thermosetting properties of the block copolymer. The molar ratio between the repeat unit of formula (I) and the repeat unit of formula (II) in the block chain (A) in the block copolymer of the present invention is calculated by ^{1}H-NMR.

[0022]

The block chain (A) in the block copolymer of the present invention may optionally have a repeat unit (hereinafter, referred to as an additional repeat unit (a3)) other than the repeat unit of formula (I) and the repeat unit of formula (II) as long as the effect of the present invention is not deteriorated. As the additional repeat unit (a3), a (meth)acrylic acid ester monomer-derived repeat unit, a (meth)acrylamide-derived repeat unit, an aromatic vinyl monomer-derived repeat unit, an isoprene-derived repeat unit, or the like is exemplified.

[0023]

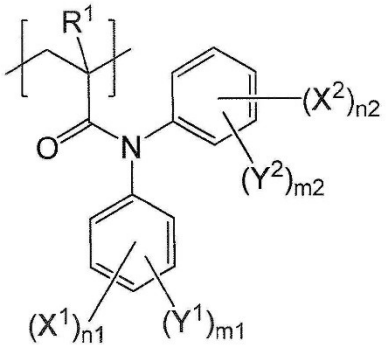
As the weight of the repeat unit of formula (I) and the repeat unit of formula (II) with respect to the total weight of the block chain (A) in the block copolymer of the present invention, for example, but not particularly limited to, 70% by weight or more, 80% by weight or more, 90% by weight or more, 95% by weight or more, 99% by weight or

more, 99.5% by weight or more, 100% by weight, or the like is exemplified.

[0024]

The block chain (B) in the block copolymer of the present invention has a repeat unit of formula (III).

[0025]



(III)

[0026]

In formula (III), R^1 represents a hydrogen atom or a methyl group.

[0027]

In formula (III), X^1 and X^2 each independently represent a C1 to C20 alkyl group, a C1 to C20 alkoxy group, a C3 to C6 cyclic alkyl group, a C3 to C6 cyclic alkoxy group, a benzyl group, a 1-phenylethyl group, or a 2-phenylpropan-2-yl group.

[0028]

As the "C1 to C20 alkyl group" for X^1 and X^2, a "C1 to C20 linear alkyl group" or a "C3 to C20 branched alkyl group" is exemplified.

As the "C1 to C20 linear alkyl group", a methyl group, an ethyl group, an n-propyl group, an n-butyl group, an n-pentyl group, an n-hexyl group, an n-heptyl group, an n-octyl group, an n-nonyl group, an n-decyl group, an n-

dodecyl group, an n-tridecyl group, an n-tetradecyl group, an n-hexadecyl group, an n-octadecyl group, an n-eicosyl group, or the like is exemplified.

As the "C3 to C20 branched alkyl group", an isopropyl group, a sec-butyl group, an isobutyl group, a tert-butyl group, a neopentyl group, an isopentyl group, a sec-pentyl group, a 1-ethylpropyl group, a tert-pentyl group, an isohexyl group, a 3-methylpentyl group, a 2,2-dimethylbutyl group, a 2,3-dimethylbutyl group, a 1,1,2,2-tetramethylpropyl group, a 1,1,3-trimethylbutyl group, a 1-ethylpentyl group, a 1,1,3,3-tetramethylbutyl group, a 2,2,3,3-tetramethylbutyl group, a 1,2,4-trimethylpentyl group, a 2,4,4-trimethylpentyl group, a 2,2,4-trimethylpentyl group, a 1-ethyl-4-methylpentyl group, a 3-ethyl-3-methylpentyl group, a 3-ethyl-4-methylpentyl group, a 1-ethyl-1-methylpentyl group, a 1,1-dimethylhexyl group, a 3,3-dimethylhexyl group, a 4,4-dimethylhexyl group, a 2-ethylhexyl group, a 3-ethylhexyl group, a 6-methylheptyl group, a 1,3,5-trimethylhexyl group, a 1,1,3-trimethylhexyl group, a 1-butyl-1-methylheptyl group, a 1-methylheptyl group, a 1-methyl-1-octylundecyl group, or the like is exemplified.

[0029]

As the "C1 to C20 alkoxy group" for X^1 and X^2, a "C1 to C20 linear alkoxy group" or a "C3 to C20 branched alkoxy group" is exemplified.

As the "C1 to C20 linear alkoxy group", a methoxy group, an ethoxy group, an n-propyloxy group, an n-butyloxy group, an n-pentyloxy group, an n-heptyloxy group, an n-octyloxy group, an n-nonyloxy group, an n-decyloxy group,

an n-dodecyloxy group, an n-tridecyloxy group, an n-tetradecyloxy group, an n-hexadecyloxy group, an n-octadecyloxy group, an n-eicosyloxy group, or the like is exemplified.

As the "C3 to C20 branched alkoxy group", an isopropyloxy group, a sec-butyloxy group, an isobutyloxy group, a tert-butyloxy group, a neopentyloxy group, an isopentyloxy group, a sec-pentyloxy group, a 1-ethylpropyloxy group, a tert-pentyloxy group, an isohexyloxy group, a 3-methylpentyloxy group, a 2,2-dimethylbutyloxy group, a 2,3-dimethylbutyloxy group, a 1,1,2,2-tetramethylpropyloxy group, a 1,1,3-trimethylbutyloxy group, a 1-ethylpentyloxy group, a 1,1,3,3-tetramethylbutyloxy group, a 2,2,3,3-tetramethylbutyloxy group, 1,2,4-trimethylpentyloxy group, a 2,4,4-trimethylpentyloxy group, a 2,2,4-trimethylpentyloxy group, a 1-ethyl-4-methylpentyloxy group, a 3-ethyl-3-methylpentyloxy group, a 3-ethyl-4-methylpentyloxy group, a 1-ethyl-1-methylpentyloxy group, a 1,1-dimethylhexyloxy group, a 3,3-dimethylhexyloxy group, a 4,4-dimethylhexyloxy group, a 2-ethylhexyloxy group, a 3-ethylhexyloxy group, a 6-methylheptyloxy group, a 1,3,5-trimethylhexyloxy group, a 1,1,3-trimethylhexyloxy group, a 1-butyl-1-methylheptyloxy group, a 1-methylheptyloxy group, a 1-methyl-1-octylundecyloxy group, or the like is exemplified.

[0030]

As the "C3 to C6 cyclic alkyl group" for X^1 and X^2, a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, or the like is exemplified.

[0031]

As the "C3 to C6 cyclic alkoxy group" for X^1 and X^2, a cyclopropyloxy group, a cyclobutyloxy group, a cyclopentyloxy group, a cyclohexyloxy group, or the like is exemplified.

[0032]

Each of X^1 and X^2 is preferably a C1 to C20 alkyl group, more preferably a C3 to C20 branched alkyl group, and particularly preferably a C7 to C20 branched alkyl group.

[0033]

In formula (III), n1 and n2 each independently represent 0 or 1.

[0034]

In formula (III), Y^1 and Y^2 each independently represent an organic group or a halogeno group.

[0035]

The "organic group" for Y^1 and Y^2 is not particularly limited as long as the organic group is chemically accepted and produces the effect of the present invention. As the organic group, a C1 to C6 alkyl group such as a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, an s-butyl group, an i-butyl group, a t-butyl group, an n-pentyl group, or an n-hexyl group, a C6 to C10 aryl group such as a phenyl group and a naphthyl group, a C1 to C6 alkoxy group such as a methoxy group, an ethoxy group, an n-propoxy group, an i-propoxy group, an n-butoxy group, an s-butoxy group, an i-butoxy group, or a t-butoxy group, a C1 to C6 haloalkyl group such as a chloromethyl group, a chloroethyl group, a trifluoromethyl group, a 1,2-

dichloro-n-propyl group, a 1-fluoro-n-butyl group, or a perfluoro-n-pentyl group, or the like is exemplified.

[0036]

As the "halogeno group" for Y^1 and Y^2, a fluoro group, a chloro group, a bromo group, or an iodo group is exemplified.

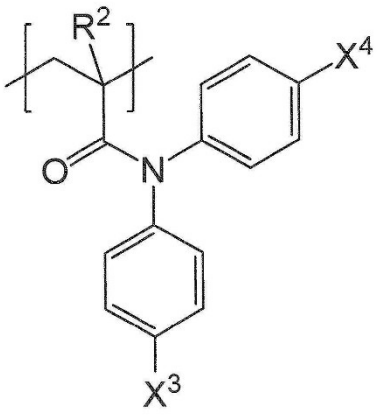
[0037]

In formula (III), m1 and m2 each independently represent any integer of 0 to 4. Each of m1 and m2 is preferably 0.

[0038]

The repeat unit of formula (III) is preferably a repeat unit of formula (V).

[0039]



(V)

[0040]

In formula (V), R^2 is a hydrogen atom or a methyl group.

[0041]

In formula (V), X^3 and X^4 each independently represent a hydrogen atom, a C1 to C20 alkyl group, a C1 to C20 alkoxy group, a C3 to C6 cyclic alkyl group, a C3 to C6 cyclic

alkoxy group, a benzyl group, a 1-phenylethyl group, or a 2-phenylpropan-2-yl group.

As the "C1 to C20 alkyl group", the "C1 to C20 alkoxy group", the "C3 to C6 cyclic alkyl group", and the "C3 to C6 cyclic alkoxy group" for X^3 and X^4, the same as those listed for X^1 and X^2 is exemplified.

[0042]

X^3 is preferably a hydrogen atom or a C1 to C20 alkyl group, more preferably a hydrogen atom or a C3 to C20 branched alkyl group, and further preferably a hydrogen atom or a C7 to C20 branched alkyl group.

X^4 is preferably a hydrogen atom or a C1 to C20 alkyl group, more preferably a hydrogen atom or C3 to C20 branched alkyl group, further preferably a hydrogen atom or a C7 to C20 branched alkyl group, and particularly preferably a C7 to C20 branched alkyl group.

[0043]

The block chain (B) in the block copolymer of the present invention may optionally have a repeat unit (hereinafter, referred to as an additional repeat unit (b1)) other than the repeat unit of formula (III) as long as the effect of the present invention is not deteriorated. As the additional repeat unit (b1), a (meth)acrylic acid ester monomer-derived repeat unit, a (meth)acrylamide-derived repeat unit, an aromatic vinyl monomer-derived repeat unit, an olefin monomer-derived repeat unit, or the like is exemplified.

[0044]

As the weight of the repeat unit of formula (III) with respect to the total weight of the block chain (B) in the

block copolymer of the present invention, for example, but not particularly limited to, 70% by weight or more, 80% by weight or more, 90% by weight or more, 95% by weight or more, 99% by weight or more, 99.5% by weight or more, 100% by weight, or the like is exemplified.

