

DESCRIPTION

TITLE OF INVENTION: COMPOUND, CURABLE RESIN COMPOSITION AND CURED
PRODUCT THEREFROM, AND METHOD FOR PRODUCING COMPOUND

5 TECHNICAL FIELD

[0001]

The present invention relates to a compound, a curable resin composition, and a
cured product thereof, as well as a method for producing the compound, which are suitably
used for electrical and electronic components such as semiconductor encapsulants, printed
10 wiring boards, and build-up laminates, lightweight and high-strength materials such as carbon
fiber reinforced plastics and glass fiber reinforced plastics, and 3D printing applications.

BACKGROUND ART

[0002]

In recent years, the laminates on which electric and electronic components are
15 mounted have come to be used in a wider range of fields, and the required characteristics have
become more extensive and sophisticated. Conventional semiconductor chips were mainly
mounted on metal lead frames, but semiconductor chips with high processing power, such as
central processing units (hereinafter referred to as CPUs), are increasingly being mounted on
laminates made of polymer materials.

20 [0003]

In particular, in semiconductor packages (hereinafter referred to as PKG) used in
smartphones and the like, there is a demand for thinner PKG substrates to meet the demand
for smaller size, thinner thickness, and higher density, but as the PKG substrate becomes
thinner, its rigidity decreases, and defects such as large warpage occur when the PKG is
25 heated during solder mounting on a motherboard (printed circuit board: PCB). To reduce this,
there is a demand for PKG substrate materials with a high Tg equal to or higher than the

solder mounting temperature.

[0004]

In addition, the fifth generation communication system "5G", whose development is currently accelerating, is expected to further increase capacity and speed of communication.

5 The need for low dielectric tangent materials is increasing, and various studies are being conducted. Patent Literature 1 describes a thermosetting resin composition containing (A) an imide compound having a maleimide group and (B) a phenol aralkyl resin having an aliphatic unsaturated bond in one molecule as essential components. Patent Literature 2 describes an allyl ether modified biphenyl aralkyl novolac resin. Patent Literature 3 describes a compound
10 having a styrene structure.

CITATION LIST

PATENT LITERATURE

[0005]

Patent Literature 1: Japanese Patent Application Publication No. H04(1992)-359911

15 Patent Literature 2: International Publication No. 2016/002704

Patent Literature 3: Japanese Patent No. 6951829

SUMMARY OF THE INVENTION

TECHNICAL PROBLEM

[0006]

20 The applicant of the present application retested Patent Publication 3 and found that when the compound synthesized by the method described in Patent Publication 3 was stored in a state dissolved in a solvent such as toluene, a problem occurred in which crystals precipitated. In order to solve the problem of crystal precipitation, the applicant also considered using a compound precursor having a high molecular weight 2-
25 bromoethylbenzene structure, but in this case, a problem occurred in which the styrenization reaction on the polymer side did not proceed completely. Furthermore, the applicant also

considered making the reaction conditions harsher in order to promote the reaction, but although the reaction progress rate (conversion) increased, other problems occurred, such as a decrease in electrical properties due to an increase in the amount of impurities, and high molecular weight and gelation due to the progress of unintended radical polymerization reactions. In other words, it was extremely difficult to achieve both stability in solvent and suppression of impurity generation (low dielectric properties).

[0007]

The present invention has been made in view of the above circumstances, and an object of the present invention is to provide a compound having excellent stability in solvent and low dielectric properties, a curable resin composition and a cured product thereof, and a method for producing the compound.

SOLUTION TO PROBLEM

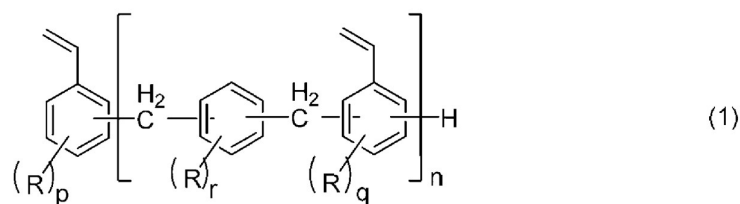
[0008]

That is, the present invention relates to the following [1] to [13]:

[1]

A compound represented by the following formula (1), in which a compound in which n in formula (1) is 1 is less than 50% of the total amount of the compound in terms of GPC area percentage:

[0009]



[0010]

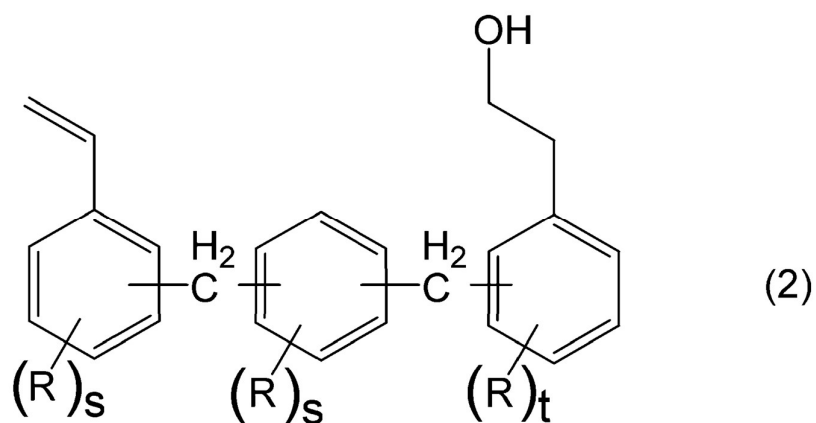
(In formula (1), each of the multiple R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p and r are integers from 0 to 4, q is an

integer from 0 to 3, and n is a repetition number, the average value n_{ave} of n satisfying $1 \leq n_{ave} \leq 20$.)

[2]

The compound according to the preceding item [1], wherein the value (α/β) obtained by dividing the sum (α) of the HP-LC peak areas of the compounds represented by the following formulas (2) to (4) by the HP-LC peak area (β) of the compound where n in formula (1) is 1 is 0.10 or less:

[0011]

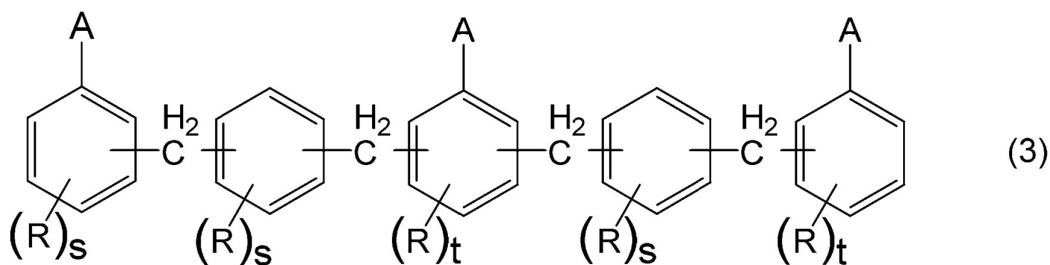


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[0012]

(In formula (2), each of the multiple R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. Each of the multiple s's independently represents an integer of 0 to 4.)

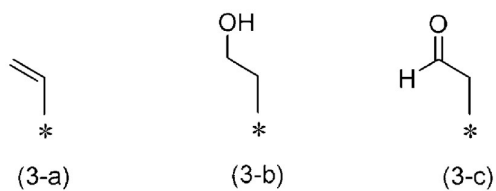
15 [0013]



[0014]

(In formula (3), each of the multiple R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. Each of the multiple A's independently represents one of the following formulae (3-a) to (3-c). Each of the multiple s's independently represents an integer of 0 to 4, and each t's independently represents an integer of 0 to 3.)

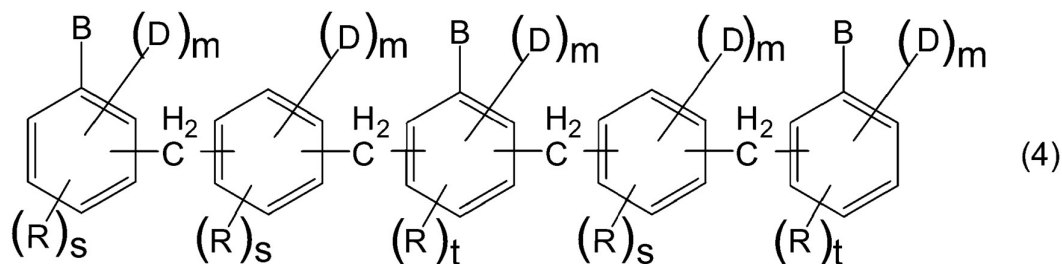
[0015]



[0016]

(In formulas (3-a) to (3-c), * represents the bonding position with the aromatic ring of the compound of formula (3).)

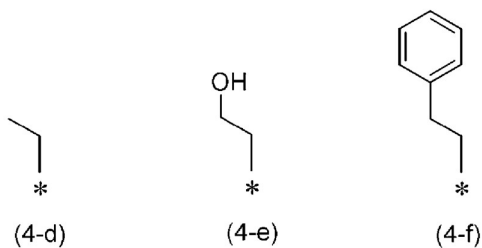
[0017]



[0018]

(In formula (4), each of the multiple R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. Each of the multiple B's independently represents the following formula (4-d) or (4-e). D represents the following formula (4-f). Each of the multiple s's independently represents an integer of 0 to 4, and t is an integer of 0 to 3. One of the five m's in formula (4) is 1, and the other four are 0.)

[0019]



[0020]

(In formulas (4-d) to (4-f), * represents a bonding position with the aromatic ring of the compound of formula (4).)

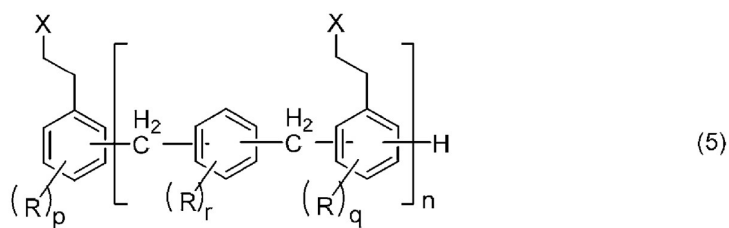
5 [3]

The compound according to the above item [1] or [2], wherein in formula (1), $p = 0$, $q = 0$, and $r = 0$.

[4]

The compound according to any one of the above items [1] to [3], wherein the compound represented by formula (1) is derived from a compound represented by the following formula (5):

[0021]



[0022]

(In formula (5), each of the multiple R's is present independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p and r are integers from 0 to 4, q is an integer from 0 to 3, n is a repetition number, and the average value n_{ave} of n satisfies $1 \leq n_{ave} \leq 20$. X represents a halogen atom.)

[5]

The mixture according to any one of items [1] to [4] above, further containing a

polymerization inhibitor.

[6]

A curable resin composition containing the compound according to any one of items [1] to [4] above, or the mixture according to item [5] above.

5 [7]

The curable resin composition according to item [6] above, containing one or more of a polyphenylene ether compound, polybutadiene and modified products thereof, and polystyrene and modified products thereof.

[8]

10 The curable resin composition according to item [6] or [7] above, containing a radical polymerization initiator.

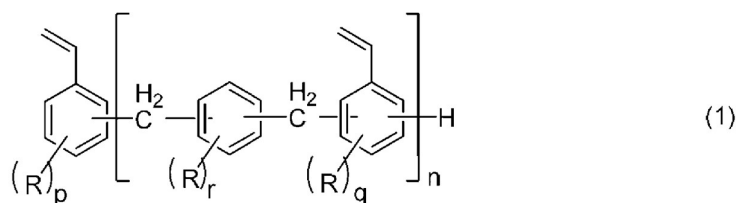
[9]

A cured product obtained by curing the compound according to any one of the preceding items [1] to [4], the mixture according to the preceding item [5], or the curable
15 resin composition according to any one of the preceding items [6] to [8].

[10]

A method for producing a compound represented by the following formula (1), which is obtained by subjecting a compound represented by the following formula (5) to a dehydrohalogenation reaction in a solvent having a volume 4 to 7 times the weight of the
20 compound represented by the following formula (5) in the presence of a basic catalyst.

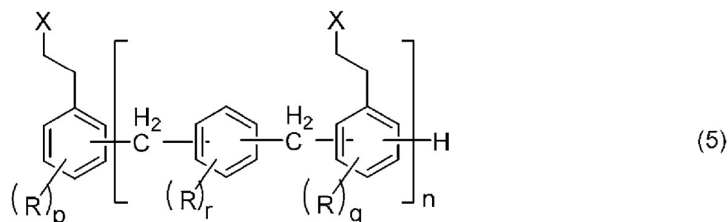
[0023]



[0024]

(In formula (1), each of the multiple R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p and r are integers of 0 to 4, q is an integer of 0 to 3, n is a number of repetitions, and the average value n_{ave} of n satisfies $1 \leq n_{ave} \leq 20$.)

5 [0025]



[0026]

(In formula (5), each of the multiple R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p and r are integers from 0 to 4, q is an integer from 0 to 3, n is a repetition number, and the average value n_{ave} of n satisfies $1 \leq n_{ave} \leq 20$. X represents a halogen atom.)

[11]

A method for producing the compound according to the above item [10], wherein the solvent is a mixed solvent of a polar aprotic solvent and a water-insoluble solvent.

15 [12]

A method for producing the compound according to the above item [11], wherein the polar aprotic solvent is used in an amount 1 to 10 times by weight relative to the water-insoluble solvent.

[13]

20 A method for producing the compound according to the above item [11] or [12], wherein the polar aprotic solvent is dimethylsulfoxide and the water-insoluble solvent is toluene.

ADVANTAGEOUS EFFECTS OF INVENTION

[0027]

The compound of the present invention has excellent solubility in a solvent and its cured product has excellent low dielectric properties, making it a useful material for sealing electric and electronic parts, circuit boards, carbon fiber composites, etc.

5 BRIEF DESCRIPTION OF DRAWINGS

[0028]

[Figure 1] A GPC chart of Synthesis Example 1.

[Figure 2] A GPC chart of Example 1.

[Figure 3] A ¹H-NMR chart of Example 1.

10 [Figure 4] A LC-MS chart of Example 1.

[Figure 5] A HP-LC chart of Example 1.

[Figure 6] A GPC chart of Example 2.

[Figure 7] A HP-LC chart of Example 2.

[Figure 8] A GPC chart of Example 3.

15 [Figure 9] A HP-LC chart of Example 3.

[Figure 10] A GPC chart of Example 4.

[Figure 11] A HP-LC chart of Example 4.

[Figure 12] A GPC chart of Comparative Synthesis Example 1.

[Figure 13] A GPC chart of Comparative Synthesis Example 2.

20 [Figure 14] A HP-LC chart of Comparative Synthesis Example 2.

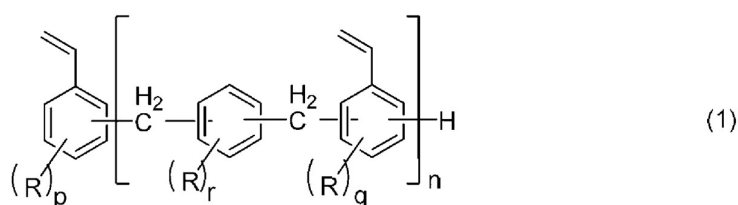
DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0029]

The compound of this embodiment is represented by the following formula (1), and
 25 in the total amount of the compound, the ratio (area percentage) of the area (time integral value of signal value) of the compound in which n in formula (1) is 1 to the sum of the areas

(time integral values of signal value) of the compounds having the structure represented by formula (1) in a chromatogram obtained by gel permeation chromatography (hereinafter also referred to as GPC) is less than 50%. If the area percentage of the compound in which n in formula (1) is 1 is 50% or more, there is a risk that crystals will precipitate (i.e., the solubility in a solvent will decrease) when a resin solution containing the compound represented by formula (1) is stored.

[0030]



[0031]

- (In formula (1), each of the multiple R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p and r are integers from 0 to 4, and q is an integer from 0 to 3. n is the number of repetitions, and the average value n_{ave} of n satisfies $1 \leq n_{\text{ave}} \leq 20$.)

[0032]

- In the formula (1), p and r are usually 0 to 4, preferably 0 to 2, and more preferably 0. q is usually 0 to 3, preferably 0 to 2, and more preferably 0. n_{ave} is usually $1 \leq n_{\text{ave}} \leq 20$, preferably $1.1 \leq n_{\text{ave}} \leq 20$, more preferably $1.1 \leq n_{\text{ave}} \leq 10$, and particularly preferably $1.1 \leq n_{\text{ave}} \leq 5$. The value of n_{ave} can be calculated from the value of the number average molecular weight (M_n) determined by GPC measurement of the compound of formula (1). The number average molecular weight is preferably 200 or more and less than 5000, more preferably 300 or more and less than 3000, and particularly preferably 400 or more and less than 2000. If the number average molecular weight is less than 5000, purification by washing with water is easy, and if it is 200 or more, the target compound does not volatilize in the solvent

distillation step.

