

NOVEL COPOLYMER AND PHOTORESIST COMPOSITION COMPRISING THE
SAME

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a copolymer that intensifies contrast and resolution power in the patterning of a photoresist, and a photoresist composition containing the copolymer. More particularly, the present invention
10 relates to a novel copolymer that can be used for preparing a resist which is useful in microprocessing using various radiations, including far-ultraviolet radiation such as krypton fluoride (KrF) excimer laser radiation, argon fluoride (ArF) excimer laser radiation or F₂ excimer laser
15 radiation; X-rays such as synchrotron radiation; and charged particle beams such as extreme ultraviolet (EUV) beam, and to a photoresist composition containing the copolymer.

Description of the Related Art

20 The recent high integration of semiconductor devices has led to a demand for ultrafine patterns with a line width of 0.10 micrometers or less in the production of ultra-large scale integration (LSI) and the like. Accordingly, attention is focused on researches concerning lithographic
25 processes using an exposure light having a far shorter wavelength compared with the conventionally used exposure light having a wavelength in the region of g-rays or i-rays,

such as far-ultraviolet radiation, KrF excimer laser radiation, ArF excimer laser radiation, EUV, X-rays and electron beam.

5 In particular, a light source that attracts the most attention in the field of lithography demanding the next-generation patterns with a line width of 0.10 micrometer or less, is ArF excimer laser radiation.

10 A photoresist composition used for the purposes as described above usually contains a component having an acid-sensitive functional group (hereinafter, referred to as "polymer"), a component that generates acid when irradiated (hereinafter, referred to as "acid generator"), and a solvent, and depending on the purpose, basic additives and the like may also be added.

15 A polymer that is used as a main raw material of the photoresist composition, needs to have appropriate compatibility with developing solutions, an adhesive power to substrates, resistance to etching, and functional groups imparting excellent resolution power.

20 Specific examples of such functional groups include a hydroxyl group, a lactone group, a carboxyl group and the like, as the functional groups for enhancing the compatibility with developing solutions and the adhesive power to substrates; a cyclic alkyl group having no oxygen atom in the main chain, such as in a norbornene derivative
25 and an adamantane derivative, as the functional groups for enhancing the resistance to etching; and the like. However,

as a factor for enhancing the resolution, the fluidity of acid due to a photoacid generator is more weighted than any special functional groups from the aspect of polymer structure.

5 A number of inventions have been developed until recently, so as to satisfy such properties. Specifically, there may be mentioned, for example, a copolymer of adamantane acrylate and cyclolactone acrylate [SPIE (1997, 3049, 519), or US Patent No. 6,013,416], a copolymer of
10 maleic anhydride and an olefin (KP No. 0672889), a pure olefin copolymer [SPIE (1997, 3049, 92)], a hybrid copolymer synthesized using these monomers in a mixture [SPIE (1997, 3049, 85), US Patent No. 6,677,419, and KP No. 2000-0022340], and the like. However, although the performances of these
15 polymers are being enhanced, since finer patterns are ever increasingly demanded, there is always a request for new resins and compositions exhibiting appropriate resolution power.

20 SUMMARY OF THE INVENTION

It is an object of the present invention to provide a copolymer that is quickly dissolved in general solvents, is easily dissolved in most of solvents, and can be produced without a molecular weight controlling agent.

25 It is another object of the present invention to provide a chemically amplified photoresist composition that is sensitized by KrF excimer laser radiation, ArF excimer

laser radiation, EUV, X-rays, electron beam or the like,
which composition has less dependency on the substrate, has
excellent transparency in the far-ultraviolet region, and
has excellent contrast, sensitivity, resolution and
5 developability. The photoresist composition provided by the
present invention is also capable of ameliorating the
decrease of the residual film ratio occurring when a topcoat
material is used in the liquid immersion exposure method
using ArF, capable of enhancing the resolution power by
10 facilitating fluidity and diffusion of acid upon irradiation
of ArF laser radiation, and capable of enhancing the
development properties manifested by developer solutions and
the adhesive power to substrates.

15 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing the nuclear magnetic
resonance data of the monomer produced in Monomer Synthesis
Example 2 of the present invention;

Fig. 2 is a graph showing the nuclear magnetic
20 resonance data of the copolymer produced in Copolymer
Synthesis Example 1 of the present invention;

Fig. 3 is a graph showing the results of gel permeation
chromatography measurement for the copolymer produced in
Copolymer Synthesis Example 1 of the present invention;

25 Fig. 4 is a graph showing the results of nuclear
magnetic resonance data of the copolymer produced in
Copolymer Synthesis Example 2 of the present invention;

Fig. 5 is a graph showing the results of gel permeation chromatography measurement for the copolymer produced in Copolymer Synthesis Example 2 of the present invention;

Fig. 6 is a graph showing the results of nuclear magnetic resonance data of the copolymer produced in Copolymer Synthesis Example 3 of the present invention;

Fig. 7 is a graph showing the results of gel permeation chromatography measurement for the copolymer produced in Copolymer Synthesis Example 3 of the present invention;

Fig. 8 is a graph showing the results of nuclear magnetic resonance data of the copolymer produced in Copolymer Synthesis Example 5 of the present invention;

Fig. 9 is a graph showing the results of gel permeation chromatography measurement for the copolymer produced in Copolymer Synthesis Example 5 of the present invention;

Fig. 10 is a diagram showing the results of an analysis using a thermal analyzer, performed on BOC-HAMA itself produced in Monomer Synthesis Example 2 of the present invention; and

Fig. 11 is a diagram showing the results of an analysis using a thermal analyzer, performed on a mixture of 92 parts by weight of BOC-HAMA and 8 parts by weight of toluenesulfonic acid.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

All of the compounds or substituents mentioned herein may be unsubstituted or substituted, unless stated otherwise.

Here, the term "substituted" means a hydrogen atom on a compound or substituent is substituted with any one selected from the group consisting of a halogen atom, a hydroxy group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy 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 stated otherwise herein, the term "halogen atom" means an atom of any one selected from fluorine, chlorine, bromine, iodine and combinations thereof.

Unless stated otherwise herein, the term "perfluoroalkyl group" means an "alkyl group" having a part or the entirety of its hydrogen atoms substituted with fluorine.

Unless stated otherwise herein, the term "heterocycloalkyl group" or "heteroaryl group" means a "cycloalkyl group" or "aryl group" containing, within a ring, 1 to 3 heteroatoms selected from the group consisting of nitrogen (N), oxygen (O), sulfur (S) and phosphorus (P), and carbon atoms for the rest.

Unless stated otherwise herein, the term "alkyl group" means a linear or branched alkyl group having 1 to 30 carbon atoms; the term "perfluoroalkyl group" means a linear or branched perfluoroalkyl group having 1 to 30 carbon atoms; the term "cycloalkyl group" means a cycloalkyl group having 3 to 30 carbon atoms; the term "heterocycloalkyl group"

means a heterocycloalkyl group having 2 to 30 carbon atoms; and the term "aryl group" means an aryl group having 6 to 30 carbon atoms.

