

DESCRIPTION

Title of Invention

5 (METH)ACRYLIC COPOLYMER, METHOD FOR PRODUCING SAME, RESIN
COMPOSITION AND ANTIFOULING PAINT COMPOSITION

TECHNICAL FIELD

[0001]

10 The present invention relates to a (meth)acrylic copolymer, a method for
producing the same, a polymerizable monomer, a resin composition, and an antifouling
paint composition.

Priority is claimed on Japanese Patent Application No. 2017-065457, filed on
March 29, 2017, the content of which is incorporated herein by reference.

15

BACKGROUND ART

[0002]

It is known that marine structures or ships are coated with antifouling paints in
order to prevent adhesion of marine organisms that cause corrosion of a portion in
20 contact with sea water or a decrease in sailing speed. In the related art, self-polishing
antifouling paints are known as antifouling paints. A self-polishing antifouling paint
typically contains a hydrolyzable resin and an antifouling agent. In a case of a coating
film obtained from such an antifouling paint, the surface of the coating film is gradually
dissolved in sea water to renew the surface (self-polished), and the surface of the coating
25 film is constantly exposed to an antifouling agent. Therefore, an antifouling effect is

exhibited for a long period of time.

[0003]

As the self-polishing antifouling paint, for example, a paint composition (PTL 1) which contains a copolymer having a constituent unit derived from a silicon-containing polymerizable monomer and a constituent unit derived from a metal atom-containing polymerizable monomer having a divalent metal atom, and an antifouling paint composition (PTL 2) which contains a hydrolyzable resin containing a silicon-containing group and a triorganosilyloxycarbonyl group have been suggested.

10 Citation List

Patent Literature

[0004]

[PTL 1] Japanese Unexamined Patent Application, First Publication No. 2004-300410

15 [PTL 2] PCT International Publication No. 2011/046087

DISCLOSURE OF INVENTION

Technical Problem

[0005]

20 The paint composition described in PTL 1 forms a coating film that exhibits an excellent antifouling effect even in a case where the paint composition does not contain an antifouling agent. However, there is a problem in that the surface smoothness of the coating film is degraded.

The antifouling paint composition described in PTL 2 has a problem of degraded surface smoothness of a coating film to be formed, compared to the paint composition

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described in PTL 1.

[0006]

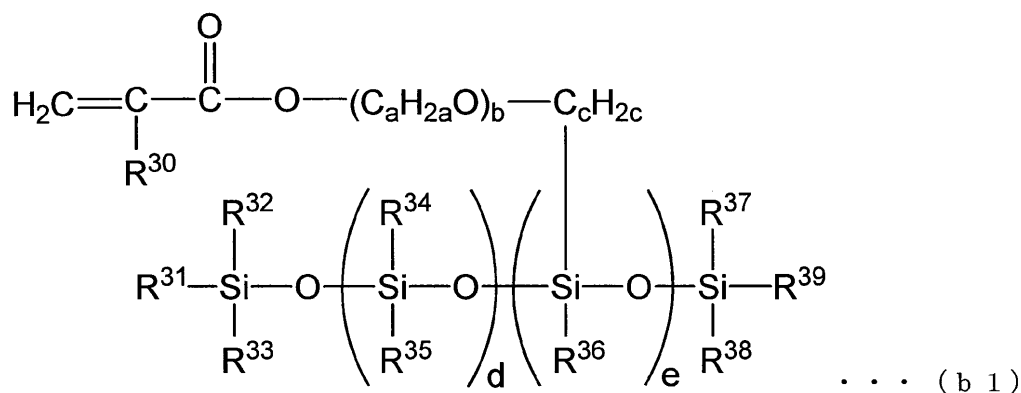
An object of the present invention is to provide a (meth)acrylic copolymer which enables formation of a coating film with excellent surface smoothness, a resin composition and an antifouling paint composition, and a method for producing the (meth)acrylic copolymer.

Solution to Problem

[0007]

The present invention has the following aspects.

[1] A (meth)acrylic copolymer, including: a constituent unit (B) derived from a polysiloxane block-containing polymerizable monomer (b) represented by Formula (b1).

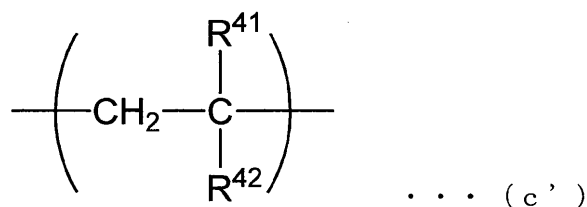


(in Formula (b1), R^{30} represents a hydrogen atom or a methyl group, a represents an integer of 2 to 5, b represents a number of 0 to 50, c represents an integer of 0 to 18, d represents a number of 1 to 1000, e represents a number of 1 to 80, R^{31} to R^{39} each represents an alkyl group, an alkoxy group, a phenyl group, a substituted phenyl group, a phenoxy group, or a substituted phenoxy group)

[2] The (meth)acrylic copolymer according to [1], further including: a

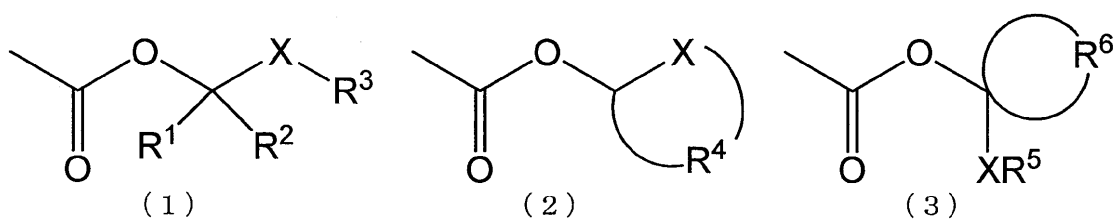
constituent unit (C) derived from a macromonomer (c).

[3] The (meth)acrylic copolymer according to [2], in which the macromonomer (c) has two or more constituent units represented by Formula (c').

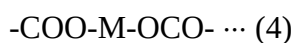


- 5 (in Formula (c'), R⁴¹ represents a hydrogen atom, a methyl group, or CH₂OH, R⁴² represents OR⁴³, a halogen atom, COR⁴⁴, COOR⁴⁵, CN, CONR⁴⁶R⁴⁷, or R⁴⁸, R⁴³ to R⁴⁷ each independently represents a hydrogen atom, an alkyl group having an unsubstituted or substituted group, an alicyclic group having an unsubstituted or substituted group, an aryl group having an unsubstituted or substituted group, a
- 10 heteroaryl group having an unsubstituted or substituted group, a non-aromatic heterocyclic group having an unsubstituted or substituted group, an aralkyl group having an unsubstituted or substituted group, an alkaryl group having an unsubstituted or substituted group, or an organosilyl group having an unsubstituted or substituted group, and R⁴⁸ represents an aryl group having an unsubstituted or substituted group or a
- 15 heteroaryl group having an unsubstituted or substituted group)

- [4] The (meth)acrylic copolymer according to any one of [1] to [3], further including: at least one constituent unit (A) selected from the group consisting of a constituent unit (A1) having at least one structure (I) represented by Formula (1), Formula (2), or Formula (3), a constituent unit (A2) containing a
- 20 triorganosilyloxycarbonyl group, and a constituent unit (A3) having at least one structure (III) represented by Formula (4) or Formula (5).

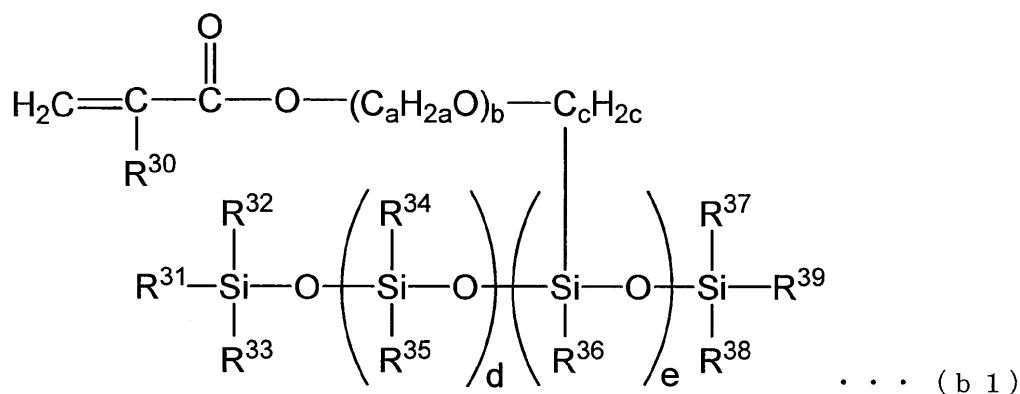


(in Formulae (1) to (3), X represents -O-, -S-, or -NR¹⁴-, R¹⁴ represents a hydrogen atom or an alkyl group, R¹ and R² each represents a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, R³ and R⁵ each represents an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group, or an aryl group, and R⁴ and R⁶ each represents an alkylene group having 1 to 10 carbon atoms)



(in Formulae (4) and (5), M represents Zn, Cu, Mg, or Ca, and R²² represents a monovalent organic acid residue)

[5] A method for producing a (meth)acrylic copolymer, including: a step of polymerizing a monomer mixture which contains a polysiloxane block-containing polymerizable monomer (b) represented by Formula (b1) and a polymerizable monomer different from the polysiloxane block-containing polymerizable monomer (b) to obtain a (meth)acrylic copolymer.



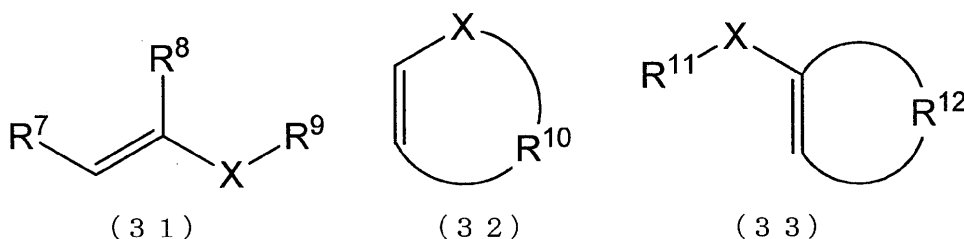
(in Formula (b1), R^{30} represents a hydrogen atom or a methyl group, a represents an integer of 2 to 5, b represents a number of 0 to 50, c represents an integer of 0 to 18, d represents a number of 1 to 1000, e represents a number of 1 to 80, R^{31} to R^{39} each represents an alkyl group, an alkoxy group, a phenyl group, a substituted phenyl group, a phenoxy group, or a substituted phenoxy group)

[6] A resin composition, including: the (meth)acrylic copolymer according to any one of [1] to [4].

[7] The resin composition according to [6], further including: silicone oil.

[8] The resin composition according to [6] or [7], further including: an organic solvent.

[9] The resin composition according to any one of [6] to [8], in which the (meth)acrylic copolymer has the constituent unit (A1), and the resin composition further contains at least one compound (Y) selected from the group consisting of a compound represented by Formula (31), a compound represented by Formula (32), and a compound represented by Formula (33).



(in Formulae (31) to (33), X represents -O-, -S-, or -NR¹⁴-, R¹⁴ represents a hydrogen atom or an alkyl group, R⁷ represents a hydrogen atom or an alkyl group having 1 to 9 carbon atoms, R⁸ represents a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, R⁹ and R¹¹ each represents an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group, or an aryl group, R¹⁰ represents a single bond or an alkylene group

having 1 to 9 carbon atoms, and R¹² represents an alkylene group having 1 to 9 carbon atoms)

[10] An antifouling paint composition, including: the resin composition according to any one of [6] to [9].

5 [11] The antifouling paint composition according to [10], further including: an antifouling agent.

[12] The antifouling paint composition according to [10] or [11], further including: a thermoplastic resin other than the (meth)acrylic copolymer.

10 Advantageous Effects of Invention

[0008]

According to the present invention, it is possible to provide a (meth)acrylic copolymer which enables formation of a coating film with an excellent surface smoothness, a resin composition and an antifouling paint composition, and a method for
15 producing the (meth)acrylic copolymer.

BEST MODE FOR CARRYING OUT THE INVENTION

[0009]

The definitions of the following terms apply throughout the present specification
20 and claims.

The term “constituent unit” indicates a constituent unit derived from a polymerizable monomer formed by polymerizing a polymerizable monomer or a constituent unit obtained by treating a polymer so that a part of a constituent unit is converted to another structure.

25 The term “(meth)acrylate” is a general term for acrylate and methacrylate, the

term “(meth)acrylic acid” is a general term for acrylic acid and methacrylic acid, the term “(meth)acryloyl group” is a general term for an acryloyl group and a methacryloyl group, and the term “(meth)acrylamide” is a general term for acrylamide and methacrylamide.

The term “(meth)acrylic copolymer” indicates a copolymer in which at least some
 5 constituent units are constituent units derived from a (meth)acrylic monomer.

The (meth)acrylic copolymer may further have a constituent unit derived from a monomer other than a (meth)acrylic monomer (for example, a vinyl-based monomer such as styrene).

The term “(meth)acrylic monomer” indicates a monomer containing an acryloyl
 10 group or a methacryloyl group.

The term “volatile organic compound (VOC)” indicates an organic compound (volatile organic compound) which easily volatilizes at room temperature under normal pressure. Further, room temperature indicates a temperature range of 10°C to 30°C and normal pressure indicates a pressure range of 1000 Pa to 1050 Pa.

15 [0010]

[(Meth)acrylic copolymer]

The (meth)acrylic copolymer (hereinafter, also referred to as a “copolymer (X)”) of the present invention has the following constituent unit (B).

The copolymer (X) may further have the following constituent unit (C).

20 The copolymer (X) may further have the following constituent unit (A).

The copolymer (X) may further have the following constituent unit (D).

The copolymer (X) may further have a constituent unit (hereinafter, also referred to as a “constituent unit (E)”) other than the constituent unit (B), the constituent unit (C), the constituent unit (A), and the constituent unit (D).

25 The copolymer (X) has constituent units derived from a (meth)acrylic monomer,

and at least some of the constituent units are constituent units (B). The proportion of the constituent units derived from a (meth)acrylic monomer with respect to the total amount (100% by mass) of all constituent units in the copolymer (X) is preferably in a range of 20% to 100% by mass and more preferably in a range of 40% to 100% by mass.

5 [0011]

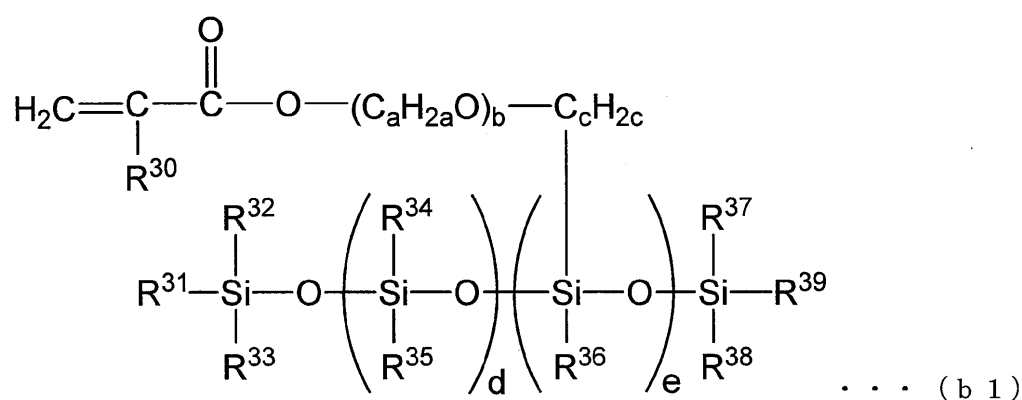
<Constituent unit (B)>

The constituent unit (B) is a constituent unit derived from a polysiloxane block-containing polymerizable monomer (b) (hereinafter, also referred to as a “polymerizable monomer (b)”) represented by Formula (b1).

10 In a case where the copolymer (X) has the constituent unit (B), marine organisms or various kinds of dirt are unlikely to be attached to the surface of the coating film containing the copolymer (X) derived from a polysiloxane block, and the coating film exhibits antifouling properties even in a case where the coating film does not contain an antifouling agent. Further, since the polysiloxane block is derived from the

15 polymerizable monomer (b), the surface smoothness and the crack resistance of the coating film containing the copolymer (X) are improved.

[0012]



(In Formula (b1), R³⁰ represents a hydrogen atom or a methyl group, a

represents an integer of 2 to 5, b represents a number of 0 to 50, c represents an integer of 0 to 18, d represents a number of 1 to 1000, e represents a number of 1 to 80, R^{31} to R^{39} each represents an alkyl group, an alkoxy group, a phenyl group, a substituted phenyl group, a phenoxy group, or a substituted phenoxy group.)

5 [0013]

In Formula (b1), a represents an integer of 2 to 5.

In Formula (b1), b represents a number of 0 to 50, preferably greater than 0 and 30 or less, more preferably greater than 0 and 25 or less, and particularly preferably greater than 0 and 20 or less. In a case where b is less than or equal to the above-
 10 described upper limit, the water resistance of the coating film tends to be improved. It is particularly preferable that b be 20 or less from the viewpoint of excellent recoatability with an old coating film.

In Formula (b1), c represents an integer of 0 to 18, preferably 2 or 3, and more preferably 3.

15 [0014]

In a case where d in Formula (b1) is greater than or equal to the above-described lower limit, the coating film formed of the antifouling paint composition tends to exhibit the antifouling effect even in a case where the antifouling paint composition containing the copolymer (X) does not contain an antifouling agent. In a case where d in Formula
 20 (b1) is less than or equal to the above-described upper limit, the compatibility between the polymerizable monomer (b) and a polymerizable monomer forming the constituent unit (A) and the solubility of the copolymer (X) in a solvent tend to be improved.

In Formula (b1), d represents an integer of 1 to 1000, preferably an integer of 1 to 200, more preferably an integer of 1 to 100, and particularly preferably an integer of 1
 25 to 60. In a case where d is greater than 1000, the compatibility with another

polymerizable monomer at the time of synthesizing a polymer tends to be degraded.

[0015]

In a case where e in Formula (b1) is greater than or equal to the above-described lower limit, the antifouling properties tend to be further improved. In a case where e is less than or equal to the above-described upper limit, the solvent solubility, the consumption degree, and the crack resistance tend to be improved. In Formula (b1), e preferably represents 80 or less, more preferably 50 or less, still more preferably 10 or less, and particularly preferably 5 or less.

Further, d + e preferably represents 2 to 1000 and more preferably 2 to 500.

[0016]

The numbers of carbon atoms of the alkyl group and the alkoxy group as R^{31} to R^{39} are each and preferably in a range of 1 to 18. Examples of the substituent in the substituted phenyl group and the substituted phenoxy group include an alkyl group and an alkoxy group.

R^{31} to R^{39} each preferably represents an alkyl group having 1 to 18 carbon atoms, more preferably a methyl group or an ethyl group, and particularly preferably a methyl group.

[0017]

In Formula (b1), a siloxane unit provided with d and a siloxane unit provided with e may be arranged randomly or in blocks. In a case where the siloxane units are arranged in blocks, the number of blocks of each siloxane unit may be one or more.

Further, each of a to e and R^{30} to R^{39} is independent. In a case where the same symbols are present in or between molecules, these may be different from each other.

A group of molecules in which c represents the same and the type of R^{30} to R^{39} and $(C_aH_{2a}O)$ constituting $(C_aH_{2a}O)_b$ is the same can be regarded as one compound even

in a case where one or more of b, d, and e are different, and b, d, and e is an average value per one molecule.

[0018]

The polymerizable monomer (b) may be used alone or in combination of two or
5 more kinds thereof.

[0019]

<Constituent unit (C)>

The constituent unit (C) is a constituent unit derived from a macromonomer (c).

The macromonomer (c) is a compound containing a radically polymerizable
10 group and having two or more constituent units derived from a monomer (hereinafter, also referred to as a “monomer (c1)”) containing a radically polymerizable group. Two or more constituent units of the macromonomer (c) may be the same as or different from each other.

In a case where the copolymer (X) has the constituent unit (C), the viscosity can
15 be lowered even with the same solid content, and the VOC content can be further reduced.

[0020]

A group having an ethylenically unsaturated bond is preferable as the radically
polymerizable group contained in the macromonomer (c). Examples of the group
20 having an ethylenically unsaturated bond include $\text{CH}_2=\text{C}(\text{COOR})-\text{CH}_2-$, a (meth)acryloyl group, a 2-(hydroxymethyl)acryloyl group, and a vinyl group.

Here, R represents a hydrogen atom, an unsubstituted or substituted alkyl group, an unsubstituted or substituted alicyclic group, an unsubstituted or substituted aryl group, and an unsubstituted or substituted heterocyclic group.

25 [0021]

Examples of the alkyl group as R include a branched or linear alkyl group having 1 to 20 carbon atoms. Specific examples of the branched or linear alkyl group having 1 to 20 carbon atoms include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, a t-butyl group, an i-butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, a tetradecyl group, a pentadecyl group, a hexadecyl group, a heptadecyl group, an octadecyl group, a nonadecyl group, and an icosyl group.

[0022]

10 The alicyclic group as R may be monocyclic or polycyclic, and examples thereof include an alicyclic group having 3 to 20 carbon atoms. As the alicyclic group, a saturated alicyclic group such as a cycloalkyl group is preferable, and specific examples thereof include a cyclopropyl group, a cyclobutyl group, a cyclopentyl group, a cyclohexyl group, a cycloheptyl group, a bicyclo[2.2.1]heptyl group, a cyclooctyl group, 15 and an adamantyl group.

[0023]

Examples of the aryl group as R include an aryl group having 6 to 18 carbon atoms. Specific examples of the aryl group having 6 to 18 carbon atoms include a phenyl group and a naphthyl group.

20 [0024]

Examples of the heterocyclic group as R include a heterocyclic group having 5 to 18 carbon atoms. Specific examples of the heterocyclic group having 5 to 18 carbon atoms include an oxygen atom-containing heterocyclic group such as a γ -butyrolactone group or a ϵ -caprolactone group, a nitrogen atom-containing heterocyclic group such as a 25 pyridyl group, a carbazolyl group, a pyrrolidinyl group, or a pyrrolidone group, and a

morpholino group.

[0025]

Each of the alkyl group, the alicyclic group, the aryl group, and the heterocyclic group may have a substituent. Examples of the substituent include at least one selected from the group consisting of an alkyl group (here, excluding a case where R represents an alkyl group having a substituent), an aryl group, $-\text{COOR}^{51}$, a cyano group, $-\text{OR}^{52}$, $-\text{NR}^{53}\text{R}^{54}$, $-\text{CONR}^{55}\text{R}^{56}$, a halogen atom, an allyl group, an epoxy group, a siloxy group, and a hydrophilic or ionic group.

Here, R^{51} to R^{56} each independently represents a hydrogen atom, an alkyl group, an alicyclic group, or an aryl group. Examples of these groups are the same as those described above.

[0026]

Examples of the alkyl group and the aryl group as the substituents are the same as those exemplified as the alkyl group and the aryl group represented by R.