[0033]

In the formula (1), R is a hydrocarbon group or halogenated alkyl group having 1 to 10 carbon atoms, preferably a hydrocarbon group having 1 to 10 carbon atoms, more preferably a hydrocarbon group having 1 to 5 carbon atoms, and particularly preferably a hydrocarbon group having 1 to 3 carbon atoms. When R has a small number of carbon atoms, molecular vibration is unlikely to occur when exposed to high frequency waves, and therefore, when R is a hydrocarbon group having 1 to 3 carbon atoms among the above, the electrical properties are particularly excellent.

10 [0034]

The GPC measurement in this embodiment is carried out under the following conditions.

<GPC>

GPC: Online degassing unit (DGU-20A3R), binary liquid delivery unit (LC-20AD), autosampler (SIL-20AHT), differential refractive index detector (RID-20A), column oven (CTO-20A), system controller (CBM-20A) (all manufactured by Shimadzu Corporation)

Column: Shodex KF-603 x 1, KF-602.5 x 1, KF-602 x 1, KF-601 x 1 (all manufactured by Showa Denko K.K.)

Guard column: Shodex KF-G 4A (manufactured by Showa Denko K.K.)

20 Connected eluent: tetrahydrofuran

Flow rate: 1.5 ml/min.

Column temperature: 40°C

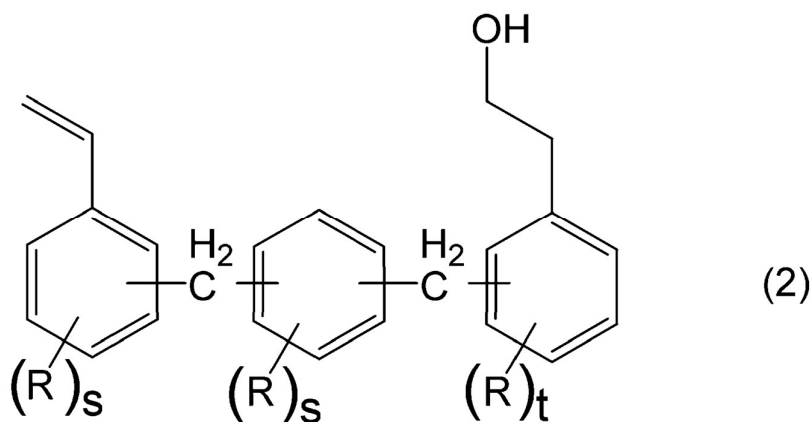
Detection: RI (differential refractive index detector)

[0035]

25 The compound represented by formula (1) may contain compounds represented by the following formulas (2) to (4) as by-products, and the sum (α) of the peak areas of the

compounds represented by the following formulas (2) to (4) in a chromatogram obtained by high performance liquid chromatography (HP-LC) divided by the HP-LC peak area (β) of the compound in which n in formula (1) is 1 (α/β) is preferably 0.10 or less, more preferably 0.07 or less. Here, the "peak area" is the area surrounded by a straight line connecting both bottoms of the peak and the peak. In practice, it is determined by an approximation value by the half-width method or the number of counts obtained by integrating the output at the peak (JIS K0214:2013). This is because the compounds represented by the following formulas (2) to (4) have polar groups in their structures, and the dielectric properties deteriorate when the content of them increases. The lower limit of the value of (α/β) may be 0, but it is more preferable that it is 0.01. When the ratio is 0.01 or more, the adhesiveness, solubility in a solvent, and compatibility with a compound having a polar group are improved.

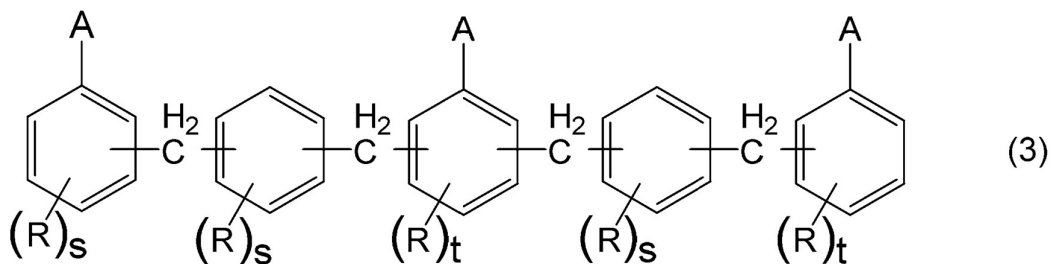
[0036]



[0037]

(In formula (2), each of the multiple R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. s is an integer of 0 to 4.)

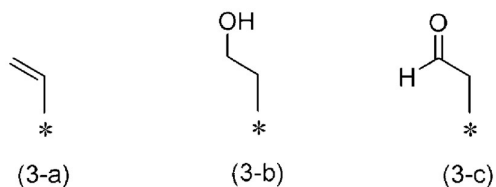
[0038]



[0039]

(In formula (3), each of the multiple R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. Each of the multiple A's independently represents one of the following formulae (3-a) to (3-c). s is an integer of 0 to 4, and t is an integer of 0 to 3.)

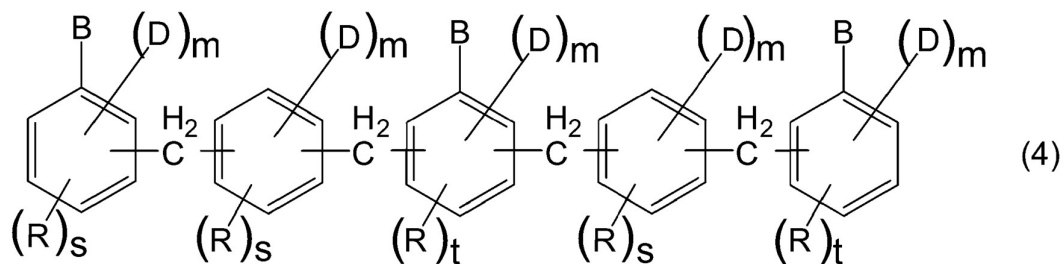
[0040]



[0041]

(In formulas (3-a) to (3-c), * represents the bonding position with the aromatic ring of the compound of formula (3).)

[0042]



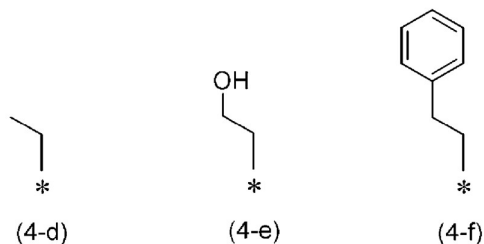
[0043]

(In formula (4), each of the multiple R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. Each of the multiple B's independently represents one of the following formulae (4-a) to (4-c). m is an integer of 0 to 4, and n is an integer of 0 to 3.)

represents the following formula (4-d) or (4-e). D represents the following formula (4-f). Each of the multiple s's independently represents an integer of 0 to 4, and t is an integer of 0 to 3.

One of the five m's in formula (4) is 1, and the other four are 0.)

[0044]



[0045]

(In formulas (4-d) to (4-f), * represents the bonding position with the aromatic ring of the compound of formula (4).)

[0046]

10 Generally, by-products such as the compounds represented by the formulas (2) to (4) can be removed by purification, but in the case of the compound represented by the formula (1), it is difficult to remove the compounds represented by the formulas (2) to (4) by purification methods such as distillation, recrystallization, and water washing. To be more specific, since the compound represented by the formula (1) has a styrene structure as a functional group, it is highly reactive, and unintended polymerization will proceed in a purification method that requires overheating such as distillation. In addition, as can be seen from the fact that the compound represented by the formula (1) is a liquid compound after distillation of the solvent, it is difficult to form a crystalline structure, so it is difficult to recrystallize it with a high yield. Furthermore, water washing has already been performed in Patent Literature 3, but the effect is small.

15

20

For these reasons, in this embodiment, the production amount of the compounds represented by the formulas (2) to (4) is controlled by adjusting the reaction temperature, the amount of solvent, and the mixing ratio of the solvent in the synthesis process of the

compound represented by the formula (1). The details of the synthesis method of the compound represented by the formula (1) will be described later.

[0047]

In this embodiment, the structure is analyzed by liquid chromatography mass spectrometry (hereinafter, also referred to as LC-MS), and the contents of the compounds represented by the formulas (2) to (4) are analyzed by high performance liquid chromatography (hereinafter, also referred to as HP-LC).

<LC-MS>

Apparatus: Ultra-high performance liquid chromatograph (UHPLC) system (Ultimate 3000), mass spectrometer (Q-Exactive (registered trademark)) (both manufactured by Thermo Fisher Scientific)

Column: ODS-2 (manufactured by GL Sciences)

Connected eluent: Tetrahydrofuran: water = 3: 1 (no gradient)

Flow rate: 0.5 ml/min.

Ionization mode: ESI

Mass range: $m/z = 150-2000$

<HP-LC>

Apparatus: Binary liquid delivery unit (LC-20AB), online degassing unit (DGU-20A3R), autosampler (SIL-20A), column oven (CTO-20A), system controller (CBM-20A), photodiode array detector (SPD-M20A) (all manufactured by Shimadzu Corporation)

Column: ODS-2 (manufactured by GL Sciences)

Connected eluent: Tetrahydrofuran: water = 3:1 (no gradient)

Flow rate: 0.5 ml/min.

Column temperature: 40°C

Detection: PDA (photodiode array detector)

Detector: 274 nm

[0048]

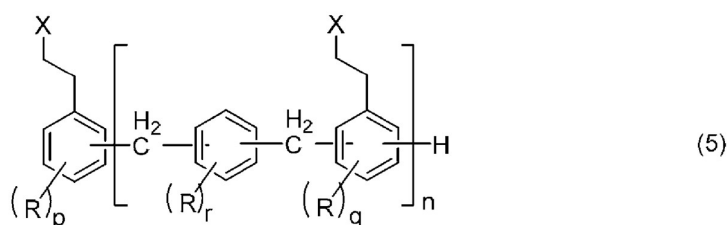
The hydroxyl value of the compound represented by formula (1) is preferably 100,000 g/eq. or less. When the hydroxyl value is 100,000 g/eq. or less, the adhesion, solubility in a solvent, and compatibility with compounds having a polar group are improved without impairing the electrical characteristics and low heat properties.

[0049]

The compound represented by the formula (1) is derived from a compound represented by the following formula (5).

[0050]

10



[0051]

(In formula (5), each of the multiple R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p and r are integers of 0 to 4, q is an integer of 0 to 3, n is the number of repetitions, and the average value n_{ave} of n satisfies $1 \leq n_{ave} \leq 20$. X represents a halogen atom.)

[0052]

The definition of R in the formula (5) and the preferred range of p, r, q, and the average value n_{ave} of n are the same as those in the formula (1). From the viewpoint of reactivity and stability of raw materials, when R represents a halogenated alkyl group, the halogen atom in R and X are preferably a bromine atom or a chlorine atom, and particularly preferably a bromine atom.

[0053]

The compound represented by formula (1) can be obtained, for example, by a method of subjecting the compound represented by formula (5) to a dehydrohalogenation reaction in a solvent in the presence of a basic catalyst. The amount of the solvent used is preferably 4 to 7
5 times by weight of the compound represented by formula (5).

[0054]

The solvent to be used is preferably a polar aprotic solvent, and examples thereof include dimethylsulfone, dimethylsulfoxide, dimethylformamide, dimethylacetamide, 1,3-dimethyl-2-imidazolidinone, and N-methylpyrrolidone, and two or more of these may be used
10 in combination.

It is also preferable to use a polar aprotic solvent in combination with a water-insoluble solvent to form a mixed solvent. In this case, the polar aprotic solvent is preferably dimethylsulfoxide, dimethylformamide, 1,3-dimethyl-2-imidazolidinone, or N-methylpyrrolidone. The water-insoluble solvent is preferably benzene, toluene, xylene,
15 mesitylene, hexane, cyclohexane, or methylcyclohexane. Of these, the most preferred combination is a combination of dimethylsulfoxide and toluene.

In the mixed solvent, the polar aprotic solvent is preferably used in an amount 1 to 10 times by weight, more preferably 1 to 8 times, and particularly preferably 2 to 6 times, the amount of the water-insoluble solvent. If the amount is less than 1 time, the reaction is
20 difficult to proceed, and there is a risk that raw materials will remain. If it exceeds 10 times, the reaction promotion effect is high, but the amounts of the compound represented by the formulas (2) to (4) produced are likely to increase. Since the reaction proceeds in a state in which the polar aprotic solvent layer and the water-insoluble solvent layer are separated into two layers in the latter half of the reaction, the above range is preferable from the viewpoint
25 of controlling the reactivity at the interface.

The total amount of the solvent used is preferably 1 to 9 times by weight, more

preferably 2 to 8 times by weight, and particularly preferably 3 to 7 times by weight, relative to the compound represented by the formula (5). If it is less than 1 time by weight, stirring may become difficult due to precipitation of salt, and if it is more than 9 times by weight, the kettle efficiency (the amount of resin that can be synthesized in one batch) may be significantly reduced.

[0055]

The reaction temperature is preferably 0 to 80°C, more preferably 10 to 70°C, and further preferably 26 to 60°C. If the temperature is less than 0°C, the reaction may not proceed sufficiently, and if the temperature is higher than 80°C, a polymerization reaction of the styrene structure may occur at the same time, which may cause gelation.

[0056]

The catalyst is not particularly limited, and examples thereof include basic catalysts such as sodium hydroxide, potassium hydroxide, and potassium carbonate. Since it is difficult to completely proceed with the dehydrohalogenation reaction, a polar aprotic solvent may be used in large excess relative to the substrate, and the dehydrohalogenation reaction may be repeated two or more times. For example, the dehydrohalogenation reaction of the compound represented by the formula (2) may be carried out in an organic solvent in the presence of a base catalyst, and the resulting solution may be washed with water and then returned to the reaction vessel, and the base catalyst may be added to cause the reaction again. This can increase the progress of the dehydrohalogenation reaction. That is, it is possible to reduce the mass concentration of the residual halogen contained in the target compound. The mass concentration of the residual halogen in the target is preferably 1 to 10,000 ppm, more preferably 1 to 1,000 ppm, and even more preferably 1 to 750 ppm. If the mass concentration of the residual halogen contained in the compound represented by the formula (1) is high, molecular vibration may occur when exposed to high frequency waves, which may adversely affect electrical properties, particularly dielectric tangent. Furthermore, if the mass

concentration of the residual halogen is high, there is a risk of causing defects such as metal corrosion and ion migration in environmental tests such as HAST tests (High Accelerated Stress Tests), so the halogen content is preferably within the above range.

[0057]

5 The method for producing the compound represented by the formula (5) is not particularly limited, and for example, a compound having a (2-bromoethyl)benzene structure may be reacted with a bishalogenated methylaryl compound (or a bishydroxymethylaryl compound, etc.) in the presence of an acid catalyst such as hydrochloric acid, sulfonic acid, or activated clay, or a compound having a (2-bromoethyl)benzene structure may be reacted with
10 a bishydroxymethylaryl compound in the presence of an acid catalyst such as hydrochloric acid, sulfonic acid, or activated clay. When sulfonic acid or the like is used as a catalyst, the mixture may be neutralized with an alkali metal such as sodium hydroxide or potassium hydroxide before proceeding to the extraction step. In the extraction step, an aromatic hydrocarbon solvent such as toluene or xylene may be used alone, or a non-aromatic
15 hydrocarbon such as cyclohexane or toluene may be used in combination. After extraction, the organic layer is washed with water until the wastewater becomes neutral, and the solvent and the excess compound having a (2-bromoethyl)benzene structure are distilled off using an evaporator or the like, thereby obtaining a compound having at least two or more 2-bromoethyl ethylbenzene structures in the target molecule.

20 [0058]

 The charge ratio of the compound having a (2-bromoethyl)benzene structure is preferably 1.0 to 4.0 times, more preferably 1.0 to 3.0 times, and even more preferably 1.0 to 2.0 times, per mole of the bishalogenated methylaryl compound (or bishydroxymethylaryl compound, etc.). If the charge ratio is 4.0 times or less, significant crystal precipitation can be
25 avoided when the resin solution containing the compound represented by the formula (1) is stored in a refrigerator or freezer. If the charge ratio is 1.0 times or more, significant

generation of high molecular weight substances can be avoided, and purification by washing with water is possible.