[0045]

The block chain (B) in the block copolymer of the present invention specifically encompasses the following block chains:

I) a block chain consisting of one type of repeat unit of formula (III),

II) a block chain consisting of two or more types of repeat units of formula (III),

III) a block chain consisting of one type of repeat unit of formula (III) and at least one type of additional repeat unit (b1), and

IV) a block chain consisting of two or more types of repeat units of formula (III) and at least one type of additional repeat unit (b1).

[0046]

The block chain (B) in the block copolymer of the present invention is preferably the block chain I) or III), and more preferably the block chain I).

[0047]

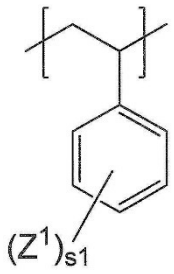
Among the block chains described above, the block chains II) to IV) may be any block chain in which the repeat units of different types are randomly arranged, alternately arranged, or block-arranged.

[0048]

In the block copolymer of the present invention, the weight ratio between the block chain (A) and the block chain (B) is preferably 10:90 to 90:10, and more preferably 20:80 to 70:30.

[0049]

The block copolymer of the present invention may have one or more block chains (A) and one or more block chains (B). The block copolymer of the present invention may optionally contain a block chain other than the block chain (A) and the block chain (B) as long as the effect of the present invention is not deteriorated. As the block chain other than the block chain (A) and the block chain (B), for example, but not particularly limited to, a block chain (C) having a repeat unit of formula (IV) is exemplified.



(IV)

In formula (IV), Z^1 represents a C1 to C10 alkyl group, a C1 to C10 alkoxy group, a C3 to C6 cyclic alkyl group, a C3 to C6 cyclic alkoxy group, a phenyl group, a halogeno group, an amino group, a dialkylamino group, a C1 to C6 alkylcarbonyl group, a C1 to C6 alkylcarbonyloxy group, a trialkylsilyl group, a trialkoxysilyl group, a cyano group, or a nitro group, and s1 represents any integer of 0 to 5.

[0050]

As the "C1 to C10 alkyl group", the "C1 to C10 alkoxy group", the "C3 to C6 cyclic alkyl group", and the "C3 to

C6 cyclic alkoxy group" for Z^1, the same as those listed for X^1 and X^2 is exemplified.

As the "halogeno group" for Z^1, the same as those listed for Y^1 and Y^2 is exemplified.

[0051]

As the "dialkylamino group" for Z^1, a dimethylamino group, a diethylamino group, a di-normal propylamino group, a methylethylamino group, or the like is exemplified.

[0052]

As the "C1 to C6 alkylcarbonyl group" for Z^1, an acetyl group, a propionyl group, or the like is exemplified.

[0053]

As the "C1 to C6 alkylcarbonyloxy group" for Z^1, an acetyloxy group, a propionyloxy group, or the like is exemplified.

[0054]

As the "trialkylsilyl group" for Z^1, a trimethylsilyl group, a triethylsilyl group, or the like is exemplified.

[0055]

As the "trialkoxysilyl group" for Z^1, a trimethoxysilyl group, a triethoxysilyl group, or the like is exemplified.

[0056]

s1 is preferably 0 or 1, and more preferably 0.

[0057]

The block chain (C) in the block copolymer of the present invention may optionally have a repeat unit (hereinafter, referred to as an additional repeat unit (c1)) other than the repeat unit of formula (IV) as long as the effect of the present invention is not deteriorated. As

the additional repeat unit (c1), a (meth)acrylic acid ester monomer-derived repeat unit, a (meth)acrylamide-derived repeat unit, an aromatic vinyl monomer-derived repeat unit, an olefin monomer-derived repeat unit, or the like is exemplified.

[0058]

As the weight of the repeat unit of formula (IV) with respect to the total weight of the block chain (C) in the block copolymer of the present invention, for example, but not particularly limited to, 70% by weight or more, 80% by weight or more, 90% by weight or more, 95% by weight or more, 99% by weight or more, 99.5% by weight or more, 100% by weight, or the like is exemplified.

[0059]

As a preferred embodiment of the block copolymer of the present invention, a diblock copolymer consisting of the block chain (A) and the block chain (B); or a triblock copolymer consisting of the block chain (A), the block chain (B), and the block chain (C) is exemplified.

[0060]

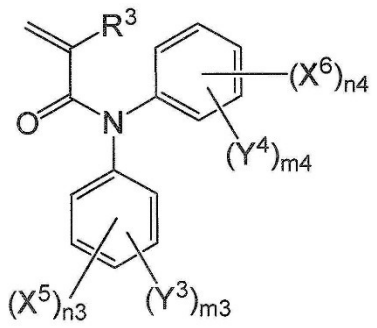
As the weight-average molecular weight (Mw) of the block copolymer of the present invention, for example, but not particularly limited to, 1,000 to 100,000, 4,000 to 100,000, 1,000 to 30,000, 4,000 to 30,000, 6,000 to 20,000, 6,000 to 18,000, 6,500 to 20,000, 6,500 to 18,000, 10,000 to 20,000, 10,000 to 18,000, or the like is exemplified. The weight-average molecular weight (Mw) of the block copolymer of the present invention is measured by gel permeation chromatography (GPC) with polystyrene as a standard substance.

[0061]

As a method for producing the block copolymer of the present invention, for example, but not particularly limited to, the following production method is exemplified.

1,3-Butadiene is mixed in the presence of a polymerization solvent and an anionic polymerization initiator to polymerize the 1,3-butadiene (step 1). After step 1, a stabilizer is added thereto, and a compound of formula (VI) is further mixed to polymerize the compound of formula (VI) (step 2).

[0062]



(VI)

In formula (VI), R^3 represents a hydrogen atom or a methyl group, X^5 and X^6 each independently represent a C1 to C20 alkyl group, a C1 to C20 alkoxy group, a C3 to C6 cyclic alkyl group, a C3 to C6 cyclic alkoxy group, a benzyl group, a 1-phenylethyl group, or a 2-phenylpropan-2-yl group, n3 and n4 each independently represent 0 or 1, Y^3 and Y^4 each independently represent an organic group or a halogeno group, and m3 and m4 each independently represent any integer of 0 to 4.

[0063]

As the "C1 to C20 alkyl group", the "C1 to C20 alkoxy group", the "C3 to C6 cyclic alkyl group", and the "C3 to

C6 cyclic alkoxy group" for X^5 and X^6, the same as those listed for X^1 and X^2 is exemplified.

[0064]

As the "organic group" and the "halogeno group" for Y^3 and Y^4, the same as those listed for Y^1 and Y^2 is exemplified.

[0065]

As the polymerization solvent in the method for producing the block copolymer of the present invention, for example, but not particularly limited to, a hydrocarbon solvent such as propane, butane, pentane, hexane, heptane, isooctane, cyclopentane, cyclohexane, methylcyclohexane, decane, benzene, or toluene; or an ether solvent such as 1,2-dimethoxyethane, 1,2-diethoxyethane, tetrahydrofuran, 2-methoxymethyltetrahydrofuran, diethyl ether, triethylene glycol dimethyl ether, or cyclopentylmethyl ether is exemplified. These solvents may be used alone or used as a mixed solvent of two or more thereof. As the solvent, an ether solvent or a mixed solvent of an ether solvent and a hydrocarbon solvent is preferably used from the viewpoint of increasing the proportion of the repeat unit of formula (I) in the block chain (A).

[0066]

As the anionic polymerization initiator in the method for producing the block copolymer of the present invention, for example, but not particularly limited to, an organolithium compound such as methyl lithium, ethyl lithium, propyl lithium, n-butyl lithium, sec-butyl lithium, t-butyl lithium, isobutyl lithium, hexyl lithium, octyl lithium, tetramethylene dilithium, pentamethylene dilithium,

hexamethylene dilithium, phenyl lithium, tolyl lithium, or lithium naphthalenide; metal sodium, or the like is exemplified.

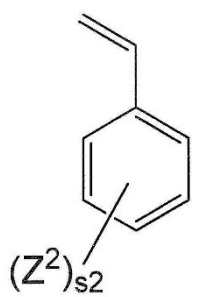
[0067]

The stabilizer in the method for producing the block copolymer of the present invention is a reagent that may control a polymerization rate and/or suppress side reaction by stabilizing a growing chain end during anionic polymerization. As the stabilizer in the method for producing the block copolymer of the present invention, for example, but not particularly limited to, lithium chloride, methoxy ethoxide-type alkoxy lithium, potassium t-butoxide, tetramethylethylenediamine, a derivative of tetramethylethylenediamine, an organic magnesium compound such as dibutyl magnesium, an organic zinc compound such as diethyl zinc, an organic aluminum compound such as triethyl aluminum, or the like is exemplified.

[0068]

The method for producing the block copolymer of the present invention may comprise, before or after step 1, step 3 of mixing a compound of formula (VII) to polymerize the compound of formula (VII).

[0069]



(VII)

Z^2 represents a C1 to C10 alkyl group, a C1 to C10 alkoxy group, a C3 to C6 cyclic alkyl group, a C3 to C6 cyclic alkoxy group, a phenyl group, a halogeno group, an amino group, a dialkylamino group, a C1 to C6 alkylcarbonyl group, a C1 to C6 alkylcarbonyloxy group, a trialkylsilyl group, a triethoxysilyl group, a cyano group, or a nitro group, and s2 represents any integer of 0 to 5.

As the "C1 to C10 alkyl group", the "C1 to C10 alkoxy group", the "C3 to C6 cyclic alkyl group", and the "C3 to C6 cyclic alkoxy group" for Z^2, the same as those listed for X^1 and X^2 is exemplified.

As the "halogeno group" for Z^2, the same as those listed for Y^1 and Y^2 is exemplified.

As the "dialkylamino group", the "C1 to C6 alkylcarbonyl group", the "C1 to C6 alkylcarbonyloxy group", the "trialkylsilyl group", and the "trialkoxysilyl group" for Z^2, the same as those listed for Z^1 is exemplified.

s2 is preferably 0 or 1, and more preferably 0.

[0070]

As a polymerization temperature in step 1, step 2, and step 3, for example, but not particularly limited to, -78°C to 70°C, -78°C to 35°C, -78°C to 25°C, -78°C to 10°C, -10°C to 70°C, -10°C to 35°C, -10°C to 25°C, -10°C to 10°C, -5°C to 70°C, -5°C to 35°C, -5°C to 25°C, -5°C to 10°C, -5°C to 5°C, or the like is exemplified.

[0071]

As a method for producing the compound of formula (VI), for example, but not particularly limited to, a production method described in WO2018/070079, WO2020/071456, WO2021/201207, WO2021/201208, or the like is exemplified.

[0072]

The resin composition of the present invention comprises the block copolymer of the present invention.