The recent high integration of semiconductor devices
5 has led to an ever-increasing demand for ultrafine patterns with a line width of 0.10 micrometers or less in the production of ultra-large scale integration (LSI) and the like.

In this regard, as the method of increasing the
10 resolution, there may be mentioned a method of using short wavelengths for the exposure wavelength, as can be seen in Rayleigh's equation, $R = k\lambda/NA^2$, and a method of increasing the numerical aperture (NA). Therefore, attention is focused on researches concerning lithographic processes that
15 use an exposure light having a far shorter wavelength, such as far-ultraviolet radiation, KrF excimer laser radiation, ArF excimer laser radiation, EUV, X-rays and electron beam, as compared with the conventionally used exposure light having a wavelength in the region of g-rays or i-rays, in
20 order to obtain high resolution by changing the exposure wavelength to a shorter wavelength.

On the other hand, in the method of increasing the numerical aperture (NA), the maximum NA value is substantially maintained at 0.93, and therefore, in order to
25 obtain an effect of increasing the NA, use is made of a liquid immersion exposure method, which utilizes a medium having a high refractive index in between the laser

radiation and a coated wafer. Since water is currently used as such a medium, a top coat substance is used on a photoresist so as to prevent leaching from the photoresist to water. At this time, the photoresist should not be
5 damaged by the solvent of the top coat used thereon, and thus the film loss after exposure serves as an important factor in the liquid immersion exposure method of using ArF.

Therefore, in order to improve the residual film ratio of the photoresist, it is desirable not to use a hydroxyl
10 group or a carboxylic acid in the constitution of the resin used in the composition.

However, if a hydroxyl group or a carboxylic acid is not used, there are problems such as that the adhesive power to the substrate is lowered, and a monomer having a bulky
15 hydrocarbon structure should be used to acquire etching resistance.

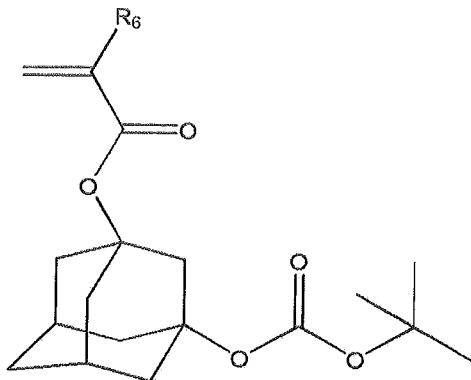
Accordingly, in the present invention, a monomer having a structure such as hydroxyadamantane is used to enhance etching resistance, and at the same time, the hydroxyl group
20 is substituted with a tert-butoxycarbonate (t-BOC) structure to improve the residual film ratio of the resin.

Furthermore, the t-BOC moiety is liable in the presence of the acid generated after exposure, and the isoprene and hydroxy structure generated as a result of decomposition of
25 the t-BOC yield an effect of aiding in the flow of acid and improving the resolution.

Monomers and copolymers

The structure of a monomer having the t-BOC moiety that can be used in the present invention, may be represented by the following formula 1, but the present invention is not intended to be limited to this.

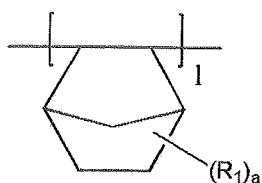
5 [General Formula 1]



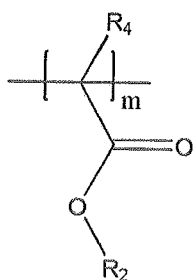
In the general formula 1, R_6 represents any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group,
 10 an epoxy group, an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group.

The copolymer according to an aspect of the present invention can be synthesized using monomers represented by the general formula 1 shown above, and includes monomers
 15 represented by the following formulas 1 to 4.

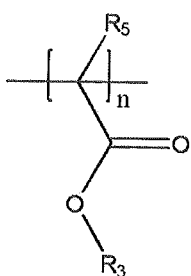
[Formula 1]



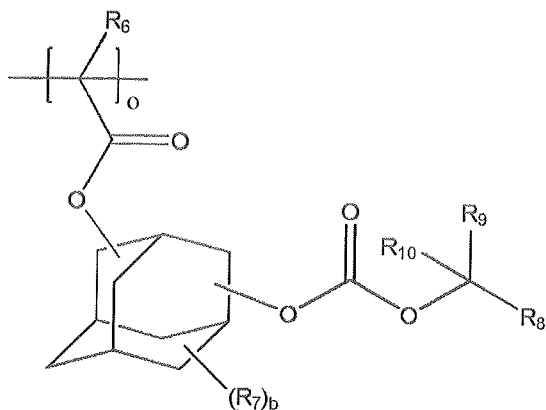
[Formula 2]



[Formula 3]



[Formula 4]



5

wherein in the formulas 1 to 4,

R₁ to R₁₀ each independently represent any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group,
 10 an epoxy group, an alkyl group, a cycloalkyl group, a

heterocycloalkyl group, an aryl group and a heteroaryl group;

a is an integer from 0 to 10;

b is an integer from 0 to 14;

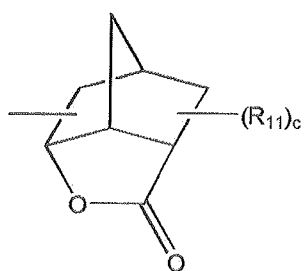
5 l, m, n and o are integers satisfying the relationships such as that $l+m+n+o=1$, $0.01 < l/(l+m+n+o) < 0.4$, $0 < m/(l+m+n+o) < 0.6$, $0 \leq n/(l+m+n+o) < 0.6$, and $0 < o/(l+m+n+o) < 0.4$.

10 In regard to the monomers represented by the formulas 1 to 3, any one selected from the group consisting of R_1 to R_3 and combinations thereof, may be any one selected from the group consisting of an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group. Any one group selected from the group consisting of the alkyl group, cycloalkyl group, heterocycloalkyl group, aryl

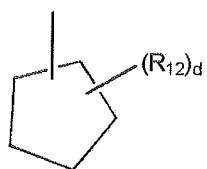
15 group and heteroaryl group mentioned above, may include any one selected from the group consisting of an ether group, an ester group, a carbonyl group, an acetal group, an amine group and combinations thereof, in the middle of the carbon chain.

20 Specifically, the one selected from the group consisting of R_1 to R_3 and combinations thereof, may be represented by any one formula selected from the group consisting of the following formulas 5 to 11, but the present invention is not intended to be limited to these.