The content of the compound in which n in formula (5) is 1 among the compounds represented by the formula (5) can be determined by obtaining slice data of a chromatogram using an RI (differential refractive index) detector for GPC analysis, and calculating the ratio (area percentage) of the area of the slice data corresponding to the compound r in which n in formula (5) is 1 to the sum of the areas (time integral values of signal values) of the slice data corresponding to the compounds represented by the formula (5). The content (area percentage) of the compound in which n is 1 in the formula (5) is preferably 25 to 75%, more preferably 30 to 60%, and even more preferably 35 to 50%. If it is more than 75%, there is a risk of significant crystal precipitation when a resin solution containing the compound represented by the formula (1) is stored in a refrigerator or freezer. If it is less than 25%, the reactivity of the high molecular weight material may decrease. This is because, when the compound represented by the formula (1) derived from the compound represented by the formula (5) is synthesized under the above-mentioned preferred conditions, the higher the molecular weight, the more difficult the reaction proceeds.

[0059]

Examples of compounds having a (2-bromoethyl)benzene structure include, but are not limited to, (2-bromoethyl)benzene, 1-(2-bromoethyl)-2-methylbenzene, 1-(2-bromoethyl)-3-methylbenzene, 1-(2-bromoethyl)-4-methylbenzene, 1-(2-bromoethyl)-2,3-dimethylbenzene, 1-(2-bromoethyl)-2,4-dimethylbenzene, 1-(2-bromoethyl)-2,5-dimethylbenzene, and 1-(2-bromoethyl)-2,6-dimethylbenzene. These may be used alone or in combination of two or more. A large number of carbon atoms improves solubility in a solvent, but reduces heat resistance. So it is preferably unsubstituted or substituted with an alkyl group having 1 to 3 carbon atoms, more preferably unsubstituted or substituted with an alkyl group having 1 to 2 carbon atoms, and most preferably unsubstituted or substituted with a methyl

group.

[0060]

Examples of the bishalogenated methylaryl compound include, but are not limited to, o-xylylene difluoride, m-xylylene difluoride, p-xylylene difluoride, o-xylylene dichloride, m-xylylene dichloride, p-xylylene dichloride, o-xylylene dibromide, m-xylylene dibromide, p-xylylene dibromide, o-xylylene diiodide, m-xylylene diiodide, and p-xylylene diiodide. These may be used alone or in combination of two or more. From the viewpoint of the reactivity of the raw material during synthesis, chloride-based compounds, bromide-based compounds, and iodide-based compounds are preferred, and chloride-based compounds and bromide-based compounds are more preferred.

[0061]

Examples of bishydroxymethylaryl compounds include, but are not limited to, o-benzenedimethanol, m-benzenedimethanol, and p-benzenedimethanol. These may be used alone or in combination of two or more. The amount of these compounds used is preferably 0.05 to 0.8 parts by mass, more preferably 0.1 to 0.6 parts by mass, per part by mass of the compound having a (2-bromoethyl)benzene structure.

[0062]

In the reaction of a compound having a (2-bromoethyl)benzene structure with a halogenated methylaryl compound or the like, as well as hydrochloric acid, phosphoric acid, sulfuric acid, formic acid, p-toluenesulfonic acid, and methanesulfonic acid; Lewis acids such as aluminum chloride and zinc chloride; solid acids such as activated clay, acidic clay, white carbon, zeolite, and silica alumina; and acidic ion exchange resins can be used as catalysts as necessary. These can be used alone or in combination of two or more. The amount of catalyst used is 0.05 to 0.8 mol, preferably 0.1 to 0.7 mol, per mol of the compound having a (2-bromoethyl)benzene structure used. If the amount of catalyst used is too large, the viscosity of the reaction solution may be too high, making stirring difficult, and if the amount is too small,

the reaction may proceed slowly. The reaction may be carried out using an organic solvent such as hexane, cyclohexane, octane, toluene, or xylene, as necessary, or may be carried out without a solvent. For example, after adding an acidic catalyst to a mixed solution of a compound having a (2-bromoethyl)benzene structure, a halogenated methylaryl compound, and a solvent, if the catalyst contains water, the water is removed from the system by azeotropy. Thereafter, the reaction is carried out at 40 to 180°C, preferably 50 to 170°C, for 0.5 to 40 hours. After the reaction is completed, the acidic catalyst may be neutralized with an alkaline aqueous solution, but it is also possible to proceed to the water washing step without neutralizing it. In the water washing step, a water-insoluble organic solvent is added to the oil layer and water washing is repeated until the wastewater becomes neutral.

[0063]

The softening point of the compound represented by formula (5) is preferably 80°C or less, more preferably 70°C or less. When the softening point is 80°C or less, the viscosity when the compound represented by formula (5) is derived to the compound represented by formula (1) is low. This makes it easy to ensure fluidity, impregnation to fibrous materials such as glass cloth and carbon fiber is not impaired, and makes it easy to make the curable resin composition semi-cured (B-staged) such as prepreg. If the viscosity is reduced by increasing the dilution solvent, there is a possibility that the curable resin composition will not sufficiently adhere to the fibrous material in the impregnation step.

[0064]

[Polymerization inhibitor]

The compound and the curable resin composition of the present embodiment may contain a polymerization inhibitor. By containing a polymerization inhibitor, storage stability is improved and the reaction initiation temperature can be controlled. By controlling the reaction initiation temperature, the fluidity of the curable resin composition can be easily ensured, impregnation into glass cloth and the like is not impaired, and B-stage such as

prepreg formation is facilitated. If the polymerization reaction proceeds too much during prepreg formation, problems such as lamination becoming difficult in the lamination process are likely to occur.

[0065]

5 The polymerization inhibitor may be added during or after the synthesis of the compound represented by the formula (1). The amount of the polymerization inhibitor used is 0.008 to 1 part by weight, preferably 0.01 to 0.5 parts by weight, based on 100 parts by weight of the compound represented by the formula (1).

[0066]

10 Examples of the polymerization inhibitor include phenol-based, sulfur-based, phosphorus-based, hindered amine-based, nitroso-based, and nitroxyl radical-based polymerization inhibitors. The polymerization inhibitor may be used alone or in combination. Among these, in the present embodiment, phenol-based, hindered amine-based, nitroso-based, and nitroxyl radical-based polymerization inhibitors are preferred.

15 [0067]

 Examples of the phenol-based polymerization inhibitor include, but are not limited to: monophenols such as 2,6-di-t-butyl-p-cresol, butylated hydroxyanisole, 2,6-di-t-butyl-p-ethylphenol, stearyl- β -(3,5-di-t-butyl-4-hydroxyphenyl)propionate, isooctyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate, 2,4-bis-(n-octylthio)-6-(4-hydroxy-3,5-di-t-butylanilino)-1,3,5-triazine, and 2,4-bis[(octylthio)methyl]-o-cresol; bisphenols such as 2,2'-methylenebis(4-methyl-6-t-butylphenol), 2,2'-methylenebis(4-ethyl-6-t-butylphenol), 4,4'-thiobis(3-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), triethylene glycol-bis[3-(3-t-butyl-5-methyl-4-hydroxyphenyl)propionate], 1,6-hexanediol-bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], N,N'-hexamethylenebis(3,5-di-t-butyl-4-hydroxy-
20 hydrocinnamamide), 2,2'-thio-diethylenebis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate], 3,5-di-t-butyl-4-hydroxybenzylphosphonate-diethyl ester, 3,9-bis[1,1-dimethyl-2- β -(3-t-

butyl-4-hydroxy-5-methylphenyl)propionyloxy}ethyl]2,4,8,10-tetraoxaspiro[5,5]undecane, bis(3,5-di-t-butyl-4-hydroxybenzylsulfonate ethyl)calcium; and other polymeric phenols such as 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane, 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene, tetrakis-[methylene-3-(3',5'-di-t-butyl-4'-hydroxyphenyl)propionate]methane, bis[3,3'-bis-(4'-hydroxy-3'-t-butylphenyl)butyric acid]glycol ester, tris-(3,5-di-t-butyl-4-hydroxybenzyl)-isocyanurate, 1,3,5-tris(3',5'-di-t-butyl-4'-hydroxybenzyl)-S-triazine-2,4,6-(1H,3H,5H)trione, tocopherol.

[0068]

Examples of the sulfur-based polymerization inhibitor include, but are not limited to, dilauryl-3,3'-thiodipropionate, dimyristyl-3,3'-thiodipropionate, and distearyl-3,3'-thiodipropionate.

[0069]

Examples of the phosphorus-based polymerization inhibitor include, but are not limited to: phosphites such as triphenyl phosphite, diphenyl isodecyl phosphite, phenyl diisodecyl phosphite, tris(nonylphenyl)phosphite, diisodecyl pentaerythritol phosphite, tris(2,4-di-t-butylphenyl)phosphite, cyclic neopentane tetrayl bis(octadecyl)phosphite, cyclic neopentane tetrayl bis(2,4-di-t-butylphenyl)phosphite, cyclic neopentane tetrayl bis(2,4-di-t-butyl-4-methylphenyl)phosphite, bis[2-t-butyl-6methyl-4-{2-(octadecyloxycarbonyl)ethyl}phenyl]hydrogenphosphite; and oxaphosphaphenanthrene oxides such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-(3,5-di-t-butyl-4-hydroxybenzyl)-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide, 10-decyloxy-9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide.

[0070]

Examples of the hindered amine-based polymerization inhibitor include, but are not limited to: ADK STAB LA-40MP, ADK STAB LA-40Si, ADK STAB LA-402AF, ADK STAB LA-87, ADK STAB LA-82, ADK STAB LA-81, ADK STAB LA-77Y, ADK STAB

LA-77G, ADK STAB LA-72, ADK STAB LA-68, ADK STAB LA-63P, ADK STAB LA-57, and ADK STAB LA-52, all of which are manufactured by ADEKA CORPORATION; and Chimassorb 2020FDL, Chimassorb 944FDL, Chimassorb 944LD, Tinuvin 622SF, Tinuvin PA144, Tinuvin 765, Tinuvin 770DF, Tinuvin XT55FB, Tinuvin 111FDL, Tinuvin 783FDL, 5 Tinuvin 791FB manufactured by BASF Japan Ltd.

[0071]

Examples of the nitroso-based polymerization inhibitor include, but are not limited to, p-nitrosophenol, N-nitrosodiphenylamine, ammonium salt of N-nitrosophenylhydroxyamine (cupferron), etc. Among these, the ammonium salt of N- 10 nitrosophenylhydroxyamine (cupferron) is preferred.

[0072]

Examples of the nitroxyl radical polymerization inhibitor include, but are not limited to, di-tert-butyl nitroxide, 2,2,6,6-tetramethylpiperidine-1-oxyl, 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, 4-oxo-2,2,6,6-tetramethylpiperidine-1-oxyl, 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl, 4-methoxy-2,2,6,6-tetramethylpiperidine-1-oxyl, 4-acetoxy- 15 2,2,6,6-tetramethylpiperidine-1-oxyl, 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl, etc.

[0073]

[Polyphenylene ether compound]

The curable resin composition of the present embodiment may contain a 20 polyphenylene ether compound.

As the polyphenylene ether compound, from the viewpoint of heat resistance and electrical properties, a polyphenylene ether compound having an ethylenically unsaturated bond is preferable, and a polyphenylene ether compound having an acrylic group, a methacrylic group, or a styrene structure is more preferable. Commercially available products 25 include SA-9000 (manufactured by SABIC, a polyphenylene ether compound having a methacrylic group) and OPE-2St 1200 (manufactured by Mitsubishi Gas Chemical Co., Ltd.,

a polyphenylene ether compound having a styrene structure).

The number average molecular weight (M_n) of the polyphenylene ether compound is preferably 500 to 5000, more preferably 2000 to 5000, and more preferably 2000 to 4000. If the molecular weight is less than 500, the heat resistance of the cured product tends to be insufficient. In addition, if the molecular weight is greater than 5000, the melt viscosity becomes high and sufficient fluidity cannot be obtained, which tends to cause molding defects. In addition, the reactivity is also reduced, the curing reaction takes a long time, and the amount of unreacted material that is not incorporated into the curing system increases, which leads to a decrease in the glass transition temperature of the cured product and a decrease in the heat resistance of the cured product.

If the number average molecular weight of the polyphenylene ether compound is 500 to 5000, excellent heat resistance and moldability can be achieved while maintaining excellent dielectric properties. The number average molecular weight here can be specifically measured using gel permeation chromatography or the like.

[0074]

The polyphenylene ether compound may be one obtained by a polymerization reaction, or one obtained by a redistribution reaction of a high molecular weight polyphenylene ether compound having a number average molecular weight of about 10,000 to 30,000. In addition, these may be used as raw materials and reacted with a compound having an ethylenically unsaturated bond, such as methacryl chloride, acrylic chloride, or chloromethylstyrene, to impart radical polymerizability. The polyphenylene ether compound obtained by the redistribution reaction is obtained, for example, by heating a high molecular weight polyphenylene ether compound in a solvent such as toluene in the presence of a phenolic compound and a radical initiator to cause a redistribution reaction. The polyphenylene ether compound obtained by the redistribution reaction in this way has hydroxy groups derived from a phenolic compound that contributes to curing at both ends of

the molecular chain, and is therefore preferable in that it can maintain even higher heat resistance, and that functional groups can be introduced at both ends of the molecular chain even after modification with a compound having an ethylenically unsaturated bond. In addition, the polyphenylene ether compound obtained by the polymerization reaction is
5 preferable in that it exhibits excellent fluidity.

[0075]

The molecular weight of the polyphenylene ether compound can be adjusted by adjusting the polymerization conditions, etc., in the case of a polyphenylene ether compound obtained by a polymerization reaction. In addition, in the case of a polyphenylene ether
10 compound obtained by a redistribution reaction, the molecular weight of the obtained polyphenylene ether compound can be adjusted by adjusting the conditions of the redistribution reaction, etc. More specifically, it is possible to adjust the amount of the phenolic compound used in the redistribution reaction. That is, the greater the amount of the phenolic compound, the lower the molecular weight of the obtained polyphenylene ether
15 compound. In this case, poly(2,6-dimethyl-1,4-phenylene ether) or the like can be used as the high molecular weight polyphenylene ether compound that undergoes the redistribution reaction. In addition, the phenolic compound used in the redistribution reaction is not particularly limited, but for example, a multifunctional phenolic compound having two or more phenolic hydroxy groups in the molecule, such as bisphenol A, phenol novolac, cresol
20 novolac, etc., is preferably used. These may be used alone or in combination of two or more.

[0076]

The content of the polyphenylene ether compound is not particularly limited, but is preferably 5 to 1000 parts by mass, and more preferably 10 to 750 parts by mass, relative to 100 parts by mass of the compound represented by formula (1). When the content of the
25 polyphenylene ether compound is within the above range, it is preferable in that a cured product is obtained that is not only excellent in heat resistance, etc., but also fully exhibits the

excellent dielectric properties of the polyphenylene ether compound.

[0077]

[Polybutadiene and its modified product]

The curable resin composition of the present embodiment may contain polybutadiene
5 and its modified product.

Polybutadiene and its modified product are polybutadiene or compounds having a structure derived from polybutadiene in the molecule. Some or all of the unsaturated bonds of the structure derived from polybutadiene may be converted to single bonds by hydrogenation.

Examples of polybutadiene and its modified products include polybutadiene,
10 hydroxy group-terminated polybutadiene, terminal (meth)acrylated polybutadiene, carboxylic acid-terminated polybutadiene, amine-terminated polybutadiene, styrene butadiene rubber, etc., but are not limited thereto. In addition, these may be used alone or in combination. Of these, polybutadiene or styrene butadiene rubber is preferred from the viewpoint of dielectric properties. Examples of styrene butadiene rubber (SBR) include RICON-100, RICON-181,
15 and RICON-184 (all manufactured by Cray Valley Corporation), and 1,2-SBS (manufactured by Nippon Soda Co., Ltd.). Examples of polybutadiene include B-1000, B-2000, and B-3000 (all manufactured by Nippon Soda Co., Ltd.). The molecular weight of polybutadiene and styrene butadiene rubber is preferably a weight average molecular weight of 500 to 10,000, more preferably 750 to 7,500, and even more preferably 1,000 to 5,000. Below the lower limit
20 of the above range, the amount of volatilization is large, making it difficult to adjust the solid content when preparing the prepreg, and above the upper limit of the above range, the compatibility with other curable resins is deteriorated. In general, in the case of compounds containing heteroatoms such as oxygen and nitrogen, such as bismaleimide and polymaleimide, it is difficult to ensure compatibility with low-polarity compounds such as
25 compounds mainly composed of hydrocarbons or compounds composed only of hydrocarbons due to their polarity. On the other hand, the compound represented by the formula (1) does not

have a skeleton design in which heteroatoms such as oxygen and nitrogen are actively introduced, and therefore has excellent compatibility with materials having low polarity and low dielectric properties, and with compounds composed only of hydrocarbons.

