

DESCRIPTION

COMPOUND, POLYMER COMPRISING THE COMPOUND, AND CHEMICALLY
AMPLIFIED RESIST COMPOSITION COMPRISING THE POLYMER

5 Technical Field

The present invention relates to a novel compound, a polymer containing the compound, and a chemically amplified resist composition containing the polymer, which uses the compound and the polymer produced by polymerizing the compound as a monomer, thereby allowing uniform dispersion of the composition and making the
10 composition suitable for the formation of fine patterns, which has characteristics such as high adhesive force, high sensitivity and high thermal stability with a reduced amount of gas generation, and which can improve resolution and the line edge roughness. More particularly, the present invention relates to a novel compound which can be used to produce a resist that is capable of forming patterns using various radiations, such as far-
15 infrared radiations of a KrF excimer laser, an ArF excimer laser and the like, X-rays such as synchrotron radiation, and charged-particle radiations such as an electron beam, and is therefore useful for microprocessing; a polymer produced by polymerizing the compound as a monomer; and a chemically amplified resist composition containing the polymer.

20 Background Art

As the lithography technology that is used in the semiconductor industry and the like has been recently replaced by sub-50-nanometer technology, it is anticipated that more new and improved technologies will emerge. Although a lithography technology using extreme ultraviolet (EUV) radiation is one of important technologies capable of
25 such patterning, technologies realizing sub-32-nanometer patterns require very difficult

processes. A lithography technology using a wavelength of 193 nm is considered as an important means that can realize a technology for fabricating sub-32-nanometer patterns in the future, and this technology can be made possible by increasing the numerical aperture (NA).

5 According to Rayleigh's equation, the numerical aperture can be increased in order to increase the refractive index of an immersion fluid or an immersion resist, and the resolution can be simultaneously increased. Further, an increase in the refractive index may increase the depth of field (DOF).

$$R = (K1 \cdot \lambda) / (NA), \quad NA = n \sin \theta$$

10 R = resolution, λ = wavelength, NA = numerical aperture, n = refractive index, θ = incident angle

There has been an on-going demand for a new resist composition intended for an improvement of properties such as resolution, sensitivity, refractive index, and line edge roughness (LER), and investigations have been conducted on resist technologies to increase the refractive index of currently available resists and to obtain higher sensitivity. However, the results of these investigations are not satisfactory in the realization of finer semiconductor integrated circuits, and there is a problem that the photospeed is decreased.

15 Furthermore, there is an increasing demand for a chemically amplified resist composition which allows introduction of a photoacid generator in a photoacid generator, has higher sensitivity and higher stability with a reduced amount of gas discharge, and has high resolution and low line edge roughness.

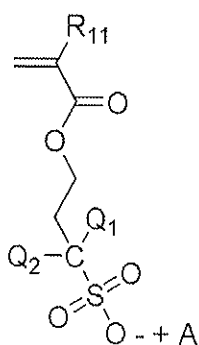
Disclosure of the Invention

25 An object of the present invention is to provide a novel compound that can be used as a photoacid generator or a monomer in a chemically amplified resist. Another object of

the invention is to provide a polymer containing the aforementioned compound as a monomer, which can be used in a chemically amplified resist composition having excellent sensitivity and higher stability with a reduced amount of gas discharge and also having high resolution and low line edge roughness.

5 In order to achieve the objects described above, a compound according to an aspect of the present invention is represented by the following formula (1):

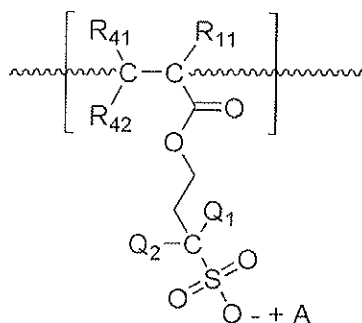
[Formula 1]



10 wherein in the formula (1), R₁₁ represents any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms; Q₁ and Q₂ each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom; and A⁺ represents an organic counterion.

15 A polymer according to another aspect of the present invention contains a repeating unit represented by the following formula (2):

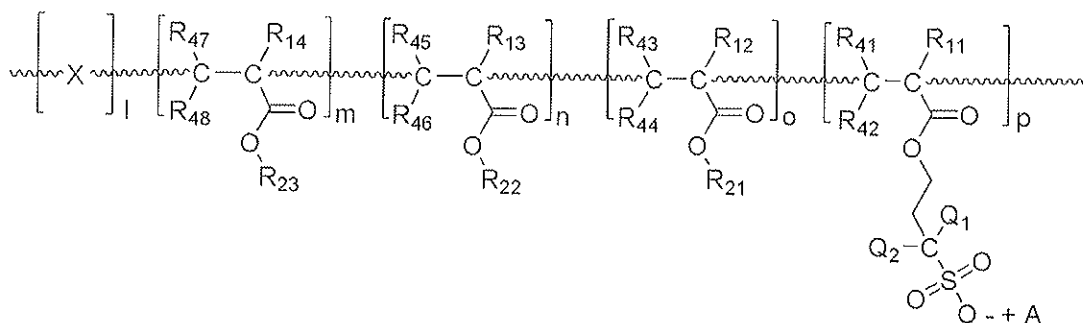
[Formula 2]



wherein in the formula (2), R_{11} , R_{41} and R_{42} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms; Q_1 and Q_2 each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom; and A^+ represents an organic counterion.

The polymer may be a polymer represented by the following formula (3):

[Formula 3]



wherein in the formula (3), R_{11} , R_{12} , R_{13} , R_{14} , R_{41} , R_{42} , R_{43} , R_{44} , R_{45} , R_{46} , R_{47} and R_{48} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms; Q_1 and Q_2 each independently represent any one selected from the group consisting of a hydrogen atom and a halogen

atom; R_{21} , R_{22} and R_{23} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group, a heteroalkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group, a heteroaryl group and combinations thereof; A^+ represents an organic counterion; X represents a polymerized unit derived from an olefinic monomer; and l , m , n , o and p are respectively in the ranges of $0 < l \leq 0.4$, $0 < m \leq 0.5$, $0 \leq n \leq 0.5$, $0 \leq o \leq 0.5$, and $0 < p \leq 0.2$, while $l+m+n+o+p = 1$.

The polymer may have a weight average molecular weight of 2,000 to 100,000, and may have a molecular weight distribution of 1 to 5.

A chemically amplified resist composition according to another aspect of the present invention includes the polymer containing the repeating unit of formula (2).

Hereinafter, the present invention will be described in more detail.

The terms used in the present specification are defined as follows.

Unless particularly stated otherwise herein, the halogen atom means any one selected from the group consisting of fluorine, chlorine, bromine and iodine.

Unless particularly stated otherwise herein, examples of the alkyl group include a primary alkyl group, a secondary alkyl group, and a tertiary alkyl group.

Unless particularly stated otherwise herein, the perfluoroalkyl group means an alkyl group in which a part of the hydrogen atoms or all the hydrogen atoms are substituted with fluorine atoms.

Unless particularly stated otherwise herein, the perfluoroalkoxy group means an alkoxy group in which a part of the hydrogen atoms or all the hydrogen atoms are substituted with fluorine atoms.

Unless particularly stated otherwise herein, all of the compounds and substituents may be substituted or unsubstituted. Here, being substituted means that a hydrogen atom has been replaced with any one selected from the group consisting of a halogen atom, a

hydroxyl group, a carboxyl group, a cyano group, a nitro group, an amino group, a thio group, a methylthio group, an alkoxy group, a nitrile group, an aldehyde group, an epoxy group, an ether group, an ester group, a carbonyl group, an acetal group, a ketone group, an alkyl group, a perfluoroalkyl group, a cycloalkyl group, a heterocycloalkyl group, an allyl group, a benzyl group, an aryl group, a heteroaryl group, derivatives thereof, and combinations thereof.

Unless particularly stated otherwise herein, the prefix "hetero-" means that carbon atoms are substituted with one to three heteroatoms selected from the group consisting of N, O, S and P. For example, a heteroalkyl group means that one to three carbon atoms of the carbon atoms of an alkyl group are substituted with heteroatoms.

Unless particularly stated otherwise herein, the alkyl group means a linear or branched alkyl group having 1 to 30 carbon atoms; the heteroalkyl group means an heteroalkyl group having 1 to 3 carbon atoms; the alkoxy group means an alkoxy group having 1 to 10 carbon atoms; the perfluoroalkyl group means a perfluoroalkyl group having 1 to 10 carbon atoms; the perfluoroalkoxy group means a perfluoroalkoxy group having 1 to 10 carbon atoms; the cycloalkyl group means a cycloalkyl group having 3 to 32 carbon atoms; the heterocycloalkyl group means a heterocycloalkyl group having 2 to 32 carbon atoms; the aryl group having an aryl group having 6 to 30 carbon atoms; and the heteroaryl group means a heteroaryl group having 2 to 30 carbon atoms.

Unless particularly stated otherwise herein, examples of the cycloalkyl group include monocyclic, bicyclic, tricyclic and tetracyclic cycloalkyl groups. Examples of the cycloalkyl group also include an adamantyl group, a norbornyl group, and a polycyclic cycloalkyl group containing a norbornyl group.