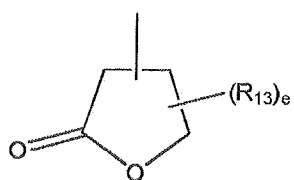
25 [Formula 5]



[Formula 6]

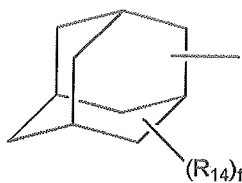


[Formula 7]

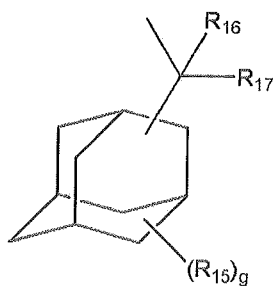


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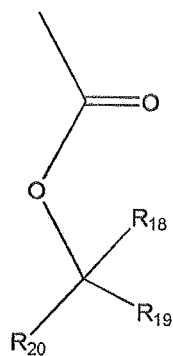
[Formula 8]



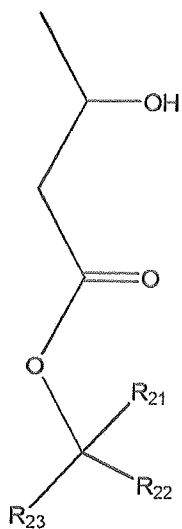
[Formula 9]



[Formula 10]



[Formula 11]



5

wherein in the formulas 5 to 11,

R_{11} to R_{23} each independently represent any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group,

an epoxy group, an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group;

c is an integer from 0 to 9;

5 d is an integer from 0 to 4;

e is an integer from 0 to 4;

f is an integer from 0 to 14; and

g is an integer from 0 to 14.

The aforementioned copolymer may have an acrylate
10 derivative of methylacrylic acid 3-t-butoxycarbonyloxyadamantan-1-yl ester (BOC-HAMA), and another acrylate monomer and a norbornene derivative as repeating units.

The copolymer is generally insoluble or sparingly
15 soluble per se in alkaline aqueous solutions, but in some occasions, the copolymer may be soluble. The copolymer generally has an acid-labile functional group in the side chain moiety, but in some occasions, the copolymer may not have a functional group.

20 The solubility of the copolymer may be increased or decreased, depending on the type of the monomer included in the copolymer and the content variation of the monomer. In general, as the proportion of hydrophobic groups increases, the solubility in alkaline aqueous solutions decreases. As
25 such, when a copolymer obtained by adjusting the type and content of monomers is used, a photoresist composition excellent in the adhesiveness to substrates, substrate-

independency, sensitivity and resolution can be obtained.

In the copolymer of the present invention, the norbornene functional group in the norbornene derivative represented by the formula 1 has a characteristic of inducing the copolymer to acquire a modified spiral structure, thereby largely improving the disadvantage of poor solubility in solvents, which is exhibited by existing methacrylic copolymers. Furthermore, at the time of copolymerization of acrylics only, it is difficult to control the molecular weight, and it is not easy to produce low molecular weight compounds. However, when a norbornene derivative represented by the formula 1 is introduced into the reaction, the derivative helps in controlling the degree of polymerization of the acrylics and in producing low molecular weight copolymers. Thus, the norbornene derivatives represented by the formula 1 is characterized by playing a role as a molecular weight controlling agent, and by enhancing etching resistance.

The acrylic derivative represented by the formula 2 or 3 can have an acid-labile functional group introduced thereto, and can also have a functional group related to an improvement of adhesive power, introduced thereto to reinforce the adhesive power. In order to reinforce such adhesive power, an acrylic monomer containing lactone can be mainly used. Furthermore, while a functional group formed from an acid-labile functional group and lactone, which is intended for the reinforcement of adhesiveness to substrates,

can be used, a bulky hydrocarbon compound that increases resistance to etching can also be introduced at the same time.

On the other hand, the repeating unit represented by
5 the formula 4 is advantageous in that, when t-BOC is introduced into hydroxyadamantane (meth)acrylate, the residual film ratio required in the ArF liquid immersion exposure method can be reinforced; at the time of light irradiation, when the acid-labile group, t-BOC, is
10 decomposed, the fluidity of acid can be enhanced to thus improve the resolution; and pattern profiles having good perpendicularity can be obtained by a contrast enhancing effect.

The copolymer of the present invention may be a block
15 copolymer a random copolymer or a graft copolymer.

The copolymer of the present invention can be polymerized by any conventional method, but radical polymerization is preferable. In the case of performing radical polymerization, the radical polymerization initiator
20 is not particularly limited as long as it is a commonly used radical polymerization initiator, such as azobisisobutyronitrile (AIBN), benzoyl peroxide (BPO), lauryl peroxide, azobisisocapronitrile, azobisisovaleronitrile, or t-butyl hydroperoxide.

25 The polymerization may be carried out by methods such as bulk polymerization, solution polymerization, suspension polymerization, bulk suspension polymerization and emulsion

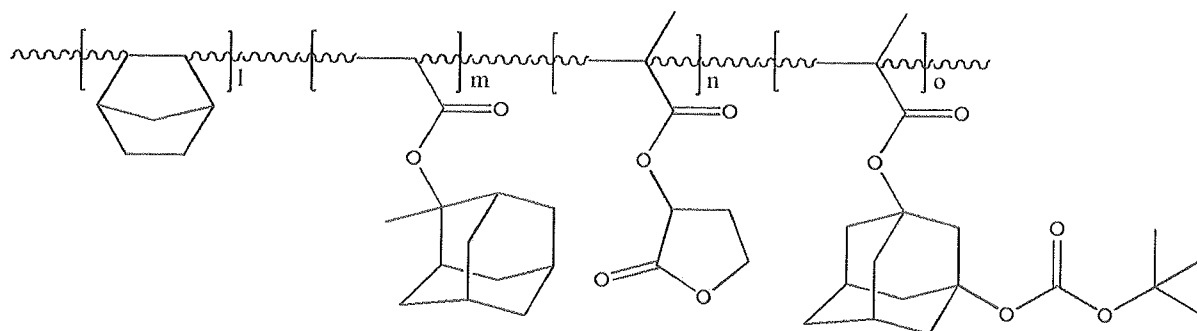
polymerization, and as for the polymerization solvent, one or more may be selected for use, from benzene, toluene, xylene, halogenated benzene, diethyl ether, tetrahydrofuran, esters, ethers, lactones, ketones, amides and alcohols.

5 The temperature for the polymerization of the copolymer can be appropriately selected and used depending on the type of catalyst. The molecular weight distribution of the copolymer can be appropriately adjusted by changing the amount of polymerization initiator used and the reaction
10 time. After completion of the polymerization, any unreacted monomers and side products remaining in the reaction mixture are preferably removed by a precipitation method using a solvent.