[0078]

5 The content of polybutadiene and modified products thereof is not particularly limited, but is preferably 5 to 1000 parts by mass, and more preferably 10 to 750 parts by mass, relative to 100 parts by mass of the compound represented by formula (1). When the content of polybutadiene and modified products thereof is within the above range, it is preferable in that a cured product is obtained that is not only excellent in heat resistance, etc.,
10 but also fully exhibits the excellent dielectric properties of polybutadiene and modified products thereof.

[0079]

[Polystyrene and modified products thereof]

 The curable resin composition of the present embodiment may contain polystyrene
15 and modified products thereof.

 Polystyrene and modified products thereof are polystyrene or compounds having a structure derived from polystyrene in the molecule.

 Examples of polystyrene and modified products thereof include polystyrene, styrene-2-isopropenyl-2-oxazoline copolymers (Epocross RPS-1005, RP-61, both manufactured by
20 Nippon Shokubai Co., Ltd.), SEP (styrene-ethylene-propylene copolymer: Septon 1020, manufactured by Kuraray Co., Ltd.), SEPS (styrene-ethylene-propylene-styrene copolymer: Septon 2002, Septon 2004F, Septon 2005, Septon 2006, Septon 2063, Septon 2104, all manufactured by Kuraray Co., Ltd.), SEEPS (styrene-ethylene/ethylene-propylene-styrene block copolymer: Septon 4003, Septon 4044, Septon 4055, Septon 4077, Septon 4099, all
25 manufactured by Kuraray Co., Ltd.), and SEBS (styrene-ethylene-butylene-styrene block copolymer: Septon 8004, Septon 8006, Septon 8007L, all manufactured by Kuraray Co.,

Ltd.), SEEPS-OH (styrene-ethylene/ethylene propylene-styrene block copolymer having a
 hydroxy group at the end: SEPTON HG252, manufactured by Kuraray Co., Ltd.), SIS
 (styrene-isoprene-styrene block copolymer: SEPTON 5125, SEPTON 5127, manufactured by
 Kuraray Co., Ltd.), hydrogenated SIS (hydrogenated styrene-isoprene-styrene block
 5 copolymer: HYBRAR 7125F, HYBRAR 7311F, manufactured by Kuraray Co., Ltd.), SIBS
 (styrene-isobutylene-styrene block copolymer: SIBSTAR073T, SIBSTAR102T,
 SIBSTAR103T (all manufactured by Kaneka Corporation), SEPTON V9827 (manufactured
 by Kuraray Co., Ltd.)). These may be used alone or in combination. It is preferable that
 polystyrene and modified products thereof do not have unsaturated bonds in order to have
 10 higher heat resistance and less susceptible to oxidative deterioration. The weight average
 molecular weight of polystyrene and modified products thereof is not particularly limited as
 long as it is 10,000 or more, but if it is too large, the compatibility with not only
 polyphenylene ether compounds but also low molecular weight components with a weight
 average molecular weight of about 50 to 1,000 and oligomer components with a weight
 15 average molecular weight of about 1,000 to 5,000 deteriorates, making it difficult to ensure
 mixing and stability in solvent, so it is preferably about 10,000 to 300,000.

[0080]

The content of polystyrene and modified products thereof is not particularly limited,
 but is preferably 5 to 1000 parts by mass, and more preferably 10 to 750 parts by mass,
 20 relative to 100 parts by mass of the compound represented by the formula (1). Styrene and
 modified products thereof in the above range are preferable in that a cured product is obtained
 that is not only excellent in heat resistance, but also fully exhibits the excellent dielectric
 properties of polystyrene and modified products thereof.

[0081]

25 [Inorganic filler]

The curable resin composition of the present embodiment may contain an inorganic

filler. Examples of inorganic fillers include: powders such as fused silica, crystalline silica, porous silica, alumina, zircon, calcium silicate, calcium carbonate, quartz powder, silicon carbide, silicon nitride, boron nitride, zirconia, aluminum nitride, graphite, forsterite, steatite, spinel, mullite, titania, talc, clay, iron oxide asbestos, and glass powder; and inorganic fillers
 5 obtained by making these into a spherical or crushed shape, but are not limited thereto. In addition, these may be used alone or in combination.

[0082]

When a curable resin composition for semiconductor encapsulation is obtained, the amount of the inorganic filler used is preferably 80 to 92 parts by mass, and more preferably
 10 83 to 90 parts by mass, based on 100 parts by mass of the curable resin composition. When a curable resin composition for an interlayer insulating layer forming material, or a substrate material such as a copper-clad laminate, prepreg, or RCC is obtained, the amount of the inorganic filler used is preferably 5 to 80 parts by mass, and more preferably 10 to 60 parts by mass, based on 100 parts by mass of the curable resin composition.

15 [0083]

[Curing Accelerator]

The curable resin composition of the present embodiment can also have improved curability by adding a curing accelerator. As the curing accelerator, an anionic curing accelerator that accelerates the curing reaction by generating anions upon irradiation with
 20 ultraviolet light or visible light or heating, or a cationic curing accelerator that accelerates the curing reaction by generating cations upon irradiation with ultraviolet light or visible light or heating, is preferred.

Examples of the anionic curing accelerator include: imidazoles such as 2-methylimidazole, 2-ethylimidazole, and 2-ethyl-4-methylimidazole; trialkylamines such as
 25 triethylamine and tributylamine; 4-dimethylaminopyridine, benzyldimethylamine, 2,4,6-tris(dimethylaminomethyl)phenol, and 1,8-diazabicyclo(5,4,0)-undecene, and 4-

dimethylaminopyridine and 1,8-diazabicyclo(5,4,0)-undecene are preferred. Other examples of the cationic curing accelerator include phosphines such as triphenylphosphine; and quaternary ammonium salts such as tetrabutylammonium salts, triisopropylmethylammonium salts, trimethyldecanylammonium salts, cetyltrimethylammonium salts, and
 5 hexadecyltrimethylammonium hydroxide.

Examples of the cationic curing accelerator include: quaternary phosphonium salts such as triphenylbenzylphosphonium salts, triphenylethylphosphonium salts, and tetrabutylphosphonium salts (the counter ions of the quaternary salts are halogens, organic acid ions, hydroxide ions, and the like, and are not particularly specified, but organic acid ions
 10 and hydroxide ions are particularly preferred.); and transition metal compounds (transition metal salts) such as tin octylate, zinc carboxylate (zinc 2-ethylhexanoate, zinc stearate, zinc behenate, zinc myristate), and zinc phosphate esters (zinc octylphosphate, zinc stearylphosphate), but are not limited thereto. In addition, these may be used alone or in combination.

15 [0084]

The amount of the curing accelerator to be blended is 0.01 to 5.0 parts by mass per 100 parts by mass of the total of the nonvolatile contents excluding the inorganic filler in the curable resin composition, as required.

[0085]

20 [Polymerization initiator]

The curable resin composition of the present embodiment can also improve the curability by adding a polymerization initiator. The polymerization initiator is a compound capable of polymerizing an olefin functional group such as an ethylenically unsaturated bond, and includes an olefin metathesis polymerization initiator, an anionic polymerization initiator,
 25 a cationic polymerization initiator, and a radical polymerization initiator. Among these, it is preferable to use a radical polymerization initiator having curability and moderate stability. In

the case of an olefin metathesis polymerization initiator such as a Schrock catalyst having molybdenum as a central metal, an anionic polymerization initiator such as BuLi, or a cationic polymerization initiator such as triethylaluminum, they are poor in stability, as they react with moisture in the air.

5 The radical polymerization initiator refers to a compound that generates radicals by irradiation with ultraviolet light or visible light or heating, and initiates a chain polymerization reaction. Examples of radical polymerization initiators that can be used include organic peroxides, azo compounds, and benzopinacoles, and it is preferable to use an organic peroxide because it has little effect on curing temperature control, outgassing suppression, and
10 electrical properties of decomposition products.

 Examples of the organic peroxides include, but are not limited to: ketone peroxides such as methyl ethyl ketone peroxide and acetylacetone peroxide; diacyl peroxides such as benzoyl peroxide; dialkyl peroxides such as dicumyl peroxide and 1,3-bis-(t-butylperoxyisopropyl)-benzene; peroxyketals such as t-butylperoxybenzoate and 1,1-di-t-butylperoxycyclohexane; alkyl peresters such as α -cumylperoxyneodecanoate, t-butylperoxyneodecanoate, t-butylperoxypivalate, 1,1,3,3-tetramethylbutylperoxy-2-ethylhexanoate, t-amylperoxy-2-ethylhexanoate, t-butylperoxy-2-ethylhexanoate, t-butylperoxy-2-ethylhexanoate, t-amylperoxy-3,5,5-trimethylhexanoate, t-butylperoxy-3,5,5-tromethylhexanoate, t-amylperoxybenzoate; peroxycarbonates such as di-2-ethylhexyl
15 peroxydicarbonate, bis(4-t-butylcyclohexyl)peroxydicarbonate, t-butylperoxyisopropyl carbonate, 1,6-bis(t-butylperoxycarbonyloxy)hexane; t-butyl hydroperoxide, cumene hydroperoxide, t-butyl peroxyoctoate, lauroyl peroxide, etc. These may be used alone or in combination. Among the above organic peroxides, ketone peroxides, diacyl peroxides, hydroperoxides, dialkyl peroxides, peroxyketals, alkyl peresters, peroxycarbonates, and the
20 like are preferred, with dialkyl peroxides being more preferred.

 Examples of the azo compounds include, but are not limited to,

azobisisobutyronitrile, 4,4'-azobis(4-cyanovaleric acid), 2,2'-azobis(2,4-dimethylvaleronitrile), and the like. These may be used alone or in combination.

[0086]

The amount of the polymerization initiator added is preferably 0.01 to 5 parts by mass, particularly preferably 0.01 to 3 parts by mass, when the total amount of nonvolatile matters in the curable resin composition excluding the inorganic filler is taken as 100 parts by mass. If the amount of the polymerization initiator used is less than 0.01 part by mass, there is a risk that the molecular weight will not be sufficiently extended during the polymerization reaction, and if it is more than 5 parts by mass, there is a risk that the dielectric properties such as the dielectric constant and the dielectric tangent will be impaired.

[0087]

[Flame retardant]

The curable resin composition of the present embodiment may contain a flame retardant. Examples of the flame retardant include halogen-based flame retardants, inorganic flame retardants (antimony compounds, metal hydroxides, nitrogen compounds, boron compounds, etc.), and phosphorus-based flame retardants. From the viewpoint of achieving halogen-free flame retardancy, phosphorus-based flame retardants are preferred.

The phosphorus-based flame retardant may be either a reactive type or an additive type. Specific examples include: phosphoric acid esters such as trimethyl phosphate, triethyl phosphate, tricresyl phosphate, trixylenyl phosphate, cresyl diphenyl phosphate, cresyl-di-2,6-xilylenyl phosphate, 1,3-phenylene bis(dixylenyl phosphate), 1,4-phenylene bis(dixylenyl phosphate), and 4,4'-biphenyl(dixylenyl phosphate); phosphanes such as 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and 10(2,5-dihydroxyphenyl)-10H-9-oxa-10-phosphaphenanthrene-10-oxide, as well as phosphorus-containing epoxy compounds obtained by reacting an epoxy resin with the active hydrogen of the phosphanes, red phosphorus, and the like, but are not limited thereto. These may be used alone or in combination. Of the above-

listed substances, phosphoric acid esters, phosphanes, or phosphorus-containing epoxy compounds are preferred, with 1,3-phenylenebis(dixylenyl phosphate), 1,4-phenylenebis(dixylenyl phosphate), 4,4'-biphenyl(dixylenyl phosphate) or phosphorus-containing epoxy compounds being particularly preferred.

5 [0088]

The content of the flame retardant is preferably in the range of 0.1 to 0.6 parts by mass, per 100 parts by mass of the total of the nonvolatile contents excluding the inorganic filler in the curable resin composition. If the content is less than 0.1 part by mass, the flame retardancy may be insufficient, and if the content is more than 0.6 part by mass, the

10 hygroscopicity and dielectric properties of the cured product may be adversely affected.

[0089]

[Light stabilizer]

The curable resin composition of the present embodiment may contain a light stabilizer. As the light stabilizer, a hindered amine light stabilizer, particularly HALS, etc., is

15 preferable. Examples of HALS include reaction products of dibutylamine, 1,3,5-triazine, N,N'-bis(2,2,6,6-tetramethyl-4-piperidyl)-1,6-hexamethylenediamine and N-(2,2,6,6-tetramethyl-4-piperidyl)butylamine, reaction products of dimethyl succinate-1-(2-hydroxyethyl)-4-hydroxy-2,2,6,6-tetramethylpiperidine, poly[6-(1,1,3,3-tetramethylbutyl)amino-1,3,5-triazine-2,4-diyl} {(2,2,6,6-tetramethyl-4-piperidyl)imino} hexamethylene {(2,2,6,6-tetramethyl-4-piperidyl)imino}], bis(1,2,2,6,6-pentamethyl-4-piperidyl)[[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]methyl]butyl malonate, bis(2,2,6,6-tetramethyl-4-piperidyl)sebacate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)sebacate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)sebacate, 2-(3,5-di-t-butyl-4-hydroxybenzyl)-2-n-butylmalonate bis(1,2,2,6,6-pentamethyl-4-piperidyl) and the like, but

20 are not limited thereto. These may be used alone or in combination.

[0090]

The content of the light stabilizer is preferably in the range of 0.001 to 10 parts by mass, per 100 parts by mass of the total of the non-volatile contents excluding inorganic fillers in the curable resin composition. If the content is less than 0.001 part by mass, it may be insufficient to exhibit a light stabilizing effect, and if the content is more than 10 parts by mass, it may have an adverse effect on the hygroscopicity and dielectric properties of the cured product.

[0091]

[Binder Resin]

The curable resin composition of the present embodiment may use a binder resin.

Examples of binder resins include, but are not limited to, butyral resins, acetal resins, acrylic resins, epoxy-nylon resins, NBR-phenol resins, epoxy-NBR resins, and silicone resins. These may be used alone or in combination.

[0092]

The amount of the binder resin is preferably within a range that does not impair the flame retardancy and heat resistance of the cured product, and is preferably 0.05 to 50 parts by mass, and more preferably 0.05 to 20 parts by mass, per 100 parts by mass of the total non-volatile content excluding the inorganic filler in the curable resin composition.

[0093]

[Additives]

The curable resin composition of the present embodiment may contain additives, such as modified acrylonitrile copolymers, polyethylene, fluororesins, silicone gels, silicone oils, surface treatment agents for fillers such as silane coupling agents, release agents, and colorants such as carbon black, phthalocyanine blue, and phthalocyanine green.

[0094]

The amount of the additive is preferably 1,000 parts by mass or less, and more preferably 700 parts by mass or less, based on 100 parts by mass of the curable resin

composition.

[0095]

The curable resin composition of the present embodiment may further include epoxy resins, active ester compounds, phenolic resins, amine resins, maleimide compounds, compounds having ethylenically unsaturated bonds, isocyanate resins, polyamide resins, polyimide resins, cyanate ester resins, etc., and these may be used alone or in combination. Among these compounds, it is preferable to include compounds having ethylenically unsaturated bonds and cyanate ester resins in view of the balance of heat resistance, adhesion, and dielectric properties. By containing these compounds, the brittleness of the cured product can be improved and adhesion to metals can be improved, and cracks in the package during solder reflow and reliability tests such as thermal cycles can be suppressed.

[0096]

Unless otherwise specified, the amount of the above compounds used is preferably 10 times by mass or less, more preferably 5 times by mass or less, and particularly preferably 3 times by mass or less, relative to the compound represented by formula (1). The preferred lower limit is 0.1 times by mass or more, more preferably 0.25 times by mass or more, and even more preferably 0.5 times by mass or more. By being within the above range, the effects of each compound added can be added while making use of the effects of the heat resistance and dielectric properties of the compound represented by formula (1). As these components, the following examples can be used.

[0097]

[Epoxy resin]

Preferred examples of the epoxy resin are shown below, but are not limited to these. The epoxy resin may be liquid or solid, and may be used alone or in combination.