It is preferable that R^{51} in $-\text{COOR}^{51}$ as the substituent represent a hydrogen atom or an alkyl group. That is, it is preferable that $-\text{COOR}^{51}$ represent a carboxy group or an alkoxycarbonyl group. Examples of the alkoxycarbonyl group include a methoxycarbonyl group.

It is preferable that R^{52} in $-\text{OR}^{52}$ as the substituent represent a hydrogen atom or an unsubstituted alkyl group. That is, it is preferable that $-\text{OR}^{52}$ represent a hydroxy group or an alkoxy group. Examples of the alkoxy group include an alkoxy group having 1 to 12 carbon atoms, and specific examples thereof include a methoxy group.

[0027]

Examples of $-\text{NR}^{53}\text{R}^{54}$ as the substituent include an amino group, a monomethylamino group, and a dimethylamino group.

Examples of $-\text{CONR}^{55}\text{R}^{56}$ as the substituent include a carbamoyl group ($-\text{CONH}_2$), an N-methylcarbamoyl group ($-\text{CONHCH}_3$), and an N,N-dimethylcarbamoyl group (dimethylamide group: $-\text{CON}(\text{CH}_3)_2$).

[0028]

5 Examples of the halogen atom as the substituent include a fluorine atom, a chlorine atom, a bromine atom, and an iodine atom.

Examples of the hydrophilic or ionic group as the substituent include an alkali salt of a carboxy group or an alkali salt of a sulfoxy group, a poly(alkylene oxide) group such as a polyethylene oxide group or a polypropylene oxide group, and a cationic

10 substituent such as a quaternary ammonium.

[0029]

R preferably represents an alkyl group or a saturated alicyclic group and more preferably an alkyl group or a saturated alicyclic group containing an alkyl group as an unsubstituted or substituted group.

15 Among these, from the viewpoint of availability, a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, a t-butyl group, a pentyl group, a hexyl group, a heptyl group, or an octyl group is preferable, and a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, a t-butyl group, a cyclopropyl group, a cyclobutyl group, an isobornyl group, or an adamantyl group is
20 more preferable.

[0030]

As the radically polymerizable group contained in the monomer (c1), a group having an ethylenically unsaturated bond is preferable, similar to the radically polymerizable group contained in the macromonomer (c).

25 As the monomer (c1), various monomers can be used, and examples thereof

include hydrocarbon group-containing (meth)acrylic acid ester such as methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, t-butyl (meth)acrylate, isoamyl (meth)acrylate, hexyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, octyl (meth)acrylate, lauryl (meth)acrylate, stearyl (meth)acrylate, isostearyl (meth)acrylate, hexadecyl (meth)acrylate, nonyl (meth)acrylate, isononyl (meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate, cyclohexyl (meth)acrylate, tetrahydrofurfuryl (meth)acrylate, isobornyl (meth)acrylate, 3,5,5-trimethylcyclohexyl (meth)acrylate, dicyclopentanyl (meth)acrylate, dicyclopentenyl (meth)acrylate, dicyclopentenylxyethyl (meth)acrylate, terpene acrylate or a derivative thereof, hydrogenated rosin acrylate or a derivative thereof, or docosyl (meth)acrylate; hydroxyl group-containing (meth)acrylic acid ester such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 2-hydroxybutyl (meth)acrylate, 3-hydroxybutyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, or glycerol (meth)acrylate; a carboxyl group-containing vinyl-based monomer such as (meth)acrylic acid, 2-(meth)acryloyloxyethyl hexahydrophthalic acid, 2-(meth)acryloyloxypropyl hexahydrophthalic acid, 2-(meth)acryloyloxyethylphthalic acid, 2-(meth)acryloyloxypropylphthalic acid, 2-(meth)acryloyloxyethylmaleic acid, 2-(meth)acryloyloxypropylmaleic acid, 2-(meth)acryloyloxyethylsuccinic acid, 2-(meth)acryloyloxypropylsuccinic acid, crotonic acid, fumaric acid, maleic acid, itaconic acid, citraconic acid, monomethyl maleate, monoethyl maleate, monooctyl maleate, monomethyl itaconate, monoethyl itaconate, monobutyl itaconate, monooctyl itaconate, monomethyl fumarate, monoethyl fumarate, monobutyl fumarate, monooctyl fumarate, or monoethyl citraconate; an acid anhydride group-containing vinyl-based monomer such as maleic anhydride or itaconic anhydride; an unsaturated dicarboxylic acid diester monomer such as dimethyl maleate, dibutyl maleate, dimethyl fumarate, dibutyl

- fumarate, dibutyl itaconate, or diperfluorocyclohexyl fumarate; an epoxy group-containing vinyl-based monomer such as glycidyl (meth)acrylate, glycidyl α -ethyl acrylate, or 3,4-epoxybutyl (meth)acrylate; an amino group-containing (meth)acrylic acid ester-based vinyl-based monomer such as dimethylaminoethyl (meth)acrylate or
- 5 diethylaminoethyl (meth)acrylate; a vinyl-based monomer containing an amide group such as (meth)acrylamide, N-t-butyl (meth)acrylamide, N-methylol (meth)acrylamide, N-isopropylacrylamide, hydroxyethylacrylamide, N-methoxymethyl (meth)acrylamide, N-butoxymethyl (meth)acrylamide, diacetone acrylamide, maleic acid amide, or maleimide; a vinyl-based monomer such as styrene, α -methylstyrene, vinyl toluene,
- 10 (meth)acrylonitrile, vinyl chloride, vinyl acetate, or vinyl propionate; a polyfunctional vinyl-based monomer such as divinyl benzene, ethylene glycol di(meth)acrylate, 1,3-butylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, tripropylene
- 15 glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, allyl (meth)acrylate, triallyl cyanurate, diallyl maleate, polypropylene glycol diallyl ether, or N,N'-methylene bis(meth)acrylamide; acryloyl morpholine, polyethylene glycol
- 20 (meth)acrylate, polypropylene glycol (meth)acrylate, methoxyethyl (meth)acrylate, ethoxyethyl (meth)acrylate, n-butoxyethyl (meth)acrylate, isobutoxyethyl (meth)acrylate, t-butoxyethyl (meth)acrylate, ethoxyethoxyethyl (meth)acrylate, phenoxyethyl (meth)acrylate, nonylphenoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, acetoxyethyl (meth)acrylate, "PLACCEL FM" (trade name (registered trademark),
- 25 manufactured by Daicel Corporation, caprolactone addition monomer), "BLEMMER

PME-100” (trade name (registered trademark), manufactured by NOF Corporation, methoxypolyethylene glycol methacrylate (the number of chains of ethylene glycol is 2), “BLEMMER PME-200” (trade name (registered trademark), manufactured by NOF Corporation, methoxypolyethylene glycol methacrylate (the number of chains of ethylene glycol is 4), “BLEMMER PME-400” (trade name (registered trademark), manufactured by NOF Corporation, methoxypolyethylene glycol methacrylate (the number of chains of ethylene glycol is 9), “BLEMMER 50POEP-800B” (trade name (registered trademark), manufactured by NOF Corporation, octoxypolyethylene glycol-polypropylene glycol-methacrylate (the number of chains of ethylene glycol is 8 and the number of chains of propylene glycol is 6), “BLEMMER 20ANEP-600” (trade name (registered trademark), manufactured by NOF Corporation, nonyl phenoxy (ethylene glycol-polypropylene glycol) monoacrylate), “BLEMMER AME-100” (trade name (registered trademark), manufactured by NOF Corporation), “BLEMMER AME-200” (trade name (registered trademark), manufactured by NOF Corporation), “BLEMMER 50AOEP-800B” (trade name (registered trademark), manufactured by NOF Corporation), “SILAPLANE FM-0711” (trade name (registered trademark), manufactured by JNC Corporation), “SILAPLANE FM-0721” (trade name (registered trademark), manufactured by JNC Corporation), “SILAPLANE FM-0725” (trade name (registered trademark), manufactured by JNC Corporation), “SILAPLANE TM-0701” (trade name (registered trademark), manufactured by JNC Corporation), “SILAPLANE TM-0701T” (trade name (registered trademark), manufactured by JNC Corporation), X-22-174ASX (trade name (registered trademark), manufactured by Shin-Etsu Chemical Co., Ltd.), X-22-174DX (trade name (registered trademark), manufactured by Shin-Etsu Chemical Co., Ltd.), X-22-2426 (trade name (registered trademark), manufactured by Shin-Etsu Chemical Co., Ltd.), X-22-2475 (trade name (registered trademark), manufactured by Shin-Etsu

Chemical Co., Ltd.), a silane coupling agent-containing monomer such as 3-(meth)acryloxypropyltrimethoxysilane, 3-(meth)acryloxypropylmethyldiethoxysilane, 3-(meth)acryloxypropyltriethoxysilane, 3-acryloxypropyltrimethoxysilane, vinyltrimethoxysilane, or vinyltriethoxysilane; an organosilyl group-containing monomer other than the silane coupling agent-containing monomer, such as the monomer (a2) described below; a halogenated olefin such as vinyl chloride, vinylidene chloride, vinyl fluoride, vinylidene fluoride, or chlorotrifluoroethylene; a fluorine-containing monomer (here, excluding the halogenated olefin) such as 2,2,2-trifluoroethyl (meth)acrylate, 2,2,3,3,3-pentafluorophenyl (meth)acrylate, 2-(perfluorobutyl)ethyl (meth)acrylate, 3-(perfluorobutyl)-2-hydroxypropyl (meth)acrylate, 2-(perfluorohexyl)ethyl (meth)acrylate, 3-perfluorohexyl-2-hydroxypropyl (meth)acrylate, 3-(perfluoro-3-methylbutyl)-2-hydroxypropyl (meth)acrylate, 2,2,3,3-tetrafluoropropyl (meth)acrylate, 1H,1H,5H-octafluoropentyl (meth)acrylate, 1H,1H,2H,2H-tridecafluorooctyl (meth)acrylate, 1H-1-(trifluoromethyl)trifluoroethyl (meth)acrylate, 1H,1H,3H-hexafluorobutyl (meth)acrylate, or 1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl (meth)acrylate, a monomer having an acetal structure such as 1-butoxyethyl (meth)acrylate, 1-(2-ethylhexyloxy)ethyl (meth)acrylate, 1-(cyclohexyloxy)ethyl methacrylate, or 2-tetrahydropyranyl (meth)acrylate, 4-methacryloyloxy benzophenone, and 2-isocyanate ethyl (meth)acrylate. These monomers may be used alone or in combination of two or more kinds thereof.

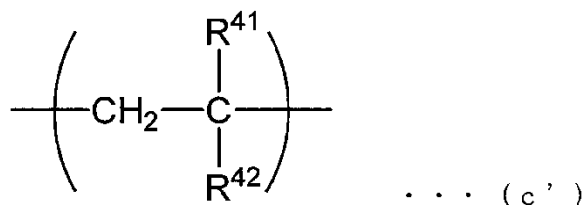
It is preferable that at least a part of the monomer (c1) be a (meth)acrylic monomer.

[0031]

As the constituent unit derived from the monomer (c1), a constituent unit represented by Formula (c') (hereinafter, also referred to as a "constituent unit (c'") is preferable. That is, it is preferable that the macromonomer (c) contain a radically

polymerizable group and two or more constituent units (c').

[0032]



(In Formula (c'), R⁴¹ represents a hydrogen atom, a methyl group, or CH₂OH,

5 R⁴² represents OR⁴³, a halogen atom, COR⁴⁴, COOR⁴⁵, CN, CONR⁴⁶R⁴⁷, or R⁴⁸, R⁴³ to

R⁴⁷ each independently represents a hydrogen atom, an alkyl group having an

unsubstituted or substituted group, an alicyclic group having an unsubstituted or

substituted group, an aryl group having an unsubstituted or substituted group, a

heteroaryl group having an unsubstituted or substituted group, a non-aromatic

10 heterocyclic group having an unsubstituted or substituted group, an aralkyl group having

an unsubstituted or substituted group, an alkaryl group having an unsubstituted or

substituted group, or an organosilyl group having an unsubstituted or substituted group,

and R⁴⁸ represents an aryl group having an unsubstituted or substituted group or a

heteroaryl group having an unsubstituted or substituted group)

15 [0033]

Examples of the alkyl group, the alicyclic group, and the aryl group as R⁴³ to R⁴⁷

are the same as those exemplified as the alkyl group, the alicyclic group, and the aryl

group as R described above.

Examples of the heteroaryl group include a pyridyl group and a carbazolyl

20 group.

Examples of the non-aromatic heterocyclic group include a pyrrolidinyl group

and a pyrrolidone group.

Examples of the aralkyl group include a benzyl group and a phenylethyl group.

Examples of the organosilyl group include a triorganosilyl group.

Examples of the triorganosilyl group are the same as those exemplified as the triorganosilyl group (such as $-\text{SiR}^{14}\text{R}^{15}\text{R}^{16}$) in the triorganosilyloxycarbonyl group of the constituent unit (A2) described below.

[0034]

Each of the alkyl group, the alicyclic group, the aryl group, the heteroaryl group, the non-aromatic heterocyclic group, the aralkyl group, the alkaryl group, and the organosilyl group may have a substituent. Examples of the substituent include a carboxylic acid group (COOH), a carboxylic acid ester group, an epoxy group, a hydroxy group, an alkoxy group, a primary amino group, a secondary amino group, a tertiary amino group, an isocyanate group, a sulfonic acid group (SO_3H), and a halogen atom.

Examples of the carboxylic acid ester group include a group in which R^{51} in $-\text{COOR}^{51}$ described in the section of R represents an alkyl group, an alicyclic group, or an aryl group.

Examples of the alkoxy group include a group in which R^{52} in OR^{52} represents an alkyl group.

Examples of the secondary amino group include a group in which R^{53} in $-\text{NR}^{53}\text{R}^{54}$ represents a hydrogen atom and R^{54} represents an alkyl group, an alicyclic group, or an aryl group.

Examples of the tertiary amino group include a group R^{53} and R^{54} in $-\text{NR}^{53}\text{R}^{54}$ each represents an alkyl group, an alicyclic group, or an aryl group.

Examples of the alkyl group, the aryl group, and the halogen atom are the same as described above.

[0035]

Examples of the aryl group and the heteroaryl group as R^{48} are the same as those described above.

Each of the aryl group and the heteroaryl group may have a substituent.

Examples of the substituent include a carboxylic acid group, a carboxylic acid ester group, an epoxy group, a hydroxy group, an alkoxy group, a primary amino group, a secondary amino group, a tertiary amino group, an isocyanate group, a sulfonic acid group, and a halogen atom.

Examples of the carboxylic acid ester group, the alkoxy group, the primary amino group, the secondary amino group, the tertiary amino group, the alkyl group, the aryl group, and the halogen atom are the same as those described above.

Examples of the olefin group include an allyl group. The olefin group may have a substituent. Examples of the substituent in the olefin group are the same as those exemplified as the substituent represented by R^{48} .

[0036]

As the constituent unit (c'), a constituent unit in which R^{41} represents a hydrogen atom or a methyl group and R^{42} represents $COOR^{45}$ is preferable. It is preferable that R^{45} represent a hydrogen atom, an alkyl group, a saturated alicyclic group, an aryl group, a heteroaryl group, or a non-aromatic heterocyclic group.

[0037]

The constituent unit (c') is a constituent unit derived from $CH_2=CR^{41}R^{42}$.

Specific examples of $CH_2=CR^{41}R^{42}$ include a hydrophobic group-containing (meth)acrylic acid ester monomer such as substituted or unsubstituted alkyl (meth)acrylate [for example, methyl (meth)acrylate, ethyl (meth)acrylate, n-propyl (meth)acrylate, i-propyl (meth)acrylate, n-butyl (meth)acrylate, i-butyl (meth)acrylate, t-butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, lauryl (meth)acrylate, stearyl

- (meth)acrylate, behenyl (meth)acrylate, 1-methyl-2-methoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, or 3-methyl-3-methoxybutyl (meth)acrylate], substituted or unsubstituted aralkyl (meth)acrylate [for example, benzyl (meth)acrylate, m-methoxyphenylmethyl (meth)acrylate, or p-methoxyphenylethyl (meth)acrylate],
- 5 substituted or unsubstituted aryl (meth)acrylate [for example, phenyl (meth)acrylate, m-methoxyphenyl (meth)acrylate, p-methoxyphenyl (meth)acrylate, or o-methoxyphenylethyl (meth)acrylate], alicyclic (meth)acrylate [for example, isobornyl (meth)acrylate or cyclohexyl (meth)acrylate], or halogen atom-containing (meth)acrylate [for example, trifluoroethyl (meth)acrylate, perfluorooctyl (meth)acrylate, or
- 10 perfluorocyclohexyl (meth)acrylate]; an oxyethylene group-containing (meth)acrylic acid ester monomer such as 2-methoxyethyl (meth)acrylate, 2-ethoxyethyl (meth)acrylate, 2-butoxyethyl (meth)acrylate, butoxydiethylene glycol (meth)acrylate, methoxytriethylene glycol (meth)acrylate, methoxypolyethylene glycol (meth)acrylate, phenoxyethyl (meth)acrylate, or 2-(2-ethylhexaoxy)ethyl (meth)acrylate;
- 15 a hydroxyl group-containing (meth)acrylic acid ester monomer such as 2-hydroxyethyl (meth)acrylate, 2-hydroxypropyl (meth)acrylate, 4-hydroxybutyl (meth)acrylate, or glycerol (meth)acrylate; a terminal alkoxy allylated polyether monomer such as methoxypolyethylene glycol allyl ether, methoxypolypropylene glycol allyl ether, butoxypolyethylene glycol allyl ether, butoxypolypropylene glycol allyl ether,
- 20 methoxypolyethylene glycol-polypropylene glycol allyl ether, or butoxypolyethylene glycol-polypropylene glycol allyl ether; an epoxy group-containing vinyl monomer such as glycidyl (meth)acrylate, glycidyl α -ethyl acrylate, or 3,4-epoxybutyl (meth)acrylate;
- a primary or secondary amino group-containing vinyl monomer such as butyl aminoethyl (meth)acrylate or (meth)acrylamide; a tertiary amino group-containing vinyl
- 25 monomer such as dimethylaminoethyl (meth)acrylate, diethylaminoethyl (meth)acrylate,

dimethylaminopropyl (meth)acrylate, dimethylaminobutyl (meth)acrylate, dibutylaminoethyl (meth)acrylate, dimethylaminoethyl (meth)acrylamide, or dimethylaminopropyl (meth)acrylamide; a heterocyclic basic monomer such as vinylpyrrolidone, vinylpyridine, or vinyl carbazole; an organosilyl group-containing

5 vinyl monomer such as trimethyl silyl (meth)acrylate, triethyl silyl (meth)acrylate, tri-n-propyl silyl (meth)acrylate, tri-n-butyl silyl (meth)acrylate, tri-n-amyl silyl (meth)acrylate, tri-n-hexyl silyl (meth)acrylate, tri-n-octyl silyl (meth)acrylate, tri-n-dodecyl silyl (meth)acrylate, triphenyl silyl (meth)acrylate, tri-p-methyl phenyl silyl (meth)acrylate, tribenzyl silyl (meth)acrylate, triisopropyl silyl (meth)acrylate, triisobutyl

10 silyl (meth)acrylate, tri-s-butyl silyl (meth)acrylate, tri-2-methylisopropylsilyl (meth)acrylate, tri-t-butyl silyl (meth)acrylate, ethyl dimethyl silyl (meth)acrylate, n-butyl dimethyl silyl (meth)acrylate, diisopropyl-n-butyl silyl (meth)acrylate, n-octyl di-n-butyl silyl (meth)acrylate, diisopropyl stearyl silyl (meth)acrylate, dicyclohexyl phenyl silyl (meth)acrylate, t-butyl diphenyl silyl (meth)acrylate, or lauryl diphenyl silyl

15 (meth)acrylate, a carboxy group-containing ethylenically unsaturated monomer such as methacrylic acid, acrylic acid, vinylbenzoic acid, tetrahydrophthalic acid monohydroxyethyl (meth)acrylate, tetrahydrophthalic acid monohydroxypropyl (meth)acrylate, tetrahydrophthalic acid monohydroxybutyl (meth)acrylate, phthalic acid monohydroxyethyl (meth)acrylate, phthalic acid monohydroxypropyl (meth)acrylate,

20 succinic acid monohydroxyethyl (meth)acrylate, succinic acid monohydroxypropyl (meth)acrylate, maleic acid monohydroxyethyl (meth)acrylate, or maleic acid monohydroxypropyl (meth)acrylate; a cyano group-containing vinyl monomer such as acrylonitrile or methacrylonitrile; a vinyl ether monomer such as alkyl vinyl ether [for example, ethyl vinyl ether, propyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, or 2-

25 ethyl hexyl vinyl ether], or cyanoalkyl vinyl ether [such as cyclohexyl vinyl ether];

a vinyl ester monomer such as vinyl acetate, vinyl propionate, vinyl butyrate, or vinyl benzoate; an aromatic vinyl monomer such as styrene, vinyl toluene, or α -methyl styrene; and a halogenated olefin such as vinyl chloride or vinyl fluoride.

[0038]

5 The macromonomer (c) may further have constituent units other than the constituent unit (c'). Examples of other constituent units include a constituent unit derived from a monomer that do not correspond to $\text{CH}_2=\text{CR}^{41}\text{R}^{42}$ among the examples of the monomer (c1) described above.

Specific preferred examples of other constituent units include constituent units
10 derived from the following monomers.

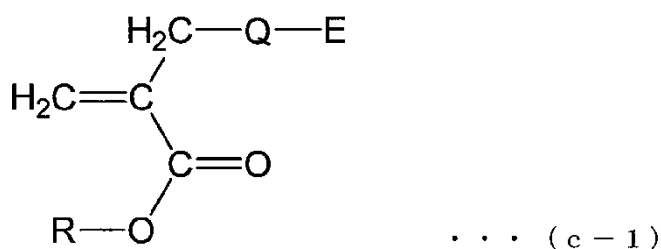
Examples thereof include an organosilyl group-containing vinyl monomer such as triisopropyl silyl methyl malate, triisopropyl silyl amyl fumarate, tri-n-butylsilyl-n-butyl fumarate, t-butyl diphenyl silyl methyl fumarate, t-butyl diphenylsilyl-n-butyl fumarate, triisopropyl silyl methyl fumarate, triisopropyl silyl amyl fumarate, tri-n-
15 butylsilyl-n-butyl fumarate, t-butyl diphenyl silyl methyl fumarate, or t-butyl diphenylsilyl-n-butyl fumarate; an acid anhydride group-containing vinyl monomer such as maleic anhydride or itaconic anhydride; a carboxy group-containing ethylenically unsaturated monomer such as crotonic acid, fumaric acid, itaconic acid, maleic acid, citraconic acid, monomethyl maleate, monoethyl maleate, monobutyl maleate, monooctyl
20 maleate, monomethyl itaconate, monoethyl itaconate, monobutyl itaconate, monooctyl itaconate, monomethyl fumarate, monoethyl fumarate, monobutyl fumarate, monooctyl fumarate, or monoethyl citraconate; an unsaturated dicarboxylic acid diester monomer such as dimethyl maleate, dibutyl maleate, dimethyl fumarate, dibutyl fumarate, dibutyl itaconate, or diperfluorocyclohexyl fumarate; a halogenated olefin such as vinylidene
25 chloride, vinylidene fluoride, or chlorotrifluoroethylene; and a polyfunctional monomer

such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, polyethylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol tetra(meth)acrylate, dipentaerythritol hexa(meth)acrylate, allyl methacrylate, triallyl cyanurate, diallyl maleate, or polypropylene glycol diallyl ether.