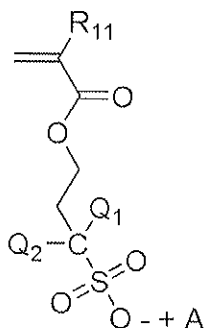
Unless particularly stated otherwise herein, the aryl group means a compound containing a benzene ring, or a derivative thereof, and examples of the aryl group include

toluene and xylene, in which an alkyl side chain is attached to a benzene ring; biphenyls in which two or more benzene rings are linked by single bonds; fluorene, xanthene and anthraquinone, in which two or more benzene rings are linked via a cycloalkyl group or a heterocycloalkyl group; and naphthalene and anthracene, in which two or more benzene rings are fused.

Unless particularly stated otherwise herein, the olefin means an unsaturated hydrocarbon compound containing a double bond. Examples thereof include, but are not limited to, alkylenes, acrylates, styrene, norbornene, indene, acenaphthylene, and furandione.

The compound according to an aspect of the present invention is represented by the following formula (1).

[Formula 1]



In the formula (1),

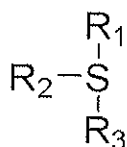
R₁₁ represents any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms, and may be preferably any one selected from a hydrogen atom, a trifluoromethyl group, an alkyl group having 1 to 5 carbon atoms, and an alkoxy group having 1 to 5 carbon atoms;

Q₁ and Q₂ each independently represent any one selected from the group consisting

of a hydrogen atom and a halogen atom, and may be preferably a fluorine atom; and

Λ^+ represents an organic counterion, and the organic counterion may be preferably a group represented by the following formula (5) or the following formula (6):

[Formula 5]



wherein in the formula (5), R_1 , R_2 and R_3 each independently represent any one selected from the group consisting of an alkyl group, a heteroalkyl group, a perfluoroalkyl group, an alkoxy group, an aryl group and a heteroaryl group; and

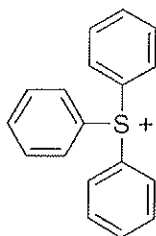
[Formula 6]



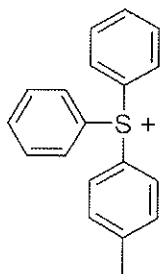
wherein R_4 and R_5 each independently represent any one selected from the group consisting of an alkyl group, a heteroalkyl group, a perfluoroalkyl group, an alkoxy group, an aryl group and a heteroaryl group.

The formula (5) may be any one selected from the group consisting of the following formulas (5-i) to (5-xxii):

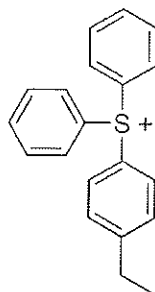
[Formulas 5-i to 5-xxii]



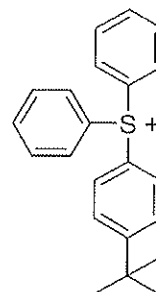
[5-i]



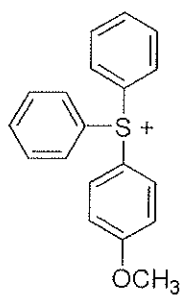
[5-ii]



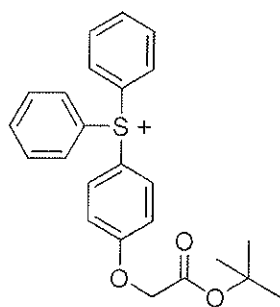
[5-iii]



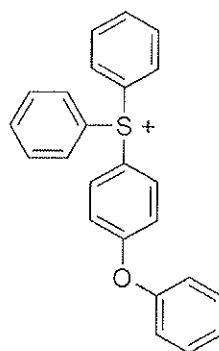
[5-iv]



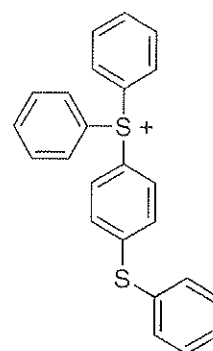
[5-v]



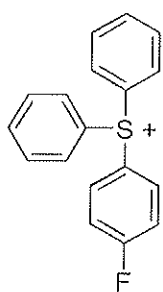
[5-vi]



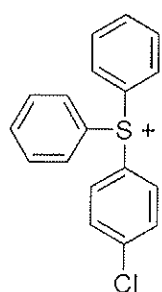
[5-vii]



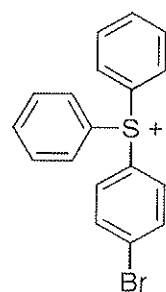
[5-viii]



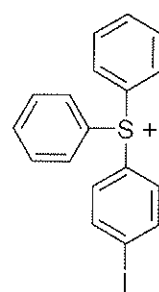
[5-ix]



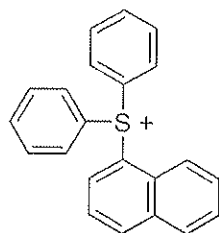
[5-x]



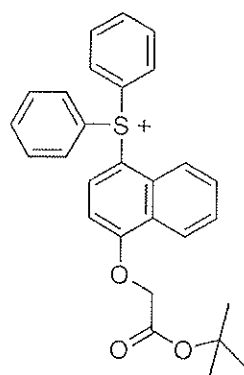
[5-xi]



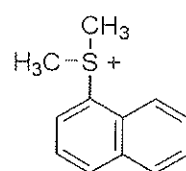
[5-xii]



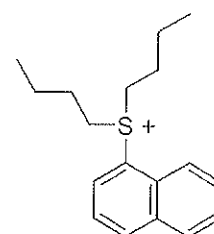
[5-xiii]



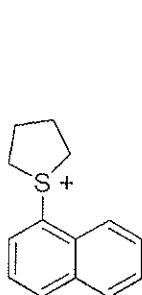
[5-xiv]



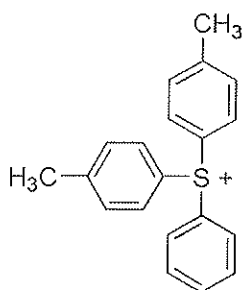
[5-xv]



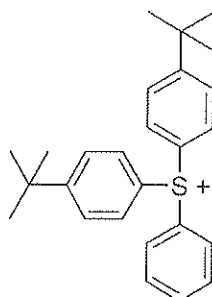
[5-xvi]



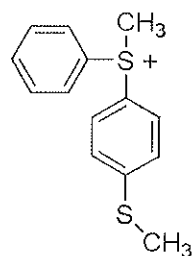
[5-xvii]



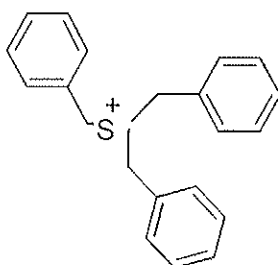
[5-xviii]



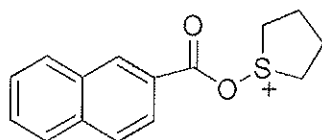
[5-xix]



[5-xx]



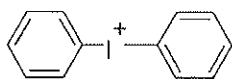
[5-xxi]



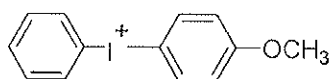
[5-xxii]

The formula (6) may be any one selected from the group consisting of the following formulas (6-i) to (6-ix):

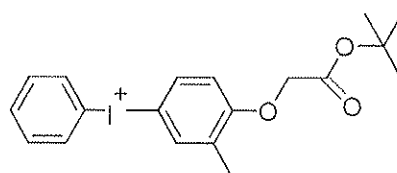
5 [Formulas 6-i to 6-ix]



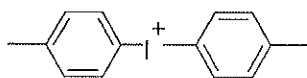
[6-i]



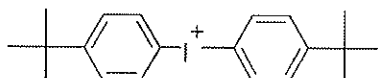
[6-ii]



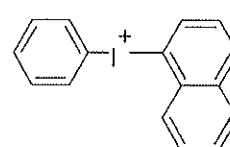
[6-iii]



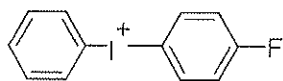
[6-iv]



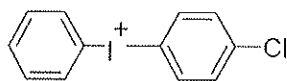
[6-v]



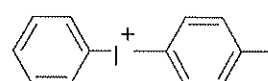
[6-vi]



[6-vii]



[6-viii]

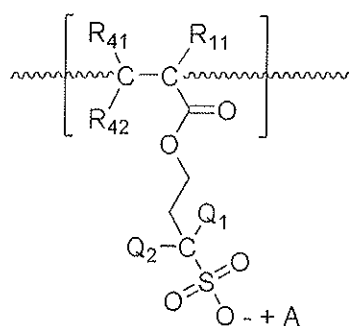


[6-ix]

The compound of the formula (1) serves as a monomer as well as a photoacid generator. In this case, resolution and the LER characteristics can be improved by regulating the carbon number of the main chain of the compound (1), and thereby securing a space in which the acid generated by exposure of a polymer obtained by polymerizing the compound (1) as a monomer, while also regulating the diffusion distance of acid appropriately for patterning.

The polymer according to another aspect of the present invention contains a repeating unit represented by the following formula (2).