[0098]

Examples of liquid epoxy resins include bisphenol A type epoxy resins, bisphenol F

type epoxy resins, bisphenol AF type epoxy resins, naphthalene type epoxy resins, glycidyl ester type epoxy resins, glycidyl amine type epoxy resins, phenol novolac type epoxy resins, alicyclic epoxy resins having an ester skeleton, cyclohexane type epoxy resins, cyclohexane dimethanol type epoxy resins, and epoxy resins having a butadiene structure. Specific

5 examples include "RE310S", "RE410S" (all manufactured by Nippon Kayaku Co., Ltd., bisphenol A type epoxy resin), "RE303S", "RE304S", "RE403S", "RE404S" (all manufactured by Nippon Kayaku Co., Ltd., bisphenol F type epoxy resin), "HP4032", "HP4032D", "HP4032SS" (all manufactured by DIC Corporation, naphthalene type epoxy resin), "828US", "jER828EL", "825", "828EL" (all manufactured by Mitsubishi Chemical

10 Corporation, bisphenol A type epoxy resin), "jE807", "1750" (all manufactured by Mitsubishi Chemical Corporation, bisphenol F type epoxy resin), "jER152" (manufactured by Mitsubishi Chemical Corporation, phenol Novolac type epoxy resin), "630", "630LSD" (all manufactured by Mitsubishi Chemical Corporation, glycidylamine type epoxy resin), "ZX1059" (manufactured by Nippon Steel & Sumitomo Metal Chemical Co., Ltd., a mixture

15 of bisphenol A type epoxy resin and bisphenol F type epoxy resin), "EX-721" (manufactured by Nagase ChemteX Corporation, glycidyl ester type epoxy resin), "Celloxide 2021P" (manufactured by Daicel Corporation, alicyclic epoxy resin having an ester skeleton), "PB-3600" (manufactured by Daicel Corporation, epoxy resin having a butadiene structure), "ZX1658", "ZX1658GS" (all manufactured by Nippon Steel & Sumitomo Metal Chemical

20 Co., Ltd., liquid 1,4-glycidylcyclohexane type epoxy resin), and the like. These may be used alone or in combination of two or more.

[0099]

Preferred examples of solid epoxy resins include bixylenol type epoxy resins, naphthalene type epoxy resins, naphthalene type tetrafunctional epoxy resins, cresol novolac

25 type epoxy resins, dicyclopentadiene type epoxy resins, trisphenol type epoxy resins, naphthol type epoxy resins, biphenyl type epoxy resins, naphthylene ether type epoxy resins,

anthracene type epoxy resins, bisphenol A type epoxy resins, bisphenol AF type epoxy resins, and tetraphenylethane type epoxy resins, and examples of such solid epoxy resins include naphthol type epoxy resins, bisphenol AF type epoxy resins, naphthalene type epoxy resins, and biphenyl type epoxy resins. Specific examples include "HP4032H" (manufactured by

5 DIC Corporation, naphthalene type epoxy resin), "HP-4700", and "HP-4710" (all manufactured by DIC Corporation, naphthalene type tetrafunctional epoxy resin), "N-690" (manufactured by DIC Corporation, cresol novolac type epoxy resin), "N-695" (manufactured by DIC Corporation, cresol novolac type epoxy resin), "HP-7200" (manufactured by DIC Corporation, dicyclopentadiene type epoxy resin), "HP-7200", "HP-7200HH", and "HP-

10 7200H" (all manufactured by DIC Corporation, dicyclopentadiene type epoxy resin), "EXA-7311", "EXA-7311-G3", "EXA-7311-G4", "EXA-7311-G4S", "HP-6000" (all manufactured by DIC Corporation, naphthylene ether type epoxy resin), "EPPN-502H" (manufactured by Nippon Kayaku Co., Ltd., trisphenol type epoxy resin), "NC-7000L", "NC-7300" (all manufactured by Nippon Kayaku Co., Ltd., naphthol-cresol novolac type epoxy resin), "NC-

15 3000H", "NC-3000", "NC-3000L", "NC-3100" (all manufactured by Nippon Kayaku Co., Ltd., biphenyl aralkyl type epoxy resin), "XD-1000-2L", "XD-1000-L", "XD-1000-H" (all manufactured by Nippon Kayaku Co., Ltd., dicyclopentadiene type epoxy resin), "ESN475V" (manufactured by Nippon Steel & Sumikin Chemical Co., Ltd., naphthol type epoxy resin), "ESN485" (manufactured by Nippon Steel & Sumikin Chemical Co., Ltd., naphthol novolac

20 type epoxy resin), "YX-4000H", "YX-4000", "YL6121" (all manufactured by Mitsubishi Chemical Corporation, biphenyl type epoxy resin), "YX-4000HK" (manufactured by Mitsubishi Chemical Corporation, bixylenol type epoxy resin), "YX-8800" (manufactured by Mitsubishi Chemical Corporation, anthracene type epoxy resin), "PG-100", "CG-500" (manufactured by Osaka Gas Chemicals Co., Ltd., fluorene type epoxy resin), "YL-7760"

25 (manufactured by Mitsubishi Chemical Corporation, bisphenol AF type epoxy resin), "YL-7800" (manufactured by Mitsubishi Chemical Corporation, fluorene type epoxy resin),

"jER1010" (manufactured by Mitsubishi Chemical Corporation, solid bisphenol A type epoxy resin), "jER1031S" (manufactured by Mitsubishi Chemical Corporation, tetraphenylethane type epoxy resin), etc. These may be used alone or in combination of two or more.

[0100]

5 [Active ester compound]

The active ester compound refers to a compound that contains at least one ester bond in the structure and has an aliphatic chain, an aliphatic ring, or an aromatic ring bonded to both sides of the ester bond. Examples of the active ester compound include compounds having two or more highly reactive ester groups in one molecule, such as phenol esters, thiophenol esters, N-hydroxyamine esters, and esters of heterocyclic hydroxy compounds, and are obtained by a condensation reaction between at least one compound of a carboxylic acid compound, an acid chloride, or a thiocarboxylic acid compound and at least one compound of a hydroxy compound or a thiol compound. In particular, from the viewpoint of improving heat resistance, it is preferable to obtain the active ester compound from a carboxylic acid compound or an acid chloride and a hydroxy compound, and the hydroxy compound is preferably a phenol compound or a naphthol compound. The active ester compound may be used alone or in combination of two or more types.

[0101]

Examples of the carboxylic acid compound include benzoic acid, acetic acid, succinic acid, maleic acid, itaconic acid, phthalic acid, isophthalic acid, terephthalic acid, and pyromellitic acid.

[0102]

Examples of the acid chloride include acetyl chloride, acrylic acid chloride, methacrylic acid chloride, malonyl chloride, succinic acid dichloride, diglycolyl chloride, glutaric acid dichloride, suberic acid dichloride, sebacic acid dichloride, adipic acid dichloride, dodecandioyl dichloride, azelaoyl chloride, 2,5-furandicarbonyl dichloride,

phthaloyl chloride, isophthaloyl chloride, terephthaloyl chloride, trimesic acid chloride, bis(4-chlorocarbonylphenyl) ether, 4,4'-diphenyldicarbonyl chloride, and 4,4'-azodibenzoyl dichloride.

[0103]

5 Examples of the phenol compound and naphthol compound include hydroquinone, resorcin, bisphenol A, bisphenol F, bisphenol S, phenolphthaline, methylated bisphenol A, methylated bisphenol F, methylated bisphenol S, phenol, o-cresol, m-cresol, p-cresol, catechol, α -naphthol, β -naphthol, 1,5-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, dihydroxybenzophenone, trihydroxybenzophenone,
10 tetrahydroxybenzophenone, phloroglucin, benzenetriol, dicyclopentadiene-type diphenol compound, phenol novolac, and phenol resins described below. Here, the term "dicyclopentadiene-type diphenol compound" refers to a diphenol compound obtained by condensing one molecule of dicyclopentadiene with two molecules of phenol.

[0104]

15 Preferred specific examples of the active ester compound include an active ester compound containing a dicyclopentadiene-type diphenol structure, an active ester compound containing a naphthalene structure, an active ester compound containing an acetylated product of phenol novolac, an active ester compound containing a benzoylated product of phenol novolac, a compound described in Example 2 of WO 2020/095829, and a compound
20 disclosed in WO 2020/059625. Among them, an active ester compound containing a naphthalene structure and an active ester compound containing a dicyclopentadiene-type diphenol structure are more preferred. The dicyclopentadiene-type diphenol structure refers to a divalent structural unit consisting of phenylene-dicyclopentylene-phenylene.

[0105]

25 Commercially available active ester compounds include, for example: active ester compounds containing a dicyclopentadiene-type diphenol structure such as "EXB9451",

"EXB9460", "EXB9460S", "HPC-8000-65T", "HPC-8000H-65TM", "EXB-8000L-65TM", and "EXB-8150-65T" (manufactured by DIC Corporation), active ester compounds containing a naphthalene structure such as "EXB9416-70BK" (manufactured by DIC Corporation); active ester compounds containing an acetylated phenol novolac such as "DC808" (manufactured by Mitsubishi Chemical Corporation); active ester compounds containing a benzoylated phenol novolac such as "YLH1026", "YLH1030", and "YLH1048" (manufactured by Mitsubishi Chemical Corporation); an active ester curing agent which is an acetylated phenol novolac such as "DC808" (manufactured by Mitsubishi Chemical Corporation), and an active ester curing agent containing a phosphorus atom such as "EXB-9050L-62M" (manufactured by DIC Corporation).

[0106]

Regarding a mixing ratio of the active ester compound and the epoxy resin, the ratio (α/β) of the active ester equivalent (α) to the epoxy equivalent (β) is preferably 0.5 to 1.5, more preferably 0.8 to 1.2, and even more preferably 0.90 to 1.10. If it is out of the above range, there is a risk that excess epoxy groups or active ester groups will remain in the system, and the characteristics may deteriorate in a high-temperature storage test (e.g., 150°C, 1000 hours) or a long-term reliability test under high-temperature and high-humidity conditions (e.g., temperature: 85°C, humidity: 85%).

[0107]

[Phenol resin]

Phenol resin is a compound having two or more phenolic hydroxy groups in the molecule. Examples of phenol resin include, but are not limited to, reaction products of phenols and aldehydes, reaction products of phenols and diene compounds, reaction products of phenols and ketones, reaction products of phenols and substituted biphenyls, reaction products of phenols and substituted phenyls, reaction products of bisphenols and aldehydes, etc. Furthermore, these may be used alone or in combination.

Specific examples of the above-mentioned raw materials are shown below, but are not limited to these.

<Phenols>

Phenol, alkyl-substituted phenol, aromatic-substituted phenol, hydroquinone,
 5 resorcin, naphthol, alkyl-substituted naphthol, dihydroxybenzene, alkyl-substituted
 dihydroxybenzene, dihydroxynaphthalene, etc.

<Aldehydes>

Formaldehyde, acetaldehyde, alkyl aldehyde, benzaldehyde, alkyl-substituted
 benzaldehyde, hydroxybenzaldehyde, naphthaldehyde, glutaraldehyde, phthalaldehyde,
 10 crotonaldehyde, cinnamaldehyde, furfural, etc.

<Diene compounds >

Dicyclopentadiene, terpenes, vinylcyclohexene, norbornadiene, vinylnorbornene,
 tetrahydroindene, divinylbenzene, divinylbiphenyl, diisopropenylbiphenyl, butadiene,
 isoprene, etc.

15 <Ketones>

Acetone, methyl ethyl ketone, methyl isobutyl ketone, acetophenone, benzophenone,
 fluorenone, etc.

<Substituted biphenyls>

4,4'-bis(chloromethyl)-1,1'-biphenyl, 4,4'-bis(methoxymethyl)-1,1'-biphenyl, 4,4'-
 20 bis(hydroxymethyl)-1,1'-biphenyl, etc.

<Substituted phenyls>

1,4-bis(chloromethyl)benzene, 1,4-bis(methoxymethyl)benzene, 1,4-
 bis(hydroxymethyl)benzene, etc.

[0108]

25 [Amine resin]

Amine resin is a compound having two or more amino groups in the molecule.

Examples of amine resins include diaminodiphenylmethane, diaminodiphenylsulfone, isophoronediamine, naphthalenediamine, aniline novolak (a reaction product of aniline and formalin), N-methylaniline novolak (a reaction product of N-methylaniline and formalin), orthoethylaniline novolak (a reaction product of orthoethylaniline and formalin), a reaction product of 2-methylaniline and formalin, a reaction product of 2,6-diisopropylaniline and formalin, a reaction product of 2,6-diethylaniline and formalin, a reaction product of 2-ethyl-6-ethylaniline and formalin, a reaction product of 2,6-dimethylaniline and formalin, and an aniline resin obtained by reacting aniline and xylylene chloride, a reaction product of aniline and a substituted biphenyl (4,4'-bis(chloromethyl)-1,1'-biphenyl and 4,4'-bis(methoxymethyl)-1,1'-biphenyl, etc.) disclosed in Japanese Patent No. 6429862, a reaction product of aniline and a substituted phenyl (1,4-bis(chloromethyl)benzene, 1,4-bis(methoxymethyl)benzene and 1,4-bis(hydroxymethyl)benzene, etc.), 4,4'-(1,3-phenylenediisopropylidene)bis(aniline), 4,4'-(1,4-phenylenediisopropylidene)bis(aniline), a reaction product of aniline and diisopropenylbenzene, dimer diamine, etc. Furthermore, these may be used alone or in combination.

[0109]

[Maleimide compound]

A maleimide compound is a compound having one or more maleimide groups in the molecule. The curable resin composition of the present embodiment may contain a maleimide compound. Examples of the maleimide compound include, but are not limited to: 4,4'-diphenylmethane bismaleimide, polyphenylmethane maleimide, m-phenylene bismaleimide, 2,2'-bis[4-(4-maleimidophenoxy)phenyl]propane, 3,3'-dimethyl-5,5'-diethyl-4,4'-diphenylmethane bismaleimide, 4-methyl-1,3-phenylene bismaleimide, 4,4'-diphenylether bismaleimide, 4,4'-diphenylsulfone bismaleimide, 1,3-bis(3-maleimidophenoxy)benzene, 1,3-bis(4-maleimidophenoxy)benzene, and Xylox type maleimide compounds (anilix-maleimide, manufactured by Mitsui Chemicals Fine Co., Ltd.), biphenylaralkyl-type maleimide

compound (solidified by distilling off the solvent under reduced pressure from a resin solution containing the maleimide compound (M2) described in Example 4 of JP 2009-001783 A), bisaminocumylbenzene-type maleimide (maleimide compound described in WO 2020/054601 A), maleimide compounds having an indane structure described in JP6629692B or

5 WO2020/217679, maleimide compounds disclosed in “Continued Epoxy Resin CAS Number Story - Hardener CAS Number Memorandum No. 31 Bismaleimide (1)”, MATERIAL STAGE Vol. 18, No. 12, 2019” and “Continued Epoxy Resin CAS Number Story - Hardener CAS Number Memorandum No. 32 Bismaleimide (2)”, MATERIAL STAGE Vol. 19, No. 2, 2019. These compounds may be used alone or in combination.

10 [0110]

The amount of the maleimide compound added is preferably 10 times by mass or less, more preferably 5 times by mass or less, and particularly preferably 3 times by mass or less, relative to the compound represented by formula (1). The preferred lower limit is 0.01 times by mass or more, and more preferably 0.1 times by mass or more. Within the above

15 range, the effects of the heat resistance, dielectric properties, and low water absorption of the compound represented by formula (1) can be utilized.

[0111]

[Compound containing an ethylenically unsaturated bond]

The compound containing an ethylenically unsaturated bond is a compound that has

20 one or more ethylenically unsaturated bonds in the molecule that can be polymerized by heat or light, regardless of whether a polymerization initiator is used or not.

Examples of the compound containing an ethylenically unsaturated bond include, but are not limited to, a reaction product of the phenol resin with an ethylenically unsaturated bond-containing halogen-based compound (chloromethylstyrene, allyl chloride, methallyl

25 chloride, acrylic acid chloride, methacrylic acid chloride, etc.), a reaction product of an ethylenically unsaturated bond-containing phenol (2-allylphenol, 2-propenylphenol, 4-

allylphenol, 4-propenylphenol, eugenol, isoeugenol, etc.) with a halogen-based compound (1,4-bis(chloromethyl)benzene, 4,4'-bis(chloromethyl)biphenyl, 4,4'-difluorobenzophenone, 4,4'-dichlorobenzophenone, 4,4'-dibromobenzophenone, cyanuric chloride, etc.), a reaction product of an epoxy resin or alcohols with (meth)acrylic acids (acrylic acid, methacrylic acid, etc.), and an acid-modified product thereof. In addition, these may be used alone or in combination.