[0039]

As the macromonomer (c), a macromonomer obtained by introducing a radically polymerizable group to a terminal of the main chain having two or more constituent units (c') is preferable, and a macromonomer represented by Formula (c-1) is more preferable.

[0040]



(In Formula (c-1), R has the same definition as described above, Q represents a main chain moiety having two or more constituent units (c'), and E represents a terminal group.)

[0041]

In Formula (c-1), R has the same definition as that for R in $\text{CH}_2=\text{C}(\text{COOR})-\text{CH}_2-$, and the preferable aspects thereof are the same as described above.

Two or more constituent units (c') contained in Q may be the same as or different from one another.

Q may be formed of only the constituent unit (c') and may further have constituent units other than the constituent unit (c').

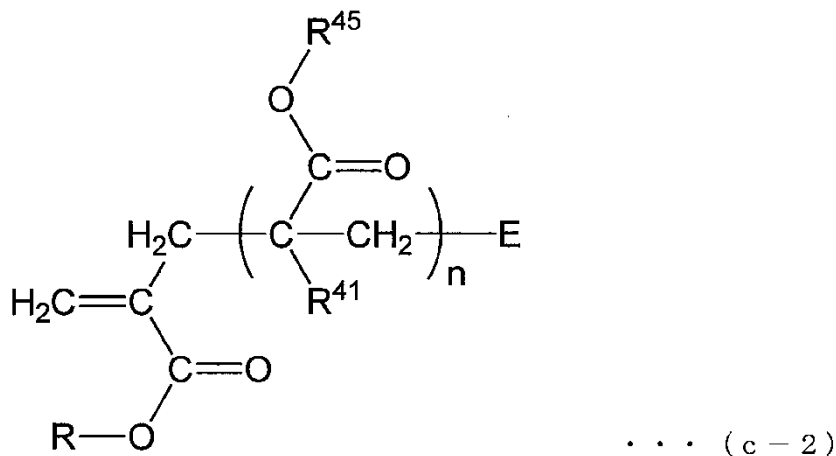
It is preferable that the number of constituent units constituting Q be set to a value such that the number-average molecular weight of the macromonomer (c) is in the
5 preferable range described below.

E represents a hydrogen atom, a group derived from a radical polymerization initiator, or a radically polymerizable group, similar to a terminal group of a polymer obtained by carrying out known radical polymerization.

[0042]

10 As the macromonomer (c), a macromonomer represented by Formula (c-2) is particularly preferable.

[0043]



(In Formula (c-2), R, R⁴¹, R⁴⁵, and E each has the same definition as described
15 above, and n represents a natural number of 2 or greater.)

[0044]

In Formula (c-2), it is preferable that n be set to a value such that the number-average molecular weight (M_n) of the macromonomer (c) is in a range of 500 to 50000. A more preferable range of the number-average molecular weight thereof is as follows.

In Formula (c-2), n R^{41} 's may be the same as or different from one another. n R^{45} 's may be the same as or different from one another.

[0045]

The number-average molecular weight (M_n) of the macromonomer (c) is preferably in a range of 500 to 50000, more preferably 500 or greater and less than 50000, still more preferably in a range of 800 to 30000, and particularly preferably in a range of 1000 to 20000. In a case where the number-average molecular weight of the macromonomer (c) is greater than or equal to the above-described lower limit, the hardness and the water resistance of the coating film are further improved. In a case where the number-average molecular weight of the macromonomer (c) is less than or equal to the above-described upper limit, the storage stability of the solution containing the copolymer (X), the resin composition containing the solution, and the antifouling paint composition is further improved.

The number-average molecular weight of the macromonomer (c) is measured by gel permeation chromatography (GPC) using polyethylene as a reference substance.

The number-average molecular weight of the macromonomer (c) can be adjusted based on the amount of a polymerization initiator or a chain transfer agent to be used at the time of production of the macromonomer (c).

[0046]

Therefore, as the macromonomer (c), a macromonomer having two or more constituent units (c') and a number-average molecular weight (M_n) of 500 to 50000 is preferable. The preferable kind of the constituent unit (c') in the macromonomer and the preferable range of the number-average molecular weight thereof are the same as described above.

[0047]

The glass transition temperature of the macromonomer (c) is preferably in a range of -50°C to 120°C and more preferably in a range of -20°C to 100°C. In a case where the glass transition temperature of the macromonomer (c) is greater than or equal to the above-described lower limit, the hardness and the water resistance of the coating film are further improved. In a case where the glass transition temperature of the macromonomer (c) is less than or equal to the above-described upper limit, the storage stability of the solution containing the copolymer (X) and the compositions containing the solution (the resin composition or the antifouling paint composition) is further improved. Further, the solution and the compositions can be easily formed to have a high solid content and a low viscosity.

The glass transition temperature of the macromonomer (c) can be measured using a differential scanning calorimeter (DSC).

The glass transition temperature of the macromonomer (c) can be adjusted based on the composition and the like of the monomer forming the macromonomer (c).

[0048]

The macromonomer (c) may be produced according to a known method, or a commercially available product may be used as the macromonomer.

Examples of the method for producing the macromonomer (c) include a production method of using a cobalt chain transfer agent, a method of using an α -substituted unsaturated compound such as an α -methylstyrene dimer as a chain transfer agent, a method of chemically bonding a radically polymerizable group to a polymer, and a method of carrying out thermal decomposition.

Examples of the combination of an addition-reactive functional group and a functional group that can react with this functional group include the following combinations.

The method of chemically bonding a radically polymerizable group to a polymer can be carried out by reacting an addition-reactive functional group with a vinyl-based monomer containing a functional group that can react with this functional group after a polymer containing the addition-reactive functional group is obtained.

5 Examples of the combination include a combination of a hydroxyl group and a carboxyl group or an acid anhydride group; a combination of an isocyanate group and a hydroxyl group or a thiol group or a carboxyl group; a combination of an epoxy group and an amino group; a combination of a carboxyl group and an epoxy group or a carbodiimide group; a combination of an amino group and a carboxyl group; a
10 combination of an amide group and a carboxyl group; and a combination of a thiol group and an epoxy group.

Among these, from the viewpoint that the number of production steps is small and a catalyst with a high chain transfer constant is used, the production method of using a cobalt chain transfer agent is preferable as the method for producing the
15 macromonomer (c). Further, the macromonomer (c) in a case of being produced using a cobalt chain transfer agent has a structure represented by Formula (c-1).

In a case where the macromonomer (c) contains a radically polymerizable group, the number of radically polymerizable groups in the macromonomer (c) may be one or more, but is preferably one.

20 [0049]

Examples of the method for producing the macromonomer (c) using a cobalt chain transfer agent include a bulk polymerization method, a solution polymerization method, and an aqueous dispersion polymerization method such as a suspension polymerization method or an emulsion polymerization method. From the viewpoint
25 that a recovery step is simple, the aqueous dispersion polymerization method is

preferable.

Examples of chemically bonding a radically polymerizable group to a polymer include a production method of substituting a halogen group of a polymer containing the halogen group with a radically polymerizable compound having a carbon-carbon double
 5 bond; a method of reacting a vinyl-based monomer containing an acid group with a vinyl-based polymer containing an epoxy group; a method of reacting a vinyl-based polymer containing an epoxy group with a vinyl-based monomer containing an acid group; and a method of reacting a vinyl-based polymer containing a hydroxyl group with a diisocyanate compound to obtain a vinyl-based polymer containing an isocyanate group
 10 and reacting this vinyl-based polymer with a vinyl-based monomer containing a hydroxyl group. The production may be carried out using any of the above-described methods.

[0050]

<Constituent unit (A)>

The constituent unit (A) is at least one constituent unit selected from the group
 15 consisting of a constituent unit (A1), a constituent unit (A2), and a constituent unit (A3).

The constituent unit (A1), the constituent unit (A2), and the constituent unit (A3) are common in that these constituent units have a hydrolyzable structure. In a case where the copolymer (X) has the constituent unit (A), the copolymer (X) has hydrolyzability, and a coating film containing the copolymer (X) shows self-polishing
 20 properties in water (particularly in sea water). That is, the copolymer (X) has any one or more of a structure (I), a triorganosilyloxycarbonyl group, and a structure (III) and is not dissolved in sea water or the like in this state. However, in a case where this structure is hydrolyzed due to contact with sea water or the like, a carboxy group or the like is generated so that the copolymer (X) can be dissolved in sea water or the like.
 25 The surface of the coating film is gradually dissolved in sea water, and thus the surface of

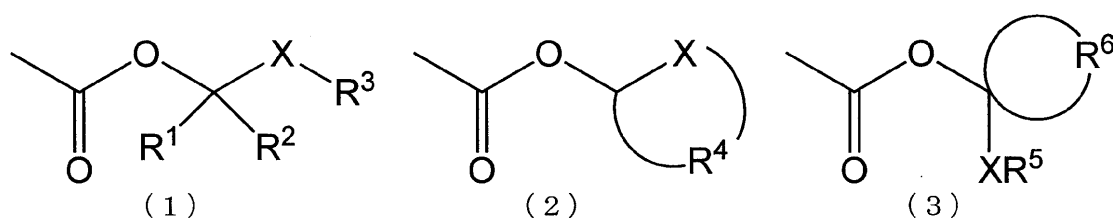
the coating film is renewed (self-polished) and the antifouling properties tend to be improved.

[0051]

(Constituent unit (A1))

- 5 The constituent unit (A1) is a constituent unit having at least one structure (I).
The structure (I) is represented by Formula (1), Formula (2), or Formula (3). In each of the formulae, among single lines extending from carbon atoms of a carbonyl group, the line that is not bonded to an oxygen atom indicates a bonding site.

[0052]



10

- (In Formulae (1) to (3), X represents -O-, -S-, or -NR¹⁴-, R¹⁴ represents a hydrogen atom or an alkyl group, R¹ and R² each represents a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, R³ and R⁵ each represents an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group, or an aryl group, and R⁴ and R⁶ each represents an alkylene group having 1 to 10 carbon atoms.)
- 15

[0053]

In Formulae (1) to (3), X may represent any of -O- (an etheric oxygen atom), -S- (a sulfide-based sulfur atom), or -NR¹⁴-, and it is preferable that X represent -O-.

[0054]

- 20 In Formula (1), examples of the alkyl group having 1 to 10 carbon atoms as R¹ and R² include a methyl group, an ethyl group, a propyl group, an isopropyl group, a

butyl group, an isobutyl group, a pentyl group, a hexyl group, and a 2-ethylhexyl group.

The number of carbon atoms in the alkyl group as R^1 and R^2 is preferably in a range of 1 to 4, more preferably in a range of 1 to 3, and still more preferably 1 or 2.

[0055]

5 Preferred examples of a combination of R^1 and R^2 in Formula (1) include a combination of a hydrogen atom and a methyl group, a combination of a methyl group and a methyl group, a combination of a hydrogen atom and an alkyl group having 2 to 10 carbon atoms (hereinafter, also referred to as a “long chain alkyl group”), a combination of a methyl group and a long chain alkyl group, a combination of a hydrogen atom and a
10 hydrogen atom, and a combination of a long chain alkyl group and a long chain alkyl group. Among these, from the viewpoint of the hydrolyzability, the combination of a hydrogen atom and a methyl group is preferable.

[0056]

In Formula (1), examples of the alkyl group having 1 to 20 carbon atoms as R^3
15 include the alkyl groups exemplified as the alkyl group having 1 to 10 carbon atoms above, a decyl group, a dodecyl group, and a tetradecyl group. The number of carbon atoms in the alkyl group as R^3 is preferably in a range of 1 to 10.

As the cycloalkyl group, a cycloalkyl group having 4 to 8 carbon atoms is preferable, and examples thereof include a cyclohexyl group and a cyclopentyl group.

20 As the aryl group, an aryl group having 6 to 20 carbon atoms is preferable, and examples thereof include a phenyl group and a naphthyl group.

It is preferable that R^3 represent an alkyl group having 1 to 10 carbon atoms or a cycloalkyl group.

[0057]

25 The alkyl group, the cycloalkyl group, or the aryl group may be substituted with

a substituent selected from the group consisting of a cycloalkyl group, an aryl group, an alkoxy group, an alkanoyloxy group, an aralkyl group, and an acetoxy group. In a case where the group is substituted with a substituent, the number of substituents may be one or more.

5 Examples of the cycloalkyl group and the aryl group as a substituent are the same as those described above. Examples of the alkoxy group include a methoxy group, an ethoxy group, a propoxy group, and a butoxy group. Examples of the alkanoyloxy group include an ethanoyloxy group. Examples of the aralkyl group include a benzyl group.

10 [0058]

In Formula (2), examples of the alkylene group having 1 to 10 carbon atoms as R^4 include a methylene group, an ethylene group, a propylene group, a butylene group, and a hexylene group.

15 The number of carbon atoms in the alkylene group as R^4 is preferably in a range of 2 to 7 and more preferably 3 or 4.

20 The alkylene group may be substituted with a substituent selected from the group consisting of a cycloalkyl group, an aryl group, an alkoxyl group, an alkanoyloxy group, an aralkyl group, and an acetoxy group. In a case where the group is substituted with a substituent, the number of substituents may be one or more. Specific examples of the substituent which may be substituted with the alkylene group are the same as those exemplified as the substituent as R^3 in Formula (1).

[0059]

In Formula (3), R^5 has the same definition as that for R^3 in Formula (1), and the preferable aspects thereof are the same as described above.

25 R^6 has the same definition as that for R^4 in Formula (2), and the preferable

aspects thereof are the same as described above.

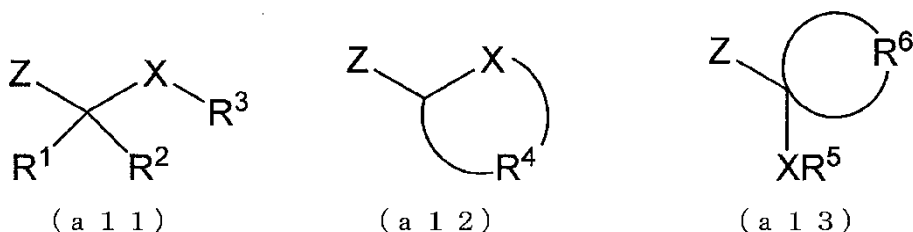
[0060]

Examples of the constituent unit (A1) include a constituent unit derived from a polymerizable monomer (a1) having a structure (I). The polymerizable monomer (a1) typically has the structure (I) and an ethylenically unsaturated bond (polymerizable carbon-carbon double bond).

From the viewpoint that the viscosity at the time of dissolving the copolymer (X) in an organic solvent becomes lower, it is preferable that the polymerizable monomer (a1) be a monofunctional monomer having one ethylenically unsaturated bond.

Examples of the polymerizable monomer (a1) include a compound represented by Formula (a11), a compound represented by Formula (a12), and a compound represented by Formula (a13).

[0061]



(In Formulae (a11) to (a13), Z represents $\text{CH}_2=\text{CH}-\text{COO}-$, $\text{CH}_2=\text{C}(\text{CH}_3)-\text{COO}-$, $\text{CHR}^{\text{X}}=\text{CH}-\text{COO}-$, $\text{CH}_2=\text{C}(\text{CH}_2\text{R}^{\text{X}})-\text{COO}-$, or $\text{CH}_2=\text{CR}^{\text{X}}-\text{CH}_2\text{COO}-$, R^{X} represents the structure (I) shown above or an alkyl ester group, X represents -O-, -S-, or $-\text{NR}^{14}$, R^{14} represents a hydrogen atom or an alkyl group, and R^1 to R^6 each has the same definition as described above.)

[0062]

In Formulae (a11) to (a13), $\text{CH}_2=\text{CH}-\text{COO}-$ as Z represents an acryloyloxy

group, and $\text{CH}_2=\text{C}(\text{CH}_3)\text{-COO-}$ represents a methacryloyloxy group.

$\text{CH}(\text{CH}_3)=\text{CH-COO-}$ represents a crotonoyloxy group (an ethylenically unsaturated bond is of a trans type) or an isocrotonoyloxy group (an ethylenically unsaturated bond is of a cis type).

5 $\text{CHR}^{\text{X}}=\text{CH-COO-}$ represents a maleinoyloxy group (an ethylenically unsaturated bond is of a cis type) or a fumaroyloxy group (an ethylenically unsaturated bond is of a trans type), in which a carboxy group is substituted with a structure (I) or an alkyl ester group.

10 In Formulae (a11) to (a13), the structure (I) in R^{X} has the same definition as described above. It is preferable that R^{X} have the same structure as that of the group to which Z is bonded. For example, in a case of the compound represented by Formula (a11), it is preferable that R^{X} represent a group represented by $-\text{CR}^1\text{R}^2\text{-OR}^3$.

15 In Formulae (a11) to (a13), the alkyl ester group as R^{X} is represented by $-\text{COOR}^{\text{X}1}$. $\text{R}^{\text{X}1}$ represents an alkyl group. As the alkyl group represented by $\text{R}^{\text{X}1}$, an alkyl group having 1 to 6 carbon atoms is preferable, and a methyl group is particularly preferable.

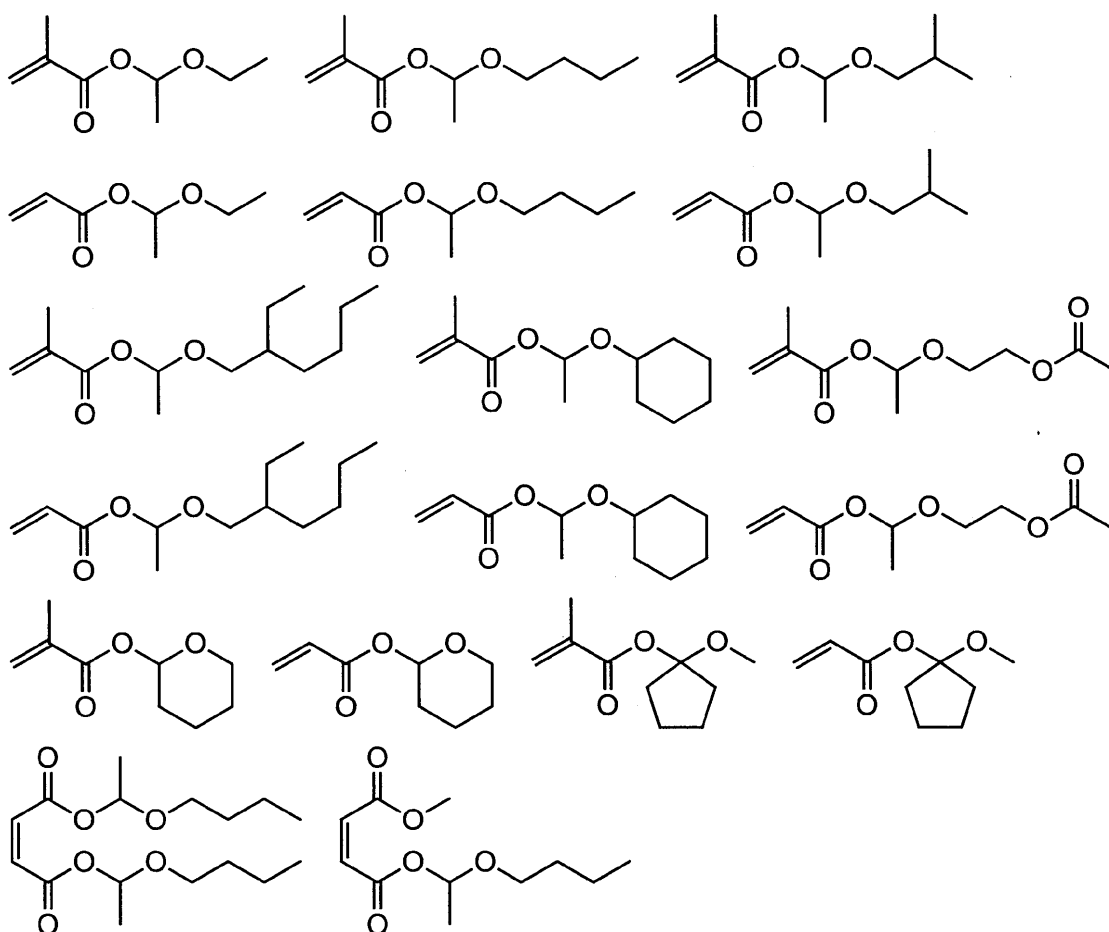
$\text{CH}_2=\text{C}(\text{CH}_2\text{R}^{\text{X}})\text{-COO-}$ or $\text{CH}_2=\text{CR}^{\text{X}}\text{-CH}_2\text{COO-}$ represents an itaconoyloxy group in which a carboxy group is substituted with a structure (I) or an alkyl ester group. R^{X} has the same definition as described above.

20 In Formulae (a11) to (a13), it is preferable that Z represent $\text{CH}_2=\text{CH-COO-}$ or $\text{CH}(\text{CH}_3)=\text{CH-COO-}$.

[0063]

Specific examples of the polymerizable monomer (a1) are the same as those described below.

25 [0064]



[0065]

As the polymerizable monomer (a1), a commercially available product may be used or the monomer can be appropriately synthesized according to a known method.

- 5 For example, the polymerizable monomer (a1) can be synthesized by converting a carboxy group in a polymerizable monomer (m0) containing the carboxy group to a structure (I).

- Examples of the polymerizable monomer (m0) include (meth)acrylic acid, crotonic acid, isocrotonic acid, maleic acid, fumaric acid, itaconic acid, monomethyl
10 maleate, and monomethyl fumarate.

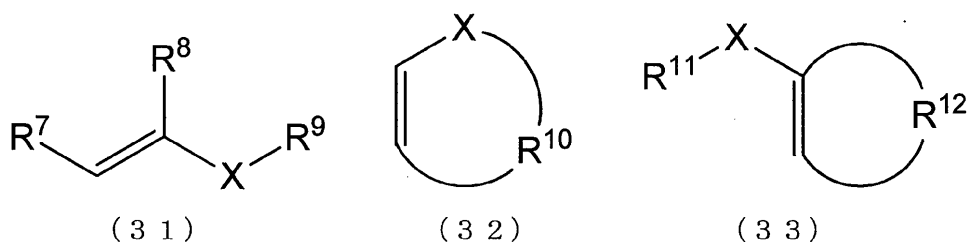
[0066]

Examples of the method of converting the carboxy group in the polymerizable

monomer (m0) to the structure (I) include a method of causing a reaction (addition reaction) between the polymerizable monomer (m0) and at least one compound (Y) selected from the group consisting of a compound represented by Formula (31), a compound represented by Formula (32), and a compound represented by Formula (33).

- 5 The compound (Y) may be used alone or in combination of two or more kinds thereof.