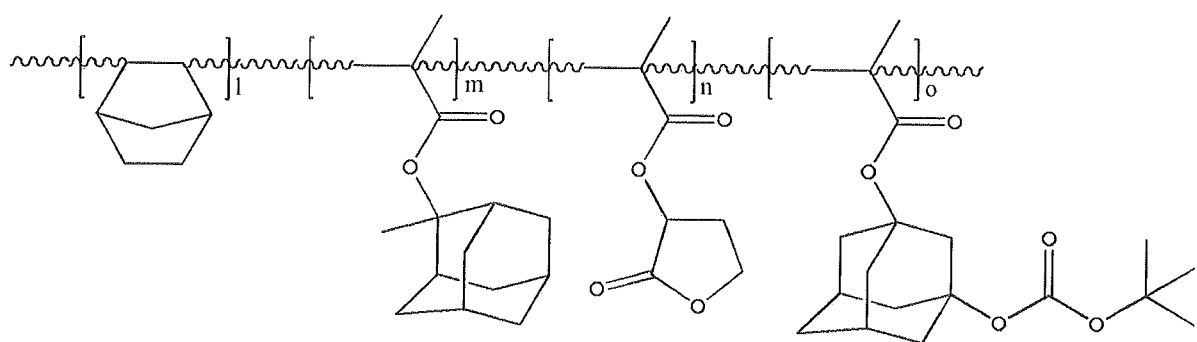
 The weight average molecular weight (hereinafter,
15 referred to as "Mw") of the copolymer of the present invention as measured by gel permeation chromatography (GPC) and calculate relative to polystyrene standards, is usually 2,000 to 1,000,000, and is preferably 3,000 to 50,000, from the viewpoints of sensitivity as photoresist, developability,
20 coatability, thermal resistance and the like. The molecular weight distribution of the copolymer is preferably 1.0 to 5.0, and particularly preferably 1.0 to 3.0.

 Specifically, a copolymer including the monomers represented by the formulas 1 to 4, can be represented by
25 any one formula selected from the group consisting of the following formulas 12 to 21, but the present invention is not intended to be limited to these.

[Formula 12]

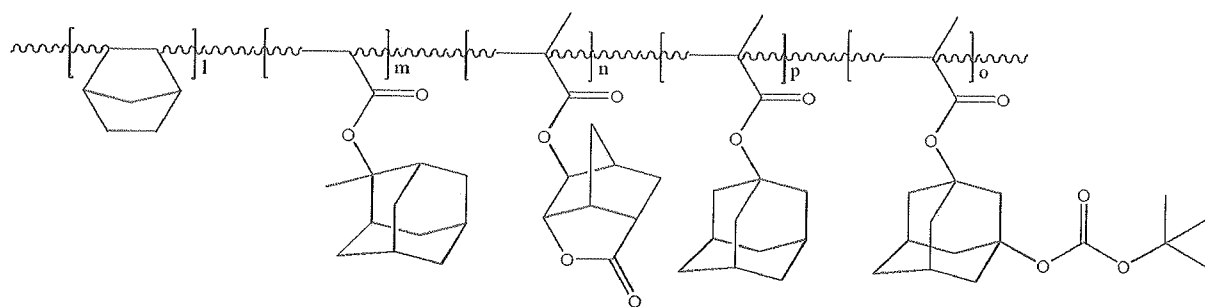


[Formula 13]

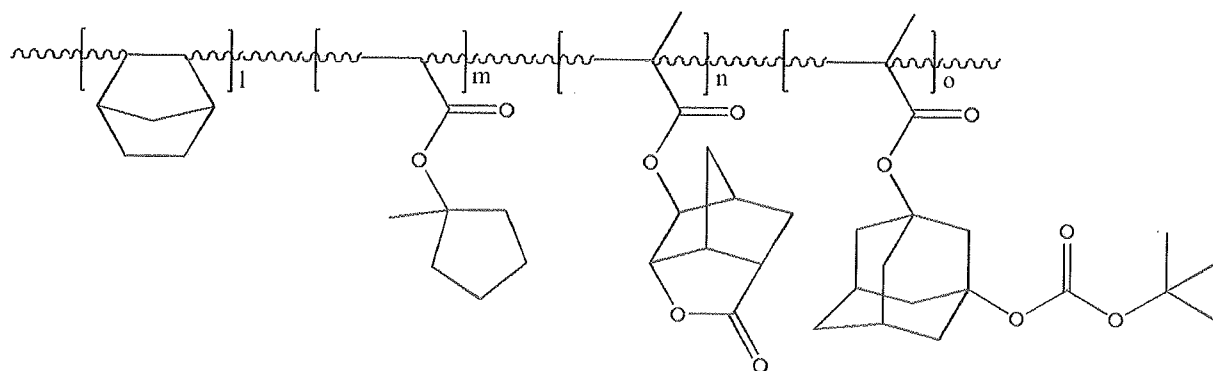


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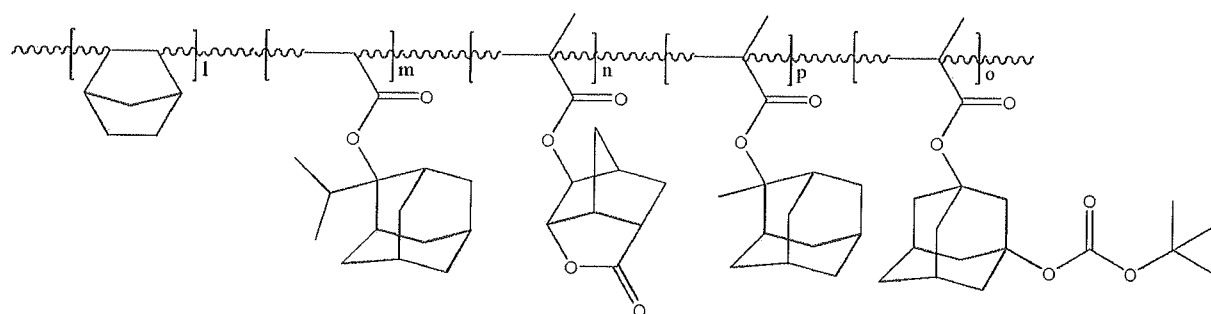
[Formula 14]



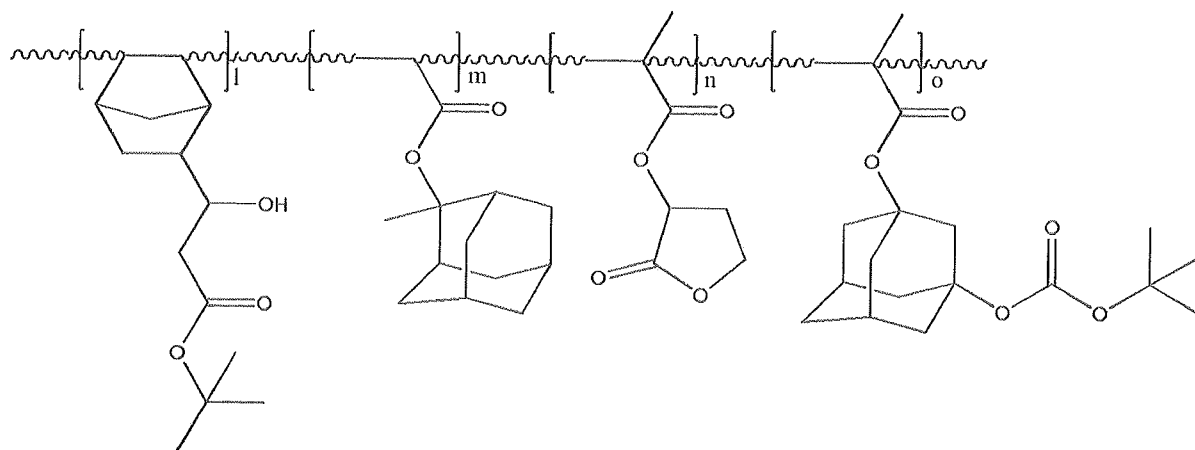
[Formula 15]