[Formula 2]



In the formula (2),

R_{11} , R_{41} and R_{42} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms, and may be preferably any one selected from a hydrogen atom, a trifluoromethyl group, an alkyl group having 1 to 5 carbon atoms, and an alkoxy group

having 1 to 5 carbon atoms;

Q_1 and Q_2 each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom, and may be preferably a fluorine atom; and

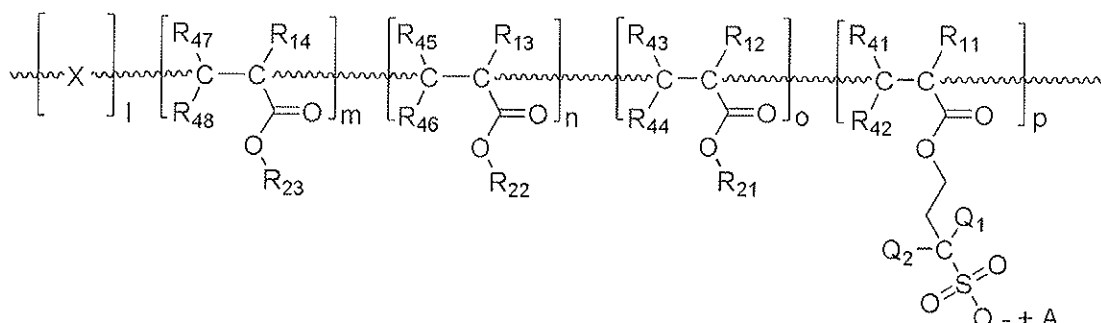
A^+ represents an organic counterion. This A^+ has the same definition as described
5 with regard to the formula (1), and thus further descriptions on A^+ will not be repeated.

The polymer is produced by directly polymerizing the compound of formula (1), which plays the role of a photoacid generator, into a polymer, and thereby allows introduction of the photoacid generator in a large amount. Therefore, a polymer which enables a resist containing the polymer to have higher sensitivity at the time of exposure
10 and higher stability, and which has a low LER with a reduced amount of discharge gas that is generated after exposure, can be produced.

The polymer is a multi-component copolymer, and may be a block copolymer, a random copolymer or a graft copolymer. Furthermore, the polymer containing the repeating unit represented by the formula (2) may be a polymer containing any one
15 repeating unit selected from the group consisting of a repeating unit having an acid labile group, a repeating unit containing a hydroxyl group, a repeating unit containing an adhesive group of lactone ring, and combinations thereof.

More specifically, the polymer may be a polymer represented by the following formula (3):

20 [Formula 3]



In the formula (3),

R_{11} , R_{12} , R_{13} , R_{14} , R_{41} , R_{42} , R_{43} , R_{44} , R_{45} , R_{46} , R_{47} and R_{48} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms, and may be preferably any one selected from a hydrogen atom, a trifluoromethyl group, an alkyl group having 1 to 5 carbon atoms, and an alkoxy group having 1 to 5 carbon atoms;

Q_1 and Q_2 each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom, and may be preferably a fluorine atom;

A^+ represents an organic counterion, and since A^+ has the same definition as described with regard to A^+ in the formula (1), further descriptions thereon will not be repeated;

symbols l , m , n , o and p are respectively in the ranges of $0 < l \leq 0.4$, $0 < m \leq 0.5$, $0 \leq n \leq 0.5$, $0 \leq o \leq 0.5$, and $0 < p \leq 0.2$, while $l+m+n+o+p = 1$; and

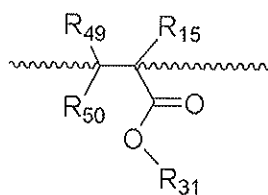
X represents a polymerized unit derived from an olefinic monomer.

The olefinic monomer may be preferably any one selected from the group consisting of acrylate, styrene, norbornene, indene, acenaphthylene, furandione and derivatives thereof.

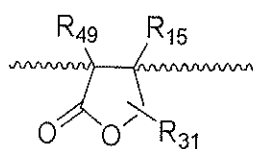
X may be preferably a polymerized unit represented by one of the following

formulas (3-a) to (3-f):

[Formula 3-a]

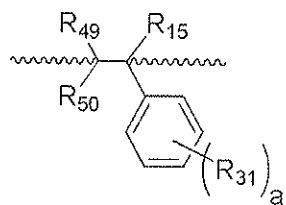


[Formula 3-b]

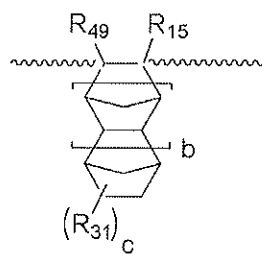


5

[Formula 3-c]

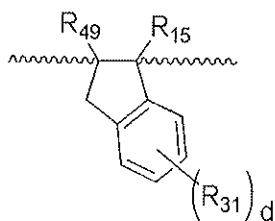


[Formula 3-d]

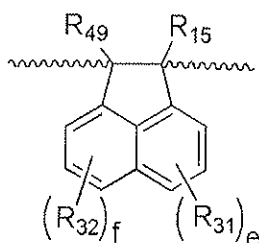


10

[Formula 3-e]



[Formula 3-f]



In the formula (3-a) to the formula (3-f),

- 5 R_{15} , R_{49} and R_{50} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms, and may be each preferably any one selected from a hydrogen atom, a trifluoromethyl group, an alkyl group having 1 to 5 carbon atoms, and an alkoxy group
10 having 1 to 5 carbon atoms;

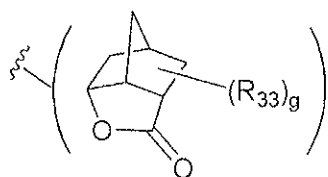
- R_{31} and R_{32} each independently represent any one selected from the group consisting of a halogen atom, a hydroxyl group, a cyano group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy group, a nitro group, an amino group, a thio group, a methylthio group, an alkyl group, an alkoxy group, a perfluoroalkoxy group, a
15 hydroxyalkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group, a heteroaryl group, COOR' and COR' , wherein R' represents any one selected from the group consisting of an alkyl group, a perfluoroalkyl group, a cycloalkyl group, an aryl group and a cycloaryl group;

a represents an integer from 0 to 5, b represents an integer from 0 to 5, c represents an integer from 0 to 8, d represents an integer from 0 to 4, e represents an integer from 0 to 3, and f represents an integer from 0 to 3.

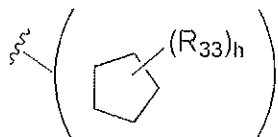
In the formula (3),

5 R_{21} , R_{22} and R_{23} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group, a heteroalkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group, a heteroaryl group and combinations thereof, and may be preferably any one selected from the group consisting of the following formulas (3-i) to (3-ix):

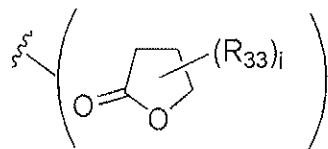
10 [Formula 3-i]



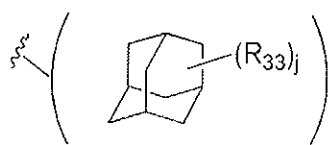
[Formula 3-ii]



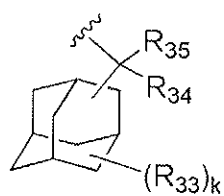
[Formula 3-iii]



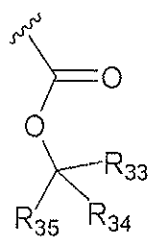
15 [Formula 3-iv]



[Formula 3-v]

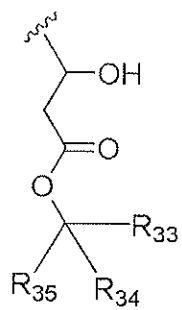


[Formula 3-vi]

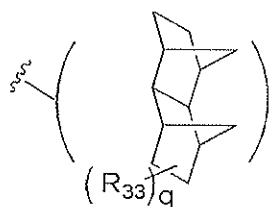


5

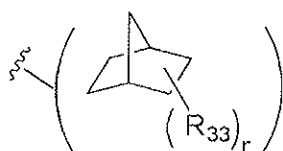
[Formula 3-vii]



[Formula 3-viii]



[Formula 3-ix]



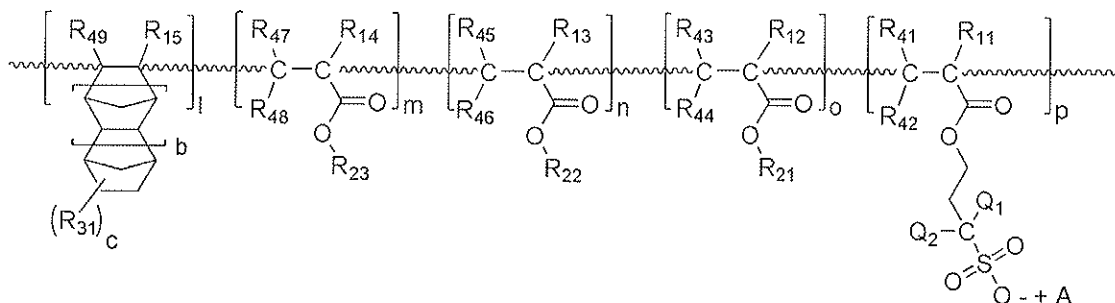
In the formulas (3-i) to (3-ix),

5 R_{33} to R_{35} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group, an alkoxy group, a perfluoroalkyl group, a perfluoroalkoxy group, a hydroxyalkyl group, a halogen atom, a hydroxyl group, a cyano group, a nitro group, an amino group, a thio group, a methylthio group, an ether group and a methoxy group, and preferably, R_{33} to R_{35} may be each independently any one selected
10 from the group consisting of a hydrogen atom, an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, a perfluoroalkyl group having 1 to 4 carbon atoms, a perfluoroalkoxy group having 1 to 4 carbon atoms, a hydroxyalkyl group having 1 to 6 carbon atoms, a halogen atom, a hydroxyl group, a cyano group, a nitro group, an amino group, a thio group, a methylthio group and a methoxy group.