As the content of the block copolymer of the present invention in the resin composition of the present invention, for example, but not particularly limited to, an amount of 10 to 95% by weight, 10 to 90% by weight, 20 to 90% by weight, 30 to 90% by weight, 10 to 75% by weight, 20 to 75% by weight, or 30 to 75% by weight with respect to the total weight of the resin composition is exemplified.

[0073]

The resin composition of the present invention may further comprise a radical polymerization initiator. As the radical polymerization initiator for use in the resin composition of the present invention, an azo-based initiator, a peroxide-based initiator, or the like is exemplified.

[0074]

As the azo-based initiator, for example, azobisisobutyronitrile, 1,1'-azobis(cyclohexane-1-carbonitrile), 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-(hydroxymethyl)propionitrile], 2,2'-azobis(2, 4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2, 4-dimethylvaleronitrile), dimethyl 2,2'-azobisisobutyrate, 2,2'-azobis[2-(2-imidazolin-2-yl)propane], 2,2'-azobis{2-methyl-N-[1, 1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}, or the like is exemplified.

[0075]

As the peroxide-based initiator, benzoyl peroxide, cumene hydroperoxide, 2,5-dimethylhexane-2,5-dihydroperoxide, α,α'-di(t-butylperoxy)diisopropylbenzene, 2,5-dimethyl-2,5-di(t-butylperoxy)hexine-3, di-t-butyl peroxide, 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, trimethylsilyltriphenylsilyl peroxide, diisopropylbenzene hydroperoxide, or the like is exemplified.

[0076]

The radical polymerization initiator for use in the resin composition of the present invention is preferably a peroxide-based initiator.

[0077]

As the content of the radical polymerization initiator in the resin composition of the present invention, for example, but not particularly limited to, an amount of 0.1 to 20% by weight, 0.1 to 10% by weight, or 0.1 to 5% by weight with respect to the total weight of the resin composition may be exemplified.

[0078]

The resin composition of the present invention may optionally contain other components as long as the effect of the present invention is not deteriorated. As other components, a thermosetting resin, an organic solvent, a cross-linking agent, a thermoplastic resin, an inorganic

filler, an organic filler, a flame retardant, other additives, or the like may be exemplified.

[0079]

As the thermosetting resin, for example, but not particularly limited to, a monomer, a prepolymer, an oligomer, a polymer, or the like having a vinyl group, a (meth)acryloyl group, an epoxy group, an oxetanyl group, or a maleimide group may be used. Among them, a polyfunctional resin is preferably used. As a specific example of the thermosetting resin, for example, the following components A-1 to A-5 may be exemplified.

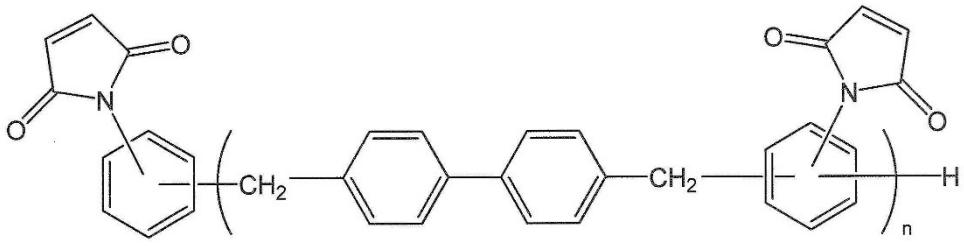
[0080]

[Component A-1]

Component A-1 is a maleimide compound. The maleimide compound is not particularly limited as long as the compound has one or more maleimide groups in a molecule. As a specific example thereof, for example, N-phenylmaleimide, N-hydroxyphenylmaleimide, bis(4-maleimidophenyl)methane, 2,2-bis{4-(4-maleimidophenoxy)-phenyl}propane, bis(3,5-dimethyl-4-maleimidophenyl)methane, bis(3-ethyl-5-methyl-4-maleimidophenyl)methane, bis(3,5-diethyl-4-maleimidophenyl)methane, polytetramethylene oxide-bis(4-maleimidobenzoate), 2,2-bis[4-(4-maleimidophenoxy)phenyl]propane, 4,4'-diphenylmethane bismaleimide, bis-(3-ethyl-5-methyl-4-maleimidophenyl)methane, 2,2-bis-[4-(4-maleimidophenoxy)phenyl]propane, a maleimide compound of formula (IV) given below, a prepolymer of such a maleimide compound, or a prepolymer of the maleimide compound and an amine compound may be exemplified. As the maleimide

compound, a commercially available product may be used. As the commercially available product, for example, MIR-3000 (manufactured by Nippon Kayaku Co., Ltd.), MIR-3000-70MT (manufactured by Nippon Kayaku Co., Ltd.), BMI (manufactured by K-I Chemical Industry Co., Ltd.), BMI-70 (manufactured by K-I Chemical Industry Co., Ltd.), BMI-80 (manufactured by K-I Chemical Industry Co., Ltd.), or the like may be exemplified. These compounds may be used alone or used by appropriate mixing of two or more thereof.

[0081]



(1)

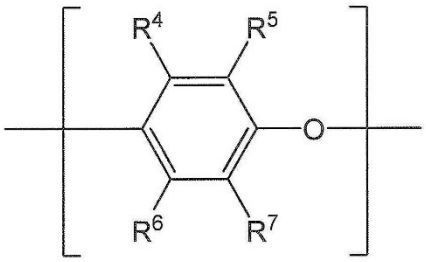
In formula (1), n represents any integer of 1 to 100. n is preferably 1 to 50, more preferably 1 to 20, and further preferably 1 to 5.

[0082]

[Component A-2]

Component A-2 is a polyphenylene ether compound. The polyphenylene ether compound as component A-2 is not particularly limited as long as the compound is a polymer having a repeat unit of the following formula (2).

[0083]



(2)

In formula (2), R^4 to R^7 each independently represent a hydrogen atom, a C1 to C6 alkyl group, a C2 to C6 alkenyl group, a C2 to C6 alkynyl group, a C1 to C6 alkylcarbonyl group, or a C2 to C6 alkenylcarbonyl group.

As the "C1 to C6 alkyl group" for R^4 to R^7, the same as those listed for X^1 and X^2 is exemplified.

As the "C2 to C6 alkenyl group" for R^4 to R^7, a vinyl group, an allyl group, or the like is exemplified.

As the "C2 to C6 alkynyl group" for R^4 to R^7, an ethynyl group, a 2-propynyl group, or the like may be exemplified.

As the "C1 to C6 alkylcarbonyl group" for R^4 to R^7, the same as those listed for Z^1 is exemplified.

As the "C2 to C6 alkenylcarbonyl group" for R^4 to R^7, an acryloyl group, a methacryloyl group, or the like is exemplified.

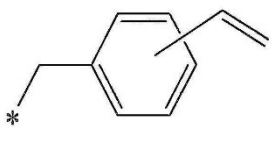
[0084]

The polyphenylene ether compound as component A-2 may be modified at its end. As the terminally modified polyphenylene ether compound, a terminally hydroxy group-modified polyphenylene ether compound, or a polyphenylene ether compound modified with a substituent having a carbon-carbon unsaturated double bond may be exemplified.

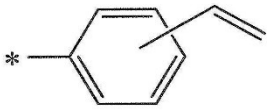
[0085]

As the substituent having a carbon-carbon unsaturated double bond, a group of formula (3), a group of formula (4), an acryloyl group, or a methacryloyl group may be exemplified.

[0086]



(3)



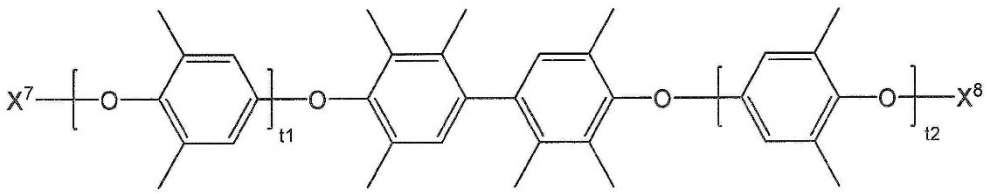
(4)

* in formula (3) and formula (4) represents a binding position.

[0087]

As the polyphenylene ether compound modified with the substituent having a carbon-carbon unsaturated double bond, a compound of formula (5) or formula (6) is specifically exemplified.

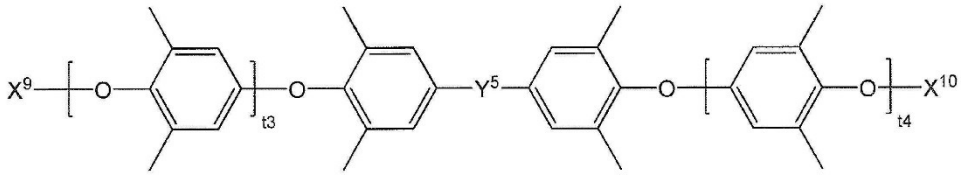
[0088]



(5)

In formula (5), X^7 and X^8 each independently represent a group of formula (3), a group of formula (4), an acryloyl group, or a methacryloyl group, and t1 and t2 each independently represent an integer of 0 to 20. The group of formula (3) and the group of formula (4) for X^7 and X^8 are as described above.

[0089]



(6)

In formula (6), X^9 and X^{10} each independently represent a group of formula (3), a group of formula (4), an acryloyl group, or a methacryloyl group, and t3 and t4 each independently represent an integer of 0 to 20, and Y^5 represents a C1 to C6 alkylene group. The group of formula (3) and the group of formula (4) for X^9 and X^{10} are as described above. As the C1 to C6 alkylene group for Y^5, a methylene group, an ethylene group, a methylmethylene group, a dimethylmethylene group, or the like may be exemplified.

[0090]

Although the number-average molecular weight (Mn) of the polyphenylene ether compound as component A-2 is not particularly limited, 1,000 to 7,000, 1,000 to 5,000, 1,000 to 3,000, or the like may be exemplified. The number-average molecular weight (Mn) is a value converted from data measured by gel permeation chromatography (GPC) with tetrahydrofuran as a solvent, on the basis of the molecular weight of standard polystyrene.

[0091]

As the polyphenylene ether compound as component A-2, a known compound or a commercially available product may be used. As the commercially available product, for example, SA90 (manufactured by SABIC Innovative Plastics), SA9000 (manufactured by SABIC Innovative Plastics), OPE-2st (manufactured by Mitsubishi Gas Chemical Co, Inc.), or the like may be exemplified.

In the case of synthesizing the polyphenylene ether compound, this compound may be synthesized by a method described in WO2014/203511 or the like and a method equivalent thereto.

[0092]

[Component A-3]

Component A-3 is polybutadiene having a molar ratio between a 1,2-bond structure and a 1,4-bond structure of 70:30 to 100:0. The polybutadiene as component A-3 may be polybutadiene unmodified at its backbone and end or may be polybutadiene modified at its backbone and end.