[0067]



(In Formulae (31) to (33), X represents -O-, -S-, or -NR¹⁴-, R¹⁴ represents a

hydrogen atom or an alkyl group, R⁷ represents a hydrogen atom or an alkyl group

- 10 having 1 to 9 carbon atoms, R⁸ represents a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, R⁹ and R¹¹ each represents an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group, or an aryl group, R¹⁰ represents a single bond or an alkylene group having 1 to 9 carbon atoms, and R¹² represents an alkylene group having 1 to 9 carbon atoms.)

15 [0068]

In a case where a compound represented by Formula (31) is used as the compound (Y), a compound in which R¹ in Formula (a11) represents CH₂R⁷, R² represents R⁸, and R³ represents R⁹ is obtained as the polymerizable monomer (a1).

- 20 In Formula (31), the alkyl group having 1 to 9 carbon atoms as R⁷ has the same definition as that for the alkyl group having 1 to 10 carbon atoms as R¹ except that the number of carbon atoms thereof is 9 or less.

In Formula (31), R^8 and R^9 each has the same definition as that for R^2 and R^3 in Formula (a11).

[0069]

Examples of the compound represented by Formula (31) include 1-alkenyl alkyl
 5 ether in which X in Formula (31) represents -O-, 1-alkenyl alkyl sulfide in which X in
 Formula (31) represents -S-, and 1-alkenyl dialkylamine in which X in Formula (31)
 represents $-NR^{14}$ -. Examples of the 1-alkenyl alkyl ether include vinyl ethers such as
 alkyl vinyl ether (such as ethyl vinyl ether, butyl vinyl ether, isobutyl vinyl ether, t-butyl
 vinyl ether, or 2-ethyl hexyl vinyl ether) and cycloalkyl vinyl ether (such as cyclohexyl
 10 vinyl ether); 1-propenyl ethers such as ethyl-1-propenyl ether; and 1-butenyl ethers such
 as ethyl-1-butenyl ether. Examples of the 1-alkenyl alkyl sulfide include 1-alkenyl alkyl
 sulfides such as 1-(ethenylthio)ethane, 1-(ethenylthio)propane, 1-(ethenylthio)butane, 2-
 (ethenylthio)butane, 1-(ethenylthio)-2-methylpropane, 1-(propylthio)-1-propene, and 2-
 (propylthio)-1-propene. Examples of the 1-alkenyl dialkylamine include 1-alkenyl
 15 dialkylamines such as N,N-dimethyl ethenamine, N-methyl-N-ethyl ethenamine, N,N-
 diethyl ethenamine, and N-vinylpyrrolidone.

Among these, 1-alkenyl alkyl ether is preferable, and vinyl ethers and 1-
 propenyl ethers are more preferable.

[0070]

20 In a case where a compound represented by Formula (32) is used as the
 compound (Y), a compound in which R^4 in Formula (a12) represents CH_2-R^{10} is obtained
 as the polymerizable monomer (a1).

In Formula (32), the alkylene group having 1 to 9 carbon atoms as R^{10} has the
 same definition as that for the alkylene group as R^4 except that the number of carbon
 25 atoms thereof is 9 or less.

[0071]

Examples of the compound represented by Formula (32) include dihydrofurans such as 2,3-dihydrofuran, and 5-methyl-2,3-dihydrofuran; dihydropyrans such as 3,4-dihydro-2H-pyran and 5,6-dihydro-4-methoxy-2H-pyran; dihydrothiophenes such as 2,3-dihydrothiophene; dihydrothiopyrans such as 3,4-dihydro-2H-thiopyran; dihydropyrroles such as 2,3-dihydro-1-methylpyrrole; and tetrahydropyridines such as 1,2,3,4-tetrahydro-1-methylpyridine.

Among these, dihydrofurans and dihydropyrans are preferable, and dihydropyrans are more preferable.

10 [0072]

In a case where a compound represented by Formula (33) is used as the compound (Y), a compound in which R^5 in Formula (a13) represents R^{11} and R^6 represents CH_2-R^{12} is obtained as the polymerizable monomer (a1).

In Formula (33), R^{11} has the same definition as that for R^5 in Formula (a13).

15 R^{12} has the same definition as that for R^6 in Formula (a13) except that the carbon atoms thereof is 9 or less.

[0073]

Examples of the compound represented by Formula (33) include 1-alkoxy-1-cycloalkylenes such as 1-methoxy-1-cyclopentene, 1-methoxy-1-cyclohexene, 1-methoxy-1-cycloheptene, 1-ethoxy-1-cyclopentene, 1-ethoxy-1-cyclohexene, 1-butoxy-1-cyclopentene, and 1-butoxy-1-cyclohexene; substituent-containing 1-alkoxy-1-cycloalkylenes such as 1-ethoxy-3-methyl-1-cyclohexene; 1-(alkylthio)-1-cycloalkylenes such as 1-(methylthio)-1-cyclopentene and 1-(methylthio)-1-cyclohexene; and 1-(1-pyrrolidinyl)-1-cycloalkylenes such as 1-(1-pyrrolidinyl)-1-cyclopentene and 1-(1-pyrrolidinyl)-1-cyclohexene.

20

25

As the compound (Y), a commercially available product may be used or the compound can be appropriately synthesized.

[0074]

The reaction between the polymerizable monomer (m0) and the compound (Y) proceeds under relatively mild conditions. For example, a target object can be obtained by carrying out the reaction while maintaining the reaction temperature at 40°C to 100°C for 5 to 10 hours in the presence or absence of an acidic catalyst such as hydrochloric acid, sulfuric acid, or phosphoric acid.

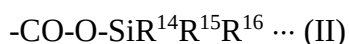
After completion of the reaction, the target monomer can be recovered by carrying out vacuum distillation under predetermined conditions.

[0075]

(Constituent unit (A2))

The constituent unit (A2) is a constituent unit containing a triorganosilyloxycarbonyl group.

Examples of the triorganosilyloxycarbonyl group include a group represented by Formula (II).



(In Formula (II), R^{14} to R^{16} each represents a hydrocarbon group having 1 to 20 carbon atoms.)

[0076]

In Formula (II), examples of the hydrocarbon group as R^{14} to R^{16} include an alkyl group having 1 to 20 carbon atoms such as a methyl group, an ethyl group, an n-propyl group, an isopropyl group, an n-butyl group, an isobutyl group, a sec-butyl group, a tert-butyl group, a pentyl group, a hexyl group, a heptyl group, an octyl group, a nonyl group, a decyl group, an undecyl group, a dodecyl group, a tridecyl group, or a tetradecyl

group; a cycloalkyl group such as a cyclohexyl group; and an aryl group such as a phenyl group or a naphthyl group.

Each of the cycloalkyl group and the aryl group may have a substituent.

Examples of the substituent include a halogen atom, an alkyl group, an acyl group, a
 5 nitro group, and an amino group. The number of carbon atoms in the alkyl group as a substituent is preferably in a range of 1 to 18.

R^{14} to R^{16} may be the same as or different from one another.

From the viewpoints of obtaining a coating film exhibiting a stabilized polishing rate and maintaining the stabilized antifouling performance for a long period of time, it is
 10 preferable that at least one of R^{14} to R^{16} represent an isopropyl group and particularly preferable that all of R^{14} and R^{16} represent an isopropyl group.

[0077]

Examples of the constituent unit (A2) include a constituent unit derived from the polymerizable monomer (a2) containing a triorganosilyloxycarbonyl group. The
 15 polymerizable monomer (a2) typically has a triorganosilyloxycarbonyl group and an ethylenically unsaturated bond (polymerizable carbon-carbon double bond).

From the viewpoint that the viscosity at the time of dissolution of the copolymer (X) in an organic solvent becomes lower, it is preferable that the polymerizable monomer (a2) be a monofunctional monomer having one ethylenically unsaturated bond.

20 [0078]

Examples of the polymerizable monomer (a2) include a monomer represented by Formula (a21) and a monomer represented by Formula (a22). Among these, a compound represented by Formula (a21) is preferable.



(In Formulae (a21) and (a22), R^{14} to R^{16} each has the same definition as described above, R^{17} represents a hydrogen atom or a methyl group, and R^{18} represents an alkyl group.)

[0079]

5 Specific examples of the monomer represented by Formula (a21) include trimethylsilyl (meth)acrylate, triethylsilyl (meth)acrylate, tri-n-propylsilyl (meth)acrylate, tri-n-butylsilyl (meth)acrylate, tri-n-amylsilyl (meth)acrylate, tri-n-hexylsilyl (meth)acrylate, tri-n-octylsilyl (meth)acrylate, tri-n-dodecylsilyl (meth)acrylate, triphenylsilyl (meth)acrylate, tri-p-methylphenylsilyl (meth)acrylate, tribenzylsilyl (meth)acrylate, triisopropylsilyl (meth)acrylate, triisobutylsilyl (meth)acrylate, tri-s-butylsilyl (meth)acrylate, tri-2-methylisopropylsilyl (meth)acrylate, tri-t-butylsilyl (meth)acrylate, ethyldimethylsilyl (meth)acrylate, n-butyl dimethylsilyl (meth)acrylate, diisopropyl-n-butylsilyl (meth)acrylate, n-octyl di-n-butylsilyl (meth)acrylate, diisopropylstearyl silyl (meth)acrylate, dicyclohexylphenylsilyl (meth)acrylate, t-butyl diphenylsilyl (meth)acrylate, and lauryl diphenylsilyl (meth)acrylate.

[0080]

In Formula (a22), examples of the alkyl group as R^{18} include an alkyl group having 1 to 5 carbon atoms.

20 Specific examples of the compound represented by Formula (a22) include triisopropylsilyl methyl fumarate, triisopropylsilyl amyl fumarate, tri-n-butylsilyl-n-butyl malate, t-butyl diphenylsilyl methyl malate, t-butyl diphenylsilyl-n-butyl malate, triisopropylsilyl methyl fumarate, triisopropylsilyl amyl fumarate, tri-n-butylsilyl-n-butyl fumarate, t-butyl diphenylsilyl methyl fumarate, and t-butyl diphenylsilyl-n-butyl fumarate.

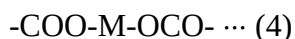
25 As the polymerizable monomer (a2), a commercially available product may be

used or the monomer can be appropriately synthesized according to a known method.

[0081]

(Constituent unit (A3))

The constituent unit (A3) is a constituent unit having at least one structure (III)
5 represented by Formula (4) or (5).



(In Formulae (4) and (5), M represents Zn, Cu, Mg, or Ca, and R^{22} represents a monovalent organic acid residue.)

10 [0082]

In Formulae (4) and (5), it is preferable that M represent Zn or Cu.

In Formula (5), the organic acid residue as R^{22} indicates a remaining part obtained by removing one proton from an organic acid (for example, a remaining part obtained by removing a proton from a carboxy group of a carboxylic acid) and is ion-
15 bonded to M in place of this proton.

As the organic acid, a carboxylic acid is preferable, and examples thereof include a monocarboxylic acid such as monochloroacetic acid, monofluoroacetic acid, acetic acid, propionic acid, octylic acid, versatic acid, isostearic acid, palmitic acid, cresotic acid, α -naphthoic acid, β -naphthoic acid, benzoic acid, 2,4,5-
20 trichlorophenoxyacetic acid, 2,4-dichlorophenoxyacetic acid, quinolinecarboxylic acid, nitrobenzoic acid, nitronaphthalenecarboxylic acid, pyruvic acid, naphthenic acid, abietic acid, hydrogenated abietic acid, or (meth)acrylic acid.

From the viewpoint of the storage stability, it is preferable that R^{22} represent an organic acid residue other than the (meth)acryloyloxy group.

25 From the viewpoint of obtaining a coating film with high durability which can

prevent cracking or peeling for a long period of time, it is preferable that R^{22} represent a fatty acid residue (aliphatic monocarboxylic acid residue) having 1 to 20 carbon atoms.

[0083]

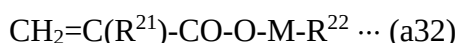
Examples of the constituent unit (A3) include a constituent unit derived from the
5 polymerizable monomer (a3) having a structure (III).

Examples of the polymerizable monomer (a3) having the structure (III) include a
monomer in which a vinyl group having an unsubstituted or substituted group is bonded
to both terminals of a group represented by Formula (4) and a monomer in which a vinyl
group having an unsubstituted or substituted group is bonded to one terminal (a side
10 opposite to the R^{22} side) of a group represented by Formula (5).

Examples of the monomer in which the vinyl group is bonded to both terminals
of a group represented by Formula (4) include a monomer (hereinafter, also referred to as
a “monomer (a31)”) represented by formula (a31).

Examples of the monomer in which the vinyl group is bonded to one terminal of
15 a group represented by Formula (5) include a monomer (hereinafter, also referred to as a
“monomer (a32)”) represented by Formula (a32).

[0084]



20 In Formulae (a31) and (a32), M represents Zn, Cu, Mg, or Ca, R^{21} represents a
hydrogen atom or a methyl group, and R^{22} represents a monovalent organic acid residue.

M and R^{22} each has the same definition as described above, and the preferable
aspects thereof are the same as described above.

[0085]

25 Examples of the monomer (a31) include zinc acrylate $[(\text{CH}_2=\text{CHCOO})_2\text{Zn}]$,

zinc methacrylate $[(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})_2\text{Zn}]$, copper acrylate $[(\text{CH}_2=\text{CHCOO})_2\text{Cu}]$, copper methacrylate $[(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})_2\text{Cu}]$, magnesium acrylate $[(\text{CH}_2=\text{CHCOO})_2\text{Mg}]$, magnesium methacrylate $[(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})_2\text{Mg}]$, calcium acrylate $[(\text{CH}_2=\text{CHCOO})_2\text{Ca}]$, and calcium methacrylate $[(\text{CH}_2=\text{C}(\text{CH}_3)\text{COO})_2\text{Ca}]$.

5 These may be used alone or in combination of two or more kinds thereof.

Among these, from the viewpoint that the transparency of the copolymer (X) is improved and the color tone of the coating film containing the copolymer (X) tends to be beautiful, zinc (meth)acrylate or copper (meth)acrylate is preferable.

[0086]

10 Examples of the monomer (a32) include magnesium monochloroacetate (meth)acrylate, calcium monochloroacetate (meth)acrylate, zinc monochloroacetate (meth)acrylate, and copper monochloroacetate (meth)acrylate; magnesium monofluoroacetate (meth)acrylate, calcium monofluoroacetate (meth)acrylate, zinc monofluoroacetate (meth)acrylate, and copper monofluoroacetate (meth)acrylate;

15 magnesium acetate (meth)acrylate, calcium acetate (meth)acrylate, zinc acetate (meth)acrylate, and copper acetate (meth)acrylate; magnesium propionate (meth)acrylate, calcium propionate (meth)acrylate, zinc propionate (meth)acrylate, and copper propionate (meth)acrylate; magnesium octylate (meth)acrylate, calcium octylate (meth)acrylate, zinc octylate (meth)acrylate, and copper octylate (meth)acrylate;

20 magnesium versatate (meth)acrylate, calcium versatate (meth)acrylate, zinc versatate (meth)acrylate, and copper versatate (meth)acrylate; magnesium isostearate (meth)acrylate, calcium isostearate (meth)acrylate, zinc isostearate (meth)acrylate, and copper isostearate (meth)acrylate; magnesium palmitate (meth)acrylate, calcium palmitate (meth)acrylate, zinc palmitate (meth)acrylate, and copper palmitate

25 (meth)acrylate; magnesium cresotinate (meth)acrylate, calcium cresotinate

(meth)acrylate, zinc cresotinate (meth)acrylate, and copper cresotinate (meth)acrylate; magnesium α -naphthoate (meth)acrylate, calcium α -naphthoate (meth)acrylate, zinc α -naphthoate (meth)acrylate, and copper α -naphthoate (meth)acrylate; magnesium β -naphthoate (meth)acrylate, calcium β -naphthoate (meth)acrylate, zinc β -naphthoate (meth)acrylate, and copper β -naphthoate (meth)acrylate; magnesium benzoate (meth)acrylate, calcium benzoate (meth)acrylate, zinc benzoate (meth)acrylate, and copper benzoate (meth)acrylate; magnesium 2,4,5-trichlorophenoxy acetate (meth)acrylate, calcium 2,4,5-trichlorophenoxy acetate (meth)acrylate, zinc 2,4,5-trichlorophenoxy acetate (meth)acrylate, and copper 2,4,5-trichlorophenoxy acetate (meth)acrylate; magnesium 2,4-dichlorophenoxy acetate (meth)acrylate, calcium 2,4-dichlorophenoxy acetate (meth)acrylate, zinc 2,4-dichlorophenoxy acetate (meth)acrylate, and copper 2,4-dichlorophenoxy acetate (meth)acrylate; magnesium quinoline carboxylate (meth)acrylate, calcium quinoline carboxylate (meth)acrylate, zinc quinoline carboxylate (meth)acrylate, and copper quinoline carboxylate (meth)acrylate; magnesium nitrobenzoate (meth)acrylate, calcium nitrobenzoate (meth)acrylate, zinc nitrobenzoate (meth)acrylate, and copper nitrobenzoate (meth)acrylate; magnesium nitronaphthalene carboxylate (meth)acrylate, calcium nitronaphthalene carboxylate (meth)acrylate, zinc nitronaphthalene carboxylate (meth)acrylate, and copper nitronaphthalene carboxylate (meth)acrylate; and magnesium pyruvate (meth)acrylate, calcium pyruvate (meth)acrylate, zinc pyruvate (meth)acrylate, and copper pyruvate (meth)acrylate. These may be used alone or in combination of two or more kinds thereof.

Among these, from the viewpoint that the transparency of the copolymer (X) is improved and the color tone of the coating film containing the copolymer (X) tends to be

beautiful, a zinc-containing monomer in which M represents Zn is preferable. Further, from the viewpoint of the durability of the coating film to be obtained, fatty acid zinc (meth)acrylate (in which M in Formula (a32) represents Zn and R²² represents a fatty acid residue) or fatty acid copper (meth)acrylate (in which M in Formula (a32) represents Cu and R²² represents a fatty acid residue) is more preferable.

[0087]

From the viewpoints of maintaining self-polishing properties of the coating film for a long period of time and obtaining excellent antifouling properties, the polymerizable monomer (a3) may contain both of the monomer (a31) and the monomer (a32). That is, the copolymer (X) may contain both of a constituent unit derived from the monomer (a31) (hereinafter, also referred to as a “monomer (a31) unit”) and a constituent unit derived from the monomer (a32) (hereinafter, also referred to as a “monomer (a32) unit”).

As the combination of the monomer (a31) and the monomer (a32), a combination of zinc (meth)acrylate and fatty acid zinc (meth)acrylate or a combination of copper (meth)acrylate and fatty acid copper (meth)acrylate is preferable.

[0088]

In a case where the copolymer (X) has both of the monomer (a31) unit and the monomer (a32) unit, the ratio (molar ratio) (monomer (a31) unit/monomer (a32) unit) of the monomer (a31) unit to the monomer (a32) unit in the copolymer (X) is preferably in a range of 10/90 to 90/10, more preferably in a range of 20/80 to 80/20, and still more preferably in a range of 30/70 to 70/30. In a case where the ratio thereof is 90/10 or less, the crack resistance or the adhesiveness of the coating film becomes excellent. In a case where the ratio thereof is 10/90 or greater, the viscosity of the paint tends to be lowered.

[0089]

The polymerizable monomer (a3) may be produced according to a known method, or a commercially available product may be used as the monomer.

The monomer (a31) is obtained by reacting an inorganic metal compound
5 having a metal element corresponding to M in Formula (a31) and (meth)acrylic acid in a diluent such as an organic solvent or a reactive diluent containing a polymerizable unsaturated group such as an ethylenically unsaturated monomer. The mixture containing a metal atom-containing polymerizable monomer obtained using this method has excellent compatibility with an organic solvent or another monomer so that the
10 polymerization can be easily carried out. It is preferable that the reaction be performed in the presence of water, and the content of water in the reactant preferably be in a range of 0.01% to 30% by mass. Examples of the inorganic metal compound include an oxide, a hydroxide, and a chloride of a metal selected from Zn, Cu, Mg, and Ca.

[0090]

15 The monomer (a32) is obtained by reacting an inorganic metal compound having a metal element corresponding to M in Formula (a32), (meth)acrylic acid, and an organic acid corresponding to R²² as an organic acid residue in Formula (a32) in a diluent such as an organic solvent or a reactive diluent containing a polymerizable unsaturated group such as an ethylenically unsaturated monomer. Examples of the inorganic metal
20 compound are the same as those exemplified as the inorganic metal compound used for obtaining the monomer (a31).

[0091]

The monomer mixture containing the monomer (a31) and the monomer (a32) is obtained by reacting an inorganic metal compound having a metal element corresponding
25 to M in Formulae (a31) and (a32), (meth)acrylic acid, and an organic acid corresponding

to R²² as an organic acid residue in Formula (a32) in a diluent such as an organic solvent or a reactive diluent containing a polymerizable unsaturated group such as an ethylenically unsaturated monomer.

The amount of the organic acid to be used, which corresponds to R²², is preferably in a range of 0.01 to 3 mol times, more preferably in a range of 0.01 to 0.95 mol times, and still more preferably in a range of 0.1 to 0.7 mol times with respect to the amount of the inorganic metal compound. In a case where the content of the organic acid is 0.01 mol times or greater, precipitation of a solid in a step of producing this monomer mixture is suppressed, and the self-polishing properties and crack resistance of a coating film are improved. In a case where the content thereof is 3 mol times or less, the antifouling properties of a coating film tend to be maintained for a long period of time.

[0092]

<Constituent unit (D)>

The constituent unit (D) is a constituent unit derived from a polysiloxane block-containing polymerizable monomer other than the polymerizable monomer (b).

Another polysiloxane block-containing polymerizable monomer typically has a polysiloxane block and an ethylenically unsaturated bond.

The ethylenically unsaturated bond may be contained in a side chain of the polysiloxane block or in a terminal group bonded to a terminal of the polysiloxane block or may be contained in both of these.

The polysiloxane block may have a side chain that does not have an ethylenically unsaturated bond. Examples of the side chain that does not have an ethylenically unsaturated bond include an alkyl group, an alkoxy group, a phenyl group, a substituted phenyl group, a phenoxy group, and a substituted phenoxy group. The

number of carbon atoms in the alkyl group or the alkoxy group is preferably in a range of 1 to 18. Examples of the substituent in the substituted phenyl group or the substituted phenoxy group include an alkyl group and an alkoxy group.

A terminal group that does not have an ethylenically unsaturated bond may be bonded to a terminal of the polysiloxane block. Examples of the terminal group that does not have an ethylenically unsaturated bond are the same as the groups exemplified as the side chains that do not have an ethylenically unsaturated bond.

[0093]

As other forms of the polysiloxane block-containing polymerizable monomer, a both terminal type polysiloxane block-containing polymerizable monomer such as a polymerizable monomer (d1) represented by Formula (d1) or a polymerizable monomer (d2) represented by Formula (d2).