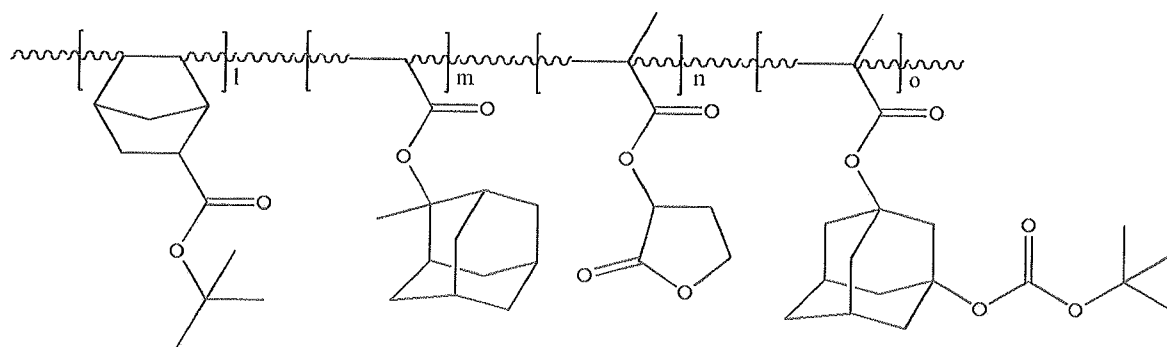
[Formula 16]



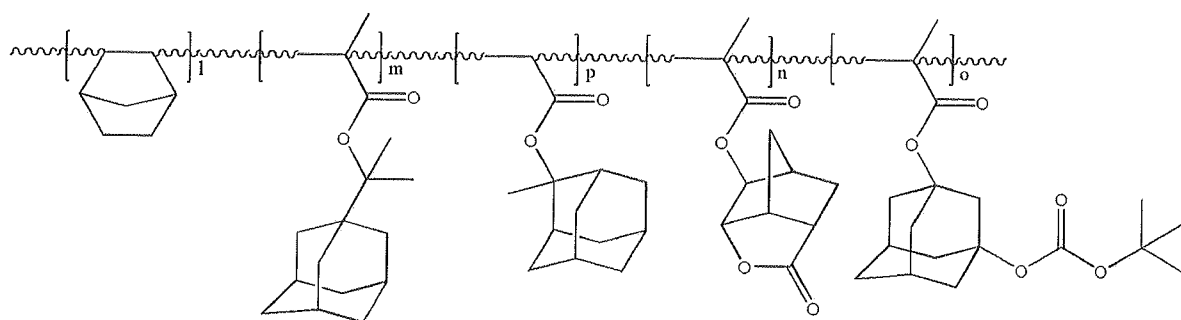
[Formula 17]



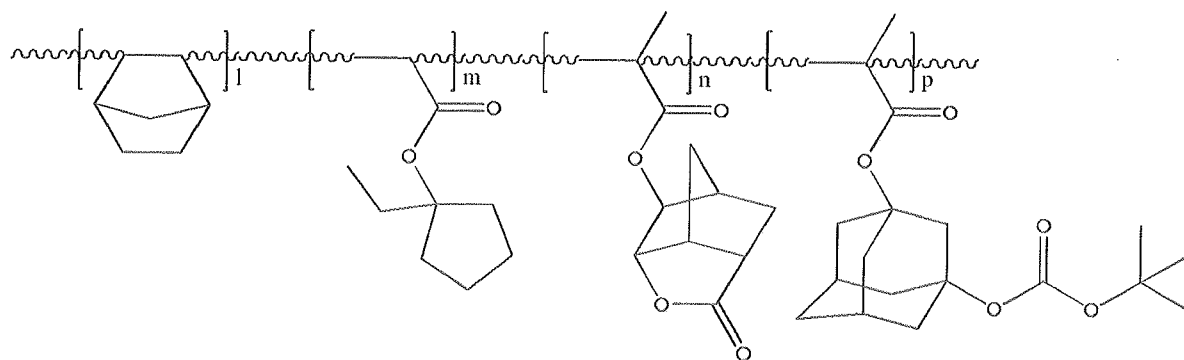
[Formula 18]



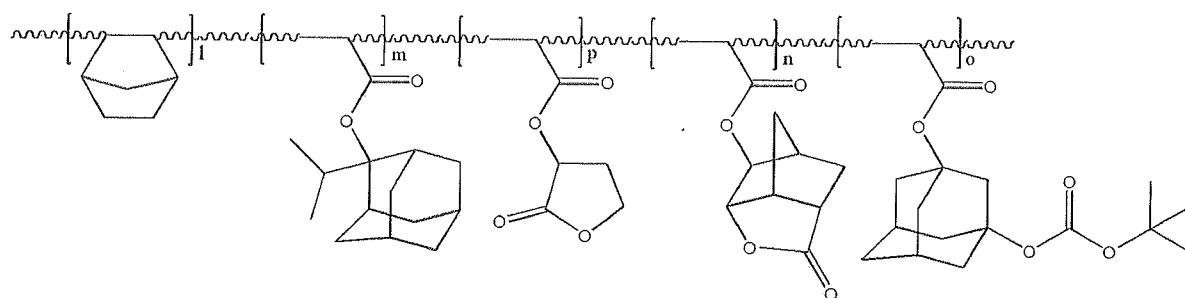
[Formula 19]



[Formula 20]



[Formula 21]



wherein in the formulas 12, 13, 15, 17, 18 and 20,

l, m, n and o are integers satisfying the relationships such as that $l+m+n+o=1$, $0.01 < l/(l+m+n+o) < 0.4$,

$0 < m/(l+m+n+o) < 0.6$, $0 \leq n/(l+m+n+o) < 0.6$, and $0 < o/(l+m+n+o) < 0.4$;

5 and in the formulas 14, 16, 19 and 21,

l, m, n, o and p are integers satisfying the relationships such as that $l+m+n+o+p=1$,

$0.01 < l/(l+m+n+o+p) < 0.4$, $0 < m/(l+m+n+o+p) < 0.6$,

$0 \leq n/(l+m+n+o+p) < 0.6$, $0 < o/(l+m+n+o+p) < 0.4$, and

10 $0 \leq p/(l+m+n+o+p) < 0.6$.

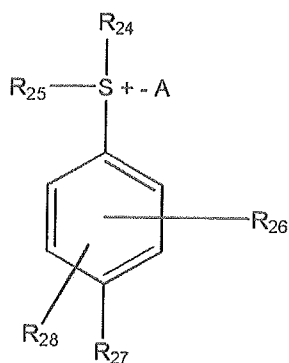
Photoresist composition

The photoresist composition according to another aspect of the present invention contains the copolymer of the present invention, an acid generator, additives, and a
15 solvent. The photoresist composition may be a positive type chemically amplified photoresist composition.