Although the weight-average molecular weight (Mw) of the polybutadiene as component A-3 is not particularly limited, 500 to 10,000, 500 to 8,000, 500 to 6,000, 500 to 5,000, or the like may be exemplified. The weight-average molecular weight (Mw) is a value converted from data measured by gel permeation chromatography (GPC) with tetrahydrofuran as a solvent, on the basis of the molecular weight of standard polystyrene.

As the polybutadiene as component A-3, a commercially available product may be used. As the commercially available product of the polybutadiene, NISSO-PB B-1000 (manufactured by Nippon Soda Co., Ltd.), NISSO-PB B-2000 (manufactured by Nippon Soda Co., Ltd.), NISSO-PB B-3000 (manufactured by Nippon Soda Co., Ltd.), or the like may be exemplified. These polybutadienes may be used alone or used by combination of two or more thereof.

[0093]

[Component A-4]

Component A-4 is a styrene-butadiene-styrene block copolymer (hereinafter, also referred to as SBS) having a molar ratio between a 1,2-bond structure and a 1,4-bond structure of 80:20 to 100:0 in the butadiene block.

Although the weight ratio between the styrene block and the butadiene block in the SBS as component A-4 is not particularly limited, 10:90 to 80:20, 10:90 to 70:30, 10:90 to 60:40, 20:80 to 80:20, 30:70 to 80:20, or 40:60 to 80:20 may be exemplified.

Although the weight-average molecular weight (Mw) of the SBS as component A-4 is not particularly limited, 2,000 to 100,000, 2,000 to 80,000, 2,000 to 60,000, or the like may be exemplified. Although the molecular weight distribution (Mw/Mn) of the styrene-butadiene-styrene block copolymer is not particularly limited, 1.00 to 3.00, 1.00 to 2.00, or the like may be exemplified. The weight-average molecular weight (Mw) and the molecular weight distribution (Mw/Mn) are measured by gel permeation chromatography (GPC) with polystyrene as a standard substance.

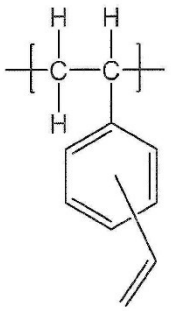
A method for producing the SBS as component A-4 is not particularly limited. The SBS may be produced by, for example, a method described in Japanese unexamined Patent Application Publication No. 6-192502, Japanese unexamined Patent Application Publication (Translation of PCT Application) No. 2000-514122, Japanese unexamined Patent Application Publication No. 2007-302901, WO2021/024679, or the like and a method equivalent thereto.

[0094]

[Component A-5]

Component A-5 is a polymer having a repeat unit of formula (7) in a molecule.

[0095]

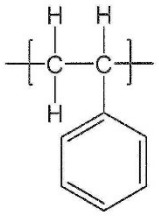


(7)

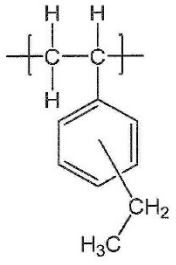
[0096]

The polymer having the repeat unit of formula (7) in a molecule as component A-5 may have a repeat unit of formula (8) and/or a repeat unit of formula (9). When the polymer having the repeat unit of formula (7) in a molecule as component A-5 has a repeat unit of formula (8) and/or a repeat unit of formula (9), the polymer having the repeat unit of formula (7) in a molecule may be a block copolymer or may be a random copolymer.

[0097]



(8)



(9)

[0098]

The weight-average molecular weight (Mw) of the polymer having the repeat unit of formula (7) in a molecule as component A-5 is preferably 1200 to 40000, more

preferably 1200 to 35000. The weight-average molecular weight (Mw) is a value converted from data measured by gel permeation chromatography (GPC) with tetrahydrofuran as a solvent, on the basis of the molecular weight of standard polystyrene.

[0099]

As the polymer having the repeat unit of formula (7) in a molecule as component A-5, a commercially available product may be used. As the commercially available product, ODV-XET-X03 (manufactured by NIPPON STEEL Chemical & Material Co., Ltd.), ODV-XET-X04 (manufactured by NIPPON STEEL Chemical & Material Co., Ltd.), ODV-XET-X05 (manufactured by NIPPON STEEL Chemical & Material Co., Ltd.), or the like may be exemplified.

[0100]

Although the organic solvent is not particularly limited, an amide-based solvent, an ether-based solvent, an ester-based solvent, an aliphatic hydrocarbon-based solvent, an aromatic hydrocarbon-based solvent, a ketone-based solvent, an organic halogen compound-based solvent, or the like may be exemplified.

As the amide-based organic solvent, N,N-dimethylformamide (DMF) or N,N-dimethylacetamide; as the ether-based organic solvent, diethyl ether, dipropyl ether, dibutyl ether, diamyl ether, or tetrahydrofuran; as the ester-based organic solvent, ethyl acetate, propyl acetate, butyl acetate, amyl acetate, heptyl acetate, ethyl butyrate, isoamyl isovalerate, or propylene glycol methyl ether acetate; as the aliphatic hydrocarbon-based organic solvent, normal hexane, normal heptane, or cyclohexane; as the

aromatic hydrocarbon-based organic solvent, toluene or xylene; as the ketone-based organic solvent, methyl ethyl ketone, methyl isobutyl ketone, or cyclohexanone; as the organic halogen compound-based organic solvent, trichloroethane or trichloroethylene; or the like may be exemplified. Alternatively, a relative inert organic solvent such as propylene glycol monomethyl ether or propylene glycol monoethyl ether may be used.

[0101]

As the cross-linking agent, for example, but not particularly limited to, a polyfunctional vinyl compound such as divinylbenzene, divinylnaphthalene, and divinyl biphenyl; a vinyl benzyl ether compound synthesized through the reaction of phenol and vinyl benzyl chloride; a styrene monomer; an allyl ether compound synthesized through the reaction of phenol and allyl chloride; trialkenyl isocyanurate such as triallyl isocyanurate (TAIC(R)) and triallyl cyanurate (TAC); a (meth)acrylate compound (methacrylate compound and acrylate compound) such as trimethylolpropane; a compound having an acenaphthylene backbone, or the like may be exemplified. These cross-linking agents may be used for enhancing heat resistance. One or more of these cross-linking agents may be used.

[0102]

As the compound having an acenaphthylene backbone, acenaphthylene; a hydroxyacenaphthylene compound such as 3-hydroxyacenaphthylene, 4-hydroxyacenaphthylene, 5-hydroxyacenaphthylene, and 5,6-dihydroxyacenaphthylene; an alkylacenaphthylene compound such as 3-methylacenaphthylene, 3-ethylacenaphthylene, 3-propylacenaphthylene, 4-

methylacenaphthylene, 4-ethylacenaphthylene, 4-propylacenaphthylene, 5-methylacenaphthylene, 5-ethylacenaphthylene, 5-propylacenaphthylene, 3,8-dimethylacenaphthylene, and 5,6-dimethylacenaphthylene; an alkoxyacenaphthylene compound such as 3-methoxyacenaphthylene, 3-ethoxyacenaphthylene, 3-butoxyacenaphthylene, 4-methoxyacenaphthylene, 4-ethoxyacenaphthylene, 4-butoxyacenaphthylene, 5-methoxyacenaphthylene, 5-ethoxyacenaphthylene, and 5-butoxyacenaphthylene; a halogenated acenaphthylene compound such as 3-chloroacenaphthylene, 3-bromoacenaphthylene, 4-chloroacenaphthylene, 4-bromoacenaphthylene, 5-chloroacenaphthylene, and 5-bromoacenaphthylene, or the like may be exemplified.

[0103]

As the thermoplastic resin, for example, but not particularly limited to, polyacrylate resin, polymethacrylate resin, polystyrene resin, polyphenylene ether resin, polyetherimide resin, polyethersulfone resin, polyphenylene sulfide resin, polycyclopentadiene resin, polycycloolefin resin, polycycloolefin copolymer resin, polyarylate resin, polyether resin, phenoxy resin, polyvinylacetal resin, polyolefin resin, polybutadiene resin, polyimide resin, polyamide imide resin, polysulfone resin, polycarbonate resin, polyether ether ketone resin, polyester resin, liquid crystal polyester resin, fluorine resin, or the like, a known thermoplastic elastomer, for example, a styrene-ethylene-propylene copolymer, a styrene-ethylene-butylene copolymer, a styrene-butadiene copolymer, a styrene-isoprene copolymer, a hydrogenated styrene-

butadiene copolymer, a hydrogenated styrene-isoprene copolymer, a (meth)acrylonitrile-butadiene-(meth)acrylic acid copolymer, a (meth)acrylonitrile-butadiene-methyl (meth)acrylate copolymer, a methyl (meth)acrylate-butadiene-styrene copolymer (MBS), and (meth)acrylonitrile-butadiene rubber (NBR), linear polyurethane, polybutadiene, polyisoprene, fluorine-based rubber, ethylene-propylene-diene rubber, or the like may be exemplified.

[0104]

As the inorganic filler, for example, but not particularly limited to, silica, alumina, glass, cordierite, silicon oxide, barium sulfate, barium carbonate, talc, clay, a mica powder, zinc oxide, hydrotalcite, boehmite, aluminum hydroxide, magnesium hydroxide, calcium carbonate, magnesium carbonate, magnesium oxide, boron nitride, aluminum nitride, manganese nitride, aluminum borate, strontium carbonate, strontium titanate, calcium titanate, magnesium titanate, bismuth titanate, titanium oxide, zirconium oxide, barium titanate, barium zirconate titanate, barium zirconate, calcium zirconate, zirconium phosphate, zirconium tungstate phosphate, or the like may be exemplified. Among them, silica is particularly suitable. As the silica, spherical silica is preferred. These inorganic fillers may be used alone or used by combination of two or more thereof.

[0105]

The inorganic filler is preferably treated with one or more surface treatment agents such as an aminosilane-based coupling agent, an epoxysilane-based coupling agent, a mercaptosilane-based coupling agent, a silane-based

coupling agent, an organosilazane compound, a titanate-based coupling agent, a vinylsilane-based coupling agent, a methacryloxysilane-based coupling agent, an acryloxysilane-based coupling agent, and a styrylsilane-based coupling agent.

[0106]

As the organic filler, for example, but not particularly limited to, a rubber particle, a fluorine resin particle (fluoropolymer particle), a fine polyamide particle, a silicone particle, or the like may be exemplified.

[0107]

As the rubber particle, a commercially available product may be used. For example, "EXL-2655" manufactured by Dow Chemical Japan Ltd., "AC3816N" manufactured by Aica Kogyo Co., Ltd., or the like may be exemplified.