[0094]

$$\text{CH}_2=\text{CR}^{1a}-\text{CO}-\text{O}-(\text{C}_k\text{H}_{2k}-\text{O})_l-\text{C}_m\text{H}_{2m}-(\text{SiR}^{1b}\text{R}^{1c}-\text{O})_n-\text{SiR}^{1d}\text{R}^{1e}-\text{C}_o\text{H}_{2o}-(\text{O}-\text{C}_p\text{H}_{2p})_q-\text{O}-\text{CO}-\text{CR}^{1f}=\text{CH}_2 \dots (\text{d1})$$

$$\text{CH}_2=\text{CR}^{2a}-\text{CO}-\text{O}-(\text{C}_{k'}\text{H}_{2k'}-\text{O})_{l'}-\text{C}_{m'}\text{H}_{2m'}-\text{Si}((\text{OSiR}^{2b}\text{R}^{2c})_r-\text{OSiR}^{2d}\text{R}^{2e}\text{R}^{2f})_2-\text{OSi}((\text{OSiR}^{2g}\text{R}^{2h})_s-\text{OSiR}^{2i}\text{R}^{2j}\text{R}^{2k})_2-\text{C}_{o'}\text{H}_{2o'}-(\text{O}-\text{C}_{p'}\text{H}_{2p'})_{q'}-\text{O}-\text{CO}-\text{CR}^{2l}=\text{CH}_2 \dots (\text{d2})$$

(In Formulae (d1) and (d2), R^{1a} and R^{1f} each represents a hydrogen atom or a methyl group, k and p each represents an integer of 2 to 5, l and q each represents a number of 0 to 50, m and o each represents an integer of 2 to 5, n represents a number of 3 to 80, R^{1b} to R^{1e} each represents an alkyl group, an alkoxy group, a phenyl group, a substituted phenyl group, a phenoxy group, or a substituted phenoxy group,

R^{2a} and R^{2l} each represents a hydrogen atom or a methyl group, k' and p' each represents an integer of 2 to 5, l' and q' each represents a number of 0 to 50, m' and o' each represents an integer of 2 to 5, r and s each represents a number of 0 to 20, and R^{2b}

to R^{2k} each represents an alkyl group.)

[0095]

In Formula (d1), R^{1b} to R^{1e} each has the same definition as that for R^{31} to R^{39} , and the preferable aspects thereof are the same as described above.

5 k and p represent an integer of 2 to 5 and preferably 2 or 3 from the viewpoint of low cost. A combination of a monomer in which k and p represent 2 and a monomer in which k and p represent 3 can be used.

l and q each has the same definition as that for b described above, and the preferable aspects thereof are the same as described above.

10 m and o represent an integer of 2 to 5 and preferably 2 or 3.

n represents an average polymerization degree of the polysiloxane structure. In a case where n is greater than or equal to the above-described lower limit, the coating film tends to exhibit the antifouling effect even in a case where the antifouling paint composition containing the copolymer (X) does not contain an antifouling agent.

15 Further, in a case where n is less than or equal to the above-described upper limit, the compatibility between the polymerizable monomer (d1) and a polymerizable monomer that does not have a polysiloxane block (for example, a polymerizable monomer forming the constituent unit (A)), and the solubility of the copolymer (X) in a solvent tend to be improved. n preferably represents 5 to 50, more preferably 7 to 40, and particularly
20 preferably 8 to 30.

Further, each of R^{1a} to R^{1f} , k, l, m, n, o, p, and q is independent. In a case where the same symbols are present in or between molecules, these may be different from each other.

[0096]

25 Specific examples of the polymerizable monomer (d1) in which l and q

represent 0 include FM-7711, FM-7721, and FM-7725 (all trade names, manufactured by JNC Corporation), and X-22-164, X-22-164AS, X-22-164C (all trade names, manufactured by Shin-Etsu Chemical Co., Ltd.).

[0097]

5 In Formula (d2), R^{2b} to R^{2k} each has the same definition as that for R^{31} to R^{39} , and the preferable aspects thereof are the same as described above.

k' and p' represent an integer of 2 to 5 and preferably 2 or 3 from the viewpoint of low cost. A combination of a monomer in which k' and p' represent 2 and a monomer in which k' and p' represent 3 can be used.

10 l' and q' each has the same definition as that for b described above, and the preferable aspects thereof are the same as described above.

m' and o' represent an integer of 2 to 5 and preferably 2 or 3.

r and s each represents an average polymerization degree of the polysiloxane structure. In a case where r and s are each lower than or equal to the above-described upper limit, the compatibility between the polymerizable monomer (d2) and a polymerizable monomer that does not have a polysiloxane block, and the solubility of the copolymer (X) in a solvent tend to be improved. r and s each preferably represents 10 or less, more preferably 5 or less.

20 Further, each of R^{2a} to R^{2l} , k' , l' , m' , n' , o' , p' , q' , r , and s is independent. In a case where the same symbols are present in or between molecules, these may be different from each other.

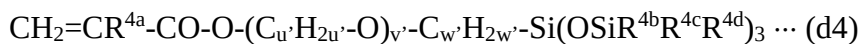
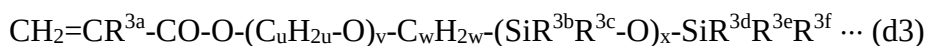
[0098]

As other forms of the polysiloxane block-containing polymerizable monomer, a one terminal type polysiloxane block-containing polymerizable monomer such as a polymerizable monomer (d3) represented by Formula (d3) or a polymerizable monomer

25

(d4) represented by Formula (d4).

[0099]



5 (In Formulae (d3) and (d4), R^{3a} represents a hydrogen atom or a methyl group, u represents an integer of 2 to 5, v represents a number of 0 to 50, w represents an integer of 2 to 5, x represents a number of 3 to 80, R^{3b} to R^{3f} each represents an alkyl group, an alkoxy group, a phenyl group, a substituted phenyl group, a phenoxy group, or a substituted phenoxy group,

10 R^{4a} represents a hydrogen atom or a methyl group, u' represents an integer of 2 to 5, v' represents a number of 0 to 50, w' represents an integer of 2 to 5, R^{4b} to R^{4d} each represents an alkyl group, $-(\text{OSiR}^{61}\text{R}^{62})_y-\text{OSiR}^{63}\text{R}^{64}\text{R}^{65}$ (here, y represents an integer of 0 to 20, and R^{61} to R^{65} represent an alkyl group), or $-\text{R}^{66}-(\text{OC}_2\text{H}_4)_{y'}-\text{OR}^{67}$ (here, y' represents an integer of 1 to 20, R^{66} represents an alkylene group, and R^{67} represents an
15 alkyl group.))

[0100]

In Formula (d3), R^{3b} to R^{3f} each has the same definition as that for R^{31} to R^{39} , and the preferable aspects thereof are the same as described above.

u represents an integer of 2 to 5 and preferably 2 or 3 from the viewpoint of low
20 cost. A combination of a monomer in which u represents 2 and a monomer in which u represents 3 can be used.

v has the same definition as that for b described above, and the preferable aspects thereof are the same as described above.

w represents an integer of 2 to 5 and preferably 2 or 3.

25 x has the same definition as that for n described above, and the preferable

aspects thereof are the same as described above.

Further, each of R^{3a} to R^{3f} , u, v, w, and x is independent. In a case where the same symbols are present in or between molecules, these may be different from each other.

5 [0101]

Specific examples of the polymerizable monomer (d3) in which v represents 0 include FM-0711, FM-0721, and FM-0725 (all trade names, manufactured by JNC Corporation), and X-24-8201, X-22-174ASX, X-22-174DX, and X-22-2426 (all trade names, manufactured by Shin-Etsu Chemical Co., Ltd.).

10 [0102]

In Formula (d4), the alkyl group as R^{4b} to R^{4d} has the same definition as that for the alkyl group as R^{31} to R^{39} , and the preferable aspects thereof are the same as described above.

y and y' each represents an average polymerization degree of the polysiloxane structure. In a case where y and y' are each lower than or equal to the above-described upper limit, the compatibility between the polymerizable monomer (d4) and a polymerizable monomer that does not have a polysiloxane block, and the solubility of the copolymer (X) in a solvent tend to be improved. y and y' each preferably represents 10 or less, more preferably 5 or less.

20 Examples of the alkyl group as R^{61} to R^{65} and R^{67} are the same as those exemplified as the alkyl group represented by R^{4b} to R^{4d} , and the preferable aspects thereof are the same as described above. The number of carbon atoms in the alkylene group as R^{66} is preferably in a range of 1 to 18.

u' represents an integer of 2 to 5 and preferably 2 or 3 from the viewpoint of low cost. A combination of a monomer in which u' represents 2 and a monomer in which u'

25

represents 3 can be used.

v' has the same definition as that for b, and the preferable aspects thereof are the same as described above.

w' represents an integer of 2 to 5 and preferably 2 or 3.

5 Further, each of R^{4a} to R^{4d} , u', v', w', y and y' is independent. In a case where the same symbols are present in or between molecules, these may be different from each other.

[0103]

Specific examples of the polymerizable monomer (d4) in which v' represents 0
10 include TM-0701 (trade name, manufactured by JNC Corporation) and X-22-2404 (trade name, manufactured by Shin-Etsu Chemical Co., Ltd.).

[0104]

Other polysiloxane block-containing polymerizable monomers may be used alone or in combination of multiple kinds thereof.

15 [0105]

<Constituent unit (E)>

The constituent unit (E) is not particularly limited, and examples thereof include a unit derived from a monomer (d) other than the polymerizable monomer (b), other polysiloxane block-containing polymerizable monomers, the macromonomer (c), the
20 polymerizable monomer (a1), the polymerizable monomer (a2), and the polymerizable monomer (a3).

The monomer (d) is not particularly limited as long as the monomer is copolymerizable with the polymerizable monomer (b) or the like, and various monomers containing a radically polymerizable group such as an ethylenically unsaturated bond can
25 be used. For example, monomers which are the same as the monomer (c1) used to

obtain the macromonomer (c), exemplified above, can be used (here, excluding the polymerizable monomer (a1), the polymerizable monomer (a2), and the polymerizable monomer (a3)).

[0106]

5 From the viewpoint that the copolymer (X) is easily formed to have a high solid content and a low viscosity at the time of being dissolved in a solvent, it is preferable that the constituent unit (E) be a constituent unit derived from a monofunctional monomer having one ethylenically unsaturated bond and particularly preferable that an ethylenically unsaturated bond be derived from an acryloyl group. That is, it is particularly preferable that the constituent unit (E) be a constituent unit derived from a monofunctional monomer containing one acryloyl group.

[0107]

(Content of each constituent unit)

15 The content of the constituent unit (B) in the copolymer (X) is preferably in a range of 1% to 80% by mass, more preferably in a range of 5% to 70% by mass, and still more preferably in a range of 10% to 60% by mass with respect to the total amount (100% by mass) of all constituent units. In a case where the content of the constituent unit (B) is greater than or equal to the above-described lower limit, the surface smoothness and the antifouling properties of a coating film are further improved. In a case where the content of the constituent unit (B) is less than or equal to the above-described upper limit, the crack resistance is further improved.

[0108]

25 The content of the constituent unit (B) is preferably 5% by mass or greater, more preferably 15% by mass or greater, and still more preferably 35% by mass or greater with respect to the total amount (100% by mass) of the constituent unit (B) and the constituent

unit (D). In a case where the proportion of the constituent unit (B) is greater than or equal to the above-described lower limit, the surface smoothness of a coating film to be formed is further improved.

[0109]

5 The content of the constituent unit (C) in the copolymer (X) is preferably in a range of 2% to 40% by mass, more preferably in a range of 8% to 30% by mass, and still more preferably in a range of 10% to 25% by mass with respect to the total amount (100% by mass) of all constituent units. In a case where the content of the constituent unit (C) is greater than or equal to the above-described lower limit, the long-term
10 antifouling properties of a coating film are further improved. In a case where the content of the constituent unit (C) is less than or equal to the above-described upper limit, the crack resistance of a coating film to be formed is further improved.

[0110]

 The content of the constituent unit (A) in the copolymer (X) is preferably in a
15 range of 1% to 80% by mass, more preferably in a range of 5% to 70% by mass, and still more preferably in a range of 10% to 60% by mass with respect to the total amount (100% by mass) of all constituent units. In a case where the content of the constituent unit (A) is greater than or equal to the above-described lower limit, the self-polishing properties of a coating film are further improved. In a case where the content of the
20 constituent unit (A) is less than or equal to the above-described upper limit, the coating film to be formed has an appropriate hydrolyzability, the self-polishing properties are maintained for a long period of time, and the antifouling effect is further improved.

[0111]

 In a case where the copolymer (X) has a constituent unit derived from
25 hydrophobic group-containing (meth)acrylic acid ester as the constituent unit (E), the

content of this constituent unit is preferably in a range of 1% to 90% by mass and more preferably in a range of 10% to 80% by mass with respect to the total amount of all constituent units. In a case where the content of this constituent unit is in the above-described range, the flexibility, the crack resistance, and the peeling resistance of a coating film to be formed are further improved, and the antifouling effect becomes excellent. In a case where the content of this constituent unit is less than or equal to the above-described upper limit, a coating film to be formed has an appropriate hydrolyzability, the self-polishing properties are maintained for a long period of time, and the antifouling effect becomes excellent.

10 [0112]

In a case where the copolymer (X) has a constituent unit derived from oxyethylene group-containing (meth)acrylic acid ester as the constituent unit (E), the content of this constituent unit is preferably in a range of 1% to 80% by mass, more preferably in a range of 5% to 60% by mass, and still more preferably in a range of 20% to 50% by mass with respect to the total amount of all constituent units. In a case where the content of this constituent unit is greater than or equal to the above-described lower limit, the hydrophilicity of a coating film to be formed is further improved, and the self-polishing properties become excellent. In a case where the content of the constituent unit is less than or equal to the above-described upper limit, the coating film to be formed has an appropriate hydrolyzability, the self-polishing properties are maintained for a long period of time, and the antifouling effect is further improved.

Further, the total content of the constituent unit (A), the constituent unit (B), the constituent unit (C), the constituent unit (D), and the constituent unit (E) is 100% by mass with respect to the total content of all constituent units.

25 The content of each constituent unit in the copolymer (X) can be measured

according to a known method such as gas chromatography, high performance liquid chromatography, or nuclear magnetic resonance spectroscopy.

[0113]

In a case where the copolymer (X) has the constituent unit (A), it is preferable
5 that the copolymer (X) be a copolymer obtained by polymerizing a monomer mixture containing at least one polymerizable monomer (a) selected from the group consisting of the polymerizable monomer (a1), the polymerizable monomer (a2), and the polymerizable monomer (a3) and the polymerizable monomer (b). In a case of such a copolymer, the water resistance of a coating film to be formed is further improved
10 compared to a copolymer obtained by polymerizing a monomer mixture containing the polymerizable monomer (m0) containing an ethylenically unsaturated bond and a carboxy group, and the polymerizable monomer (b) to obtain a copolymer (X0) containing a carboxy group and converting the carboxy group in this copolymer (X0) to any of the structure (I), a triorganosilyloxycarbonyl group, and the structure (III).

15 It is preferable that the monomer mixture be formed of 1% to 80% by mass of the polymerizable monomer (a), 1% to 80% by mass of the polymerizable monomer (b), and 0% to 98% by mass of other polymerizable monomers. The content of each monomer is the proportion thereof in the total amount of the monomer mixture. The total content of the polymerizable monomer (a), the polymerizable monomer (b), and
20 other polymerizable monomers is 100% by mass. The more preferable range of the content of each monomer is the same as the preferable range of the content of the constituent unit derived from each monomer.

[0114]

The weight-average molecular weight (M_w) of the copolymer (X) is preferably
25 in a range of 1000 to 100000, more preferably in a range of 2000 to 80000, and still more

preferably in a range of 3000 to 60000. In a case where the weight-average molecular weight is less than or equal to the above-described upper limit, the viscosity of the solution at the time of dissolving the copolymer (X) in a solvent is further decreased, and a composition with a high solid content and a low viscosity is easily obtained as the antifouling paint composition. Further, the antifouling properties of a coating film are further improved. The weight-average molecular weight thereof is greater than or equal to the above-described lower limit, the hardness and the durability of a coating film to be formed are further improved.

[0115]

10 The number-average molecular weight (M_n) of the copolymer (X) is preferably in a range of 500 to 50000 and more preferably in a range of 1000 to 40000.

The molecular weight distribution (M_w/M_n) of the copolymer (X) is preferably in a range of 1.5 to 5.0 and more preferably in a range of 2.2 to 3.0.

15 The weight-average molecular weight and the number-average molecular weight of the copolymer (X) are measured by gel permeation chromatography (GPC) using polyethylene as a reference resin.

[0116]

20 The acid value of the copolymer (X) is preferably in a range of 1 to 140 mgKOH/g, more preferably in a range of 5 to 130 mgKOH/g, and still more preferably in a range of 10 to 120 mgKOH/g. In a case where the acid value of the copolymer (X) is less than or equal to the above-described upper limit, the water resistance and the crack resistance of the coating film are further improved.

25 The acid value of the copolymer (X) is measured according to a known technique such as neutralization titration using a potassium hydroxide solution. For example, the method in examples described below may be exemplified.

[0117]

(Method for producing copolymer (X))

Examples of the method for producing the copolymer (X) include the following production method (α).

5 The production method (α) is a method of polymerizing the polymerizable monomer (b) and a monomer mixture ($\alpha 1$) containing a polymerizable monomer different from the polymerizable monomer (b).

 Examples of the polymerizable monomer different from the polymerizable monomer (b) include the macromonomer (c), the polymerizable monomer (a1), the
10 polymerizable monomer (a2), the polymerizable monomer (a3), other polysiloxane block-containing polymerizable monomers, and the monomer (e).

[0118]

 In the production method (α), the composition of the monomer mixture ($\alpha 1$), that is, the kind of the monomers constituting the monomer mixture ($\alpha 1$) and the content
15 (% by mass) of each monomer with respect to the total mass of all monomers are the same as the composition of the copolymer (X), that is, the kind of the constituent units derived from each monomer constituting the copolymer (X) and the content (% by mass) of each constituent unit with respect to the total mass of all constituent units.

[0119]

20 The method of polymerizing the monomer mixture is not particularly limited, and a known polymerization method such as a solution polymerization method, a suspension polymerization method, a bulk polymerization method, or an emulsion polymerization method can be used. From the viewpoints of the productivity and the performance of the coating film, a solution polymerization method is preferable.

The polymerization may be performed according to a known method using a known polymerization initiator. Examples of the known method include a method of allowing the monomer components to react at a reaction temperature of 60°C to 120°C for 4 to 14 hours in the presence of a radical polymerization initiator. During the
5 polymerization, a chain transfer agent may be used as necessary.

[0120]

As the radical polymerization initiator, a known initiator can be used, and examples thereof include an azo-based compound such as 2,2-azobis(isobutyronitrile), 2,2-azobis(2,4-dimethyl valeronitrile), or 2,2-azobis(2-methylbutyronitrile); and an
10 organic peroxide such as benzoyl peroxide, cumene hydroperoxide, lauryl peroxide, di-t-butyl peroxide, or t-butylperoxy-2-ethylhexanoate. The content of the polymerization initiator is not particularly limited and can be appropriately set.

As the chain transfer agent, a known agent can be used, and examples thereof include mercaptans such as n-dodecyl mercaptan, thioglycolic acid esters such as octyl
15 thioglycolate, an α -methylstyrene dimer, and terpinolene. The content of the chain transfer agent is not particularly limited and can be appropriately set.

As the solvent used for the solution polymerization, for example, a typical organic solvent such as toluene, xylene, methyl isobutyl ketone, or n-butyl acetate can be used.

20 [0121]

However, the method for producing the copolymer (X) is not limited to the above-described production method (α).

For example, in a case where the copolymer (X) has the constituent unit (A), the copolymer (X) can be produced using the following production method (β).

Production method (β): a method of polymerizing a monomer mixture ($\beta 1$) containing the polymerizable monomer ($m0$) containing an ethylenically unsaturated bond and a carboxy group, and the polymerizable monomer (b) to obtain a copolymer ($X0$) containing a carboxy group and converting the carboxy group in this copolymer ($X0$) to any of the structure (I), a triorganosilyloxycarbonyl group, and the structure (III).
 5 The monomer mixture ($\beta 1$) may further contain a polymerizable monomer other than the polymerizable monomer ($m0$) and the polymerizable monomer (b).

Examples of other polymerizable monomers include the macromonomer (c), other polysiloxane block-containing polymerizable monomers, and the monomer (e).

10 [0122]

Examples of the polymerizable monomer ($m0$) are the same as those exemplified as the polymerizable monomer ($a1$).

In the production method (β), the composition of the monomer mixture ($\beta 1$) is the same as the composition of the copolymer (X) except that the polymerizable
 15 monomer (a) is the polymerizable monomer ($m0$). The polymerization of the monomer mixture ($\beta 1$) can be carried out in the same manner as the polymerization of the monomer mixture ($\alpha 1$) in the production method (α).

[0123]

Examples of the method of converting the carboxy group in the copolymer ($X0$)
 20 to the structure (I) include a method of causing a reaction (addition reaction) between the copolymer ($X0$) and the compound (Y). The reaction between the copolymer ($X0$) and the compound (Y) can be carried out in the same manner as the reaction between the polymerizable monomer ($m0$) and the compound (Y).

Examples of the method of converting the carboxy group in the copolymer ($X0$)

to the structure (III) include a method of reacting the copolymer (X0) with an organic acid metal salt such as copper acetate or zinc acetate. The metal of the organic acid metal salt corresponds to M described above. The reaction between the copolymer (X0) and the organic acid metal salt can be carried out by increasing the temperature to the
5 reflux temperature and continuing the reaction for 10 to 20 hours while removing the mixed solution of an organic acid such as acetic acid to be distilled, water, and an organic solvent and replenishing the same amount of the organic solvent.

[0124]

(Action effects)

10 Further, since the copolymer (X) has the constituent unit (B) and the polysiloxane block, marine organisms or other kinds of dirt are unlikely to be attached onto the surface of the coating film containing the copolymer (X). Accordingly, the coating film containing the copolymer (X) can exhibit an excellent antifouling effect even in a case where the coating film does not contain an antifouling agent.

15 Further, since the copolymer (X) has the constituent unit (B), the surface smoothness of the coating film containing the copolymer (X) is excellent based on the comparison to a constituent unit derived from a polysiloxane block-containing polymerizable monomer other than the constituent unit (B). For example, a temporal increase in surface roughness of the coating film in sea water or the like is suppressed.

20 For example, the water resistance is decreased at the time of movement of a ship or the like in a case where this coating film is provided on the bottom of a ship due to the suppression of an increase in surface roughness, and this results in low fuel consumption. Further, this coating film has excellent crack resistance. It is considered that such effects are exhibited because of the improvement of the water resistance of the coating
25 film.

In a case where the copolymer (X) further has the constituent unit (C), the long-term antifouling properties are further improved.

In a case where the copolymer (X) further has the constituent unit (A), the coating film containing the copolymer (X) exhibits self-polishing properties in sea water
5 or the like, an excellent antifouling effect can be obtained.

[0125]

[Resin composition]

The resin composition of the present invention contains the copolymer (X) described above. The copolymer (X) contained in the resin composition may be used
10 alone or in combination of two or more kinds thereof.