[0112]

[Isocyanate Resin]

An isocyanate resin is a compound having two or more isocyanate groups in the molecule. Examples of the isocyanate resin include, but are not limited to: aromatic diisocyanates such as p-phenylene diisocyanate, m-phenylene diisocyanate, p-xylylene diisocyanate, m-xylylene diisocyanate, 2,4-tolylene diisocyanate, 2,6-tolylene diisocyanate, 4,4'-diphenylmethane diisocyanate, and naphthalene diisocyanate; aliphatic or alicyclic diisocyanates such as isophorone diisocyanate, hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, hydrogenated xylene diisocyanate, norbornene diisocyanate, and lysine diisocyanate; polyisocyanates such as one or more biuret forms of isocyanate monomers or isocyanate forms obtained by trimerizing the diisocyanate compounds; and polyisocyanates obtained by a urethanization reaction between the isocyanate compounds and polyol compounds. These may be used alone or in combination.

[0113]

[Polyamide resin]

Examples of polyamide resins include reaction products of one or more of diamines, diisocyanates, and oxazolines with dicarboxylic acids, reaction products of diamines with acid chlorides, and ring-opening polymers of lactam compounds. These may be used alone or in combination.

Specific examples of the above-mentioned raw materials are shown below, but are

not limited to these.

<Diamines>

- Ethylenediamine, trimethylenediamine, tetramethylenediamine,
 pentamethylenediamine, hexamethylenediamine, heptamethylenediamine,
 5 octamethylenediamine, nonamethylenediamine, decanediamine, undecanediamine,
 dodecanediamine, tridecanediamine, tetradecanediamine, pentadecanediamine,
 hexadecanediamine, heptadecanediamine, octadecanediamine, nonadecanediamine,
 eicosanediamine, 2-methyl-1,5-diaminopentane, 2-methyl-1,8-diaminooctane, dimer diamine,
 cyclohexane diamine, bis-(4-aminocyclohexyl)methane, bis(3-methyl-4-
 10 aminocyclohexyl)methane, xylylene diamine, norbornane diamine, isophorone diamine,
 bisaminomethyltricyclodecane, phenylenediamine, diethyltoluenediamine,
 naphthalenediamine, diaminodiphenylmethane, bis(4-amino-3,5-dimethylphenyl)methane,
 bis(4-amino-3,5-diethylphenyl) methane, 4,4'-methylenebis-o-toluidine, 4,4'-methylenebis-o-
 ethylaniline, 4,4'-methylenebis-2-ethyl-6-methylaniline, 4,4'-methylenebis-2,6-
 15 diisopropylaniline, 4,4'-ethylenedianiline, diaminodiphenyl sulfone, diaminodiphenyl ether,
 1,3-bis(3-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 4,4-bis(4-
 aminophenoxy)biphenyl, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, bis[4-(4-
 aminophenoxy)phenyl]sulfone, 2,2-bis(3-amino-4-hydroxyphenyl)propane, 2,2-bis(4-
 aminophenyl)hexafluoropropane, 4,4'-(1,3-phenylenediisopropylidene)bisaniline, 4,4'-(1,4-
 20 phenylenediisopropylidene)bisaniline, 9,9-bis(4-aminophenyl)fluorene, 2,7-diaminofluorene,
 aminobenzylamine, diaminobenzophenone, etc.

<Diisocyanates>

- Benzene diisocyanate, toluene diisocyanate, 1,3-bis(isocyanatomethyl)benzene, 1,3-
 bis(isocyanatomethyl)cyclohexane, bis(4-isocyanatophenyl)methane, isophorone
 25 diisocyanate, 1,3-bis(2-isocyanato-2-propyl)benzene, 2,2-bis(4-
 isocyanatophenyl)hexafluoropropane, dicyclohexylmethane-4,4'-diisocyanate, etc.

<Dicarboxylic acids>

Oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, undecanedioic acid, dodecanedioic acid, terephthalic acid, isophthalic acid, 5-hydroxyisophthalic acid, 2-chloroterephthalic acid, 2-methylterephthalic acid, 5-methylisophthalic acid, 5-sodium sulfoisophthalic acid, hexahydroterephthalic acid, hexahydroisophthalic acid, cyclohexanedicarboxylic acid, biphenyldicarboxylic acid, naphthalenedicarboxylic acid, benzophenonedicarboxylic acid, furandicarboxylic acid, 4,4'-dicarboxydiphenyl ether, 4,4'-dicarboxydiphenyl sulfide, etc.

<Acid chlorides>

Acetyl chloride, acrylic acid chloride, methacrylic acid chloride, malonyl chloride, succinic acid dichloride, diglycolyl chloride, glutaric acid dichloride, suberic acid dichloride, sebacic acid dichloride, adipic acid dichloride, dodecandioyl dichloride, azelaoyl chloride, 2,5-furandicarbonyl dichloride, phthaloyl chloride, isophthaloyl chloride, terephthaloyl chloride, trimesic acid chloride, bis(4-chlorocarbonylphenyl)ether, 4,4'-diphenyldicarbonyl chloride, 4,4'-azodibenzoyl dichloride, etc.

<Lactams>

ϵ -caprolactam, ω -undecanelactam, ω -laurolactam, etc.

[0114]

[Polyimide resin]

Examples of polyimide resins include, but are not limited to, reaction products of the diamines described above with the following tetracarboxylic dianhydrides. These may be used alone or in combination.

<Tetracarboxylic dianhydrides>

4,4'-(hexafluoroisopropylidene)diphthalic anhydride, 5-(2,5-dioxotetrahydro-3-furanyl)-3-methyl-cyclohexene-1,2 dicarboxylic anhydride, pyromellitic dianhydride, 1,2,3,4-benzenetetracarboxylic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic dianhydride,

- 2,2',3,3'-benzophenonetetracarboxylic dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride, 3,3',4,4'-diphenylsulfone tetracarboxylic dianhydride, 2,2',3,3'-biphenyltetracarboxylic dianhydride, methylene-4,4'-diphthalic dianhydride, 1,1-ethylidene-4,4'-diphthalic dianhydride, 2,2'-propylidene-4,4'-diphthalic dianhydride, 1,2-ethylene-4,4'-diphthalic dianhydride, 1,3-trimethylene-4,4'-diphthalic dianhydride, 1,4-tetramethylene-4,4'-diphthalic dianhydride, 1,5-pentamethylene-4,4'-diphthalic dianhydride, 4,4'-oxydiphthalic dianhydride dianhydride, thio-4,4'-diphthalic dianhydride, sulfonyl-4,4'-diphthalic dianhydride, 1,3-bis(3,4-dicarboxyphenyl)benzene dianhydride, 1,3-bis(3,4-dicarboxyphenoxy)benzene dianhydride, 1,4-bis(3,4-dicarboxyphenoxy)benzene dianhydride, 1,3-bis[2-(3,4-dicarboxyphenyl)-2-propyl]benzene dianhydride, 1,4-bis[2-(3,4-dicarboxyphenyl)-2-propyl]benzene dianhydride, bis[3-(3,4-dicarboxyphenoxy)phenyl]methane dianhydride, bis[4-(3,4-dicarboxyphenoxy)phenyl]methane dianhydride, 2,2-bis[3-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride, 2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride, bis(3,4-dicarboxyphenoxy)dimethylsilane dianhydride, 1,3-bis(3,4-dicarboxyphenyl)-1,1,3,3-tetramethyldisiloxane dianhydride, 2,3,6,7-naphthalene tetracarboxylic dianhydride, 1,4,5,8-naphthalene tetracarboxylic dianhydride, 1,2,5,6-naphthalene tetracarboxylic dianhydride, 3,4,9,10-perylene tetracarboxylic dianhydride, 2,3,6,7-anthracene tetracarboxylic dianhydride, 1,2,7,8-phenanthrene tetracarboxylic dianhydride, ethylene tetracarboxylic dianhydride, 1,2,3,4-butane tetracarboxylic dianhydride, 1,2,3,4-cyclobutane tetracarboxylic dianhydride, cyclopentane tetracarboxylic dianhydride, cyclohexane-1,2,3,4-tetracarboxylic dianhydride, cyclohexane-1,2,4,5-tetracarboxylic dianhydride, 3,3',4,4'-bicyclohexyltetracarboxylic dianhydride, carbonyl-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, methylene-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, 1,2-ethylene-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, 1,1-ethylidene-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, 1,1-ethylidene-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride

dianhydride, 2,2-propylidene-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, oxy-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, thio-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, sulfonyl-4,4'-bis(cyclohexane-1,2-dicarboxylic acid) dianhydride, bicyclo[2,2,2]oct-7-ene-2,3,5,6-tetracarboxylic acid dianhydride, rel-[1S,5

5 R,6R]-3-oxabicyclo[3,2,1]octane-2,4-dione-6-spiro-3'-(tetrahydrofuran-2',5'-dione), 4-(2,5-dioxotetrahydrofuran-3-yl)-1,2,3,4-tetrahydronaphthalene-1,2-dicarboxylic anhydride, ethylene glycol-bis-(3,4-dicarboxylic anhydride phenyl)ether, 4,4'-biphenyl bis(trimellitic acid monoester acid anhydride), 9,9'-bis(3,4-dicarboxyphenyl)fluorene dianhydride, etc.

[0115]

10 [Cyanate ester resin]

Cyanate ester resin is a cyanate ester compound obtained by reacting a phenol resin with a cyanogen halide, and specific examples thereof include, but are not limited to:

dicyanatobenzene, tricyanatobenzene, dicyanatonaphthalene, dicyanatobiphenyl, 2,2'-bis(4-cyanatophenyl)propane, bis(4-cyanatophenyl)methane, bis(3,5-dimethyl-4-

15 cyanatophenyl)methane, 2,2'-bis(3,5-dimethyl-4-cyanatophenyl)propane, 2,2'-bis(4-cyanatophenyl)ethane, 2,2'-bis(4-cyanatophenyl)hexafluoropropane, bis(4-cyanatophenyl)sulfone, bis(4-cyanatophenyl)thioether, phenol novolac cyanate, and one in which the hydroxy groups of phenol-dicyclopentadiene co-condensates have been converted to cyanate groups. These may be used alone or in combination.

20 Furthermore, the cyanate ester compound whose synthesis method is described in JP2005-264154A is particularly preferred as the cyanate ester compound because of its low hygroscopicity, flame retardancy, and excellent dielectric properties.

The cyanate ester resin may contain a catalyst such as zinc naphthenate, cobalt naphthenate, copper naphthenate, lead naphthenate, zinc octylate, tin octylate, lead

25 acetylacetonate, or dibutyltin maleate in order to trimerize the cyanate group to form a sym-triazine ring, if necessary.

[0116]

The catalyst is preferably used in an amount of 0.0001 to 0.10 parts by mass, and more preferably 0.00015 to 0.0015 parts by mass, per 100 parts by mass of the cyanate ester resin.

5 [0117]

The curable resin composition of the present embodiment can be obtained by preparing the above-mentioned components in a predetermined ratio, pre-curing at 130 to 180°C for 30 to 500 seconds, and then post-curing at 150 to 200°C for 2 to 15 hours, whereby a sufficient curing reaction proceeds to obtain a cured product of the present embodiment.

10 Alternatively, the components of the curable resin composition can be uniformly dispersed or dissolved in a solvent or the like, and cured after removing the solvent.

[0118]

The method for preparing the curable resin composition of the present embodiment is not particularly limited, but each component may be mixed uniformly or may be

15 prepolymerized. For example, a mixture of the compound represented by the formula (1) and other compounds is heated in the presence or absence of a curing accelerator or a polymerization initiator, and in the presence or absence of a solvent to form a prepolymer.

Similarly, compounds such as amine compounds, compounds having ethylenically unsaturated bonds, maleimide compounds, cyanate ester compounds, polybutadiene and its
20 modified products, polystyrene and its modified products, inorganic fillers, and other additives may be added to form a prepolymer. The mixing of each component or prepolymerization is carried out using, for example, an extruder, kneader, roll, etc. in the absence of a solvent, and a reaction kettle with a stirrer, etc. in the presence of a solvent.

[0119]

25 As a method of uniform mixing, the materials are mixed at a temperature in the range of 50 to 100°C by kneading with a device such as a kneader, roll, or planetary mixer to obtain

a uniform resin composition. The obtained resin composition is crushed and then molded into a cylindrical tablet shape using a molding machine such as a tablet machine, or into a granular powder or powder compact, or these compositions can be melted on a surface support and molded into a sheet shape with a thickness of 0.05 mm to 10 mm to obtain a molded curable resin composition. The obtained molded body is a non-sticky molded body at 0 to 20°C, and even if stored at -25 to 0°C for one week or more, the flowability and curability are hardly reduced.

The obtained molded body can be molded into a cured product using a transfer molding machine or a compression molding machine.

10 [0120]

The curable resin composition of the present embodiment can be made into a varnish-like composition (hereinafter, simply referred to as “varnish”) by adding an organic solvent. The curable resin composition of the present embodiment can be dissolved in a solvent such as toluene, xylene, acetone, methyl ethyl ketone, methyl isobutyl ketone, dimethylformamide, dimethylacetamide, or N-methylpyrrolidone as necessary to form a varnish, which is then impregnated into a substrate such as glass fiber, carbon fiber, polyester fiber, polyamide fiber, alumina fiber, or paper, and dried by heating to obtain a prepreg, which is then hot-press molded to obtain a cured product of the curable resin composition of the present embodiment. The solvent used in this case is in an amount that occupies 10 to 70% by weight, preferably 15 to 70% by weight, in the mixture of the curable resin composition of the present embodiment and the solvent. In addition, if the composition is in a liquid state, a cured product of the curable resin containing carbon fiber can be obtained as it is, for example, by the RTM method.

[0121]

25 The curable composition of the present embodiment can also be used as a modifier for a film-type composition. Specifically, it can be used to improve flexibility and the like in

the B-stage. Such a film-type resin composition is obtained as a sheet-like adhesive by applying the curable resin composition of the present embodiment as the curable resin composition varnish onto a release film, removing the solvent under heating, and then performing B-stage formation. This sheet-like adhesive can be used as an interlayer insulating layer in a multilayer substrate or the like.

[0122]

The curable resin composition of the present embodiment can be heated and melted to reduce the viscosity, and impregnated into reinforced fibers such as glass fibers, carbon fibers, polyester fibers, polyamide fibers, and alumina fibers to obtain a prepreg. Specific examples thereof include, but are not particularly limited to: glass fibers such as E glass cloth, D glass cloth, S glass cloth, Q glass cloth, spherical glass cloth, NE glass cloth, and T glass cloth; inorganic fibers other than glass, and organic fibers such as polyparaphenylene terephthalamide (Kevlar (registered trademark), manufactured by DuPont), all aromatic polyamides, polyester, polyparaphenylene benzoxazole, polyimide, and carbon fibers. The shape of the substrate is not particularly limited, but examples thereof include woven fabric, nonwoven fabric, roving, chopped strand mat, and the like. In addition, as the weaving method of the woven fabric, plain weave, mat weave, twill weave, and the like are known, and these known weaves can be appropriately selected and used depending on the intended use and performance. In addition, woven fabrics that have been subjected to fiber opening treatment and glass woven fabrics that have been surface-treated with a silane coupling agent or the like are preferably used. The thickness of the substrate is not particularly limited, but is preferably about 0.01 to 0.4 mm. A prepreg can also be obtained by impregnating reinforcing fibers with the varnish and drying the fibers by heating.

[0123]

Moreover, a laminate can be manufactured using the prepreg. The laminate is not particularly limited as long as it has one or more prepreps, and may have any other layer. The

manufacturing method of the laminate can be appropriately applied by a generally known method, and is not particularly limited. For example, when molding a metal foil-clad laminate, a multi-stage press machine, a multi-stage vacuum press machine, a continuous molding machine, an autoclave molding machine, etc. can be used, and the prepregs are
5 laminated together and heated and pressurized to obtain a laminate. At this time, the heating temperature is not particularly limited, but is preferably 65 to 300 °C, and more preferably 120 to 270 °C. In addition, the pressure to be applied is not particularly limited, but if the pressure is too high, it is difficult to adjust the solid content of the resin of the laminate, and the quality is not stable, and if the pressure is too low, air bubbles and adhesion between the
10 laminates are deteriorated, so that 2.0 to 5.0 MPa is preferable, and 2.5 to 4.0 MPa is more preferable. The laminate of this embodiment can be suitably used as a metal foil-clad laminate described later by providing a layer made of metal foil.

The prepreg is cut into a desired shape and laminated with copper foil or the like as necessary. The laminate is then heated and cured while applying pressure thereto by press
15 molding, autoclave molding, sheet winding molding or the like, to obtain an electrical and electronic laminate (printed wiring board) or a carbon fiber reinforced material.