15 Symbol g represents an integer from 0 to 9, h represents an integer from 0 to 9, i represents an integer from 0 to 5, j represents an integer from 0 to 15, k represents an integer from 0 to 15, q represents an integer from 0 to 17, and r represents an integer from 0 to 11.

 The polymer may be preferably a polymer represented by the following formula
20 (4):

[Formula 4]



wherein in the formula (4), R_{11} , R_{12} , R_{13} , R_{14} , R_{41} , R_{42} , R_{43} , R_{44} , R_{45} , R_{46} , R_{47} , R_{48} , Q_1 , Q_2 , A^+ , R_{21} , R_{22} , R_{23} , l , m , n , o and p respectively have the same definitions as described with
 5 regard to the formula (3), and thus further descriptions on these symbols will not be repeated.

In the formula (4), b represents an integer from 0 to 5, and c represents an integer from 0 to 8.

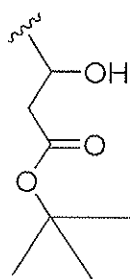
In the formula (4), R_{15} and R_{49} each independently represent any one selected from
 10 the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms, and preferably, R_{15} and R_{49} may be each independently any one selected from the group consisting of a hydrogen atom, a trifluoromethyl group, an alkyl group having 1 to 5 carbon atoms, and an alkoxy group having 1 to 5 carbon atoms.

In the formula (4), R_{31} represents any one selected from the group consisting of a
 15 halogen atom, a hydroxyl group, a cyano group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy group, a nitro group, an amino group, a thio group, a methylthio group, an alkyl group, an alkoxy group, a perfluoroalkoxy group, a hydroxyalkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group, a heteroaryl group, $COOR'$ and
 20 COR' , wherein R' represents any one selected from the group consisting of an alkyl group,

a perfluoroalkyl group, a cycloalkyl group, an aryl group and a cycloaryl group.

R_{31} may be preferably any one selected from the group consisting of an alkyl group having 1 to 6 carbon atoms, an alkoxy group having 1 to 6 carbon atoms, a perfluoroalkyl group having 1 to 4 carbon atoms, a perfluoroalkoxy group having 1 to 4 carbon atoms, a hydroxyalkyl group having 1 to 6 carbon atoms, a halogen atom, a hydroxyl group, a cyano group, a nitro group, an amino group, a thio group and a methylthio group, and more preferably, R_{31} may be any one selected from the group consisting of a hydrogen atom and the following formula 3-x:

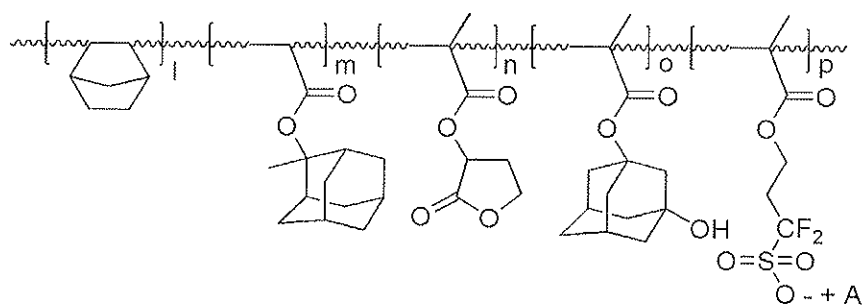
[Formula 3-x]



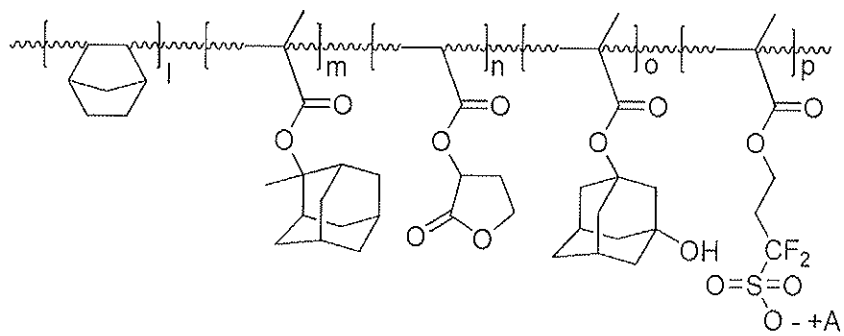
When a resist is produced using a polymer containing a (meth)acrylic polymer, the amount of light absorption is small, but there is a problem that the polymer has poor etching resistance as compared with aromatic compounds. However, in the case of introducing a cyclic olefin having a larger number of carbon atoms than (meth)acrylic polymers introduced into the main chain as shown in the formula (4), etching resistance may be highly improved, and the acid-labile moieties do not all vaporize even after pretreatments (soft baking) and partially remain in the resist film. Thus, the flow of the acid generated from the acid generator at the time of exposure may be improved, and accordingly, the patterning characteristics may be greatly improved.

The polymer may be any one selected from the group consisting of the following formulas (4-a) to (4-l):

[Formula 4-a]

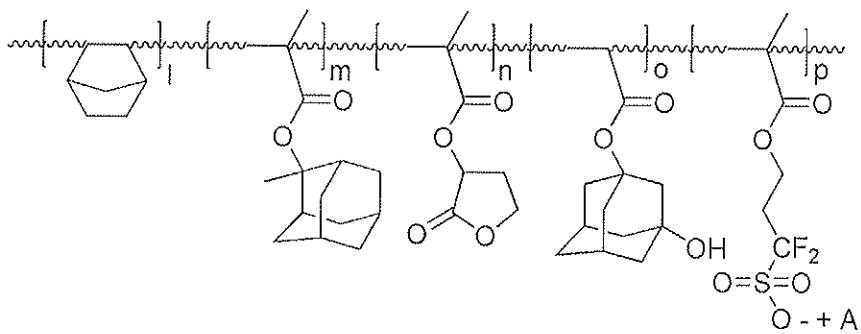


[Formula 4-b]

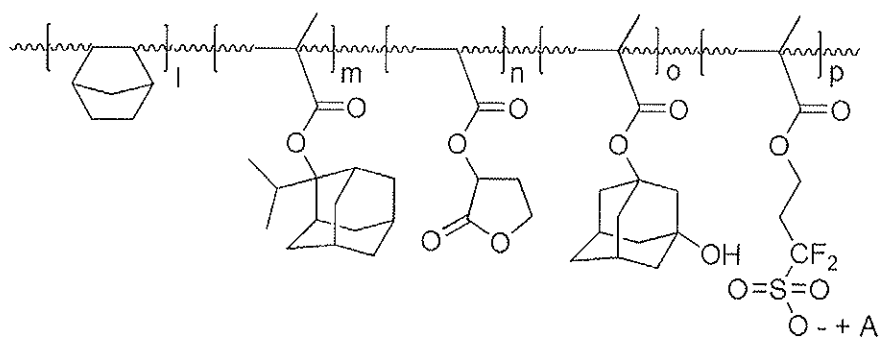


5

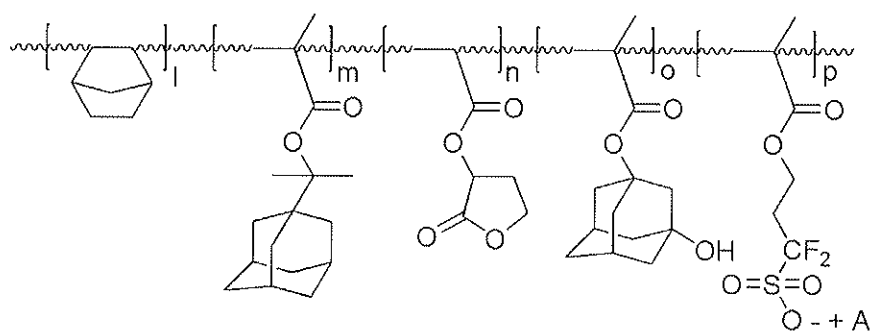
[Formula 4-c]



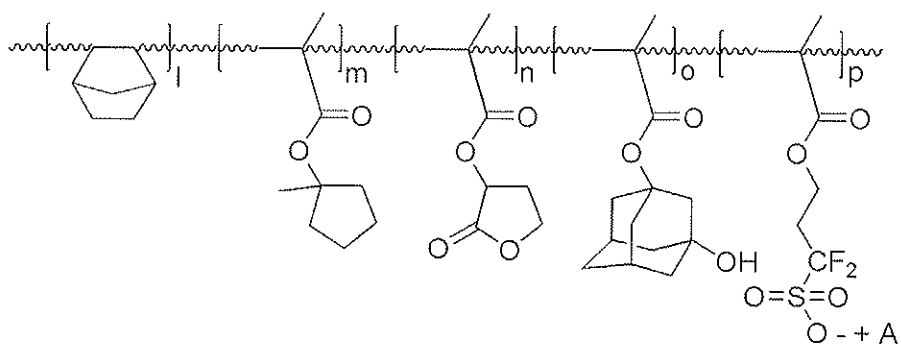
[Formula 4-d]