[0126]

The content of the copolymer (X) in the resin composition of the present invention is not particularly limited, but is preferably 45% by mass or greater, more preferably 50% by mass or greater, still more preferably 55% by mass or greater,
15 particularly preferably 60% by mass, and most preferably 64% by mass with respect to the total amount of the resin composition. In a case where the content of the copolymer (X) is greater than or equal to the above-described lower limit, an antifouling paint composition with a small VOC content can be easily obtained.

The upper limit of the content of the copolymer (X) is not particularly limited
20 and may be 100% by mass. In a case where the resin composition contains a solvent, the content of the solvent is preferably set to an amount such that the viscosity of the resin composition at 25°C to be measured using a B type viscometer is less than 5000 mPa·s (more preferably less than 3000 mPa·s). In addition, the content of the solvent varies depending on the weight-average molecular weight of the copolymer (X), the glass
25 transition temperature, and the presence of the crosslinked structure, but is preferably

85% by mass or less and more preferably 80% by mass or less.

[0127]

In a case where the copolymer (X) has the constituent unit (A1), it is preferable that the resin composition of the present invention further contain at least one selected
5 from the group consisting of a compound reacting with an acid, a basic compound, an acidic compound, and a dehydrating agent. In this manner, the storage stability of the resin composition and the antifouling paint composition containing this resin composition is improved.

In a case where the copolymer (X) has the constituent unit (A1), in the resin
10 composition containing the copolymer (X) and the antifouling paint composition containing this resin composition, the structure (I) during storage may be decomposed unintentionally. In a case where the structure (I) is decomposed, a carboxylic acid is generated. In this manner, the glass transition temperature of the copolymer (X) is increased, and the carboxylic acid and other components in the paint form a crosslinked
15 structure and thus the viscosity of the solution of the copolymer (X) or the paint containing this solution may be increased. Further, generation of a free carboxylic acid results in degradation of the stability of dissolution in an organic solvent and the water resistance. In addition, by catalytically promoting the hydrolysis reaction of the generated carboxylic acid as an acid, decomposition of the structure (I) advances. In a
20 case where the resin composition contains a compound that reacts with an acid, a carboxylic acid is captured by the compound that reacts with an acid at the time of decomposition of the structure (I) in the copolymer (X) to generate a carboxylic acid, and the storage stability is improved.

Further, in a high pH region or a low pH region, the storage stability is degraded
25 due to the decomposition of the structure (I). In a high pH region, the storage stability

is also degraded due to a decrease in the reactivity between the compound (Y) and the carboxylic acid. The decomposition of the structure (I) is suppressed and the degradation of the storage stability can be suppressed by adjusting the pH of the resin composition through addition of a basic compound or an acidic compound.

5 Further, the moisture promotes decomposition (hydrolysis) of the structure (I). In a case where the resin composition contains a dehydrating agent, the moisture in the resin composition is captured so that degradation of the storage stability can be suppressed.

[0128]

10 Examples of the compound that reacts with an acid include the compound (Y), a basic compound, and a compound containing an epoxy group.

Examples of the basic compound include dimethylamine, diethylamine, trimethylamine, trimethylamine, aniline, and pyridine.

Examples of the compound containing an epoxy group include 2-ethyloxysilane,
15 2,3-dimethyloxysilane, 2,2-dimethyloxysilane, glycidyl (meth)acrylate, glycidyl α -ethyl acrylate, and 3,4-epoxybutyl (meth)acrylate.

From the viewpoint of the storage stability, the compound (Y) is preferable as the compound that reacts with an acid. Among the examples of the compound, as the compound (Y), 1-alkenyl alkyl ether in which X in formula (31) represents -O- is
20 preferable, and vinyl ethers such as butyl vinyl ether and isobutyl vinyl ether are more preferable from the viewpoint that the effect of improving the storage stability is further improved.

[0129]

Examples of the basic compound used for adjusting the pH are the same as those
25 exemplified as the basic compound described above.

Examples of the acidic compound include abietic acid, neoabietic acid, parastrinic acid, pimaric acid, isopimaric acid, levopimaric acid, dextropimaric acid, sandaracopimaric acid, acetic acid, propionic acid, butyric acid, lauric acid, stearic acid, linoleic acid, oleic acid, chloroacetic acid, and fluoroacetic acid.

5 [0130]

Examples of the dehydrating agents include a silicate-based dehydrating agent, an isocyanate-based dehydrating agent, an ortho ester-based dehydrating agent, and an inorganic dehydrating agent. More specific examples thereof include methyl orthoformate, ethyl orthoformate, methyl orthoacetate, orthoboric acid ester, tetraethyl
10 orthosilicate, anhydrous gypsum, calcined gypsum, and synthetic zeolite (molecular sieve). Among these, a molecular sieve is particularly preferable.

[0131]

These additives can be used alone or in combination of two or more kinds thereof.

15 Examples of the combination of two or more kinds of the additives include a combination of the compound (Y) and the dehydrating agent, a combination of the compound (Y), the acidic compound, and the dehydrating agent, a combination of the compound (Y), the basic compound, the acidic compound, and the dehydrating agent, and a combination of the basic compound and the dehydrating agent.

20 [0132]

In a case where the resin composition contains the compound (Y), the content of the compound (Y) in the resin composition is preferably 20% by mole or greater, more preferably in a range of 30% to 1000% by mole, and still more preferably in a range of 40% to 800% by mole with respect to the amount of the structure (I) in the copolymer

25 (X). In a case where the content of the compound (Y) is in the above-described range,

the effect of improving the storage stability is further improved.

[0133]

In a case where the resin composition contains a basic compound and/or an acidic compound, from the viewpoint of the storage stability, as the content of the basic compound and/or the acidic compound in the resin composition, the amount of the basic compound with a concentration set such that the pH to be measured in water is in a range of 2 to 12 is preferable and the amount of the basic compound with a concentration set such that the pH is in a range of 6 to 9 is more preferable.

Here, specifically, the pH to be measured in water indicates a value to be measured by adding the basic compound in water. The pH indicates a value at 23°C.

[0134]

In a case where the resin composition contains a dehydrating agent, the content of the dehydrating agent in the resin composition is preferably in a range of 0.1% to 40% by mass and more preferably in a range of 1% to 20% by mass with respect to the total mass of the resin composition. In a case where the content of the dehydrating agent is greater than or equal to the above-described lower limit, the storage stability is further improved. In a case where the content of the dehydrating agent is less than or equal to the above-described upper limit, the dissolution stability is further improved.

[0135]

The resin composition of the present invention may further contain a silicone oil. In a case where the resin composition contains a silicone oil, the antifouling properties of a coating film to be formed are excellent.

Examples of the silicone oil include a straight silicone oil such as dimethyl silicone oil, methyl phenyl silicone oil, or methyl hydrogen silicone oil, and a modified silicone oil. A modified silicone oil indicates a silicone oil in which an organic group

(hereinafter, also referred to as a “modification group”) other than a methyl group and a phenyl group is introduced into some silicon atoms of a straight silicone oil. Examples of the modification group include a chlorophenyl group, a methylstyrene group, a long-chain alkyl group (for example, an alkyl group having 2 to 18 carbon atoms), a polyether group, a carbinol group, an aminoalkyl group, an epoxy group, and a (meth)acryloyl group. These silicone oils may be used alone or in combination of two or more kinds thereof.

[0136]

As the silicone oil, commercially available products can be used. Examples of the commercially available silicone oil include “KF-96”, “KF-50”, “KF-54”, “KF-56”, and “KF-6016” (all manufactured by Shin-Etsu Chemical Co., Ltd.), “TSF451” (manufactured by Momentive Performance Materials Inc.), “Fluid47” (manufactured by (France) Rhone-Poulenc), and “SH200”, “SH510”, “SH550”, “SH710”, “DC200”, “ST-114PA”, and “FZ209” (all manufactured by Dow Corning Toray Co., Ltd.).

[0137]

It is preferable that the resin composition of the present invention contain an organic solvent. In a case where the resin composition contains an organic solvent, the coating suitability of the antifouling paint composition obtained by using the resin composition, the water resistance of a coating film to be formed, and the film forming properties are further improved.

The organic solvent is not particularly limited as long as the copolymer (X) can be dissolved in the organic solvent, and examples thereof include a hydrocarbon-based solvent such as toluene or xylene; an ether-based solvent such as the compound (Y) or propylene glycol monomethyl ether-2-acetate; a ketone-based solvent such as methyl isobutyl ketone; and an ester-based solvent such as n-butyl acetate. These can be used

alone or in combination of two or more kinds thereof.

[0138]

From the viewpoint of reducing the VOC content in the antifouling paint composition, the content of the organic solvent in the resin composition of the present invention is preferably 60% by mass or less, more preferably 50% by mass or less, still more preferably 45% by mass or less, and particularly preferably 40% by mass or less with respect to the total amount of the resin composition.

The content of the organic solvent is preferably set to an amount such that the viscosity of the resin composition at 25°C to be measured using a B type viscometer is less than or equal to the preferable upper limit described below and varies depending on the weight-average molecular weight of the copolymer (X), the glass transition temperature thereof, the presence of a crosslinked structure, and the like, but is preferably 15% by mass or greater and more preferably 20% by mass or greater.

Further, the compound (Y) can function as an organic solvent. Therefore, in a case where the resin composition contains the compound (Y), the content of the compound (Y) is included in the content of the organic solvent.

[0139]

The resin composition of the present invention may further contain components other than the copolymer (X), the compound that reacts with an acid, the basic compound, the acidic compound, the dehydrating agent, the silicone oil, and the organic solvent.

Examples of other components are the same as those exemplified as other components in the antifouling paint composition described below.

The content of other components is preferably 200% by mass or less and may be 0% by mass with respect to the amount of the copolymer (X).

[0140]

The solid content of the resin composition of the present invention is preferably 40% by mass or greater, more preferably 50% by mass or greater, still more preferably 55% by mass or greater, and particularly preferably 60% by mass. In a case where the solid content of the resin composition is greater than or equal to the above-described lower limit, the VOC content of the antifouling paint composition is sufficiently decreased.

The upper limit of the solid content of the resin composition is not particularly limited and may be 100% by mass. In a case where the resin composition contains an organic solvent, from the viewpoint of the viscosity of the resin composition, the content thereof is preferably 85% by mass or less and more preferably 80% by mass or less.

The solid content of the resin composition is measured using the measuring method described in the examples below.

[0141]

In a case where the resin composition of the present invention contains an organic solvent, the viscosity of the resin composition to be measured at 25°C using a B type viscometer (hereinafter, also referred to as a “B type viscosity”) is preferably less than 5000 mPa·s, more preferably less than 3000 mPa·s, still more preferably less than 2000 mPa·s, and particularly preferably less than 1000 mPa·s.

The viscosity of the resin composition to be measured at 25°C using a Gardner bubble viscometer (hereinafter, also referred to as a “Gardner viscosity”) is preferably W or less and more preferably V or less.

In a case where the viscosity (the B type viscosity or the Gardner viscosity) of the resin composition is less than or equal to the above-described upper limit, a solvent

does not need to be added to the resin composition in order to dilute the resin composition, and an antifouling agent or the like can be blended or applied thereto so that an antifouling paint composition with a small VOC content can be obtained. It is preferable that the viscosity of the resin composition in a case where the solid content thereof is at least 50% by mass be lower than or equal to the above-described preferable upper limit.

The lower limit of the viscosity of the resin composition is not particularly limited. From the viewpoint of suppressing sagging of the paint at the time of application, the B type viscosity at 25°C is preferably 100 mPa·s or greater.

Therefore, the B type viscosity of the resin composition at 25°C is preferably 100 mPa·s or greater and less than 5000 mPa·s, more preferably 100 mPa·s or greater and less than 3000 mPa·s, still more preferably 100 mPa·s or greater and less than 2000 mPa·s, and particularly preferably 100 mPa·s or greater and less than 1000 mPa·s.

[0142]

The viscosity of the resin composition can be adjusted depending on the solid content of the resin composition (the content of the copolymer (X) and other components), the weight-average molecular weight of the copolymer (X), the glass transition temperature, and the presence of the crosslinked structure. For example, the viscosity tends to be lowered as the solid content, particularly the content of the copolymer(X), decreases. In addition, the viscosity tends to be lowered as the weight-average molecular weight of the copolymer (X) decreases or the glass transition temperature decreases.

[0143]

<Decomposition rate of structure (I)>

In a case where the copolymer (X) has the constituent unit (A1), the decomposition rate of the structure (I) in the copolymer (X) after storage of the resin composition at 40°C for 30 days in the resin composition of the present invention is preferably 20% or less, more preferably 7% or less, still more preferably 4% or less,

5 particularly preferably 3% or less, and most preferably 2% or less. In a case where the decomposition rate of the structure (I) after storage of the resin composition at 40°C for 30 days is less than or equal to the above-described upper limit, the storage stability of the resin composition and the antifouling paint composition is further improved.

Further, in a case where the resin composition contains an organic solvent, the stability of
10 dissolution of the copolymer (X) in an organic solvent is excellent. It is preferable that the decomposition rate thereof decrease, and the lower limit thereof may be 0%.

The decomposition rate of the structure (I) after storage of the resin composition at 40°C for 30 days can be lowered to 20% or less by allowing the resin composition to contain the compound that reacts with an acid, the basic compound, the acidic
15 compound, and the dehydrating agent.

[0144]

In the measurement of the decomposition rate of the structure (I), the storage of the resin composition is carried out by adding the resin composition to a glass bottle, sealing the bottle, and allowing the bottle to stand in a drying container under a shielded
20 environment.

The decomposition rate of the structure (I) is defined as the following value obtained by subtracting a theoretical solid acid value (b), at the time of the structure (I) contained in the copolymer (X) which is not completely decomposed, from a measured solid acid value (a) of the resin composition (after storage at 40°C for 30 days) and

dividing the obtained value by a theoretical solid acid value (c) at the time of the structure (I) contained in the copolymer (X) which is completely decomposed.

(Decomposition rate) = {(measured solid acid value (a)) - (theoretical solid acid value (b))}/(theoretical solid acid value (c)) × 100

5 The measured solid acid value will be described in the item of the solid acid value in the examples described below.

The theoretical solid acid value can be calculated according to the following equation.

$$(\text{Theoretical solid acid value}) = \Sigma(561 \times 100/Mw_i \times w_i)$$

10 In the calculation formula of the theoretical solid acid value, w_i represents a mass fraction of a monomer i containing an acid functional group among the monomers constituting the copolymer (X), and Mw_i represents a molecular weight of the monomer containing an acid functional group. The acid functional group is a functional group of a carboxylic acid or the like.

15 The acid value after decomposition is calculated by regarding the monomer as a monomer that contains an acid functional group.

The acid value before decomposition is calculated by regarding the monomer as a monomer that does not contain an acid functional group.

[0145]

20 (Method for producing resin composition)

The resin composition of the present invention can be produced using a known method. For example, a resin composition can be prepared by producing the copolymer (X) according to the production method (α) or (β) described above and blending the compound that reacts with an acid, the basic compound, the acidic compound, the

25 dehydrating agent, the silicone oil, the organic solvent, other components, and the like

into the obtained copolymer (X) as necessary.

In a case where the resin composition contains the compound (Y), the timing for blending the compound (Y) may be simultaneously with the production of the copolymer (X) or after the production of the copolymer (X) and is not particularly limited. For

5 example, according to the production method (α), the compound (Y) may coexist at the time of polymerization of the monomer mixture or the compound (Y) may be added after completion of the polymerization. According to the production method (β), after completion of the polymerization of the monomer mixture, a larger amount of the compound (Y) may be added to the carboxy group of the copolymer (X0) so that the
10 unreacted compound (Y) remains at the time of reacting the compound (Y) with the generated copolymer (X0) to obtain the copolymer (X). Since a part of the compound (Y) is radically polymerized in a case where the compound (Y) is allowed to coexist during the polymerization reaction, a method of adding the compound (Y) after completion of the polymerization is preferable.

15 A raw material containing a silicone oil may be used as the raw material of the polymerizable monomer (b) or the like. In this case, the polymerization product contains the copolymer (X) and the silicone oil.

[0146]

The resin composition of the present invention can be formed into an antifouling
20 paint composition as it is or by being mixed with an antifouling agent and the like as necessary.

The resin composition of the present invention can be used as an antifogging paint composition or the like in addition to the antifouling paint composition.

[0147]

25 (Action effects)

The resin composition of the present invention contains the copolymer (X), the coating film containing the resin composition of the present invention exhibits an excellent antifouling effect even in a case where the coating film does not contain an antifouling agent.

5 Therefore, the resin composition of the present invention is suitably used as the antifouling paint composition.

[0148]

[Antifouling paint composition]

10 The antifouling paint composition of the present invention contains the resin composition of the present invention described above. Therefore, the antifouling paint composition contains the copolymer (X).

15 From the viewpoint of the storage stability of the antifouling paint composition, it is preferable that the antifouling paint composition according to the present embodiment further contain at least one selected from the group consisting of a compound that reacts with an acid, a basic compound, an acidic compound, and a dehydrating agent. Examples of the compound that reacts with an acid, the basic compound, the acidic compound, and the dehydrating agent are each the same as those described above. The preferable contents are the same as described above.

20 From the viewpoint of antifouling properties of the coating film, the antifouling paint composition according to the present embodiment may further contain a silicone oil. Examples of the silicone oil are the same as those described above.

 The antifouling paint composition according to the present embodiment may contain an organic solvent. Examples of the organic solvent are the same as those described above.

25 The antifouling paint composition according to the present embodiment may

further contain an antifouling agent.

The antifouling paint composition according to the present embodiment may further contain components other than the copolymer (X), the compound that reacts with an acid, the basic compound, the acidic compound, the dehydrating agent, the silicone
5 oil, the organic solvent, and the antifouling agent.

In a case where the antifouling paint composition contains the compound that reacts with an acid, the basic compound, the acidic compound, the dehydrating agent, the silicone oil, the organic solvent, and other components, these components may be derived from the resin composition, may not be derived from the resin composition (those which
10 are blended at the time of preparation of the antifouling paint composition), or may be a mixture of these.

[0149]

<Antifouling agent>

Examples of the antifouling agent include inorganic antifouling agents and
15 organic antifouling agents, and one or more kinds can be appropriately selected depending on the required performance and used.

Examples of the antifouling agent include a copper-based antifouling agent such as cuprous oxide, copper thiocyanate, or copper powder, compounds of other metals (lead, zinc, nickel, and the like), an amine derivative such as diphenylamine, a nitrile
20 compound, a benzothiazole-based compound a maleimide-based compound, and a pyridine-based compound. These may be used alone or in combination of two or more kinds thereof.

[0150]

More specific examples of the antifouling agent include 4-bromo-2-(4-
25 chlorophenyl)-5-(trifluoromethyl)-1H-pyrrole-3-carbonitrile, manganese ethylene

bisdithiocarbamate, zinc dimethyl dithiocarbamate, 2-methylthio-4-t-butylamino-6-cyclopropylamino-s-triazine, 2,4,5,6-tetrachloroisophthalonitrile, N,N-dimethyldichlorophenylurea, zinc ethylene bisdithiocarbamate, copper rhodanide, 4,5-dichloro-2-n-octyl-3(2H)isothiazolone, N-(fluorodichloromethylthio)phthalimide, N,N'-dimethyl-N'-phenyl-(N-fluorodichloromethylthio)sulfamide, 2-pyridinethiol-1-oxide zinc salt, tetramethylthiuram disulfide, a Cu-10% Ni solid solution alloy, 2,4,6-trichlorophenylmaleimide 2,3,5,6-tetrachloro-4-(methylsulfonyl)pyridine, 3-iodo-2-propynyl butyl carbamate, diiodomethyl paratolyl sulfone, bisdimethyl dithiocarbamoyl zinc ethylene bisdithiocarbamate, phenyl(bispyridyl)bismuth dichloride, 2-(4-thiazolyl)-benzoimidazole, medetomidine, and pyridine triphenyl borane.

[0151]

In a case where the antifouling paint composition contains an antifouling agent, the content of the antifouling agent in the antifouling paint composition is not particularly limited, but is preferably in a range of 2 to 200 parts by mass and more preferably in a range of 10 to 150 parts by mass with respect to 100 parts by mass of the copolymer (X). In a case where the content of the antifouling agent is greater than or equal to the above-described lower limit, the antifouling effect of a coating film to be formed is excellent. In a case where the content of the antifouling agent is less than or equal to the upper limit of the above-described upper limit, the physical properties of the coating film are excellent.

[0152]

<Other components>

As other components, resins other than the copolymer (X) may be exemplified. Other resins are resins that do not have the constituent unit (B). Examples of other resins include thermoplastic resins.

It is preferable that the antifouling paint composition of the present invention contain a thermoplastic resin other than the copolymer (X). In a case where the antifouling paint composition contains a thermoplastic resin other than the copolymer (X), the physical properties of the coating film such as crack resistance and water
5 resistance are improved.

[0153]

Examples of the thermoplastic resin other than the copolymer (X) include chlorinated paraffin; chlorinated polyolefin such as chlorinated rubber, chlorinated polyethylene, or chlorinated polypropylene; polyvinyl ether; polypropylene sebacate;
10 partially hydrogenated terphenyl; polyvinyl acetate; poly(meth)acrylic acid alkyl ester such as a methyl (meth)acrylate-based copolymer, an ethyl (meth)acrylate-based copolymer, a propyl (meth)acrylate-based copolymer, a butyl (meth)acrylate-based copolymer, or a cyclohexyl (meth)acrylate-based copolymer; a polyether polyol; an alkyd resin; a polyester resin; a vinyl chloride-based resin such as a vinyl chloride-vinyl acetate
15 copolymer, a vinyl chloride-vinyl propionate copolymer, a vinyl chloride-isobutyl vinyl ether copolymer, a vinyl chloride-isopropyl vinyl ether copolymer, or a vinyl chloride-ethyl vinyl ether copolymer; waxes; fats and oils in a solid state at room temperature other than waxes; fats and oils in a liquid state at room temperature such as castor oil and refined products thereof; petroleum jelly; liquid paraffin; and rosin, hydrogenated rosin,
20 naphthenic acid, fatty acids, and divalent metal salts of these. Examples of the waxes include waxes derived from animals such as beeswax; waxes derived from plants; semi-synthetic waxes such as amide-based waxes; and synthetic waxes such as polyethylene oxide-based waxes. These thermoplastic resins may be used alone or in combination of two or more kinds thereof.

25 [0154]

The content of the thermoplastic resin other than the copolymer (X) in the antifouling paint composition is not particularly limited, but is preferably in a range of 0.1 to 50 parts by mass and more preferably in a range of 0.1 to 10 parts by mass with respect to 100 parts by mass of the copolymer (X). In a case where the content of the thermoplastic resin other than the copolymer (X) is greater than or equal to the above-described lower limit, the physical properties of the coating film such as crack resistance or water resistance are excellent. In a case where the content thereof is less than or equal to the above-described upper limit, the hydrolyzability is excellent.