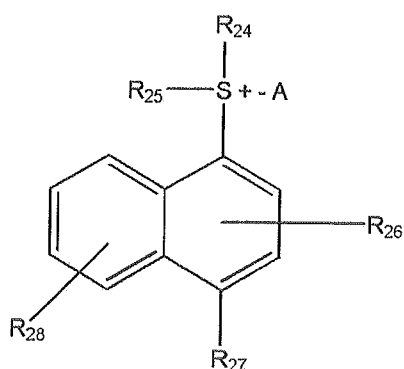
The acid generator that can be used may be an onium salt such as an iodonium salt, a sulfonium salt, a phosphonium salt, a diazonium salt or a pyridinium salt, or
20 an imide, and preferably, a compound represented by any one formula selected from the group consisting of the following formula 22, formula 23 and combinations thereof, can be used.

More preferably, by introducing a cyclic alkyl group to the anion, the acid diffusion length in the resist film can
25 be maintained appropriately short, and higher permeability property can be obtained, so that high resolution of the resist can be obtained.

[Formula 22]



[Formula 23]



5 wherein in the formulas 22 and 23,

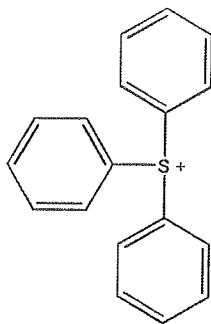
R₂₄ and R₂₅ each independently represent a substituent selected from the group consisting of an alkyl group, an allyl group, a perfluoroalkyl group, a benzyl group, and an aryl group;

10 R₂₆ to R₂₈ each independently represent a substituent selected from the group consisting of a hydrogen atom, an alkyl group, a halogen group, an alkoxy group, an aryl group, a thiophenoxy group, a thioalkoxy group, and an alkoxycarbonylmethoxy group; and

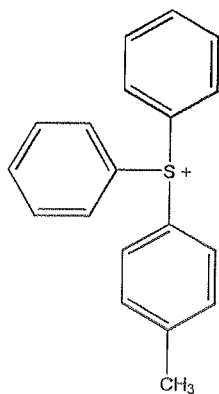
15 -A is an anion.

Preferable examples of the cation of the acid generator include compounds represented by the following general formulas 2a to 2p, but the present invention is not intended to be limited to these.

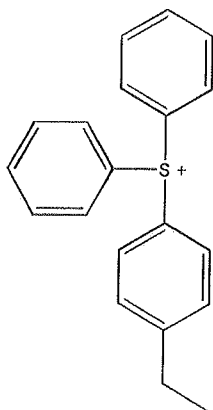
5 [General Formula 2a]



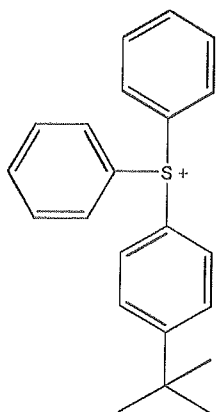
[General Formula 2b]



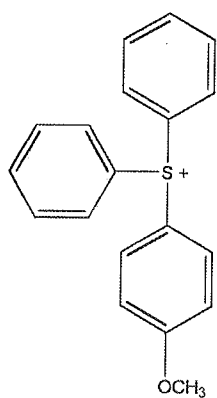
[General Formula 2c]



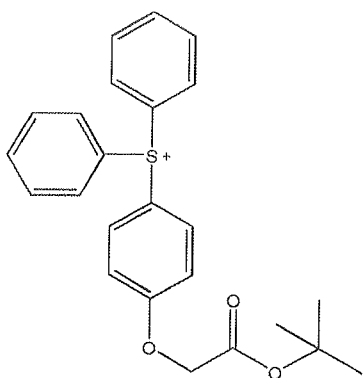
[General Formula 2d]



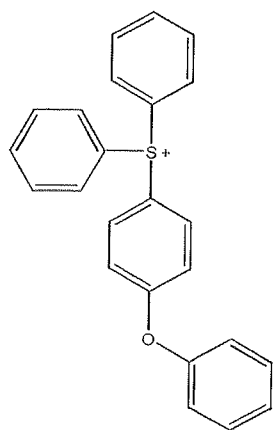
[General Formula 2e]



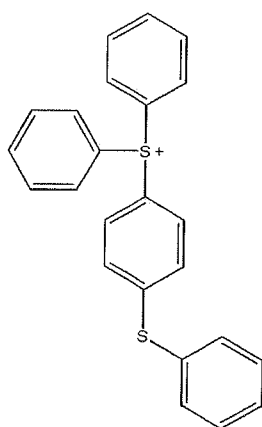
5 [General Formula 2f]



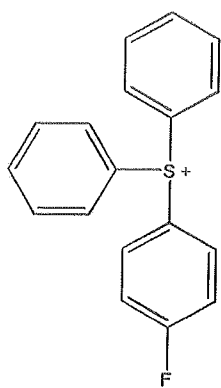
[General Formula 2g]



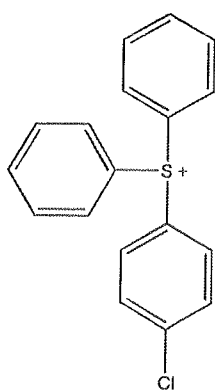
[General Formula 2h]



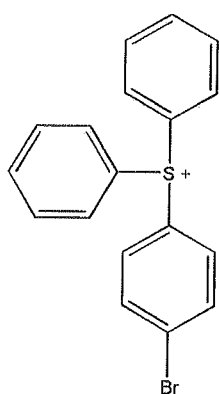
[General Formula 2i]



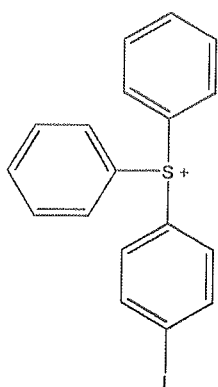
[General Formula 2j]



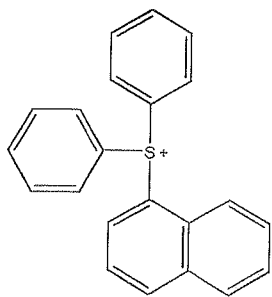
[General Formula 2k]



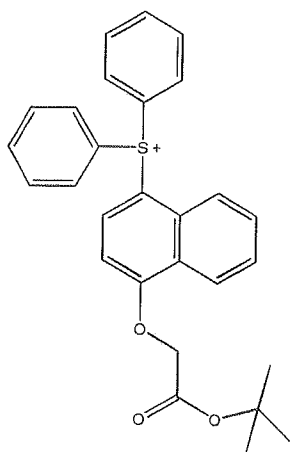
[General Formula 2l]



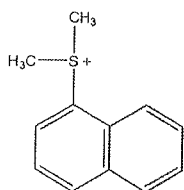
[General Formula 2m]



[General Formula 2n]