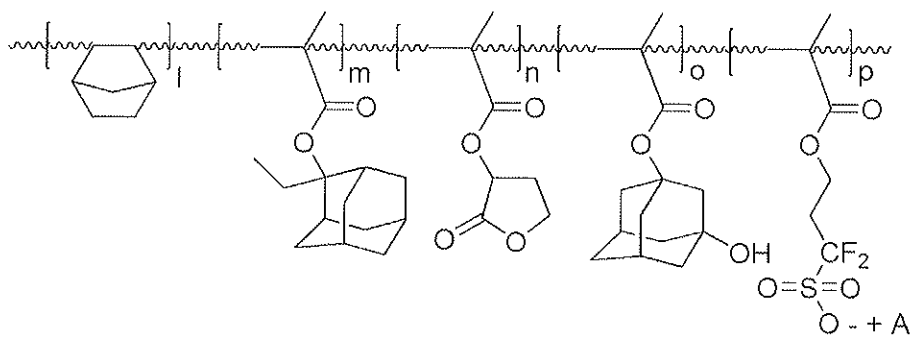
[Formula 4-e]



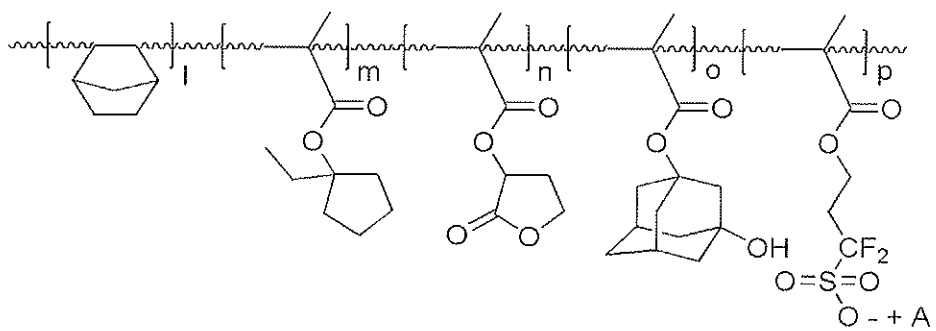
[Formula 4-f]



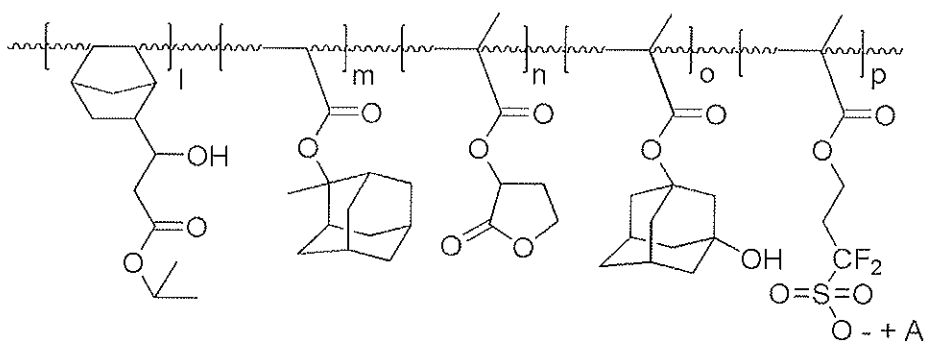
[Formula 4-g]



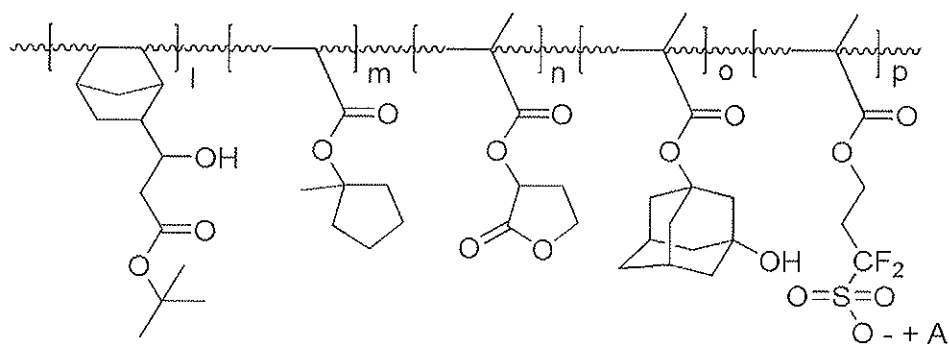
[Formula 4-h]



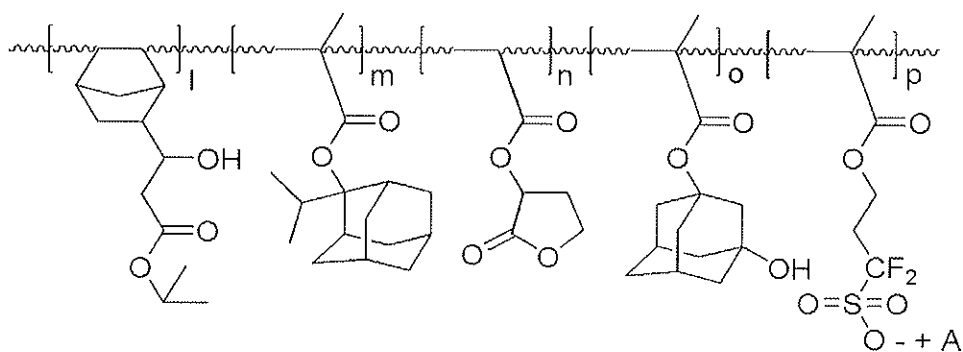
[Formula 4-i]



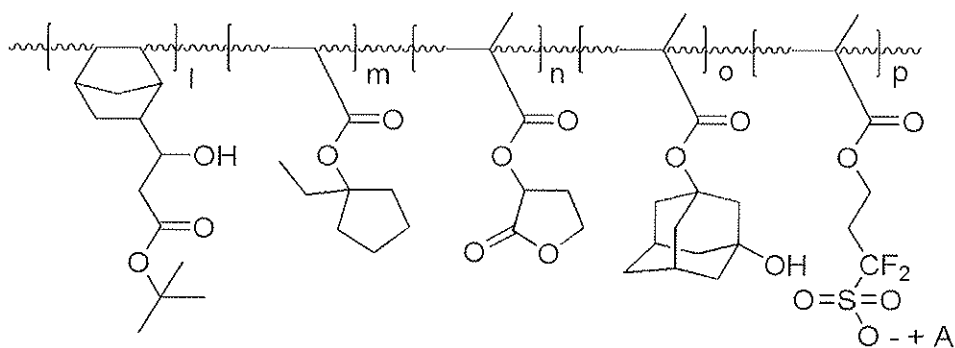
[Formula 4-j]



[Formula 4-k]



[Formula 4-l]



5

In the formulas (4-a) to (4-l),

Symbols l, m, n, o and p are respectively in the ranges of $0 < l \leq 0.4$, $0 < m \leq 0.5$, $0 \leq n \leq 0.5$, $0 \leq o \leq 0.5$, and $0 < p \leq 0.2$, while $l+m+n+o+p = 1$;

A⁺ represents an organic counterion, and since A⁺ has the same definition as
10 described with regard to A⁺ in the formula (1), further descriptions thereon will not be

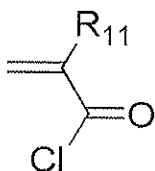
repeated.

The polymer containing the repeating unit of formula (2) may preferably have a weight average molecular weight of 2,000 to 100,000 as measured by gel permeation chromatography (GPC) relative to polystyrene standards, and a molecular weight
5 distribution of 1 to 5, and may more preferably have a weight average molecular weight of 3,000 to 30,000, and a molecular weight distribution of 1.50 to 3. If the weight average molecular weight is greater than 100,000, the solubility of the polymer may be poor when the polymer is used in a photoresist composition, and the line edge roughness may be poor. If the weight average molecular weight is less than 2,000, the mechanical strength of the
10 resin is poor, and thus there may occur a phenomenon in which patterns are not satisfactorily formed (collapse of patterns). Furthermore, if the molecular weight distribution is greater than 5, the line edge roughness may be poor. Therefore, when a polymer having the weight average molecular weight and the molecular weight distribution that fall in the ranges described above is used in a photoresist composition, the
15 photoresist composition may exhibit appropriate properties in terms of developability, coatability, and heat resistance.

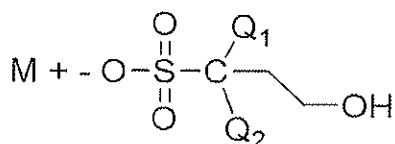
The compound represented by the formula (1) can be produced by a method such as described below.

The compound represented by the formula (1) can be produced by a method
20 including a first step of allowing a compound represented by the following formula (7) and a compound represented by the following formula (8) to react, and a second step of subjecting the reaction product produced in the first step to a substitution reaction with a compound represented by the following formula (9):

[Formula 7]



[Formula 8]



[Formula 9]

A+Z-

5

In the formula (7) to formula (9),

M+ represents any one selected from the group consisting of Li+, Na+ and K+;

Z- represents any one selected from the group consisting of (OSO₂CF₃)-, (OSO₂C₄F₉)-, (OSO₂C₈F₁₇)-, (N(CF₃)₂)-, (N(C₂F₅)₂)-, (N(C₄F₉)₂), (C(CF₃)₃)-, (C(C₂F₅)₃)-, (C(C₄F₉)₃)-, F-, Cl-, Br-, I-, BF₄-, AsF₆- and PF₆-; and

10

A+, R₁₁, Q₁ and Q₂ respectively have the same definitions as described with regard to the compound represented by the formula (1), and thus further descriptions on these symbols will not be repeated.