[0155]

In order to impart lubricity to the surface of the coating film and prevent adhesion of organisms, the antifouling paint composition of the present invention may contain a silicon compound such as dimethylpolysiloxane or a silicone oil, a fluorine-containing compound such as fluorinated hydrocarbon, or the like.

[0156]

The antifouling paint composition of the present invention may contain various pigments, antifoaming agents, leveling agents, pigment dispersants (such as antisetling agents), antisagging agents, matting agents, ultraviolet absorbing agents, antioxidants, heat resistance improvers, slipping agents, preservatives, plasticizers, and viscosity control agents.

Examples of the pigments include zinc oxide, talc, silica, barium sulfate, potassium feldspar, aluminum hydroxide, magnesium carbonate, mica, carbon black, red iron oxide, titanium oxide, phthalocyanine blue, kaolin, and gypsum.

Examples of the antisetling agent and the antisagging agent other than the thermoplastic resin include a bentonite-based agent, a fine powder silica-based agent, a stearate salt, a lecithin salt, and an alkyl sulfonate.

[0157]

Examples of the plasticizer other than the thermoplastic resin include a phthalic acid ester-based plasticizer such as dioctyl phthalate, dimethyl phthalate, dicyclohexyl phthalate, or diisodecyl phthalate; an aliphatic dibasic acid ester-based plasticizer such as isobutyl adipate or dibutyl sebacate; a glycol ester-based plasticizer such as diethylene glycol dibenzoate or pentaerythritol alkyl ester; a phosphoric acid ester-based plasticizer such as tricresyl phosphate (TCP), triaryl phosphate, or trichloroethyl phosphate; an epoxy-based plasticizer such as epoxy soybean oil or octyl epoxy stearate; an organic tin plasticizer such as dioctyl tin laurate or dibutyl tin laurate; and trioctyl trimellitate, and triacetylene. In a case where the antifouling paint composition contains a plasticizer, the crack resistance and the peeling resistance of the coating film can be improved.

[0158]

<Various characteristics of antifouling paint composition>

The VOC content of the antifouling paint composition according to the present invention is preferably 500 g/L or less, more preferably 420 g/L or less, and still more preferably 400 g/L or less.

The term “volatile organic compound (VOC)” indicates an organic compound (volatile organic compound) which easily volatilizes at room temperature under normal pressure.

The VOC content is calculated according to the following equation using the specific gravity and the solid content value of the antifouling paint composition.

$$\text{VOC content (g/L)} = \text{specific gravity of composition} \times 1000 \times (100 - \text{solid content})/100$$

The specific gravity of the antifouling paint composition is calculated by filling a specific gravity cup having a volume of 100 mL with the antifouling paint composition

at 25°C and measuring the mass thereof. The solid content (heating residue) of the antifouling paint composition is measured according to the method described in the examples below.

The VOC content can be adjusted depending on the content of the organic
5 solvent.

[0159]

The solid content of the antifouling paint composition of the present invention is preferably in a range of 55% to 100% by mass, more preferably in a range of 60% to 90% by mass, and still more preferably in a range of 65% to 80% by mass.

10 In a case where the solid content of the antifouling paint composition is greater than or equal to the above-described lower limit, the VOC content is sufficiently decreased. In a case where the solid content is less than or equal to the above-described upper limit, the viscosity of the antifouling paint composition is easily lowered.

[0160]

15 The viscosity of the antifouling paint composition of the present invention to be measured at 25°C using a B type viscometer is preferably less than 10000 mPa·s, more preferably less than 7000 mPa·s, and still more preferably less than 1000 mPa·s. In a case where the viscosity of the antifouling paint composition is less than or equal to the above-described upper limit, the antifouling paint composition is easily applied.

20 The lower limit of the viscosity of the antifouling paint composition is not particularly limited, but is preferably 100 mPa·s or greater from the viewpoint of the physical properties of the coating film.

The viscosity of the antifouling paint composition can be adjusted depending on the viscosity of the resin composition, the amount of the solvent to be added to the resin

composition, and the like.

[0161]

The antifouling paint composition of the present invention can be prepared by preparing the resin composition of the present invention, adding an antifouling agent,
5 other components, and an organic solvent as necessary, and mixing the solution.

[0162]

The antifouling paint composition of the present invention can be used for forming a coating film (antifouling coating film) on a surface of a base material, for example, underwater structures such as ships, various fishing nets, port facilities, oil
10 fences, bridges, and submarine bases.

The coating film formed of the antifouling paint composition of the present invention can be formed on a surface of a base material directly or through a ground coating film.

As the ground coating film, a wash primer, a chlorinated rubber-based primer, or
15 an epoxy-based primer, or an intermediate paint can be used for forming the coating film.

The coating film can be formed using a known method. For example, the surface of the base material or the ground coating film on the base material is coated with the antifouling paint composition by means of brush coating, spray coating, roller coating, or dip coating and dried, thereby forming a coating film. The coating amount
20 of the antifouling paint composition can be typically set such that the thickness of the dried coating film is in a range of 10 to 400 μm .

The coating film can be typically dried at room temperature and may be dried by being heated as necessary.

EXAMPLES

25 [0163]

Hereinafter, the present invention will be described in more detail based on examples and comparative examples, but the present invention is not limited to these examples. Further, parts in the examples indicate parts by mass.

The evaluation methods used in the examples are described below.

5 [0164]

<Evaluation method>

(Weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular weight distribution (M_w/M_n) of copolymer)

The measurement was performed using gel permeation chromatography (GPC)
10 (HLC-8220, manufactured by Tosoh Corporation) and tetrahydrofuran (THF) as an eluent. As the columns, TSKgel α -M (manufactured by Tosoh Corporation, 7.8 mm $\times$ 30 cm) and TSKguard column α (manufactured by Tosoh Corporation, 6.0 mm $\times$ 4 cm) were used. The calibration curve was prepared using F288/F1/F28/F80/F40/F20/F2/A1000 (manufactured by Tosoh Corporation, standard
15 polystyrene) and a styrene monomer.

[0165]

(Viscosity)

A sample was put into a dried viscosity tube (Gardner bubble viscosity tube) up to an indication line of the viscosity tube, and the tube was sealed with a cork stopper.
20 The viscosity tube with the collected sample (resin composition) was vertically immersed in a constant temperature water bath the temperature of which was adjusted to a predetermined temperature ($25.0 \pm 0.1^\circ\text{C}$) for 2 hours so that the temperature of the sample was constant, a viscosity tube serving as a reference tube and the viscosity tube to which the sample was added were allowed to rotate by 180° simultaneously, and the

viscosity (Gardner viscosity) was determined by comparing the bubble increase rate of the sample in the viscosity tube with that in the reference tube.

[0166]

(Solid content (heating residue))

- 5 0.50 g of a sample (resin composition) was measured using an aluminum dish, 3 mL of toluene was added thereto using a syringe such that the sample was evenly spread over on the bottom of the dish, and preliminary drying was performed. The preliminary drying is a treatment for easily evaporating a solvent during the main drying by spreading the measurement sample over the entire dish. In the preliminary drying, the
- 10 measurement sample and toluene were heated and dissolved in a water bath at 70°C to 80°C so as to be evaporated and dried. After the preliminary drying, the main drying was performed using a hot air dryer at 105°C for 2 hours. The solid content (heating residue) was acquired using the following equation based on the mass (mass before drying) of the measurement sample before the preliminary drying and the mass (mass
- 15 after drying) of the measurement sample after the main drying.

Solid content (% by mass) = mass after drying/mass before drying $\times$ 100

[0167]

(Solid acid value)

- Approximately 2.0 g of the sample (resin composition) was precisely weighed in
- 20 a beaker (A (g)), and a 50 mL toluene/ethanol solution was added thereto. Thereafter, several drops of phenolphthalein were added thereto, and titration was carried out using a 0.5 N KOH solution (titration amount = B (mL), titer of KOH solution = f). Further, blank measurement was performed in the above-described manner (titration amount = C ((mL))), and the solid acid value was calculated according to the following equation.

Solid acid value (mgKOH/g) = $\{(B - C) \times 0.2 \times 56.11 \times f\} / A / \text{solid content}$

[0168]

(Consumption degree)

A hard vinyl chloride plate having a size of 50 mm × 50 mm × 2 mm (thickness)

- 5 was coated with the sample (antifouling paint composition) using an applicator such that the thickness of the dried film was set to 120 μm, and the film was dried to form a coating film, thereby obtaining a test plate. This test plate was attached to a rotating drum installed in artificial seawater, the rotating drum was allowed to rotate at a circumferential speed of 7.7 m/s (15 knots), the film thickness of the coating film was
- 10 measured after 6 months, and the consumed film thickness (μm/M) per month was calculated from the measured film thickness $\{= (120 - \text{measured film thickness } (\mu\text{m})) / 6\}$. The consumption degree is preferably in a range of 1 to 150 μm/M.

[0169]

(Surface smoothness)

- 15 The consumption degree was evaluated using the coating film after 100 days from the start of the test as an index of the surface smoothness. Further, the arithmetic average roughness (Ra) was calculated by measuring the line roughness using high-accuracy shape measurement systems KS-1100 and LT-9000 (manufactured by Keyence Corporation). Based on the results, the surface smoothness was evaluated based on the
- 20 following criteria.

A: less than 1.0 μm

C: 1.0 μm or greater

[0170]

(Hardness of coating film)

A glass substrate was coated with the resin composition using a 500 μm applicator such that the thickness of the dried film was set to be in a range of 80 to 150 μm , and the film was dried at 25°C for 1 week, thereby obtaining a test plate on which a coating film formed of the resin composition was formed. The hardness (Martens
 5 hardness) of the coating film of the test plate was measured at 25°C using a micro hardness meter (trade name: HM2000, manufactured by Fischer Instruments K.K.).

The measurement was performed under conditions in which $dQRST(F)/dt$ was set to be constant, F (test force) was set to 10 mN/10 sec, C (maximum load creep time) was set to 5 seconds, the maximum indentation load was set to 10 mN, and the maximum
 10 indentation depth was set to 6 μm . The hardnesses (Martens hardness) were measured at three different sites of the coating film of the test plate, and the average value of these measured values was set as the hardness of the coating film.

Further, the Martens hardness is preferably in a range of 3.0 to 40.0 N/mm^2 and more preferably in a range of 3.5 to 30.0 N/mm^2 .

15 [0171]

(Antifouling properties)

A sandblasted plate coated with a rust-proof paint in advance was coated with a sample (the resin composition or the antifouling paint composition) such that the thickness of the dried film was set to 200 μm , thereby preparing a test plate. The
 20 coating film was allowed to stand in the bay of Aichi Prefecture and be immersed for 12 months, and the attachment area (the proportion of the area where organisms are attached in the total area of the coating film) of the attached organisms was examined. The antifouling properties were evaluated based on the following criteria.

A (good): The attachment area was less than 15%.

B (acceptable): The attachment area was in a range of 15% to 30%.

[0172]

<Production Example 1: production of polymerizable monomer (b-2)>

A polymerizable monomer (b-2) in which R³⁰ in Formula (b1) represents a
 5 methyl group, a represents 2, b represents 0, c represents 3, d represents average 12, e
 represents average 1, and R³¹ to R³⁹ each represents a methyl group was produced
 according to the following procedures.

A 1 L four-necked flask provided with a cooling pipe and a thermometer was
 charged with 188 g of 1,1,1,3,3,5,5,7,7,7-decamethyltetrasiloxane, 499 g of
 10 1,1,3,3,5,5,7,7-octamethylcyclotetrasiloxane, and 113 g of an oligomer (viscosity of 80
 mm²/s) of 3-methacryloyloxypropylmethyldimethoxysilane, and 1.20 g of
 trifluoromethanesulfonic acid was added thereto to cause a reaction at 90°C for 7 hours.
 After the reaction, the liquid temperature was increased to 40°C, 0.60 g of water, 12 g of
 sodium bicarbonate, and 12 g of sodium sulfate were sequentially added thereto, the
 15 solution was stirred for 30 minutes, and the solid content was removed by filtration.
 Thereafter, 0.27 g of BHT was added thereto, and the low boiling component was
 removed at 100°C/15 torr for 5 hours while 4% oxygen-containing nitrogen was bubbled.
 The yield of the obtained product was 625 g, the viscosity thereof was 16 mm²/s, and the
 refractive index thereof was 1.4098. It was confirmed that the obtained compound was
 20 the polymerizable monomer (b-2) (methacryl-modified silicone macromonomer) based
 on ¹H-NMR analysis (device: ECX500II (manufactured by JEOL, Ltd.), measurement
 solvent: CDCl₃).

Polymerizable monomers (b-1) and (b-3) were produced according to the same
 procedures as described above.

25 The polymerizable monomer (b-1) is a polymerizable monomer in which R³⁰ in

Formula (b1) represents a methyl group, a represents 2, b represents 0, c represents 3, d represents average 7, e represents average 1, and R^{31} to R^{39} each represents a methyl group.

The polymerizable monomer (b-3) is a polymerizable monomer in which R^{30} in Formula (b1) represents a methyl group, a represents 2, b represents 0, c represents 3, d represents average 17, e represents average 1, and R^{31} to R^{39} each represents a methyl group.

[0173]

<Production Example 2: production of polymerizable monomer (b-4)>

A polymerizable monomer (b-4) in which R^{30} in Formula (b1) represents a methyl group, a represents 2, b represents 1, c represents 3, d represents average 12, e represents average 1, and R^{31} to R^{39} each represents a methyl group was produced according to the following procedures.

The same procedures as in Production Example 1 were repeated except that 131 g of an oligomer (viscosity of 130 mm²/s) of 3-(methacryloyloxyethoxy)propylmethyldimethoxysilane was used in place of the 3-methacryloyloxypropylmethyldimethoxysilane, and the amounts of other raw materials to be used were changed to 178 g of 1,1,1,3,3,5,5,7,7,7-decamethyltetrasiloxane and 423 g of 1,1,3,3,5,5,7,7-octamethylcyclotetrasiloxane. The yield of the obtained product was 605 g, the viscosity thereof was 23 mm²/s, and the refractive index thereof was 1.4150. It was confirmed that the obtained compound was the polymerizable monomer (b-4) (methacryl-modified silicone macromonomer) based on ¹H-NMR analysis (device: ECX500II (manufactured by JEOL, Ltd.), measurement solvent: CDCl₃).

[0174]

<Production Example 4: production of metal atom-containing polymerizable

monomer mixture (MM-Zn1)>

A reaction container provided with a stirrer, a temperature adjuster, and a dropping funnel was charged with 85.4 parts of n-butanol (n-BuOH) and 40.7 parts of zinc oxide, and the mixture was heated to 75°C while being stirred. Next, a mixture
 5 formed of 43.1 parts of methacrylic acid, 36.1 parts of acrylic acid, and 5 parts of water was added dropwise from the dropping funnel at a constant speed for 3 hours. After the mixture was stirred for 2 hours, 36 parts of n-BuOH was added thereto, thereby obtaining a transparent metal atom-containing polymerizable monomer mixture (MM-Zn1) having a solid content of 44.8% by mass.

10 [0175]

<Production Example 5: production of metal atom-containing polymerizable monomer mixture (MM-Zn2)>

A four-necked flask provided with a cooling pipe, a thermometer, a dropping funnel, and a stirrer was charged with 72.4 parts of PGM and 40.7 parts of zinc oxide,
 15 and the mixture was heated to 75°C while being stirred. Next, a mixture formed of 30.1 parts of methacrylic acid, 25.2 parts of acrylic acid, and 51.6 parts of versatic acid was added dropwise from the dropping funnel at a constant speed for 3 hours. After the mixture was stirred for 2 hours, 11 parts of PGM was added thereto, thereby obtaining a transparent metal atom-containing polymerizable monomer mixture (MM-Zn2) having a
 20 solid content of 59.6% by mass.

[0176]

<Production Example 6: production of IBEMA>

90.1 parts (0.9 mol) of isobutyl vinyl ether, 0.14 parts of hydroquinone, and 0.28 parts of phenothiazine were stirred at room temperature and mixed to obtain a uniform
 25 solution. 51.7 parts (0.6 mol) of methacrylic acid was added dropwise while air (10

ml/min) was blown such that the temperature of the reaction solution was maintained at 60°C or lower. After dropwise addition, the temperature of the reaction solution was increased to 80°C and the reaction was continued for 6 hours. 158.7 parts (1.8 mol) of t-butyl methyl ether was added to the reaction solution, the solution was mixed, and the organic phase was washed once using 200 parts of a 20 mass% potassium carbonate aqueous solution. 0.03 parts of 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl was added to the organic phase so that the low boiling content was distilled off using an evaporator. The resulting residue was distilled off under reduced pressure, thereby obtaining 97.5 (0.52 mol) of 1-isobutoxyethyl methacrylate (IBEMA) having a boiling point of 60°C/3 torr.

[0177]

<Production Example: method for producing BEMA>

150.2 parts (1.5 mol) of butyl vinyl ether, 0.24 parts of hydroquinone, and 0.47 parts of phenothiazine were stirred at room temperature and mixed to obtain a uniform solution. 86.1 parts (1.0 mol) of methacrylic acid was added dropwise while air (10 mL/min) was blown such that the temperature of the reaction solution was maintained at 60°C or lower. After dropwise addition, the temperature of the reaction solution was increased to 80°C and the reaction was continued for 5 hours. 264.5 parts (3.0 mol) of t-butyl methyl ether was added to the reaction solution, the solution was mixed, and the organic phase was washed once using 350 parts of a 20 mass% potassium carbonate aqueous solution. 0.06 parts of 4-benzoyloxy-2,2,6,6-tetramethylpiperidine-N-oxyl was added to the organic phase so that the low boiling content was distilled off using an evaporator. The resulting residue was distilled off under reduced pressure, thereby obtaining 166.9 (0.91 mol) of 1-butoxyethyl methacrylate (BEMA) having a boiling

point of 70°C/5 torr (667 Pa).

[0178]

<Production Example 7>

(Production of dispersant 1)

- 5 900 parts by deionized water, 60 parts of sodium 2-sulfoethyl methacrylate, 10 parts of potassium methacrylate, and 12 parts of methyl methacrylate (MMA) were put into a polymerization device provided with a stirrer, a cooling pipe, and a thermometer, and the mixture was stirred and heated to 50°C while replacing the inside of the polymerization device with nitrogen. 0.08 parts of 2,2'-azobis(2-
- 10 methylpropionamidine) dihydrochloride was added thereto as a polymerization initiator, and the mixture was further heated to 60°C. After the mixture was heated, MMA was continuously added dropwise thereto at a rate of 0.24 parts/min for 75 minutes using a dropping pump. The reaction solution was held at 60°C for 6 hours and cooled to room temperature, thereby obtaining a dispersant 1 having a solid content of 10% by mass
- 15 which was a transparent aqueous solution.

[0179]

(Production of chain transfer agent 1)

- 1.00 g of cobalt acetate (II) tetrahydrate, 1.93 g of diphenyl glyoxime, and 80 ml of diethyl ether which had been deoxygenated by nitrogen bubbling in advance were put
- 20 into a synthesizer provided with a stirrer, and the mixture was stirred at room temperature for 30 minutes. Next, 10 ml of a boron trifluoride diethyl ether complex was added thereto, and the mixture was further stirred for 6 hours. The mixture was filtered, and the solid was washed with diethyl ether and dried in a vacuum for 15 hours, thereby obtaining 2.12 g of a chain transfer agent 1 in the form of a reddish brown solid.

[0180]

(Production of macromonomers 1 to 3)

145 g of deionized water, 0.1 parts of sodium sulfate, and 0.25 parts of the dispersant 1 (solid content of 10% by mass) were put into a polymerization device

5 provided with a stirrer, a cooling pipe, and a thermometer, and the mixture was stirred to obtain a uniform aqueous solution. Next, 100 parts of MMA, 0.008 parts of the chain transfer agent 1, and 0.80 parts of 1,1,3,3-tetramethylbutyl peroxy 2-ethylhexanoate (PEROCTA O (registered trademark), manufactured by NOF Corporation) were added thereto to obtain an aqueous suspension.

10 Thereafter, the inside of the polymerization device was replaced with nitrogen, heated to 80°C for the reaction for 1 hour, and heated to 90°C, and the state was held for 1 hour in order to increase the polymerization rate. Next, the reaction solution was cooled to 40°C to obtain an aqueous suspension containing a polymer. This aqueous suspension was filtered using nylon filter cloth having a pore size of 45 μm , and the
15 filtrate was washed with deionized water, dehydrated, and dried at 40°C for 16 hours, thereby obtaining a macromonomer 1 as listed in Table 1. The number-average molecular weight of the macromonomer 1 was 1600.

A macromonomer 2 and a macromonomer 3 were obtained according to the same method as described above except that the amounts of MMA, the chain transfer
20 agent 1, and PEROCTA O (registered trademark) to be added were changed to the amounts listed in Table 1 and MTMA listed in Table 1 was added. The number-average molecular weight of the macromonomer 2 was 2000 and the weight-average molecular weight of the macromonomer was 4000.

[0181]

[Table 1]

		Macromonomer 1	Macromonomer 2	Macromonomer 3
Monomer	MMA	100 parts	75 parts	75 parts
	MTMA	-	25 parts	25 parts
Chain transfer agent	Chain transfer agent 1	0.008 parts	0.01 parts	0.005 parts
Initiator	PEROCTA O	0.8 parts	1.5 parts	0.8 parts
Number-average molecular weight (Mn)		1600	2000	4000

[0182]

<Example 1>

A reaction container provided with a stirrer, a temperature adjuster, and a dropping funnel was charged with 59 parts of xylene, 15 parts of propylene glycol monomethyl ether (PGM), and 4 parts of EA, and the mixture was heated to 100°C while being stirred. Next, a mixture formed of 27 parts of methyl methacrylate (MMA), 19.3 parts of ethyl acrylate (EA), 21.7 parts of the metal atom-containing polymerizable monomer mixture (MM-Zn1), 40 parts of a polymerizable monomer (b-1), 10 parts of xylene, 0.3 parts of 2,2-azobis(isobutyronitrile) (AIBN), 9.0 parts of 2,2-azobis(2-methylbutyronitrile) (AMBN), and 1.0 parts of a chain transfer agent (NOFMER (registered trademark) MSD, manufactured by NOF Corporation, α -methylstyrene dimer) was added dropwise from the dropping funnel at a constant speed for 6 hours. After the dropwise addition, 0.5 parts of t-butyl peroxy octoate and 10 parts of xylene were added dropwise four times at intervals of 30 minutes, the resulting solution was further stirred for 1 hour, and 12 parts of xylene was added thereto to obtain a solution-like resin composition A-1 having a solid content of 44.8% by mass and a viscosity of B.

[0183]

<Examples 2 to 7 and Comparative Examples 1 and 2>

Each of resin compositions A-2 to A-7, A-31, and A-32 was produced in the same manner as in Example 1 except that the composition of the mixture to be added

dropwise was changed as listed in Tables 2 and 4.