[0124]

The curable resin composition of this embodiment can also be made into a resin sheet. As a method for obtaining a resin sheet from the curable resin composition of this
20 embodiment, for example, a method of applying the curable resin composition onto a support film (support), followed by drying, and forming a resin composition layer on the support film can be mentioned. When the curable resin composition of this embodiment is used for a resin sheet, it is essential that the film softens under the temperature conditions (70°C to 140°C) of lamination in the vacuum lamination method, and simultaneously with lamination of the
25 circuit board, exhibits a fluidity (resin flow) that allows resin filling in via holes or through holes present in the circuit board, and it is preferable to blend each of the above components

so as to express such characteristics. In addition, in the obtained resin sheet or circuit board (copper-clad laminate, etc.), a phenomenon of locally showing different characteristic values due to phase separation or the like does not occur, and a uniform appearance is required so that a constant performance is expressed at any part.

5 [0125]

Here, the diameter of the through-holes in the circuit board is 0.1 to 0.5 mm, and the depth is 0.1 to 1.2 mm, and it is preferable to make it possible to fill the resin within this range. When laminating both sides of the circuit board, it is preferable to fill about 1/2 of the through-holes.

10 [0126]

A specific method for producing the resin sheet includes preparing a resin composition varnished by blending an organic solvent, applying the varnished resin composition to the surface of a support film (Y), and then drying the organic solvent by heating or blowing hot air or the like to form a resin composition layer (X).

15 [0127]

As the organic solvent used here, for example: ketones such as acetone, methyl ethyl ketone, cyclohexanone, etc.; acetate esters such as ethyl acetate, butyl acetate, cellosolve acetate, propylene glycol monomethyl ether acetate, carbitol acetate, etc.; carbitols such as cellosolve, butyl carbitol, etc.; aromatic hydrocarbons such as toluene, xylene, etc.; dimethylformamide, dimethylacetamide, N-methylpyrrolidone, etc. are preferably used, and it is also preferable to use the organic solvent in a proportion such that the nonvolatile content is 30 to 60 mass %.

[0128]

The thickness of the resin composition layer (X) formed must be equal to or greater than the thickness of the conductor layer. Since the thickness of the conductor layer of the circuit board is in the range of 5 to 70 μm , the thickness of the resin composition layer (X) is

25

preferably 10 to 100 μm . The resin composition layer (X) in this embodiment may be protected with a protective film described below. By protecting the resin composition layer with a protective film, it is possible to prevent the adhesion of dirt and the like to the surface of the resin composition layer and scratches.

5 [0129]

Examples of the support film and the protective film include: polyolefins such as polyethylene, polypropylene, and polyvinyl chloride; polyesters such as polyethylene terephthalate (PET) and polyethylene naphthalate; polycarbonate, polyimide, and further release paper and metal foils such as copper foil and aluminum foil. The support film and the
10 protective film may be subjected to a mud treatment, a corona treatment, and/or a release treatment. The thickness of the support film is not particularly limited, but is in the range of 10 to 150 μm , and preferably 25 to 50 μm . The thickness of the protective film is preferably 1 to 40 μm .

[0130]

15 The support film (Y) is peeled off after laminating the resin composition layer onto a circuit board or after forming an insulating layer by heat curing the resin composition layer. If the support film (Y) is peeled off after the resin composition layer constituting the resin sheet is heat cured, adhesion of dust and the like during the curing process can be prevented. When peeling off after curing, the support film is previously subjected to a release treatment.

20 [0131]

A multilayer printed circuit board can be manufactured from the resin sheet obtained as described above. For example, when the resin composition layer (X) is protected by a protective film, the protective film is peeled off, and then the resin composition layer (X) is laminated on one or both sides of the circuit board so as to be in direct contact with the circuit
25 board, for example, by a vacuum lamination method. The lamination method may be a batch method or a continuous method using a roll. If necessary, the resin sheet and the circuit board

may be heated (preheated) before lamination. The lamination conditions are preferably a pressure bonding temperature (lamination temperature) of 70 to 140°C, a pressure bonding pressure of 1 to 11 kgf/cm² (9.8×10^4 to 107.9×10^4 N/m²), and lamination is preferably performed under reduced pressure of 20 mmHg (26.7 hPa) or less.

5 [0132]

In addition, the curable resin composition of the present embodiment can be used to manufacture a semiconductor device. Examples of the semiconductor device includes a dual in-line package (DIP), a quad flat package (QFP), a ball grid array (BGA), a chip size package (CSP), a small outline package (SOP), a thin small outline package (TSOP), a thin quad flat
10 package (TQFP), etc.

[0133]

The curable resin composition of the present embodiment and its cured product can be used in a wide range of fields. Specifically, it can be used in various applications such as molding materials, adhesives, composite materials, and paints. The cured product of the
15 curable resin composition described in this embodiment exhibits excellent heat resistance and dielectric properties, and is therefore suitable for use in electrical and electronic components such as semiconductor element encapsulants, liquid crystal display element encapsulants, organic EL element encapsulants, laminates (printed wiring boards, BGA substrates, build-up substrates, etc.), carbon fiber reinforced plastics, glass fiber reinforced plastics, and other
20 lightweight and high-strength structural composite materials, 3D printing, etc.

Example

[0134]

The present invention will now be described in more detail with reference to examples. Unless otherwise specified, all parts are by weight. However, the present invention
25 is not limited to these examples.

[0135]

The various analytical methods used in the examples are described below.

<Weight average molecular weight (Mw), number average molecular weight (Mn), and GPC area percentage of the compound in which n in formula (1) is 1 in the total amount of compounds>

5 Weight average molecular weight (Mw) and number average molecular weight (Mn) were calculated based on polystyrene equivalent using a polystyrene standard solution.

GPC: online degassing unit (DGU-20A3R), binary liquid delivery unit (LC-20AD), autosampler (SIL-20AHT), refractive index detector (RID-20A), column oven (CTO-20A), system controller (CBM-20A) (all manufactured by Shimadzu Corporation)

10 Columns: Shodex KF-603 x 1, KF-602.5 x 1, KF-602 x 1, KF-601 x 1 (all manufactured by Showa Denko K.K.)

Guard column: Shodex KF-G 4A (manufactured by Showa Denko K.K.)

Connected eluent: tetrahydrofuran

Flow rate: 1.5 ml/min.

15 Column temperature: 40°C

Detection: RI (differential refractive index detector)

Slice data of the chromatogram was obtained, and the ratio (area percentage) of the area of the slice data corresponding to the compound represented by formula (1) where n is 1 to the sum of the areas (time integral values of signal values) of the slice data corresponding to the compounds represented by formula (1) was calculated.

20

<Contents of compounds represented by formulas (2) to (4)>

HP-LC: binary liquid delivery unit (LC-20AB), online degassing unit (DGU-20A3), autosampler (SIL-20A), column oven (CTO-20A), system controller (CBM-20A), photodiode array detector (SPD-M20A) (all manufactured by Shimadzu Corporation)

25 Column: ODS-2 (manufactured by GL Sciences)

Connected eluent: tetrahydrofuran:water=3:1 (no gradient)

Flow rate: 0.5 ml/min.

Column temperature: 40°C

Detection: PDA (photodiode array detector)

Detector: 274 nm

5 The sum of the peak areas (α) of the compounds represented by formulas (2) to (4) and the peak area (β) of the compound where n in formula (1) is 1 in the chromatogram obtained by high performance liquid chromatography (HP-LC) were calculated, and (α/β) was calculated.

<Structural analysis>

10 LC-MS: ultra-high performance liquid chromatography (UHPLC) system (Ultimate 3000), mass spectrometer (Q-Exactive (registered trademark)) (both manufactured by Thermo Fisher Scientific)

Column: ODS-2 (manufactured by GL Sciences)

Connected eluent: tetrahydrofuran:water=3:1 (no gradient)

15 Flow rate: 0.5 ml/min.

Ionization mode: ESI

Mass range: m/z=150-2000

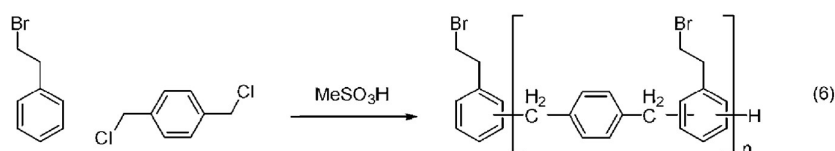
[0136]

[Synthesis Example 1]

20 An aspirator and a base trap were installed on a flask equipped with a thermometer, a condenser, and a stirrer. 370.1 parts of (2-bromoethyl)benzene (manufactured by Tokyo Chemical Industry Co., Ltd.), 175.1 parts of α,α' -dichloro-p-xylene (manufactured by Tokyo Chemical Industry Co., Ltd.), and 27.3 parts of methanesulfonic acid (manufactured by Tokyo Chemical Industry Co., Ltd.) were charged into this flask, and the reaction was carried out at
25 130°C for 6 hours while collecting the generated hydrogen chloride with the base trap. 50 parts of methanol and 700 parts of cyclohexane were added, and the mixture was neutralized

with 56.8 parts of a 30% aqueous sodium hydroxide solution, and the organic layer was washed with 100 parts of water five times. The solvent and excess (2-bromoethyl)benzene were distilled off under heating and reduced pressure to obtain 380 parts of a compound (BEB-1) having a (2-bromoethyl)benzene structure represented by the following formula (6) as a liquid resin (Mn: 938, Mw: 1290). The GPC chart of the obtained compound is shown in Figure 1. The average value n_{ave} of the repeating unit n calculated from the area percentage in the GPC chart was 2.2. In addition, the ratio of the area (area percentage) of the compound having a structure in which n in formula (6) is 1 to the total area of the compounds having a structure represented by formula (6) in the GPC chart was 45%.

10 [0137]



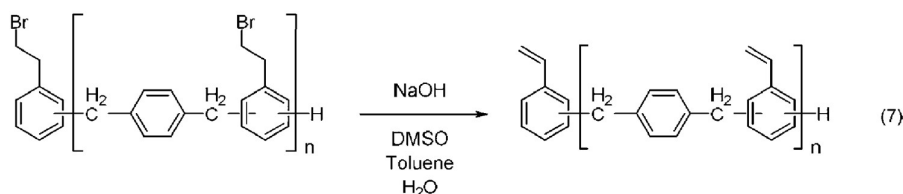
[0138]

[Example 1]

300 parts of BEB-1 obtained in Synthesis Example 1, 245 parts of toluene, 735 parts of dimethyl sulfoxide, 0.15 parts of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, and 146.4 parts of 50 wt% aqueous sodium hydroxide solution were added to a flask equipped with a thermometer, a condenser, and a stirrer, and the reaction was continued for 6 hours at 40 °C. 100 parts of water was added, the organic layer was washed, and the organic layer was returned to the reaction vessel. 735 parts of dimethyl sulfoxide and 9.8 parts of 50 wt% aqueous sodium hydroxide solution were added, and the reaction was continued for 1 hour at 40 °C again, 1050 parts of toluene were added, and the organic layer was repeatedly washed with 100 parts of water until the wastewater became neutral. The mixture was concentrated under reduced pressure using an evaporator, and 180 parts of a compound (O-1) having two or more styrene structures in the molecule represented by the following formula

(7) was obtained. The GPC chart of the obtained compound is shown in FIG. 2. ^1H -NMR data (deuterated chloroform) of the obtained compound is shown in FIG. 3. Signals derived from vinyl groups were observed at 5.10-5.30 ppm, 5.50-5.85 ppm, and 6.60-6.80 ppm in the ^1H -NMR chart. The average value n_{ave} of the repeating unit n calculated from the area percentage of the GPC chart was 2.3. In addition, the ratio of the area (area percentage) of the compound having a structure in which n in formula (7) is 1 to the total area of the compounds having a structure represented by formula (7) in the GPC chart was 40% (the average molecular weight of the resin component was M_n : 803, M_w : 1190). The LC-MS chart is shown in FIG. 4, and the HP-LC chart is shown in FIG. 5. Compounds V to Y shown in Table 1 were detected by LC-MS analysis (Table 1 shows the representative structural formulas). In compound W, the positions of the 2-phenylethanol structure and the styrene structure are in no particular order. In compound X, the positions of the 2-phenylethanol structure, the styrene structure, and the 2-phenylacetaldehyde structure are in no particular order. In compound Y, the positions of the 2-phenylethanol structure and the ethylbenzene structure are in no particular order, and the phenylethyl group may be bonded to any aromatic ring.

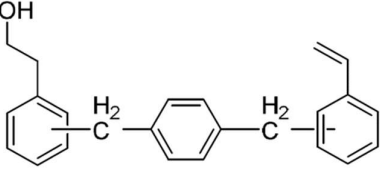
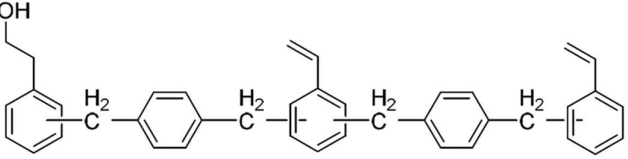
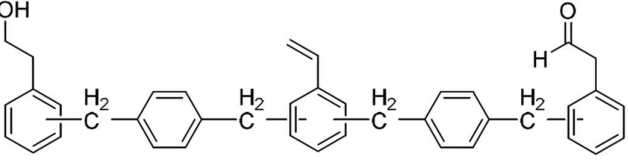
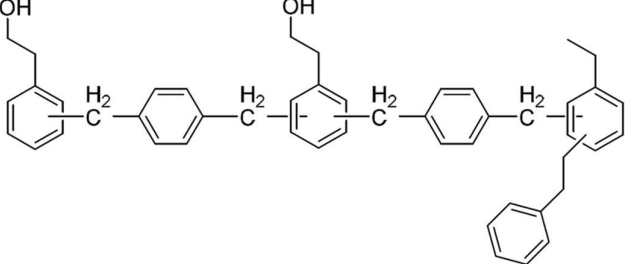
[0139]



[0140]

20 [Table 1]

Compound	HPLC Retention Time (min)	Representative Structural Formula

V	6.4	⁶² 
W	6.6	
X	7.6	
Y	8.0	

[0141]

[Example 2]

300 parts of BEB-1 obtained in Synthesis Example 1, 245 parts of toluene, 735 parts of dimethyl sulfoxide, 0.15 parts of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, and 107.4 parts of 50 wt% aqueous sodium hydroxide solution were added to a flask equipped with a thermometer, a cooling tube, and a stirrer, and the reaction was continued at 40 °C for 6 hours. 100 parts of water were added, the organic layer was washed, and the organic layer was returned to the reaction vessel. 735 parts of dimethyl sulfoxide and 9.8 parts of 50 wt% aqueous sodium hydroxide solution were added, and the reaction was continued again at 40 °C for 1 hour, 1050 parts of toluene were added, and the organic layer was repeatedly washed with 100 parts of water until the wastewater became neutral. The mixture was concentrated under reduced pressure using an evaporator, and 180 parts of a compound (O-2) having two or more styrene structures in the molecule represented by the formula (7)

was obtained. The GPC chart of the obtained compound is shown in FIG. 6. The average value n_{ave} of the repeating unit n calculated from the area percentage of the GPC chart was 2.4. In addition, the ratio (area percentage) of the area of the compound having a structure in which n in formula (7) is 1 to the total area of the compound having the structure represented by formula (7) in the GPC chart was 41% (the average molecular weight of the resin component was M_n : 799, M_w : 1297). The HP-LC chart is shown in FIG.

[0142]

[Example 3]

300 parts of BEB-1 obtained in Synthesis Example 1, 375 parts of toluene, 1125 parts of dimethyl sulfoxide, 0.15 parts of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, and 146.4 parts of 50 wt% aqueous sodium hydroxide solution were added to a flask equipped with a thermometer, a cooling tube, and a stirrer, and the reaction was continued for 6 hours at 40 °C. 100 parts of water was added, the organic layer was washed, and the organic layer was returned to the reaction vessel. 735 parts of dimethyl sulfoxide and 9.8 parts of 50 wt% aqueous sodium hydroxide solution were added, and the reaction was continued for 1 hour at 40 °C again, 1050 parts of toluene were added, and the organic layer was repeatedly washed with 100 parts of water until the wastewater became neutral. The mixture was concentrated under reduced pressure using an evaporator, and 180 parts of compound (O-3) having two or more styrene structures in the molecule represented by the formula (7) was obtained. The GPC chart of the obtained compound is shown in FIG. 8. The average value n_{ave} of the repeating unit n calculated from the area percentage of the GPC chart was 2.3. In addition, the ratio (area percentage) of the area of the compound having a structure in which n in formula (7) is 1 to the total area of the compound having the structure represented by formula (7) in the GPC chart was 35% (the average molecular weight of the resin component was M_n : 834, M_w : 1170). The HP-LC chart is shown in FIG.