The reaction of the first step may be carried out in a solvent, and as the solvent, any one selected from the group consisting of esters, ethers, lactones, ketones, amides, alcohols and combinations thereof can be used. Preferably, dichloromethane, chloroform, dichloroethane, acetonitrile, toluene, benzene, 1,4-dioxane and the like can be used.

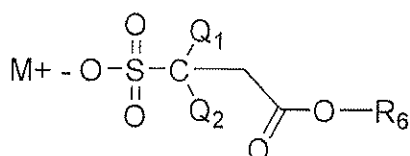
15

The reaction of the first step may be carried out in the presence of a basic catalyst, and the basic catalyst may be any one selected from the group consisting of triethylamine,

diethylamine, pyridine, diethylisopropylamine, aniline, diisopropylethylamine and combinations thereof. When the reaction of the first step is carried out in the presence of the basic catalyst, the reaction time may be shortened, the conversion ratio may be increased, and side-reactions can be reduced.

5 The compound represented by the formula (8) can be obtained by reducing a compound represented by the following formula (10):

[Formula 10]



In the formula (10),

10 M+ represents any one selected from the group consisting of Li+, Na+ and K+;

R₆ represents any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, and a heteroalkyl group in which one to three hydrogen atoms of an alkyl group having 1 to 10 carbon atoms are substituted with halogen atoms, and may be any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 5 carbon atoms, a trifluoromethyl group, a trichloromethyl group, a tribromomethyl group and a triiodomethyl group; and

15 Q₁ and Q₂ respectively have the same definitions as described with regard to the compound represented by the formula (1), and thus further descriptions on these symbols will not be repeated.

20 The process of reducing the compound represented by the formula (10) and thereby obtaining the compound represented by the formula (8), may include, specifically, the steps of dissolving the compound of formula (8) in tetrahydrofuran and an alcoholic

solvent; slowly adding dropwise a reducing agent to the solution in an ice bath; after completion of the dropwise addition, raising the temperature to 40°C to 100°C to prepare a reaction mixture liquid; allowing the reaction mixture liquid to react under stirring; subsequently terminating the reaction of the reaction mixture liquid; removing the solvent;
5 and crystallizing the reaction product. In regard to the method for crystallization, any method of crystallization that can be conventionally used can be used, but specifically, a method of acidifying the reaction mixture liquid from which the solvent has been removed, to pH 5 to 6 using a strong acid; concentrating the resultant mixture; subsequently adding an alcohol to make the resulting concentrate into a slurry; filtering the slurry, washing the
10 filtrate again using hexane; subsequently concentrating the filtrate again; and crystallizing the product from diethyl ether, can be used.

The polymer containing the repeating unit of formula (2) can be polymerized by conventional methods for producing polymers, but preferably a radical polymerization method can be used. As the polymerization initiator that can be used in radical
15 polymerization, any one selected from the group consisting of azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), lauryl peroxide, azobisisocapronitrile, azobisisovaleronitrile, tert-butyl hydroperoxide and combination thereof can be used. The polymerization reaction can be implemented by methods such as bulk polymerization, solution polymerization, suspension polymerization, bulk-suspension polymerization, and
20 emulsion polymerization. As the polymerization solvent used in the polymerization, one or more selected from benzene, toluene, xylene, halogenated benzene, diethyl ether, tetrahydrofuran, 1,2-dichloroethane, esters, ethers, lactones, ketones, and amides can be used. After the polymerization is completed, the unreacted monomers and side-products remaining in the reaction mixture liquid can be removed by conventional methods for
25 removing these monomers and side-products, and preferably, these materials can be

removed by a precipitation method using a solvent.

The chemically amplified resist composition according to another aspect of the present invention includes the polymer containing the repeating unit of formula (2). The amount of use of the monomer represented by the formula (1) in the polymer may be 0.5
5 to 15 parts by weight relative to 100 parts by weight of the total solids content of the polymer, and if the monomer represented by the formula (1) is used in an amount in the range described above, superior sensitivity and higher stability can be obtained, while the amount of gas discharge can be reduced.

The resist composition may include the polymer containing the repeating unit of
10 formula (2) in an amount of 3% by weight or greater, and preferably 5% by weight or greater, relative to the total amount of the resist composition. If the content of the polymer is less than 3% by weight, the effect of including the polymer may not be sufficiently manifested. The resist composition can also include conventional constituent elements that constitute the resist composition, such as additives or solvents, in addition to the
15 polymer.

The resist composition including the repeating unit of formula (2) can be used in the formation of patterns by a pattern forming method which includes a step of applying the resist composition on a substrate; a step of subjecting the applied resist composition to a heating treatment; and thereby exposing the resist composition with high energy rays,
20 and a step of developing the resist composition using a developer solution.

It is preferable to use a higher energy ray having a wavelength in the range of 13.5 nm to 250 nm, because the resolution can be increased, while the LER is lowered.

When the novel compound of the present invention and the polymer containing this compound are used in a chemically amplified resist composition, the resist composition
25 may have excellent sensitivity and higher stability with a reduced amount of gas discharge,

and may have higher resolution and lower line edge roughness.

Best Mode for Carrying Out the Invention

Hereinafter, the present invention will be described in detail so that those having
5 ordinary skill in the pertinent art can easily carry out the invention. However, the present invention can be implemented in various different embodiments, and is not intended to be limited to the Examples described herein.

Synthesis Examples for Compound

1) Synthesis of difluorohydroxypropane sulfonic acid sodium salt

10 83 g of 3,3-difluoro-3-sulfopropionic acid ethyl ester sodium salt was dissolved in 160 mL of methanol and 1.2 L of tetrahydrofuran (THF) in an ice bath, and 44 g of sodium borohydride was slowly added dropwise to the solution. After completion of the dropwise addition, the reaction mixture liquid was removed from the ice bath, and was heated to 60°C. The reaction mixture liquid was stirred for about 4 hours at the same temperature.

15 The reaction mixture liquid thus stirred was quenched with distilled water, and then the solvent was removed. The reaction mixture obtained after removing the solvent was dissolved again in distilled water, and the resulting solution was acidified to pH 5 to 6 with concentrated hydrochloric acid.

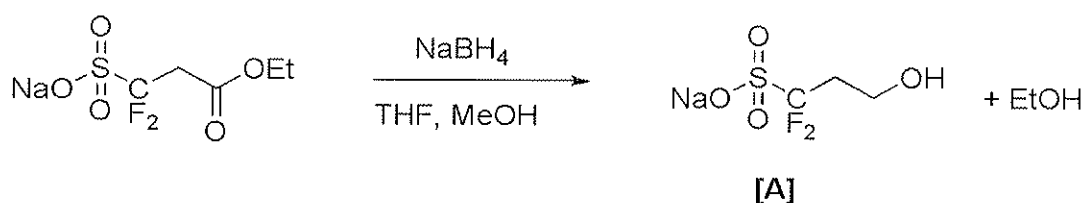
The acidified reaction mixture liquid was concentrated again, and methanol was
20 added thereto to obtain a slurry. The slurry was filtered to remove inorganic salts, and then the filtrate was washed two times with hexane. The methanol layer was concentrated again, and then was subjected to crystallization using diethyl ether.

A white solid obtained by crystallization was dried in a vacuum, and the structure
of the solid was confirmed by ¹H-NMR. Thus, 68.5 g (yield: 95%) of
25 difluorohydroxypropane sulfonic acid sodium salt (sodium 3-ethoxy-1,1-difluoro-3-

oxopropane-1-sulfonate) represented by formula [A] in the following reaction scheme (1) was obtained.

¹H-NMR (chloroform-d₃, internal standard: tetramethylsilane): δ(ppm) 3.3(t, 2H), 4.58-4.68(t, 2H)

[Reaction Scheme 1]



wherein in the reaction scheme 1, Me represents a methyl group, and Et represents an ethyl group.

2) Synthesis of 2-methylacrylic acid-2,2-difluoro-2-sulfopropyl ester sodium salt

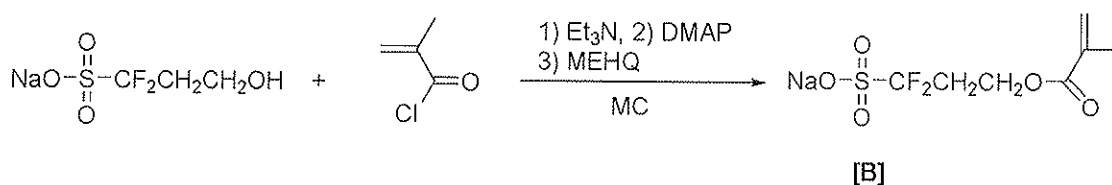
68 g of difluorohydroxylpropane sulfonic acid sodium salt (sodium 3-ethoxy-1,1-difluoro-3-oxopropane-1-sulfonate) represented by formula [A] in the reaction scheme (1), which was produced in Synthesis Example for Compound 1), and 54.6 mL of methacryloyl chloride were mixed with 500 mL of dichloromethane (MC), and the resulting mixture was stirred. Subsequently, 3.2 g of N,N'-dimethylaminopyridine (DMAP) and 50 mg of a polymerization preventing agent (hydroquinone monomethyl ether (MEHQ)) were added to the mixture at 15°C to 25°C, and the resulting mixture was mixed. 104 mL of triethylamine (Et₃N) placed in a dropping funnel was slowly added dropwise to the mixture at 15°C to 25°C, and thus a reaction mixture liquid was prepared. The reaction mixture liquid was stirred for 3 hours at 15°C to 25°C, subsequently the extent of reaction was determined by NMR, and the reaction was terminated.