[0108]

As the fluorine resin particle (fluoropolymer particle), for example, polytetrafluoroethylene (PTFE), perfluoroalkoxy alkane (PFA), a perfluoroethylene propene copolymer (FEP), an ethylene-tetrafluoroethylene copolymer (ETFE), a tetrafluoroethylene-perfluorodioxol copolymer (TFE/PDD), polyvinylidene fluoride (PVDF), polychlorotrifluoroethylene (PCTFE), an ethylene-chlorotrifluoroethylene copolymer (ECTFE), polyvinyl fluoride (PVF), or the like may be exemplified. These resins may be used alone or may be used by combination of two or more thereof.

As the fluorine resin particle (fluoropolymer particle), a commercially available product may be used.

For example, "LUBRON(R) L-2" manufactured by Daikin Industries, Ltd., "LUBRON L-5" manufactured by Daikin Industries, Ltd., "LUBRON L-5F" manufactured by Daikin Industries, Ltd., "Fluon(R) PTFE L-170JE" manufactured by AGC Inc., "FluonPTFE L-172JE" manufactured by AGC Inc., "FluonPTFE L-173JE" manufactured by AGC Inc., "KTL-500F" manufactured by Kitamura Ltd., "KTL-2N" manufactured by Kitamura Ltd., "KTL-1N" manufactured by Kitamura Ltd., or "TLP10F-1" manufactured by Mitsui-Chemours Fluoroproducts Co., Ltd. may be exemplified.

[0109]

The inorganic filler and the organic filler may contain a surface-treated particle. As the surface treatment, for example, surface treatment with a surface treatment agent is exemplified. The surface treatment agent is not particularly limited. The surface treatment agent includes a surfactant such as a nonionic surfactant, an amphoteric surfactant, a cationic surfactant, and an anionic surfactant as well as an inorganic fine particle or the like. As the surface treatment agent, a fluorine-based surfactant is preferably used from the viewpoint of affinity. As a specific example of the fluorine-based surfactant, "Surflon(R) S-243" (perfluoroalkyl-ethylene oxide adduct) manufactured by AGC Seimi Chemical Co., Ltd., "MEGAFAC(R) F-251" manufactured by DIC Corp., "MEGAFAC F-477" manufactured by DIC Corp., "MEGAFAC F-553" manufactured by DIC Corp., "MEGAFAC R-40" manufactured by DIC Corp., "MEGAFAC R-43" manufactured by DIC Corp., "MEGAFAC R-94" manufactured by DIC Corp., "FTX-218" manufactured by Neos

Corp., "Ftergent(R) 610FM" manufactured by Neos Corp., or "Ftergent 730LM" manufactured by Neos Corp. is exemplified.

[0110]

As the flame retardant, for example, but not particularly limited to, a halogen-based flame retardant, a phosphorus-based flame retardant, or the like may be exemplified.

As the halogen-based flame retardant, for example, ethylene dipentabromobenzene, ethylene bistetrabromoimide, decabromodiphenyl oxide, tetradecabromodiphenoxybenzene, or the like having a melting point of 300°C or higher may be exemplified.

As the phosphorus-based flame retardant, a phosphoric acid ester-based flame retardant such as condensed phosphoric acid ester of dixylenyl phosphate, a phosphazene-based flame retardant such as phenoxy phosphazene, a phosphinate-based flame retardant such as phosphinic acid metal salt of dialkylphosphinic acid aluminum salt, or the like may be exemplified.

The listed flame retardants may be used alone or may be used by combination of two or more thereof.

[0111]

As other additives, for example, an antifoaming agent such as a silicone-based antifoaming agent and an acrylic acid ester-based antifoaming agent, an organic metal compound such as an organic copper compound, an organic zinc compound, and an organic cobalt compound, a leveling agent, an adhesion promoter such as a silane coupling agent, a tackiness agent such as a tackifier, a heat stabilizer, an antistatic agent, a preservation stabilizer such as BHT, an

antioxidant, a light stabilizer, an ultraviolet absorber, a dye or a pigment, a lubricant, a wetting and dispersing agent, a heavy metal deactivator, an ion trapping agent, an emulsifier, an aqueous dispersion stabilizer, a mold release agent, a wax, a rheology control agent, a surfactant, or the like is exemplified.

[0112]

The resin composition of the present invention may be produced by mixing the individual components described above into an organic solvent and dispersing the components using, if necessary, a ball mill, a bead mill, a planetary mixer, a roll mill, or the like. The organic solvent may be distilled off, if necessary.

[0113]

The resin composition of the present invention is a resin composition for use in an insulating layer of a printed wiring board. The resin composition of the present invention is excellent in electrical characteristics and moisture resistance and has a high glass transition temperature of its cured product and as such, is suitable as a resin composition for use in an insulating layer of a printed wiring board. As the printed wiring board, a single-sided printed circuit board, a double-sided printed circuit board, a multilayer printed circuit board, a flexible printed circuit board, a build-up substrate, or the like is exemplified.

[0114]

The formed article of the present invention is a formed article comprising a cured product of the resin composition of the present invention. The cured product of

the resin composition of the present invention may be obtained by thermally curing the resin composition of the present invention. As the formed article of the present invention, for example, but not particularly limited to, a printed wiring board obtained by a production method comprising the step of laminating a sheeted lamination material and metal foil such as copper foil or aluminum foil in a layer configuration, and bonding the layers under pressure by heating while thermally curing the resin composition, or the like is exemplified.

As the sheeted lamination material, for example, a prepreg having a base material impregnated with the resin composition of the present invention, an adhesive film having a resin composition layer containing the resin composition of the present invention on a support film, metal foil with a resin composition having a resin composition layer containing the resin composition on metal foil, or the like is exemplified. As the base material, for example, a fibrous base material such as a glass cloth, an aramide cloth, a polyester cloth, a glass nonwoven fabric, an aramide nonwoven fabric, a polyester nonwoven fabric, pulp paper, and linter paper is exemplified. As the support film, various plastic films such as a film of polyolefin such as polyethylene, polypropylene, and polyvinyl chloride; a film of polyester such as polyethylene terephthalate (hereinafter, also abbreviated as "PET") and polyethylene naphthalate; a polycarbonate film; and a polyimide film are exemplified. As the metal foil, copper foil, aluminum foil, or the like is exemplified.

[0115]

Hereinafter, Examples of the present invention will be described. However, the technical scope of the present invention is not limited by these Examples.

Examples

[0116]

<Weight-average molecular weight (Mw) and dispersity (Mw/Mn)>

The weight-average molecular weights of polymers obtained in Examples were measured using the following apparatuses and conditions.

[Apparatus]

Sample injection apparatus: Waters 2695 alliance,

Separation column: ShodexKF-G, 803, 802, 801

Detector: Waters 2414 differential refractive index (RI) detector

2998 photodiode array (PDA) detector

Column oven: column oven manufactured by Waters Corp.

[Conditions]

Column oven temperature: 40°C

RI detector temperature: 40°C

Mobile phase: tetrahydrofuran

Flow rate: 1.0 mL/min

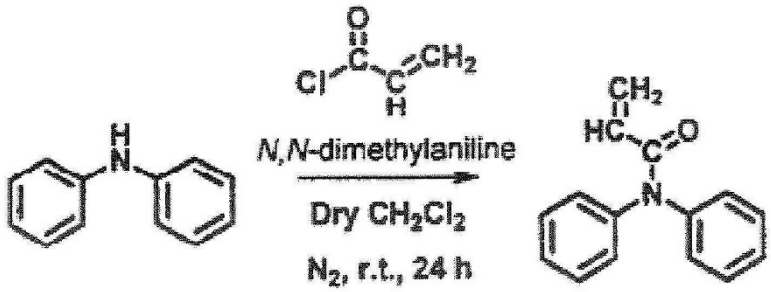
Standard injection volume: 40 μL

PDA detector extraction wave: 254.0 nm

Quantitative calculation: based on standard polystyrene

[0117]

(Synthesis Example 1) Synthesis of N,N-diphenylacrylamide (DPAm)

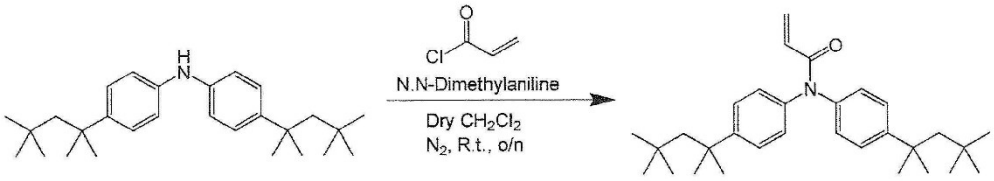


To a 1 L four-neck flask purged with nitrogen, diphenylamine (50.00 g, 0.295 mol), N,N-dimethylanline (42.97 g, 0.355 mol), and 322 mL of super-dehydrated dichloromethane were added, and stirred until uniformly dissolved. Subsequently, the reaction solution was cooled to 0°C or lower in an ice bath, and acrylic acid chloride (29.42 g, 0.325 mol) was gradually added dropwise thereto, followed by reaction for 24 hours. After the completion of reaction, the solvent was distilled off with an evaporator, and a crude product was dissolved in 250 mL of ethyl acetate. Then, the solution was washed with a 1 N aqueous hydrochloric acid solution, a saturated aqueous solution of sodium bicarbonate, and saline. An organic layer was dehydrated with magnesium sulfate, and the solvent in a filtrate was then distilled off with an evaporator. The obtained crude product was purified by recrystallization with hexane to give DPAm (52.73 g, yield: 80%). Results of mass spectrometry will be shown below.

High Resolution ESI-TOF-MS m/z Calcd. for [$C_{15}H_{13}N_1O_1$ ([M + Na]$^+$)]: 246.0889 found 246.0880.

[0118]

(Synthesis Example 2) Synthesis of N,N-bis(4-(1,1,3,3-tetramethylbutyl)phenyl)acrylamide (DODPAm)

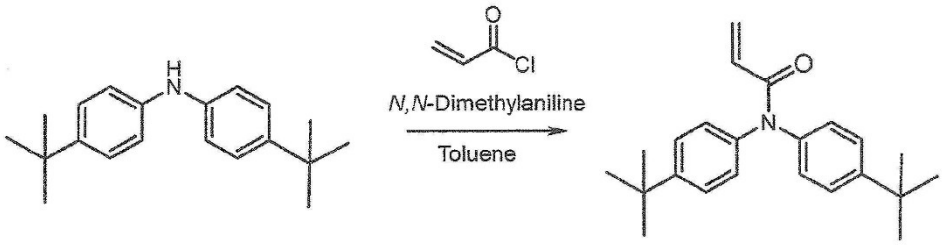


To a 1 L four-neck flask purged with nitrogen, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]amine (50.00 g, 0.127 mol), N,N-dimethylanline (46.17 g, 0.381 mol), and 477 mL of super-dehydrated dichloromethane were added, and stirred until uniformly dissolved. Subsequently, the reaction solution was cooled to 0°C or lower in an ice/ethanol bath, and acrylic acid chloride (22.99 g, 0.254 mol) was gradually added dropwise thereto, followed by reaction for 24 hours. After the completion of reaction, the solvent was distilled off with an evaporator, and a crude product was dissolved in 250 mL of ethyl acetate. Then, the solution was washed with a 1 N aqueous hydrochloric acid solution, a saturated aqueous solution of sodium bicarbonate, and saline. An organic layer was dehydrated with magnesium sulfate, and the solvent in a filtrate was then distilled off with an evaporator. The obtained crude product was purified by recrystallization with hexane to give DODPAm (38.67 g, yield: 68%). Results of mass spectrometry will be shown below.