[0184]

<Example 8>

A reaction container provided with a stirrer, a temperature adjuster, and a
5 dropping funnel was charged with 50 parts of xylene, and the mixture was heated to 90°C
while being stirred. Next, a mixture formed of 25 parts of IBEMA, 35 parts of MMA,
20 parts of the polymerizable monomer (b-2), and 25 parts of EA, and 3.0 parts of
AMBN was added dropwise from the dropping funnel at a constant speed for 4 hours.
After the dropwise addition, 2.0 parts of AMBN and 7.0 parts of xylene were added
10 thereto at a constant speed for 30 minutes, the resulting solution was further stirred for 2
hours, and 6.7 parts of isobutyl vinyl ether and 3 parts of butyl acetate were added thereto
to obtain a solution-like resin composition A-8 having a solid content of 51.0% by mass
and a viscosity of E.

[0185]

15 <Example 9>

A solution-like resin composition A-9 was produced in the same manner as in
Example 8 except that the composition of the mixture to be added dropwise was changed
as listed in Table 2.

[0186]

20 In Table 2, the abbreviations shown in the columns of the compositions of the
mixtures indicate the following materials. Further, the numerical value listed in each
column of the composition of the mixture indicates the amount (parts) of each material to
be charged.

TIPX: triisopropylsilyl acrylate

25 X-24-8201: trade name, manufactured by Shin-Etsu Chemical Co., Ltd. (one

terminal type polysiloxane block-containing polymerizable monomer in which v in Formula (d3) represents 0, R^{3a} to R^{3f} represent a methyl group, w represents 3, and x represents 25)

FM-0711: trade name, manufactured by JNC Corporation (one terminal type
5 polysiloxane block-containing polymerizable monomer in which v in Formula (d3) represents 0, R^{3a} to R^{3f} represent a methyl group, w represents 3, and x represents 10)

[0187]

<Examples 10 to 17>

Each of resin compositions A-10 to A-17 was produced in the same manner as in
10 Example 1 except that the composition of the mixture to be added dropwise was changed as listed in Tables 2 and 3.

[0188]

In Tables 2 and 3, the abbreviations shown in the columns of the compositions of the mixtures indicate the following materials. Further, the numerical value listed in
15 each column of the composition of the mixture indicates the amount (parts) of each material to be charged.

MTA: 2-methoxyethyl acrylate

nBA: normal butyl acrylate

[0189]

20 <Example 18>

A resin composition A-18 was produced in the same manner as in Example 2 except that the composition of the mixture to be added dropwise was changed as listed in Table 3.

That is, the resin composition A-18 was produced in the same manner as in
25 Example 2 except that the metal-containing monomer pure content was changed in

Example 18.

[0190]

<Examples 19 to 22>

Resin compositions A-19 to A-22 were produced in the same manner as in
5 Example 4 except that the composition of the mixture to be added dropwise was changed
as listed in Table 3.

That is, in Examples 19, 21, and 22, the macromonomer 2 was used in place of
the macromonomer 1 listed in Table 1.

Further, in Example 20, the macromonomer 3 was used in place of the
10 macromonomer listed in Table 1.

[0191]

<Example 23>

A resin composition A-23 was produced in the same manner as in Example 2
except that the composition of the mixture to be added dropwise was changed as listed in
15 Table 4.

[0192]

<Examples 24 to 27>

Resin compositions A-24 to A-27 were produced in the same manner as in
Example 8 except that the composition of the mixture to be added dropwise was changed
20 as listed in Table 4.

In Table 4, the abbreviations shown in the columns of the compositions of the
mixtures indicate the following materials. Further, the numerical value listed in each
column of the composition of the mixture indicates the amount (parts) of each material to
be charged.

25 BEMA: 1-butoxyethyl methacrylate

[0193]

<Examples 28 to 30>

Resin compositions A-28 to A-30 were produced in the same manner as in Example 8 except that the composition of the mixture to be added dropwise was changed
5 as listed in Table 4.

In Table 4, the abbreviations shown in the columns of the compositions of the mixtures indicate the following materials. Further, the numerical value listed in each column of the composition of the mixture indicates the amount (parts) of each material to be charged.

10 TIPSMA: triisopropylsilyl methacrylate

[0194]

The characteristics (the viscosity, the solid content (% by mass), and the solid acid value) of the resin compositions obtained in Examples 1 to 30 and Comparative Examples 1 and 2, the characteristics (the number-average molecular weight (M_n), the
15 weight-average molecular weight (M_w), and the molecular weight distribution) of the copolymer contained in each resin composition, and the evaluation results (the surface smoothness and the hardness of the coating film) are listed in Tables 2 to 4. The surface smoothness was noted with the value of Ra on the lower side in the evaluation result.

[0195]

[Table 2]

	Resin composition	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11
Composition of mixture (parts)	MMA	A-1 27	A-2 27	A-3 25.7	A-4 0	A-5 22.3	A-6 32.3	A-7 32.3	A-8 35	A-9 55	A-10 22.3	A-11 19
	EA	23.3	18.9	30.2	42.9	48	33.6	38	20	0	58	4
	MTA	0	0	0	0	0	0	0	0	0	0	0
	nBA	0	0	0	0	0	0	0	0	0	0	0
	MM-Zn1 (metal-containing monomer pure content)	9.7	14.1	14.1	14.1	9.7	14.1	9.7	0	0	9.7	11.7
	MM-Zn2 (metal-containing monomer pure content)	0	0	0	0	0	0	0	0	0	0	0
	IBEMA	0	0	0	0	0	0	0	25	0	0	0
	BEMA	0	0	0	0	0	0	0	0	0	0	0
	TIPX	0	0	0	0	0	0	0	0	25	0	0
	TIPSMA	0	0	0	0	0	0	0	0	0	0	0
	Macromonomer 1	0	0	0	13	0	0	0	0	0	0	0
	Macromonomer 2	0	0	0	0	0	0	0	0	0	0	0
	Macromonomer 3	0	0	0	0	0	0	0	0	0	0	0
	Polysiloxane block-containing polymerizable monomer	40	40	30	30	20	20	20	20	20	10	65
	AIBN	0.3	0.3	0.3	0.25	0.3	0.3	0.3	-	-	0.3	0.3
	AMBN	9	10.7	10.7	8.4	11	11	9	3	3	11	10.7
Compound (Y)	NOFMER MSD	1	1	1	1	1	1	1	0	0	1	1
	Isobutyl vinyl ether	-	-	-	-	-	-	-	6.7	-	-	-
Compound (Y)	Butyl vinyl ether	-	-	-	-	-	-	-	-	-	-	-
	Type	b-1	b-2	b-3	b-3	b-1	b-2	b-3	b-2	b-3	b-1	b-2
Polysiloxane block-containing polymerizable monomer	Structure	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)
Evaluation	Mw	4200	4300	4400	5500	4800	4900	4900	17000	30000	4900	5200
	Mn	1700	1600	1600	1800	1700	1700	1700	7200	8100	1800	1600
	Molecular weight distribution	2.5	2.7	2.8	3.1	2.8	2.9	2.9	2.4	3.7	2.7	3.3
	Viscosity	B	E	O	P	E	F	LM	E	CD	N	DE
	Solid content (wt%)	44.8	45.6	46.3	55.5	45.1	45.8	46.1	51	51.1	51.1	47
Evaluation	Surface smoothness (Ra (μm))	A (0.42)	A (0.40)	A (0.38)	A (0.81)	A (0.65)	A (0.65)	A (0.6)	A (0.5)	A (0.52)	A (0.78)	A (0.4)
	Hardness of coating film (N/mm ²)	8.4	9.9	9.1	10.4	6.7	8.8	7.5	6.9	6.8	5.8	4.8

[0196]

[Table 3]

	Resin composition	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21	Example 22
		Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)
Composition of mixture (parts)	MMA	20	20	20	20	20	15	27	0	0	8	0
	EA	17.2	14.2	12.2	17.2	17.2	40.9	18.9	42.9	42.9	42.9	35.9
	MTA	0	3	0	0	0	0	0	0	0	0	0
	nBA	0	0	5	0	0	0	0	0	0	0	0
	MM-Zn1 (metal-containing monomer pure content)	12.8	12.8	12.8	12.8	12.8	14.1	0	14.1	14.1	14.1	14.1
	MM-Zn2 (metal-containing monomer pure content)	0	0	0	0	0	0	14.1	0	0	0	0
	IBEMA	0	0	0	0	0	0	0	0	0	0	0
	BEMA	0	0	0	0	0	0	0	0	0	0	0
	TIPX	0	0	0	0	0	0	0	0	0	0	0
	TIPStMA	0	0	0	0	0	0	0	0	0	0	0
	Macromonomer 1	0	0	0	0	0	0	0	0	0	0	0
	Macromonomer 2	0	0	0	0	0	0	0	13	0	5	20
	Macromonomer 3	0	0	0	0	0	0	0	0	13	0	0
	Polysiloxane block-containing polymerizable monomer	50	50	50	50	50	30	40	30	30	30	30
	AIBN	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.25	0.25	0.25	0.25
	AMBN	10.7	10.7	10.7	14.7	5.9	10.7	10.7	8.4	8.4	8.4	8.4
Compound (Y)	NOFMER MSD	1	1	1	1	1	1	1	1	1	1	1
	Isobutyl vinyl ether	-	-	-	-	-	-	-	-	-	-	-
Compound (Y)	Butyl vinyl ether	-	-	-	-	-	-	-	-	-	-	-
	Type	b-2	b-2	b-2	b-2	b-2	b-3	b-2	b-3	b-3	b-3	b-3
Polysiloxane block-containing polymerizable monomer	Structure	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)	Formula (b1)
	Mw	4400	4300	4500	3800	5600	4400	4700	6000	7000	5000	7200
Mn	Mn	1600	1600	1700	1400	2000	1600	1600	1800	2500	1800	2200
	Molecular weight distribution	2.8	2.7	2.6	2.7	2.8	2.8	2.9	3.3	2.8	2.8	3.3
Viscosity	Viscosity	V	WX	W	<A	+B	B	<A	NO	W	XY	J
	Solid content (wt%)	45.1	45.2	45.1	46.1	33.2	46.3	45.2	55.1	55.2	55.5	55.2
Evaluation	Surface smoothness (Ra (μm))	A (0.36)	A (0.51)	A (0.82)	A (0.3)	A (0.4)	A (0.49)	A (0.56)	A (0.6)	A (0.71)	A (0.74)	A (0.85)
	Hardness of coating film (N/mm ²)	6.9	7.4	6.4	4.5	14.9	4.8	7.1	11.2	13.2	10.1	13.1

[0198]

<Examples 31 to 67 and Comparative Examples 3 and 4>

Each antifouling paint composition was obtained by charging a metal can with each material with the formulation listed in Tables 5 to 7, adding glass beads thereto, mixing the mixture using a stirring bar, and carrying out pigment dispersion using a rocking shaker. The consumption degree and the antifouling properties were evaluated using the obtained antifouling paint compositions. The results are listed in Tables 5 to 7.

Resin composition

		Example 31	Example 32	Example 33	Example 34	Example 35	Example 36	Example 37	Example 38	Example 39	Example 40	Example 41	Example 42	Example 43	Example 44	Example 45
Resin composition	A-1	100	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-2	-	100	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-3	-	-	100	-	-	-	-	-	-	-	-	-	-	-	-
	A-4	-	-	-	100	-	-	-	-	-	-	-	-	-	-	-
	A-5	-	-	-	-	100	-	-	-	-	-	-	-	-	-	-
	A-6	-	-	-	-	-	100	-	-	-	-	-	-	-	-	-
	A-7	-	-	-	-	-	-	100	-	-	-	-	-	-	-	-
	A-8	-	-	-	-	-	-	-	100	-	-	-	-	-	-	-
	A-9	-	-	-	-	-	-	-	-	100	-	-	-	-	-	-
	A-10	-	-	-	-	-	-	-	-	-	100	-	-	-	-	-
	A-11	-	-	-	-	-	-	-	-	-	-	100	-	-	-	-
	A-12	-	-	-	-	-	-	-	-	-	-	-	100	-	-	-
	A-13	-	-	-	-	-	-	-	-	-	-	-	-	100	-	-
	A-14	-	-	-	-	-	-	-	-	-	-	-	-	-	100	-
	A-15	-	-	-	-	-	-	-	-	-	-	-	-	-	-	100
	A-16	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-17	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-18	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-19	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-20	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-21	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-22	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-23	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-24	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-25	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-26	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-27	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-28	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-29	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	A-30	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Evaluation	Antifouling properties	B	A	A	A	A	A	B	A	A	B	B	A	A	A	A

	Consumption degree (μm/M)	18.4	10.2	6.8	11.9	18.7	26.1	9.3	3.5	8.3
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[0202]

In Tables 5 to 7, the abbreviations indicate the following materials. Further, the numerical value listed in each column indicates the amount (parts) of each material to be charged. The amount of each of the resin compositions A-1 to A-32 to be charged

5 indicates the total mass of each resin composition.

KF-6016: trade name, manufactured by Shin-Etsu Chemical Co., Ltd.,
polyether-modified silicone oil

DISPARLON (registered trademark) 4200-20: manufactured by Kusumoto
Chemicals, Ltd., oxidized polyethylene wax

10 DISPARLON A603-20X: manufactured by Kusumoto Chemicals, Ltd.,
polyamide wax

[0203]

The coating films formed of the resin compositions in Examples 1 to 30 had excellent surface smoothness. Further, the hardness was sufficiently high and exhibited

15 excellent antifouling properties.

On the contrary, the coating films formed of the resin compositions in Comparative Examples 1 and 2 in which a polysiloxane block-containing polymerizable monomer other than the polymerizable monomer (b) was used as the polymerizable monomer (b) and the coating films formed of the resin compositions in Comparative

20 Examples 3 and 4 had degraded surface smoothness.

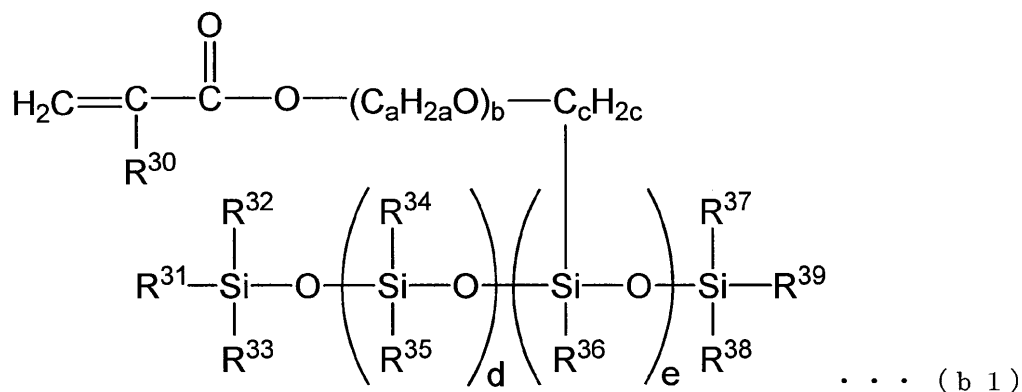
All coating films formed of the antifouling paint compositions of Examples 31 to 67, obtained by using the resin compositions of Examples 1 to 30, exhibited excellent consumption degrees and antifouling properties.

CLAIMS

1. A (meth)acrylic copolymer, comprising:

a constituent unit (B) derived from a polysiloxane block-containing

5 polymerizable monomer (b) represented by Formula (b1)



(in Formula (b1), R^{30} represents a hydrogen atom or a methyl group, a represents

an integer of 2 to 5, b represents a number of 0 to 50, c represents an integer of 0 to 18, d

represents a number of 1 to 1000, e represents a number of 1 to 80, R^{31} to R^{39} each

10 represents an alkyl group, an alkoxy group, a phenyl group, a substituted phenyl group, a phenoxy group, or a substituted phenoxy group).

2. The (meth)acrylic copolymer according to Claim 1, further comprising:

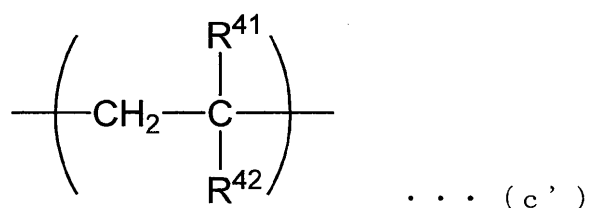
a constituent unit (C) derived from a macromonomer (c).

15

3. The (meth)acrylic copolymer according to Claim 2,

wherein the macromonomer (c) has two or more constituent units represented by

Formula (c')



(in Formula (c'), R⁴¹ represents a hydrogen atom, a methyl group, or CH₂OH, R⁴² represents OR⁴³, a halogen atom, COR⁴⁴, COOR⁴⁵, CN, CONR⁴⁶R⁴⁷, or R⁴⁸, R⁴³ to R⁴⁷ each independently represents a hydrogen atom, an alkyl group having an

5 unsubstituted or substituted group, an alicyclic group having an unsubstituted or substituted group, an aryl group having an unsubstituted or substituted group, a heteroaryl group having an unsubstituted or substituted group, a non-aromatic heterocyclic group having an unsubstituted or substituted group, an aralkyl group having an unsubstituted or substituted group, an alkaryl group having an unsubstituted or

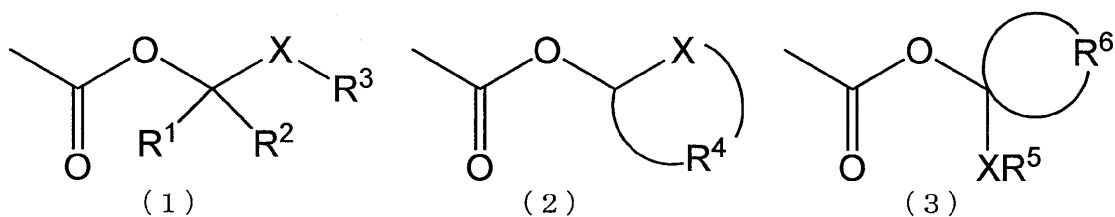
10 substituted group, or an organosilyl group having an unsubstituted or substituted group, and R⁴⁸ represents an aryl group having an unsubstituted or substituted group or a heteroaryl group having an unsubstituted or substituted group).

4. The (meth)acrylic copolymer according to any one of Claims 1 to 3, further

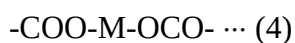
15 comprising:

at least one constituent unit (A) selected from the group consisting of a constituent unit (A1) having at least one structure (I) represented by Formula (1), Formula (2), or Formula (3), a constituent unit (A2) containing a triorganosilyloxycarbonyl group, and a constituent unit (A3) having at least one structure

20 (III) represented by Formula (4) or Formula (5)



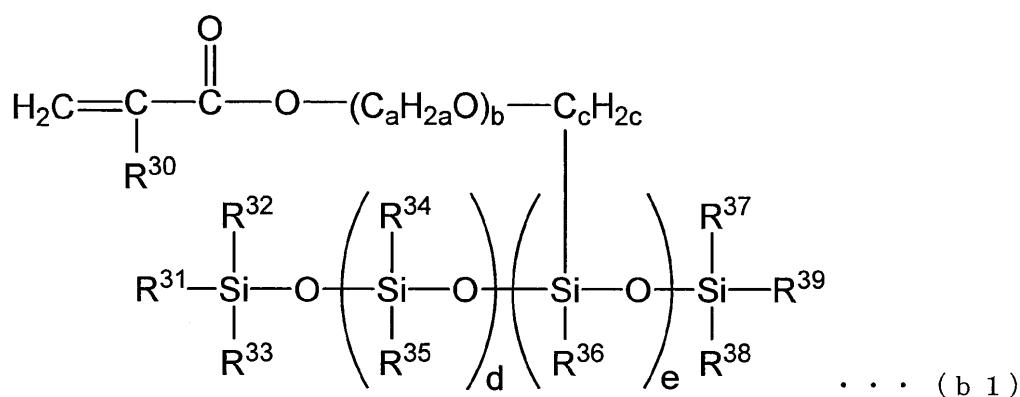
(in Formulae (1) to (3), X represents -O-, -S-, or -NR¹⁴-, R¹⁴ represents a hydrogen atom or an alkyl group, R¹ and R² each represents a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, R³ and R⁵ each represents an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group, or an aryl group, and R⁴ and R⁶ each represents an alkylene group having 1 to 10 carbon atoms)



(in Formulae (4) and (5), M represents Zn, Cu, Mg, or Ca, and R²² represents a monovalent organic acid residue).

5. A method for producing a (meth)acrylic copolymer, comprising:

a step of polymerizing a monomer mixture which contains a polysiloxane block-containing polymerizable monomer (b) represented by Formula (b1) and a polymerizable monomer different from the polysiloxane block-containing polymerizable monomer (b) to obtain a (meth)acrylic copolymer



- (in Formula (b1), R³⁰ represents a hydrogen atom or a methyl group, a represents an integer of 2 to 5, b represents a number of 0 to 50, c represents an integer of 0 to 18, d represents a number of 1 to 1000, e represents a number of 1 to 80, R³¹ to R³⁹ each represents an alkyl group, an alkoxy group, a phenyl group, a substituted phenyl group, a phenoxy group, or a substituted phenoxy group).

6. A resin composition, comprising:

the (meth)acrylic copolymer according to any one of Claims 1 to 4.

10

7. The resin composition according to Claim 6, further comprising:

silicone oil.

8. The resin composition according to Claim 6 or 7, further comprising:

15

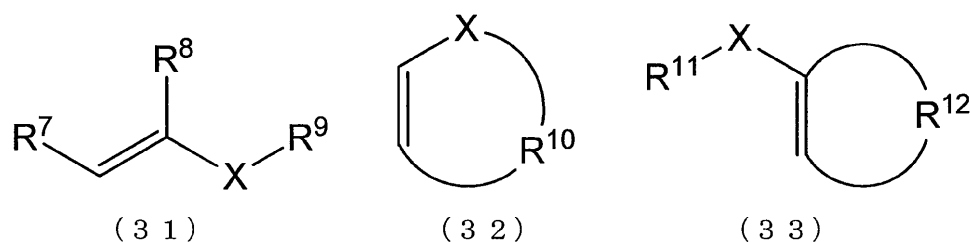
an organic solvent.

9. The resin composition according to any one of Claims 6 to 8,

wherein the (meth)acrylic copolymer has the constituent unit (A1), and

the resin composition further contains at least one compound (Y) selected from

the group consisting of a compound represented by Formula (31), a compound represented by Formula (32), and a compound represented by Formula (33)



(in Formulae (31) to (33), X represents -O-, -S-, or -NR¹⁴-, R¹⁴ represents a

- 5 hydrogen atom or an alkyl group, R⁷ represents a hydrogen atom or an alkyl group having 1 to 9 carbon atoms, R⁸ represents a hydrogen atom or an alkyl group having 1 to 10 carbon atoms, R⁹ and R¹¹ each represents an alkyl group having 1 to 20 carbon atoms, a cycloalkyl group, or an aryl group, R¹⁰ represents a single bond or an alkylene group having 1 to 9 carbon atoms, and R¹² represents an alkylene group having 1 to 9 carbon
- 10 atoms).

10. An antifouling paint composition, comprising:

the resin composition according to any one of Claims 6 to 9.

- 15 11. The antifouling paint composition according to Claim 10, further comprising:

an antifouling agent.

12. The antifouling paint composition according to Claim 10 or 11, further
- 20 comprising:

a thermoplastic resin other than the (meth)acrylic copolymer.