After termination of the reaction of the reaction mixture liquid, dichloromethane which was the reaction solvent was removed by distilling off under reduced pressure, and

300 mL of distilled water was added thereto. Subsequently, potassium carbonate was added to the reaction mixture liquid to produce a saturated solution. The saturated solution was stirred for 2 hours, and then a solid thus produced was filtered. Thus, 81 g (yield: 86%) of 2-methyl-acrylic acid-2,2-difluoro-2-sulfo-propyl ester sodium salt (sodium 1,1-difluoro-3-(methacryloyloxy)propane-1-sulfonate) represented by formula [B] in the reaction scheme 2 was obtained. The structure of the salt was confirmed by ¹H-NMR.

¹H-NMR (DMSO, internal standard: tetramethylsilane): δ(ppm) 1.91(s, 3H), 3.3(t, 2H), 4.57-4.67(t, 2H), 5.77(s, 1H), 6.11(s, 1H)

[Reaction Scheme 2]



wherein in the reaction scheme 2, Et represents an ethyl group.

3) Synthesis of 2-methylacrylic acid-2,2-difluoro-2-sulfopropyl ester diphenylmethylphenylsulfonium salt

31 g of 2-methylacrylic acid-2,2-difluoro-2-sulfopropyl ester sodium salt (sodium 1,1-difluoro-3-(methacryloyloxy)propane-1-sulfonate) produced in Synthesis Example for Compound 2), and 35 g of diphenylmethylphenylsulfonium trifluoromethanesulfonium salt represented by formula [C] in the following reaction scheme 3 were dissolved in 300 mL of dichloromethane (MC) and 300 mL of distilled water to prepare a reaction mixture, and the reaction mixture was subjected to a two-layer reaction under vigorous stirring for 3 hours.

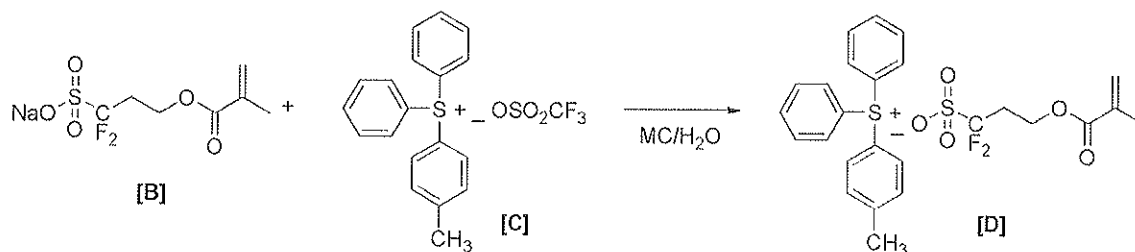
After completion of stirring, an aliquot of the organic layer was taken to check the

extent of reaction by ^{19}F -NMR, and the reaction was terminated. After termination of the reaction, the organic layer of the reaction mixture liquid was collected, and the solvent was removed. The organic layer was washed using dichloromethane, which was a good solvent, and hexane, which was a poor solvent, and the solvents were removed to obtain crystals.

The crystals thus obtained were dried under reduced pressure, and thus 40 g (yield: 96%) of 2-methylacrylic acid-2,2-difluoro-2-sulfopropyl ester diphenylmethylphenylsulfonium salt represented by formula [D] in the following reaction scheme 3 was obtained. The structure of the salt was confirmed by ^1H -NMR.

^1H -NMR (chloroform- d_3 , internal standard: tetramethylsilane): δ (ppm) 1.95(s, 3H), 2.43(s, 3H), 3.3(t, 2H), 4.82(t, 2H), 5.60(s, 1H), 6.22(s, 1H), 7.43-7.80(m, 14H)

[Reaction Scheme 3]



Synthesis Examples for Polymer

(Example 1)

As monomers for polymerization, 13 g of 2-methyl-2-adamantyl acrylate, 8.4 g of γ -butyrolactyl methacrylate, 11.6 g of 3-hydroxy-1-adamantyl methacrylate, and 1 g of 2-methylacrylic acid-2,2-difluoro-2-sulfopropyl ester diphenylmethylphenylsulfonium salt represented by formula [D] in the above reaction scheme 3 were dissolved in 58 g of 1,2-dichloroethane, and thus a monomer mixture liquid was prepared.

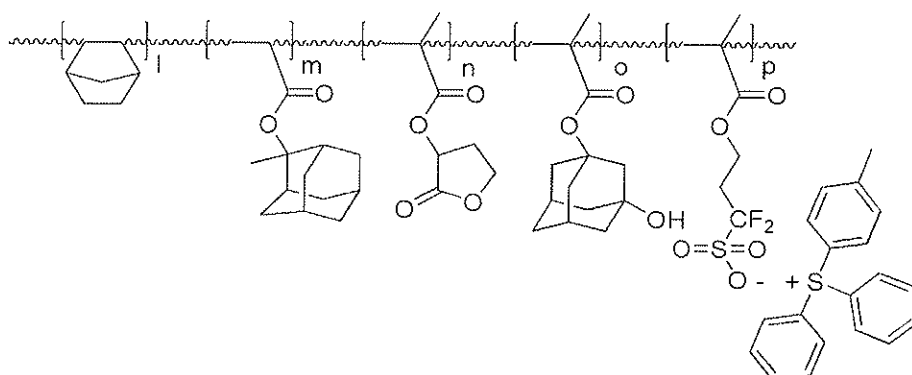
A reaction bath was provided by adding 3.7 g of norbornene, 2.5 g of

azobisisobutyronitrile (AIBN) as a polymerization initiator, and 117 g of 1,2-dichloroethane as a polymerization solvent to a 250-mL flask, and nitrogen gas was introduced into the reaction bath. The mixture was stirred for one hour while the temperature was maintained at 15°C to 25°C.

5 While the temperature of the reaction bath at 65°C, the monomer mixture liquid described above was slowly added dropwise over one hour to the reaction bath to prepare a reaction mixture liquid, and the reaction mixture liquid was allowed to react for 16 hours. After completion of polymerization, the reaction mixture liquid was cooled to 15°C to 25°C, the reaction product was precipitated with hexane, and then the precipitate was
10 filtered. The precipitate was washed several times with the same solvent during the filtration process, and crystals thus obtained were dried under reduced pressure. Thus, 37 g (yield: 79%) of a polymer of Example 1 represented by the following formula (11) was obtained. In the polymer of Example 1 represented by the following formula (11), l is 0.24, m is 0.25, n is 0.30, o is 0.20, and p is 0.01.

15 The polymer of Example 1 had a polystyrene-reduced weight average molecular weight (Mw) of 1,190, and a molecular weight distribution (ratio of weight average molecular weight and number average molecular weight, Mw/Mn) of 1.57.

[Formula 11]



(Example 2)

A polymer was produced in the same manner as in Example 1, except that the values of l, m, n, o and p in the formula (11) were changed by adjusting the respective amounts of the monomers for polymerization. The values of l, m, n, o and p in the
5 formula (11) of the polymer of Example 2 are such that l is 0.24, m is 0.25, n is 0.30, o is 0.18, and p is 0.03.

(Example 3)

A polymer was produced in the same manner as in Example 1, except that the values of l, m, n, o and p in the formula (11) were changed by adjusting the respective
10 amounts of the monomers for polymerization. The values of l, m, n, o and p in the formula (11) of the polymer of Example 3 are such that l is 0.24, m is 0.25, n is 0.30, o is 0.16, and p is 0.05.

(Example 4)

A polymer was produced in the same manner as in Example 1, except that the
15 values of l, m, n, o and p in the formula (11) were changed by adjusting the respective amounts of the monomers for polymerization. The values of l, m, n, o and p in the formula (11) of the polymer of Example 4 are such that l is 0.24, m is 0.25, n is 0.30, o is 0.14, and p is 0.07.

(Comparative Example)

20 As monomers for polymerization, 10.0 g of 2-methyl-2-adamantyl methacrylate, 7.3 g of γ -butyrolactyl methacrylate, and 10.1 g of 3-hydroxy-1-adamantyl methacrylate were mixed, and the mixture was dissolved in 82 g of 1,4-dioxane to prepare a monomer mixture liquid. The bath temperature was slowly raised to 65°C.