High Resolution ESI-TOF-MS m/z Calcd. for [$C_{31}H_{45}NO$ ([M + $Na]^+$)]: 470.3393 found 470.3317.

[0119]

(Synthesis Example 3) Synthesis of N,N-bis(4-(tert-butyl)phenyl)acrylamide (DtBPAm)



To a 1 L four-neck flask purged with nitrogen, bis(4-tert-butylphenyl)amine (100 g, 0.355 mol), N,N-dimethylanline (64.59 g, 0.533 mol), and 400 mL of super-dehydrated toluene were added, and stirred until uniformly dissolved. Subsequently, the reaction solution was cooled to 0°C or lower in an ice/ethanol bath, and acrylic acid chloride (38.59 g, 0.426 mol) was gradually added dropwise thereto, followed by reaction for 24 hours. After the completion of reaction, the solution was washed with a 1 N aqueous hydrochloric acid solution, a saturated aqueous solution of sodium bicarbonate, and saline. An organic layer was dehydrated with magnesium sulfate, and the solvent in a filtrate was then distilled off with an evaporator. The obtained crude product was purified by recrystallization with hexane to give DtBPAm (92.90 g, yield: 79%).

[0120]

(Synthesis Example 4) Production of copolymer A (butadiene/DPAm = 70/30 wt ratio)

A DPAm solution was prepared beforehand by dissolving 20.7 g of DPAm in 58 g of tetrahydrofuran. To a reaction container, 355 g of methylcyclohexane, 37 g of tetrahydrofuran, and 8.27 g of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) were added. The reaction container was cooled to 0°C, then 50 g

of 1,3-butadiene was added dropwise thereto, and the mixture was stirred for 30 minutes. To the reaction solution, 16.9 g of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was added, and the mixture was stirred for 10 minutes. To the reaction solution, the DPAm solution was added dropwise, and the mixture was stirred for 30 minutes. To the reaction solution, 1.41 g of acetic acid was added. Then, 400 g of 3% acetic acid water was added to the reaction container for separation into organic and aqueous layers. The obtained organic layer was washed with water twice, and the solvent was then distilled off to give copolymer A. As a result of conducting analysis by gel permeation chromatography (mobile phase: THF, polystyrene standard), the copolymer was confirmed to have a weight-average molecular weight (Mw) of 10,400 and a molecular weight distribution (Mw/Mn) of 1.80. Copolymer A had 94% by mol of a 1,2-bond structure in the butadiene block calculated by ^{1}H-NMR.

[0121]

(Synthesis Example 5) Production of copolymer B (butadiene/DtBPAm = 60/40 wt ratio)

A DtBPAm solution was prepared beforehand by dissolving 32.3 g of DtBPAm in 109 g of tetrahydrofuran. To a reaction container, 372 g of methylcyclohexane, 43 g of tetrahydrofuran, and 8.00 g of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) were added. The reaction container was cooled to 0°C, then 49 g of 1,3-butadiene was added dropwise thereto, and the mixture was stirred for 30 minutes. To the reaction solution, 16.6 g of diethyl zinc (solution with a concentration of 16.7%

by weight in hexane) was added, and the mixture was stirred for 10 minutes. To the reaction solution, the DtBPAm solution was added dropwise, and the mixture was stirred for 30 minutes. To the reaction solution, 1.88 g of acetic acid was added. Then, 400 g of 3% acetic acid water was added to the reaction container for separation into organic and aqueous layers. The obtained organic layer was washed with water twice, and the solvent was then distilled off to give copolymer B. As a result of conducting analysis by gel permeation chromatography (mobile phase: THF, polystyrene standard), the copolymer was confirmed to have a weight-average molecular weight (Mw) of 7,600 and a molecular weight distribution (Mw/Mn) of 1.13. Copolymer B had 93% by mol of a 1,2-bond structure in the butadiene block calculated by ^{1}H-NMR.

[0122]

(Synthesis Example 6) Production of copolymer C (butadiene/DODPAm = 68/32 wt ratio)

A DODPAm solution was prepared beforehand by dissolving 21.5 g of DODPAm in 72 g of tetrahydrofuran. To a reaction container, 302 g of methylcyclohexane, 30 g of tetrahydrofuran, and 7.37 g of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) were added. The reaction container was cooled to 0°C, then 43 g of 1,3-butadiene was added dropwise thereto, and the mixture was stirred for 30 minutes. To the reaction solution, 11.6 g of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was added, and the mixture was stirred for 10 minutes. To the reaction solution, the DODPAm solution was added dropwise, and the mixture was stirred

for 30 minutes. To the reaction solution, 1.70 g of acetic acid was added. Then, 400 g of 3% acetic acid water was added to the reaction container for separation into organic and aqueous layers. The obtained organic layer was washed with water twice, and the solvent was then distilled off to give copolymer C. As a result of conducting analysis by gel permeation chromatography (mobile phase: THF, polystyrene standard), the copolymer was confirmed to have a weight-average molecular weight (Mw) of 6,500 and a molecular weight distribution (Mw/Mn) of 1.20. Copolymer C had 94% by mol of a 1,2-bond structure in the butadiene block calculated by ^{1}H-NMR.

[0123]

(Synthesis Example 7) Production of copolymer D (butadiene/DODPAm = 54/46 wt ratio)

The same method as in Synthesis Example 6 was performed except that the amount of DODPAm was changed to 43.8 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 107 g; the amount of methylcyclohexane was changed to 355 g; the amount of tetrahydrofuran was changed to 37 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 8.10 g; the amount of 1,3-butadiene was changed to 49 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 16.8 g; and the amount of acetic acid was changed to 1.77 g. Copolymer D was confirmed to have a weight-average molecular weight (Mw) of 7,300 and a molecular weight distribution (Mw/Mn) of 1.11. Copolymer D had 94% by mol of a 1,2-bond structure in the butadiene block.

[0124]

(Synthesis Example 8) Production of copolymer E (butadiene/DODPAm = 47/53 wt ratio)

The same method as in Synthesis Example 6 was performed except that the amount of DODPAm was changed to 61.3 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 208 g; the amount of methylcyclohexane was changed to 382 g; the amount of tetrahydrofuran was changed to 40 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 9.88 g; the amount of 1,3-butadiene was changed to 55 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 20.5 g; and the amount of acetic acid was changed to 2.21 g. Copolymer E was confirmed to have a weight-average molecular weight (Mw) of 7,200 and a molecular weight distribution (Mw/Mn) of 1.17. Copolymer E had 94% by mol of a 1,2-bond structure in the butadiene block.

[0125]

(Synthesis Example 9) Production of copolymer F (butadiene/DODPAm = 37/63 wt ratio)

The same method as in Synthesis Example 6 was performed except that the amount of DODPAm was changed to 88.3 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 294 g; the amount of methylcyclohexane was changed to 503 g; the amount of tetrahydrofuran was changed to 48 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 8.60 g; the amount of 1,3-butadiene was changed to 54 g; the amount of diethyl zinc (solution with a concentration

of 16.7% by weight in hexane) was changed to 18.9 g; and the amount of acetic acid was changed to 2.25 g. Copolymer F was confirmed to have a weight-average molecular weight (Mw) of 9,700 and a molecular weight distribution (Mw/Mn) of 1.12. Copolymer F had 94% by mol of a 1,2-bond structure in the butadiene block.

[0126]

(Synthesis Example 10) Production of copolymer G (butadiene/DODPAm = 28/72 wt ratio)

The same method as in Synthesis Example 6 was performed except that the amount of DODPAm was changed to 87.5 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 292 g; the amount of methylcyclohexane was changed to 216 g; the amount of tetrahydrofuran was changed to 21 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 5.73 g; the amount of 1,3-butadiene was changed to 34 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 10.5 g; and the amount of acetic acid was changed to 1.21 g. Copolymer G was confirmed to have a weight-average molecular weight (Mw) of 9,500 and a molecular weight distribution (Mw/Mn) of 1.17. Copolymer G had 95% by mol of a 1,2-bond structure in the butadiene block.

[0127]

(Synthesis Example 11) Production of copolymer H (butadiene/DODPAm = 54/46 wt ratio)

The same method as in Synthesis Example 6 was performed except that the amount of DODPAm was changed to 42.7 g; the amount of tetrahydrofuran for dissolving DODPAm

was changed to 147 g; the amount of methylcyclohexane was changed to 350 g; the amount of tetrahydrofuran was changed to 36 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 13.8 g; the amount of 1,3-butadiene was changed to 50 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 27.5 g; and the amount of acetic acid was changed to 5.03 g. Copolymer H was confirmed to have a weight-average molecular weight (Mw) of 4,500 and a molecular weight distribution (Mw/Mn) of 1.16. Copolymer H had 94% by mol of a 1,2-bond structure in the butadiene block.

[0128]

(Synthesis Example 12) Production of copolymer I (butadiene/DODPAm = 54/46 wt ratio)

The same method as in Synthesis Example 6 was performed except that the amount of DODPAm was changed to 48.5 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 115 g; the amount of methylcyclohexane was changed to 397 g; the amount of tetrahydrofuran was changed to 40 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 5.66 g; the amount of 1,3-butadiene was changed to 56 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 10.6 g; and the amount of acetic acid was changed to 2.05 g. Copolymer I was confirmed to have a weight-average molecular weight (Mw) of 13,900 and a molecular weight distribution (Mw/Mn) of 1.17. Copolymer I had 94% by mol of a 1,2-bond structure in the butadiene block.

[0129]

(Synthesis Example 13) Production of copolymer J (butadiene/DODPAm = 54/46 wt ratio)

The same method as in Synthesis Example 6 was performed except that the amount of DODPAm was changed to 46.8 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 161 g; the amount of methylcyclohexane was changed to 386 g; the amount of tetrahydrofuran was changed to 40 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 4.34 g; the amount of 1,3-butadiene was changed to 54 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 8.91 g; and the amount of acetic acid was changed to 2.09 g. Copolymer J was confirmed to have a weight-average molecular weight (Mw) of 17,700 and a molecular weight distribution (Mw/Mn) of 1.19. Copolymer J had 94% by mol of a 1,2-bond structure in the butadiene block.