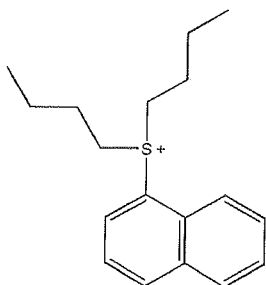


[General Formula 2o]



5

[General Formula 2p]

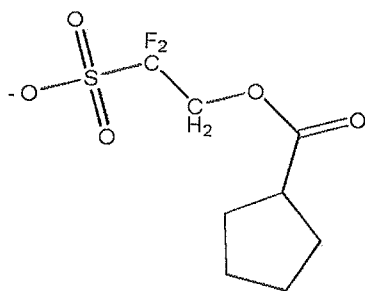


The anion -A may be any one selected from the group consisting of $-\text{OSO}_2\text{CF}_3$, $-\text{OSO}_2\text{C}_4\text{F}_9$, $-\text{OSO}_2\text{C}_8\text{F}_{17}$, $-\text{N}(\text{CF}_3)_2$, -

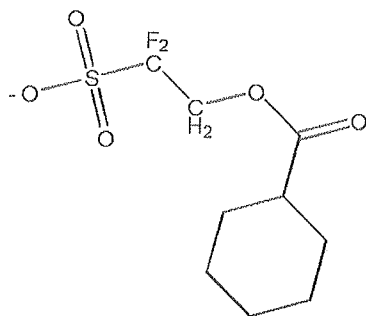
m is an integer from 0 to 2.

The anion -A selected from the group consisting of a compound represented by the formula 24 and a compound represented by the formula 25, may be preferably an anion
5 represented by any one formula selected from the group consisting of the following formulas 26 to 52, but the present invention is not intended to be limited to these.

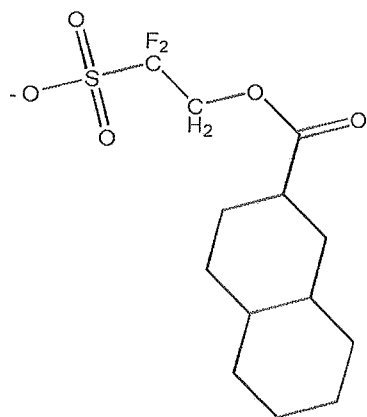
[Formula 26]



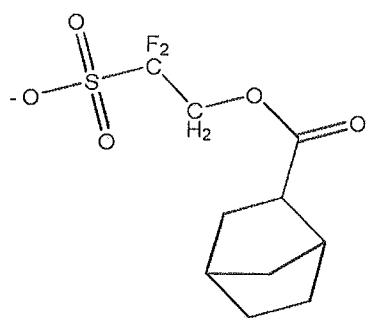
10 [Formula 27]



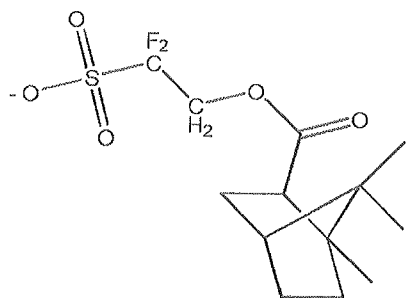
[Formula 28]



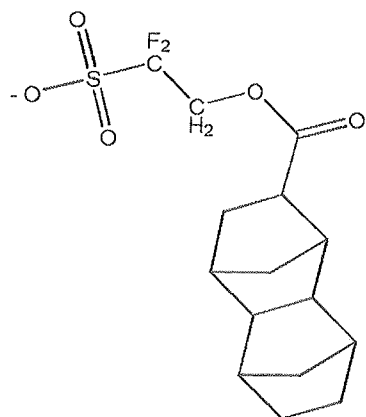
[Formula 29]



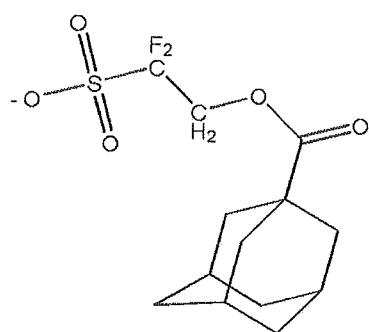
[Formula 30]



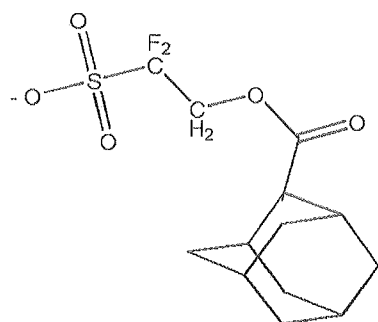
[Formula 31]



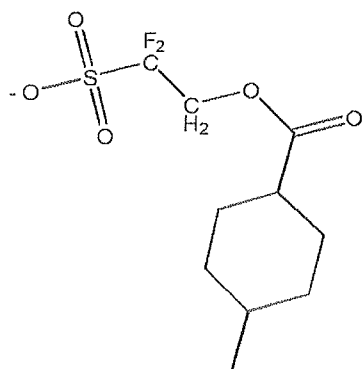
[Formula 32]



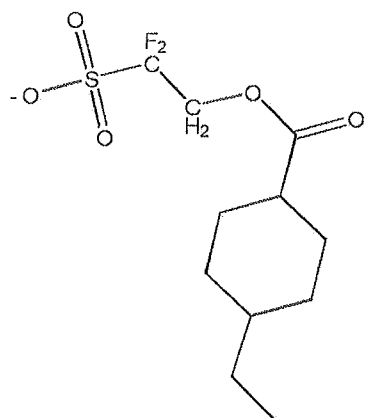
[Formula 33]



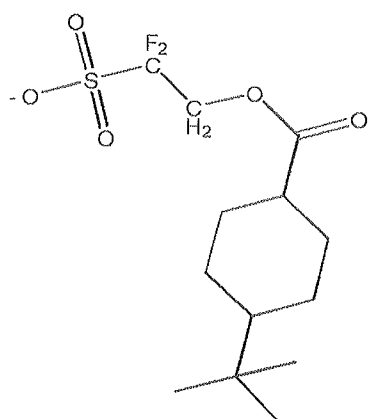
[Formula 34]



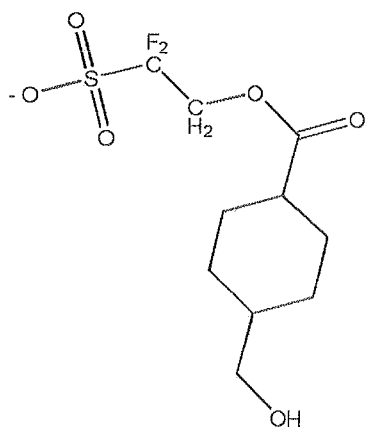
[Formula 35]



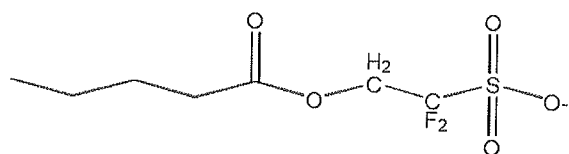
[Formula 36]