A reaction bath was provided by adding 3.7 g of norbornene, 2.5 g of
25 azobisisobutyronitrile (AIBN) as a polymerization initiator, and 117 g of 1,2-

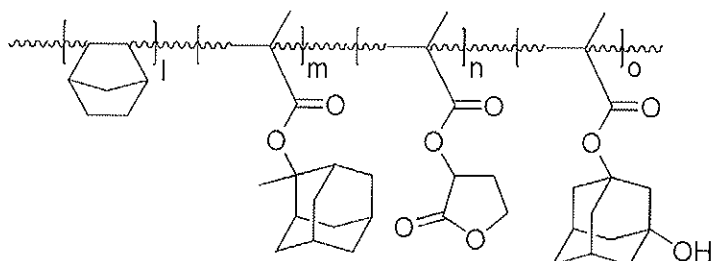
dichloroethane as a polymerization solvent to a 250-mL flask, and nitrogen gas was introduced into the reaction bath. The mixture was stirred for one hour while the temperature was maintained at 15°C to 25°C.

While the temperature of the reaction bath at 65°C, the monomer mixture liquid
5 described above was slowly added dropwise over one hour to the reaction bath to prepare a reaction mixture liquid, and the reaction mixture liquid was allowed to react for 16 hours. After completion of polymerization, the reaction mixture liquid was cooled to 15°C to 25°C, the reaction product was precipitated with hexane, and then the precipitate was filtered. The precipitate was washed several times with the same solvent during the
10 filtration process, and crystals thus obtained were dried under reduced pressure. Thus, 25 g (yield: 91%) of a polymer represented by the following formula (12) was obtained.

In the following formula (12), l is 0.28, m is 0.24, n is 0.24, and o is 0.24.

The polymer represented by the following formula (12) had a polystyrene-reduced
weight average molecular weight (Mw) of 1,780, and a molecular weight distribution
15 (ratio of weight average molecular weight and number average molecular weight, Mw/Mn) of 1.68.

[Formula 12]



Production of resist and property evaluation

20 (Example 1)

0.75 parts by weight of tetramethylammonium hydroxide as a basic additive per

100 parts by weight of the polymer of Example 1 was dissolved in 1,000 parts by weight of propylene glycol methyl ether acetate, and then the solution was filtered through a 0.2- μ m membrane filter. Thus, a resist liquid was prepared.

The resist liquid was applied on a substrate using a spinner, and was dried at 110°C for 90 seconds, to form a film having a thickness of 0.2 μ m. The film thus formed was exposed using an ArF excimer laser stepper (lens numerical aperture: 0.75), and then the film was heat-treated at 120°C for 90 seconds. The heat-treated substrate was developed with a 2.38 wt% aqueous solution of tetramethylammonium hydroxide for 40 seconds, and the substrate was washed and dried. Thus, a resist pattern was formed thereon.

(Examples 2 to 4)

Resist patterns were formed in the same manner as in Example 1 for Production of resist and property evaluation, except that 100 parts by weight each of the polymers synthesized in Examples 2 to 4 of the Synthesis Examples for Polymer were used instead of 100 parts by weight of the polymer of Example 1 for Production of resist and property evaluation. The properties of the resist patterns were evaluated.

(Comparative Examples 1 to 3)

Resist patterns were formed in the same manner as in Example 1 for Production of resist and property evaluation, except that the resist liquids having the compositions indicated in Table 1 below were produced by using the polymers of the Comparative Examples represented by the above formula (12). The properties of the resist patterns were evaluated.

[Table 1]

	Polymer	Acid generator (1)	Basic additive (2)
Comparative Example 1	100	3	1
Comparative Example 2	100	5	1

Comparative Example 3	100	7	1
-----------------------	-----	---	---

(Content: parts by weight)

(1) Acid generator: Triphenylsulfonium nonaflate

(2) Basic additive: Tetramethylammonium hydroxide

An evaluation of the properties of Examples 1 to 4 and Comparative Examples 1 to 3 was carried out in terms of sensitivity, resolution and LER, and the results are presented in Table 2 below.

In the case of sensitivity, the amount of exposure which is capable of forming a 0.10- μ m line-and-space (L/S) pattern after development to have a 1:1 line width, was defined as the amount of optimal exposure, and the amount of optimal exposure was defined as sensitivity. The minimum pattern dimension resolved at this time was defined as resolution.

The LER was measured by critical dimension scanning electron microscopy (CD SEM), and the evaluation results were rated based on 5 grades, such as 1 (very poor), 2 (poor), 3 (medium), 4 (good), and 5 (very good).

[Table 2]

	Sensitivity (mJ/cm ²)	Resolution (nm)	LER
Example 1	15	70	4
Example 2	18	70	4
Example 3	15	90	4
Example 4	13	70	5
Comparative Example 1	19	90	2
Comparative Example 2	17	80	3
Comparative Example 3	16	90	3

According to Table 2, Examples 1 to 4 exhibited generally superior sensitivity as compared with Comparative Examples 1 to 3, and also exhibited superior resolution.

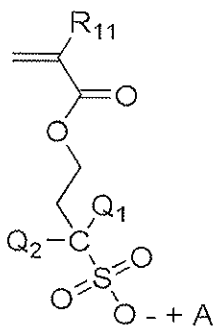
Particularly in the case of the LER, Examples 1 to 4 exhibited far superior results as compared with the Comparative Examples.

As such, preferred embodiments of the present invention have been described in detail, but the scope of the present invention is not intended to be limited thereto, and
5 various modifications and improvements that can be made by an ordinarily skilled person using the fundamental concept of the present invention as defined in the following claims are also included in the scope of the present invention.

CLAIMS

1. A compound represented by the following formula (1):

[Formula 1]



5 wherein in the formula (1),

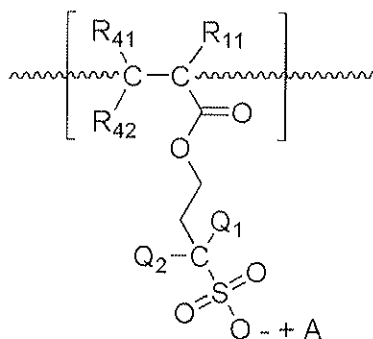
R₁₁ represents any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms;

10 Q₁ and Q₂ each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom; and

A⁺ represents an organic counterion.

2. A polymer comprising a repeating unit represented by the following formula (2):

[Formula 2]



wherein in the formula (2),

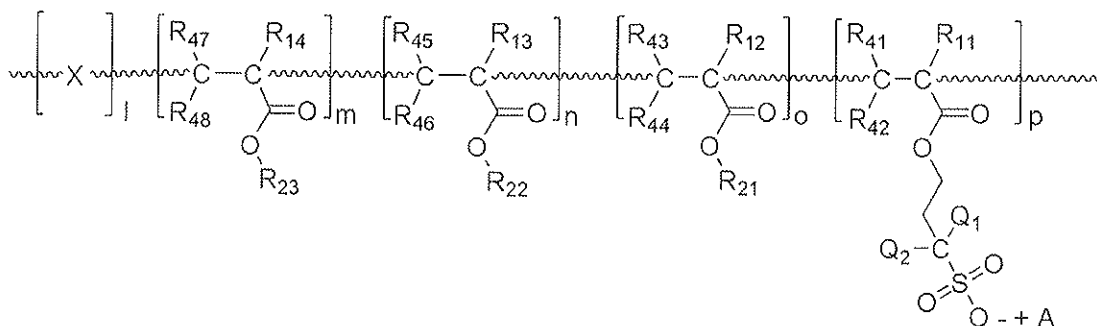
R₁₁, R₄₁ and R₄₂ each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms;

Q₁ and Q₂ each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom; and

A⁺ represents an organic counterion.

3. The polymer according to claim 2, wherein the polymer is a polymer represented by the following formula (3):

[Formula 3]



wherein in the formula (3),

R₁₁, R₁₂, R₁₃, R₁₄, R₄₁, R₄₂, R₄₃, R₄₄, R₄₅, R₄₆, R₄₇ and R₄₈ each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10 carbon atoms;

Q₁ and Q₂ each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom;

R_{21} , R_{22} and R_{23} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group, a heteroalkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group, a heteroaryl group and combinations thereof;

A^+ represents an organic counterion;

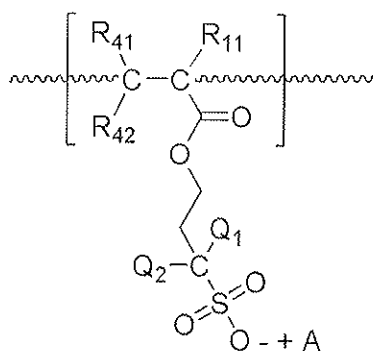
X represents a polymerized unit derived from an olefinic monomer; and

symbols l , m , n , o and p are respectively in the ranges of $0 < l \leq 0.4$, $0 < m \leq 0.5$, $0 \leq n \leq 0.5$, $0 \leq o \leq 0.5$, and $0 < p \leq 0.2$, while $l+m+n+o+p = 1$.

4. The polymer according to claim 3, wherein the polymer has a weight average molecular weight of 2,000 to 100,000, and a molecular weight distribution of 1.5 to 5.

5. A chemically amplified resist composition comprising a polymer containing a repeating unit represented by the following formula (2):

[Formula 2]



wherein in the formula (2),

R_{11} , R_{41} and R_{42} each independently represent any one selected from the group consisting of a hydrogen atom, an alkyl group having 1 to 10 carbon atoms, a perfluoroalkyl group having 1 to 10 carbon atoms, and an alkoxy group having 1 to 10

carbon atoms;

Q_1 and Q_2 each independently represent any one selected from the group consisting of a hydrogen atom and a halogen atom; and

A^+ represents an organic counterion.