[0130]

(Synthesis Example 14) Production of copolymer K (butadiene/DODPAm = 65/35 wt ratio)

The same method as in Synthesis Example 6 was performed except that the amount of DODPAm was changed to 33.6 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 112 g; the amount of methylcyclohexane was changed to 379 g; the amount of tetrahydrofuran was changed to 43 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 4.28 g; the amount of 1,3-butadiene was changed to 61 g; the amount of diethyl zinc (solution with a concentration

of 16.7% by weight in hexane) was changed to 7.96 g; and the amount of acetic acid was changed to 2.12 g. Copolymer K was confirmed to have a weight-average molecular weight (Mw) of 17,400 and a molecular weight distribution (Mw/Mn) of 1.18. Copolymer K had 94% by mol of a 1,2-bond structure in the butadiene block.

[0131]

(Synthesis Example 15) Production of copolymer L (butadiene/DODPAm = 60/40 wt ratio)

The same method as in Synthesis Example 6 was performed except that the amount of DODPAm was changed to 42.2 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 138 g; the amount of methylcyclohexane was changed to 402 g; the amount of tetrahydrofuran was changed to 43 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 4.57 g; the amount of 1,3-butadiene was changed to 63 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 9.86 g; and the amount of acetic acid was changed to 2.04 g. Copolymer L was confirmed to have a weight-average molecular weight (Mw) of 17,600 and a molecular weight distribution (Mw/Mn) of 1.16. Copolymer L had 95% by mol of a 1,2-bond structure in the butadiene block.

[0132]

(Synthesis Example 16) Production of copolymer M (styrene/butadiene/DODPAm = 16/46/37 wt ratio)

A DODPAm solution was prepared beforehand by dissolving 47.7 g of DODPAm in 160 g of tetrahydrofuran. To a reaction container, 478 g of methylcyclohexane, 46 g

of tetrahydrofuran, and 9.68 g of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) were added. The reaction container was cooled to 0°C, then 19 g of styrene was added dropwise thereto, and the mixture was stirred for 30 minutes. 57 g of 1,3-butadiene was added dropwise thereto, and the mixture was stirred for 30 minutes. To the reaction solution, 21.8 g of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was added, and the mixture was stirred for 10 minutes. To the reaction solution, the DODPAm solution was added dropwise, and the mixture was stirred for 30 minutes. To the reaction solution, 2.09 g of acetic acid was added. Then, 400 g of 3% acetic acid water was added to the reaction container for separation into organic and aqueous layers. The obtained organic layer was washed with water twice, and the solvent was then distilled off to give copolymer M. As a result of conducting analysis by gel permeation chromatography (mobile phase: THF, polystyrene standard), the copolymer was confirmed to have a weight-average molecular weight (Mw) of 8,300 and a molecular weight distribution (Mw/Mn) of 1.17. Copolymer M had 94% by mol of a 1,2-bond structure in the butadiene block calculated by ^{1}H-NMR.

[0133]

(Synthesis Example 17) Production of copolymer N (styrene/butadiene/DODPAm = 16/46/37 wt ratio)

The same method as in Synthesis Example 16 was performed except that the amount of DODPAm was changed to 46.0 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 158 g; the amount of methylcyclohexane was

changed to 440 g; the amount of tetrahydrofuran was changed to 43 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 7.27 g; the amount of 1,3-butadiene was changed to 55 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 13.8 g; and the amount of acetic acid was changed to 1.21 g. Copolymer N was confirmed to have a weight-average molecular weight (Mw) of 11,600 and a molecular weight distribution (Mw/Mn) of 1.14. Copolymer N had 96% by mol of a 1,2-bond structure in the butadiene block.

[0134]

(Synthesis Example 18) Production of copolymer O (styrene/butadiene/DODPAm = 16/46/37 wt ratio)

The same method as in Synthesis Example 16 was performed except that the amount of DODPAm was changed to 46.2 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 162 g; the amount of methylcyclohexane was changed to 450 g; the amount of tetrahydrofuran was changed to 45 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 5.70 g; the amount of 1,3-butadiene was changed to 55 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 13.9 g; and the amount of acetic acid was changed to 2.30 g. Copolymer O was confirmed to have a weight-average molecular weight (Mw) of 15,100 and a molecular weight distribution (Mw/Mn) of 1.22. Copolymer O had 94% by mol of a 1,2-bond structure in the butadiene block.

[0135]

(Synthesis Example 19) Production of copolymer P (styrene/butadiene/DODPAm = 16/46/37 wt ratio)

The same method as in Synthesis Example 16 was performed except that the amount of DODPAm was changed to 46.5 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 161 g; the amount of methylcyclohexane was changed to 448 g; the amount of tetrahydrofuran was changed to 44 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 4.20 g; the amount of butadiene was changed to 55 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 13.8 g; and the amount of acetic acid was changed to 1.21 g. Copolymer P was confirmed to have a weight-average molecular weight (Mw) of 18,600 and a molecular weight distribution (Mw/Mn) of 1.25. Copolymer P had 95% by mol of a 1,2-bond structure in the butadiene block.

[0136]

(Synthesis Example 20) Production of copolymer Q (styrene/butadiene/DODPAm = 24/41/35 wt ratio)

The same method as in Synthesis Example 16 was performed except that the amount of DODPAm was changed to 46.5 g; the amount of tetrahydrofuran for dissolving DODPAm was changed to 161 g; the amount of methylcyclohexane was changed to 448 g; the amount of tetrahydrofuran was changed to 44 g; the amount of n-butyl lithium (solution with a concentration of 14.7% by weight in hexane) was changed to 4.20 g; the amount of butadiene was changed to 55 g; the amount of diethyl zinc (solution with a concentration of 16.7% by weight in hexane) was changed to 13.8 g; and the

amount of acetic acid was changed to 1.21 g. Copolymer Q was confirmed to have a weight-average molecular weight (Mw) of 18,600 and a molecular weight distribution (Mw/Mn) of 1.25. Copolymer Q had 94% by mol of a 1,2-bond structure in the butadiene block.

[0137]

(Composition Examples 1 to 16 and Reference Examples 1 to 3)

Each reagent was added to and mixed with toluene in accordance with the composition (parts by weight) of the table such that a solid concentration was 50% by weight. Then, toluene in the obtained liquid was removed with an evaporator to give a resin composition. The resin composition was cured by heat press at 200°C for 120 minutes. The physical properties of the obtained cured product were measured as to the following items, and the results are shown in Tables 1 to 4.

<Glass transition temperature (Tg)/TMA>

A glass transition temperature (Tg) was evaluated by TMA in accordance with IPC TM650. A thermomechanical analysis (TMA) apparatus (Discovery TMA450 EM manufactured by TA Instruments Japan Inc.) was used in measurement, and the measurement was performed in the range of 0 to 250°C.

<Glass transition temperature (Tg)/DMA>

Dynamic mechanical analysis (DMA) was conducted, and a temperature at which tanδ was the maximum value was defined as Tg when the temperature was raised from room temperature to 270°C under a condition of a temperature rise at a rate of 5°C/min. The apparatus used was RAS-G2 manufactured by TA Instruments Japan Inc.

<Dielectric loss tangent before moisture absorption treatment>

Measurement was performed at 10 GHz using a cylindrical cavity resonator (TE mode resonator) manufactured by AET, Inc.

<Dielectric loss tangent after moisture absorption treatment>

A cured product used in the measurement of the dielectric loss tangent before moisture absorption treatment was exposed to an environment of 85°C and 85% RH for 72 hours in accordance with JIS K7209. The dielectric loss tangent of the cured product thus treated by moisture absorption (dielectric loss tangent after moisture absorption) was measured by the same method as in the measurement of the dielectric loss tangent before moisture absorption treatment.

<Amount of change in dielectric loss tangent (after moisture absorption treatment - before moisture absorption treatment)>

The difference between the dielectric loss tangent before moisture absorption treatment and the dielectric loss tangent after moisture absorption treatment (dielectric loss tangent after moisture absorption treatment - dielectric loss tangent before moisture absorption treatment) was calculated.

[0138]

[Table 1]

		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6
Composition (parts by weight)	Copolymer A	100					
	Copolymer B		100				
	Copolymer C			100			
	Copolymer D				100		

	Copolymer E					100	
	Copolymer F						100
	PERCUMYL D	2	2	2	2	2	2
Evaluation	Tg (°C) (DMA)	136	147	138	150	166	189
	Tg (°C) (TMA)	114	152	116	139	149	160
	Dielectric loss tangent before moisture absorption	0.0035	0.0033	0.0013	0.0013	0.0013	0.0011
	Dielectric loss tangent after moisture absorption	0.0052	0.0033	0.0013	0.0013	0.0013	0.0011
	Amount of change in dielectric loss tangent (after moisture absorption treatment - before moisture absorption treatment)	0.0017	0.0000	0.0000	0.0000	0.0000	0.0000

PERCUMYL D: dicumyl peroxide manufactured by NOF Corp.

[0139]

[Table 2]

		Example 7	Example 8	Example 9	Example 10	Example 11	Example 12
Composition (parts by weight)	Copolymer G	100					
	Copolymer H		100				
	Copolymer I			100			
	Copolymer J				100		
	Copolymer K					100	
	Copolymer L						100
	PERCUMYL D	2	2	2	2	2	2
Evaluation	Tg (°C) (DMA)	201	91	180	195	177	188
	Tg (°C) (TMA)	169	108	150	160	137	155
	Dielectric loss tangent before moisture absorption	0.0011	0.0033	0.0013	0.0013	0.0018	0.0015
	Dielectric loss tangent after moisture absorption	0.0011	0.0033	0.0013	0.0013	0.0020	0.0016
	Amount of change in dielectric loss tangent (after moisture absorption treatment - before moisture absorption treatment)	0.0000	0.0000	0.0000	0.0000	0.0002	0.0001

PERCUMYL D: dicumyl peroxide manufactured by NOF Corp.

[0140]

[Table 3]

		Example 13	Example 14	Example 15	Example 16
Composition (parts by weight)	Copolymer M	100			
	Copolymer N		100		
	Copolymer O			100	
	Copolymer P				100
	PERCUMYL D	2	2	2	2
Evaluation	Tg (°C) (DMA)	144	149	175	178
	Tg (°C) (TMA)	134	143	159	161
	Dielectric loss tangent before moisture absorption	0.0010	0.0010	0.0010	0.0010
	Dielectric loss tangent after moisture absorption	0.0010	0.0010	0.0010	0.0010

	Amount of change in dielectric loss tangent (after moisture absorption treatment - before moisture absorption treatment)	0.0000	0.0000	0.0000	0.0000

PERCUMYL D: dicumyl peroxide manufactured by NOF Corp.