[0143]

[Example 4]

300 parts of BEB-1 obtained in Synthesis Example 1, 245 parts of toluene, 735 parts of dimethyl sulfoxide, 0.15 parts of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl free radical, and 146.4 parts of 50 wt% aqueous sodium hydroxide solution were added to a flask
 5 equipped with a thermometer, a cooling tube, and a stirrer, and the reaction was continued for 6 hours at 25 ° C. 100 parts of water was added, the organic layer was washed, and the organic layer was returned to the reaction vessel. 735 parts of dimethyl sulfoxide and 9.8 parts of 50 wt% aqueous sodium hydroxide solution were added, and the reaction was continued for 1 hour at 25 °C again, 1050 parts of toluene were added, and the organic layer was
 10 repeatedly washed with 100 parts of water until the wastewater became neutral. The mixture was concentrated under reduced pressure using an evaporator, and 180 parts of compound (O-4) having two or more styrene structures in the molecule represented by the formula (7) was obtained. The GPC chart of the obtained compound is shown in FIG. 10. The average value n_{ave} of the repeating unit n calculated from the area percentage of the GPC chart was 2.5. In
 15 addition, the ratio (area percentage) of the area of the compound having a structure in which n in formula (7) is 1 to the total area of the compound having the structure represented by formula (7) in the GPC chart was 41% (the average molecular weight of the resin component was M_n : 802, M_w : 1291). The HP-LC chart is shown in FIG.

[0144]

20 Comparative Synthesis Example 1:

A flask equipped with a thermometer, a cooling tube, and a stirrer was equipped with an aspirator and a base trap. 296 parts of (2-bromoethyl)benzene (Tokyo Chemical Industry Co., Ltd.), 70 parts of α,α' -dichloro-*p*-xylene (Tokyo Chemical Industry Co., Ltd.), and 18.4 parts of methanesulfonic acid (Tokyo Chemical Industry Co., Ltd.) were charged into the
 25 flask, and the reaction was carried out at 130°C for 6 hours while collecting the generated hydrogen chloride with a base trap. 50 parts of methanol and 700 parts of cyclohexane were

added, and the mixture was neutralized with 26.8 parts of a 30% aqueous sodium hydroxide solution, and the organic layer was washed five times with 100 parts of water. The solvent and excess (2-bromoethyl)benzene were distilled off under heating and reduced pressure to obtain 171 parts of a compound (BEB-2) having a (2-bromoethyl)benzene structure represented by the formula (6) as a liquid resin (Mn: 793, Mw: 970). The GPC chart of the obtained compound is shown in Figure 12. The average value n_{ave} of repeating units n calculated from the area percentage in the GPC chart was 1.6. In addition, the ratio of the area of the compound having a structure in which n in formula (6) is 1 to the total area of the compound having a structure represented by formula (6) in the GPC chart (GPC area percentage) was 65%.

[0145]

Comparative Synthesis Example 2

: 22 parts of BEB-2 obtained in Comparative Synthesis Example 1, 50 parts of toluene, 150 parts of dimethyl sulfoxide, 15 parts of water, and 5.4 parts of sodium hydroxide were added to a flask equipped with a thermometer, a cooling tube, and a stirrer, and the reaction was continued at 40°C for 6 hours. 100 parts of toluene were added, and the organic layer was repeatedly washed with 100 parts of water until the wastewater became neutral. The mixture was concentrated under reduced pressure using an evaporator, and 12.5 parts of a compound (O-5) having two or more styrene structures in the molecule represented by the formula (7) was obtained. The GPC chart of the obtained compound is shown in FIG. 13. The average value n_{ave} of the repeating unit n calculated from the area percentage of the GPC chart was 2.2. In addition, the ratio of the area of the compound having a structure in which n in formula (7) is 1 to the total area of the compound having a structure represented by formula (7) in the product (GPC area percentage) was 65% (the average molecular weight of the resin component was Mn: 624, Mw: 778). The HP-LC chart is shown in FIG.

[0146]

As molecular weight data of compounds O-1 to O-5, the number average molecular weight (Mn), weight average molecular weight (Mw), and the area percentage of the compound in formula (1) where n is 1 are shown as the "n=1 content (GPC area %)", the sum α of the peak areas of the compounds in formulas (2) to (4) in the chromatogram obtained by HPLC are shown as the "total content of compounds V to Y in each compound (HP-LC area)", the peak area β of the compound in formula (1) where n is 1 are shown as the "n=1 content (HP-LC area)", and the value obtained by dividing α by β (α/β) are shown in Table 2.

[0147]

[Table 2]

Compound		O-1	O-2	O-3	O-4	O-5
Molecular Weight Data	Mn	803	799	834	802	624
	Mw	1190	1297	1170	1291	778
	n=1 content (GPC area)	40	41	35	41	65
α	total content of compounds V to Y in each compound (HP-LC area)	2.7	2.2	0.9	3.5	2.2
β	n=1 content (HP-LC area)	37	35	33	41	59
α / β		0.07	0.06	0.03	0.09	0.04

[0148]

[Examples 5 to 8, Comparative Example 1]

<Stability test after dissolving in solvent>

1.2 g of compounds O-1 to O-5 and 0.8 g of toluene were mixed in a 5 mL glass sample bottle, and then the mixture was stirred at 25°C for 1 hour at 100 rpm using a roller mixer (MIX-ROTAR VMR-5: manufactured by AS ONE Corporation) to prepare a toluene solution with a solid content of 60 wt% for each compound. The resulting solution was stored in a freezer at -18°C, and samples were taken out after 10 minutes and evaluated according to the following criteria. The results are shown in Table 3.

- When no crystals were precipitated: ○

- When crystals were precipitated: ×

[0149]

<Dielectric constant test/dielectric tangent test>

Compounds O-1 to O-5 were sandwiched between mirror-finished copper foil (T4X: manufactured by Fukuda Metal Copper Foil Co., Ltd.) and vacuum press molded, and cured at 220°C for 2 hours. After that, samples were cut using a laser cutter to a size of 1.7 mm wide x 100 mm long x 0.2 mm thick, and tests were performed using a 10 GHz cavity resonator manufactured by ATE Co., Ltd. by a cavity resonator perturbation method. The evaluation results are shown in Table 3.

10 [0150]

[Table 3]

		Example 5	Example 6	Example 7	Example 8	Comparative Example 1
Compound		O-1	O-2	O-3	O-4	O-5
Stability after Dissolving in Solvent		○	○	○	○	×
Dielectric property	Dielectric constant (10GHz)	2.5	2.5	2.5	2.5	2.5
	Dielectric tangent (10 GHz)	0.0015	0.0015	0.0013	0.0019	0.0016

[0151]

From the results in Table 3, it was confirmed that Examples 5 to 8 have excellent stability after dissolving in a solvent and excellent dielectric properties.

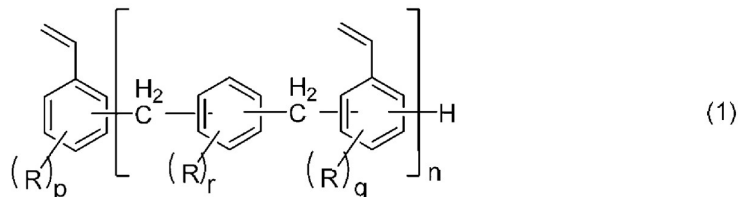
15 This application claims priority based on Japanese Patent Application No. 2022-54487 filed on March 29, 2022.

CLAIMS

[Claim 1]

A compound represented by the following formula (1), wherein the compound in which n in formula (1) is 1 is less than 50% of the total amount of the compound in terms of

5 GPC area percentage:

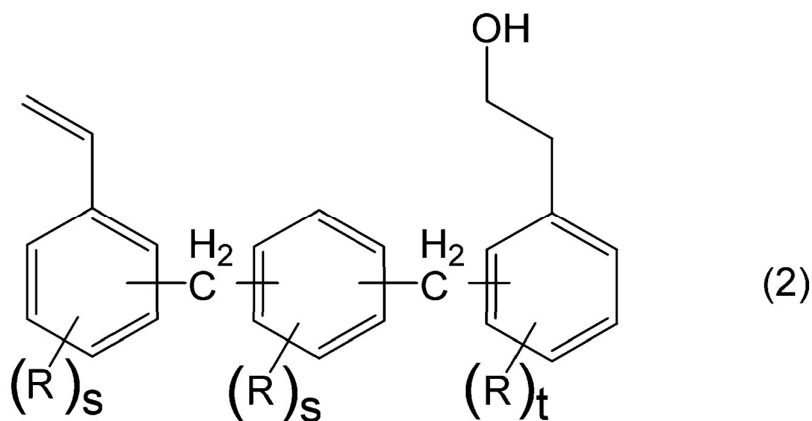


(In formula (1), each of a plurality of R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p and r are integers from 0 to 4, and q is an integer from 0 to 3. n is a number of repetitions, and the average value n_{ave} of n satisfies

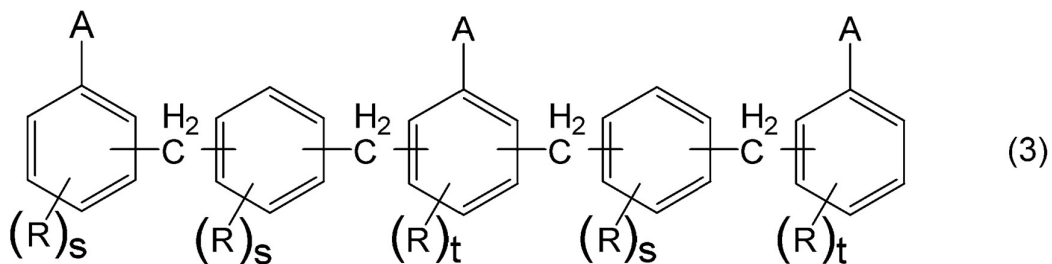
10 $1 \leq n_{ave} \leq 20$.)

[Claim 2]

The compound according to claim 1, wherein a sum (α) of HP-LC peak areas of compounds represented by the following formulas (2) to (4) divided by a HP-LC peak area (β) of the compound where n in formula (1) is 1 gives a value (α/β) of 0.10 or less.



(In formula (2), each of a plurality of R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. Each of the multiple s's independently represents an integer of 0 to 4.)

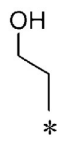


(In formula (3), each of the multiple R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. Each of the multiple A's independently represents any one of the following formulas (3-a) to (3-c). Each of the multiple s's

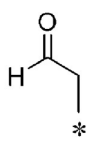
5 independently represents an integer of 0 to 4, and t is an integer of 0 to 3.)



(3-a)

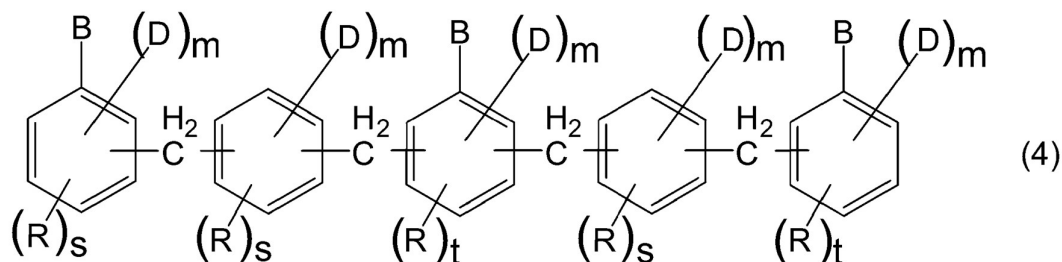


(3-b)

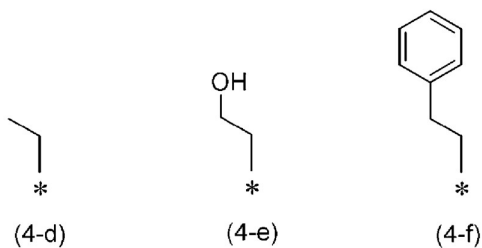


(3-c)

(In formulas (3-a) to (3-c), * represents a bonding position with the aromatic ring of the compound of formula (3).)



10 (In formula (4), each of the multiple R's independently represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. Each of the multiple B's independently represents the following formula (4-d) or (4-e). D represents the formula (4-f). Each of the multiple s's independently represents an integer from 0 to 4, and t's represent integers from 0 to 3. One of the five m's in formula (4) is 1, and the other four are 0.)



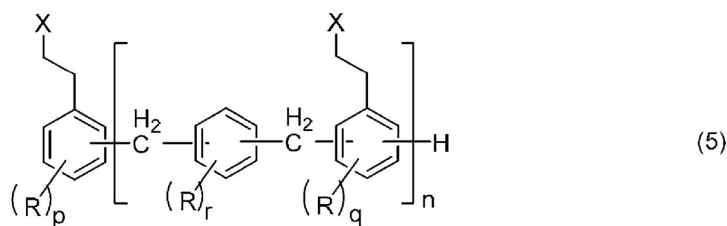
(In formulas (4-d) to (4-f), * represents a bonding position with the aromatic ring of the compound of formula (4).)

[Claim 3]

5 The compound according to claim 1 or 2, wherein in the formula (1), $p = 0$, $q = 0$, and $r = 0$.

[Claim 4]

 The compound according to any one of claims 1 to 3, wherein the compound represented by formula (1) is derived from a compound represented by formula (5):



10

(In formula (5), each of a plurality of R's exists independently and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p and r are integers of 0 to 4, q is an integer of 0 to 3, n is a number of repetitions, and the average value n_{ave} of n satisfies $1 \leq n_{ave} \leq 20$. X represents a halogen atom.)

15 [Claim 5]

 A mixture according to any one of claims 1 to 4, further comprising a polymerization inhibitor.

[Claim 6]

 A curable resin composition comprising a compound according to any one of claims
20 1 to 4 or a mixture according to claim 5.

[Claim 7]

The curable resin composition according to claim 6, containing one or more of a polyphenylene ether compound, polybutadiene and modified products thereof, and polystyrene and modified products thereof.

5 [Claim 8]

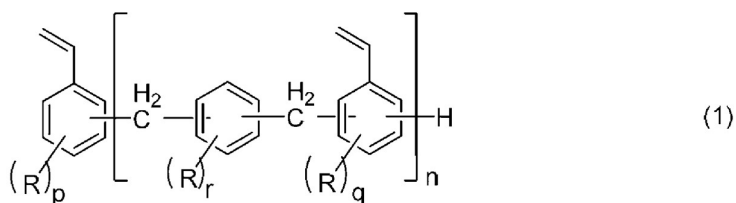
The curable resin composition according to claim 6 or 7, containing a radical polymerization initiator.

[Claim 9]

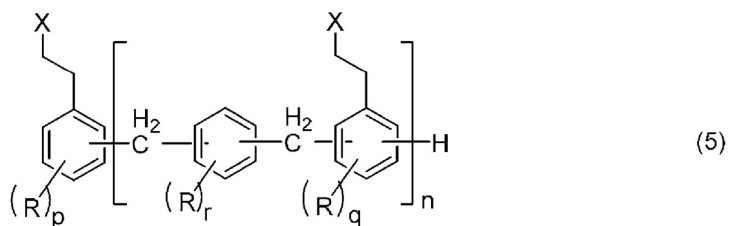
A cured product obtained by curing the compound according to any one of claims 1
10 to 4, the mixture according to claim 5, or the curable resin composition according to any one of claims 6 to 8.

[Claim 10]

A method for producing a compound represented by the following formula (1),
which is obtained by subjecting a compound represented by the following formula (5) to a
15 dehydrohalogenation reaction in a solvent having a volume 4 to 7 times the weight of the compound represented by the following formula (5) in the presence of a basic catalyst:



(In formula (1), each of a plurality of R's is independently present and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p and r are
20 integers from 0 to 4, q is an integer from 0 to 3, n is a repetition number, and the average value n_{ave} of n satisfies $1 \leq n_{ave} \leq 20$.)



(In formula (5), each of a plurality of R's is independently present and represents a hydrocarbon group or a halogenated alkyl group having 1 to 10 carbon atoms. p and r are integers from 0 to 4, q is an integer from 0 to 3, n is a repetition number, and the average value n_{ave} of n satisfies $1 \leq n_{ave} \leq 20$. X represents a halogen atom.)

[Claim 11]

The method for producing a compound according to claim 10, wherein the solvent is a mixed solvent of a polar aprotic solvent and a water-insoluble solvent.

[Claim 12]

The method for producing a compound according to claim 11, wherein the polar aprotic solvent is used in an amount 1 to 10 times by weight of the water-insoluble solvent.

[Claim 13]

The method for producing the compound according to claim 11 or 12, wherein the polar aprotic solvent is dimethyl sulfoxide, and the water-insoluble solvent is toluene.