[0141]

[Table 4]

		Reference Example 1	Reference Example 2	Reference Example 3
Composition (parts by weight)	SA9000	100		
	OPE-2St		100	
	NISSO-PB B-3000			100
	PERCUMYL D	2	2	2
Evaluation	Tg (°C) (DMA)	173	211	38
	Tg (°C) (TMA)	173	189	6
	Dielectric loss tangent before moisture absorption	0.0054	0.0048	0.0022
	Dielectric loss tangent after moisture absorption	0.0072	0.0068	0.0043
	Amount of change in dielectric loss tangent (after moisture absorption treatment - before moisture absorption treatment)	0.0018	0.0020	0.0021

SA9000: methacryl-modified polyphenylene ether compound manufactured by SABIC Innovative Plastics
OPE-2St: oligophenylene ether resin manufactured by Mitsubishi Gas Chemical Co, Inc.
NISSO-PB B-3000: liquid polybutadiene resin manufactured by Nippon Soda Co., Ltd.
PERCUMYL D: dicumyl peroxide manufactured by NOF Corp.

[0142]

(Examples 17 to 29 and Comparative Examples 1 to 9)

Each reagent was added to and mixed with toluene in accordance with the composition (parts by weight) of the table such that a solid concentration was 50% by weight. Then, toluene in the obtained liquid was removed with an evaporator to give a powdery resin composition. The resin composition was cured by heat press at 200°C for 120 minutes. The physical properties of the obtained cured product were measured as to the following items, and the results are shown in Tables 5 to 8.

<Glass transition temperature (Tg)/TMA>

A glass transition temperature (Tg) was evaluated by TMA in accordance with IPC TM650. A thermomechanical analysis (TMA) apparatus (Discovery TMA450 EM manufactured by TA Instruments Japan Inc.) was used in measurement, and the measurement was performed in the range of 0 to 250°C.

<Glass transition temperature (Tg)/DMA>

Dynamic mechanical analysis (DMA) was conducted, and a temperature at which tanδ was the maximum value was defined as Tg when the temperature was raised from room temperature to 270°C under a condition of a temperature rise at a rate of 5°C/min. The apparatus used was RAS-G2 manufactured by TA Instruments Japan Inc.

<Dielectric loss tangent>

Measurement was performed at 10 GHz using a cylindrical cavity resonator (TE mode resonator) manufactured by AET, Inc.

[0143]

[Table 5]

		Example 17	Example 18	Example 19	Example 20	Example 21	Example 22	Example 23	Example 24
Composition (parts by weight)	Copolymer Q	70	70	70	58	58	58	58	58
	SA9000	30			25	25	25	25	25
	OPE-2St		30						
	MIR-3000			30					
	TAIC				17				
	DVB					17			
	BVPE						17		
	BMI-70							17	
	B-1000								17
	PERBUTYL P	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Evaluation	Tg (°C) (DMA)	200	200	230	170	200	200	208	170
	Tg (°C) (TMA)	170	168	210	162	171	175	177	151
	Dielectric loss tangent	0.0015	0.0014	0.0017	0.0017	0.0016	0.0014	0.0023	0.0013

SA9000: methacryl-modified polyphenylene ether compound manufactured by SABIC Innovative Plastics
OPE-2St: oligophenylene ether resin manufactured by Mitsubishi Gas Chemical Co, Inc.
MIR-3000: maleimide resin manufactured by Nippon Kayaku Co., Ltd.
TAIC: triallyl isocyanurate manufactured by Tokyo Chemical Industry Co., Ltd.
DVB: divinylbenzene manufactured by FUJIFILM Wako Pure Chemical Corp.
BVPE: 1,2-bis(vinylphenyl)ethane manufactured by Hebei Honour Chemical Co., Ltd.
BMI-70: bis(3-ethyl-5-methyl-4-maleimidophenyl)methane manufactured by K-I Chemical Industry Co., Ltd.
B-1000: liquid polybutadiene resin manufactured by Nippon Soda Co., Ltd.
PERBUTYL P: bis(1-tert-butylperoxy-1-methylethyl)benzene manufactured by NOF Corp.

[0144]

[Table 6]

		Comparative Example 1	Comparative Example 2	Comparative Example 3
Composition (parts by weight)	SA9000	100		
	OPE-2St		100	
	MIR-3000			100
	PERBUTYL P	0.5	0.5	0.5
Evaluation	Tg (°C) (DMA)	190	200	>300
	Tg (°C) (TMA)	177	171	245
	Dielectric loss tangent	0.0035	0.0030	0.0038

SA9000: methacryl-modified polyphenylene ether compound manufactured by SABIC Innovative Plastics
OPE-2St: oligophenylene ether resin manufactured by Mitsubishi Gas Chemical Co, Inc.
MIR-3000: maleimide resin manufactured by Nippon Kayaku Co., Ltd.
PERBUTYL P: bis(1-tert-butylperoxy-1-methylethyl)benzene manufactured by NOF Corp.

[0145]

[Table 7]

		Example 25	Example 26	Example 27	Example 28	Example 29
Composition (parts by weight)	Copolymer L	70	70	70	70	70
	TAIC	30				
	DVB		30			
	BVPE			30		
	B-1000				30	
	1,2-SBS					30
	PERBUTYL P	0.5	0.5	0.5	0.5	0.5
Evaluation	Tg (°C) (DMA)	170	190	200	170	176
	Tg (°C) (TMA)	160	168	181	153	158
	Dielectric loss tangent	0.0016	0.0013	0.0012	0.0010	0.0010

TAIC: triallyl isocyanurate manufactured by Tokyo Chemical Industry Co., Ltd.
DVB: divinylbenzene manufactured by FUJIFILM Wako Pure Chemical Corp.
BVPE: 1,2-bis(vinylphenyl)ethane manufactured by Hebei Honour Chemical Co., Ltd.
B-1000: liquid polybutadiene resin manufactured by Nippon Soda Co., Ltd.
1,2-SBS: styrene-butadiene-styrene resin manufactured by Nippon Soda Co., Ltd.
PERBUTYL P: bis(1-tert-butylperoxy-1-methylethyl)benzene manufactured by NOF Corp.

[0146]

[Table 8]

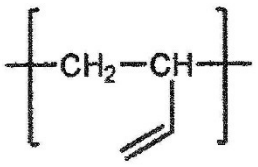
		Comparative Example 4	Comparative Example 5	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9
Composition (parts by weight)	SA9000	70	70	70			
	OPE-2St				70	70	70
	TAIC	30			30		
	DVB		30			30	
	BVPE			30			30
	PERBUTYL P	0.5	0.5	0.5	0.5	0.5	0.5
Evaluation	Tg (°C) (DMA)	173	190	190	188	200	200
	Tg (°C) (TMA)	157	180	179	162	168	170
	Dielectric loss tangent	0.0037	0.0033	0.0031	0.0033	0.0028	0.0027

SA9000: methacryl-modified polyphenylene ether compound manufactured by SABIC Innovative Plastics
OPE-2St: oligophenylene ether resin manufactured by Mitsubishi Gas Chemical Co, Inc.
TAIC: triallyl isocyanurate manufactured by Tokyo Chemical Industry Co., Ltd.
DVB: divinylbenzene manufactured by FUJIFILM Wako Pure Chemical Corp.
BVPE: 1,2-bis(vinylphenyl)ethane manufactured by Hebei Honour Chemical Co., Ltd.
PERBUTYL P: bis(1-tert-butylperoxy-1-methylethyl)benzene manufactured by NOF Corp.

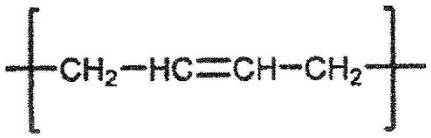
CLAIMS

[Claim 1] A block copolymer comprising

a block chain (A) having (a1) a repeat unit of formula (I), or (a2) a repeat unit of formula (I) and a repeat unit of formula (II):



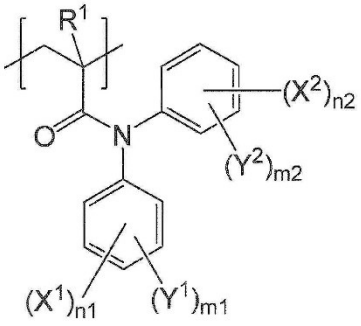
(I)



(II)

and

a block chain (B) having a repeat unit of formula (III):



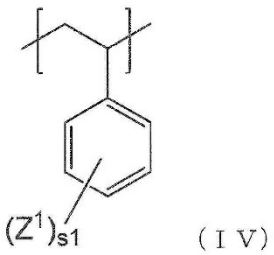
(III)

(wherein in formula (III), R^1 represents a hydrogen atom or a methyl group, X^1 and X^2 each independently represent a C1 to C20 alkyl group, a C1 to C20 alkoxy group, a C3 to C6 cyclic alkyl group, a C3 to C6 cyclic alkoxy group, a benzyl group, a 1-phenylethyl group, or a 2-phenylpropan-2-yl group, n1 and n2 each independently represent 0 or 1, Y^1 and Y^2 each independently represent an organic group or a halogeno group, and m1 and m2 each independently represent any integer of 0 to 4).

[Claim 2] The block copolymer according to claim 1, wherein a molar ratio between the repeat unit of formula (I) and the repeat unit of formula (II) in the block chain (A) is 70:30 to 100:0.

[Claim 3] The block copolymer according to claim 1 or 2, wherein a weight ratio between the block chain (A) and the block chain (B) is 10:90 to 90:10.

[Claim 4] The block copolymer according to claim 1 or 2, further comprising a block chain (C) having a repeat unit of formula (IV):



(IV)

(wherein in formula (IV), Z^1 represents a C1 to C10 alkyl group, a C1 to C10 alkoxy group, a C3 to C6 cyclic alkyl group, a C3 to C6 cyclic alkoxy group, a phenyl group, a halogeno group, an amino group, a dialkylamino group, a C1 to C6 alkylcarbonyl group, a C1 to C6 alkylcarbonyloxy group, a trialkylsilyl group, a trialkoxysilyl group, a cyano group, or a nitro group, and s1 represents any integer of 0 to 5).

[Claim 5] The block copolymer according to claim 1 or 2, wherein a weight-average molecular weight is 1,000 to 100,000.

[Claim 6] A resin composition comprising the block copolymer according to claim 1 or 2.

[Claim 7] The resin composition according to claim 6, further comprising a radical polymerization initiator.

[Claim 8] The resin composition according to claim 6 for use in an insulating layer of a printed wiring board.

[Claim 9] A formed article comprising a cured product of the resin composition according to claim 6.