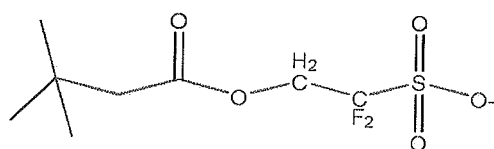
[Formula 37]



[Formula 38]

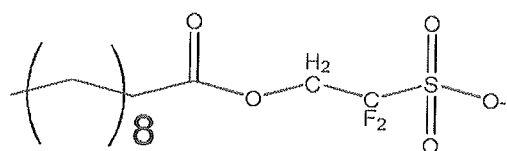


[Formula 39]

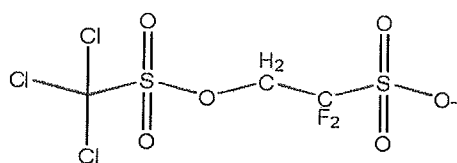


5

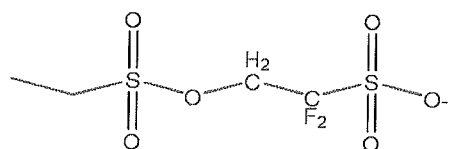
[Formula 40]



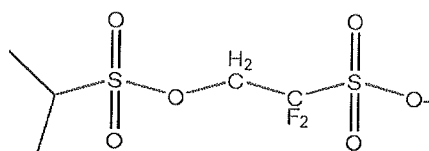
[Formula 41]



[Formula 42]

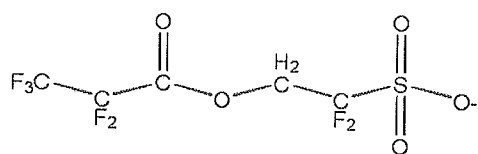


[Formula 43]

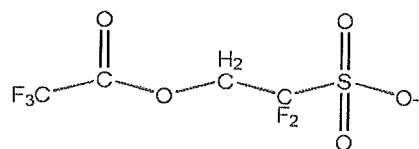


5

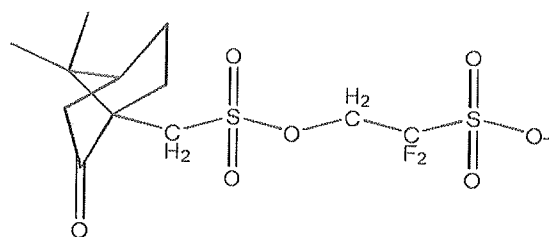
[Formula 44]



[Formula 45]

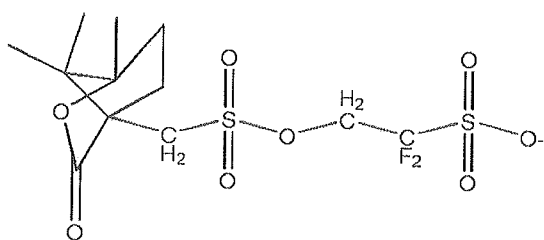


[Formula 46]

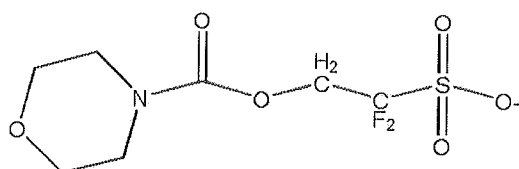


10

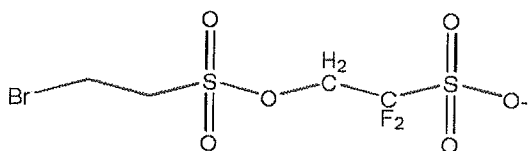
[Formula 47]



[Formula 48]

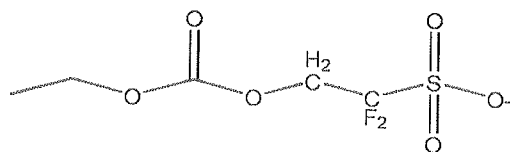


[Formula 49]

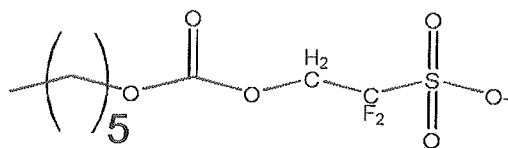


5

[Formula 50]

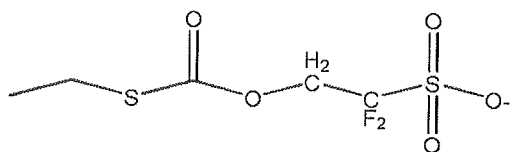


[Formula 51]



10

[Formula 52]



The photoresist composition of the present invention

may contain the acid generator in an amount of 0.5 to 15 parts by weight, and preferably 2 parts by weight to 10 parts by weight, relative to 100 parts by weight of the total solids content of the photoresist composition. If the
5 content of the acid generator exceeds 15 parts by weight, the perpendicularity of the pattern may be significantly lowered, and if the content is less than 0.5 parts by weight, the flexibility of the pattern may become poor. The acid generators mentioned above can be used individually or in
10 mixture of two or more species.

In order to obtain a uniform and flat coating film, the photoresist composition is dissolved in a solvent having an adequate rate of evaporation and viscosity, before use.

Examples of the solvent having such properties include
15 ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monopropyl ether, methylcellosolve acetate, ethylcellosolve acetate, propylene glycol monomethyl ether acetate, propylene glycol monoethyl ether acetate, propylene glycol monopropyl ether acetate, methyl
20 isopropyl ketone, cyclohexanone, methyl 2-hydroxypropionate, ethyl 2-hydroxypropionate, 2-heptanone, ethyl lactate, γ -butyrolactone, and the like. According to circumstances, these solvents may be used individually, or as mixed solvents of two or more species.

25 The amount of use of the solvent is adjusted to appropriate amounts in accordance with the properties of the solvent, namely, volatility, viscosity and the like, so that

the photoresist composition can be uniformly formed on a wafer.

The photoresist composition is prepared in the form of a solution, and is applied and dried on a wafer substrate to
5 form a resist film. In this case, a resist solution can be prepared and filtered, and then this solution can be applied onto the substrate by a method such as spin coating, cast coating, or roll coating.

The resist film applied by such a method as described
10 above is partially irradiated with radiation, to form a fine pattern thereon. The radiation used for this purpose is not particularly limited, but examples thereof include I-rays which belong to ultraviolet radiation; KrF excimer laser, ArF excimer laser, F₂ excimer laser and X-rays which belong
15 to far-ultraviolet radiation; electron beams which belong to charged particle radiation; and the like. These can be used selectively according to the type of the acid generator.

The developer solution that is used for developing the resist film can be selected from aqueous solutions
20 containing sodium hydroxide, potassium hydroxide, sodium carbonate, sodium silicate, sodium metasilicate, ammonia water, ethylamine, n-propylamine, triethylamine, tetramethylammonium hydroxide, tetraethylammonium hydroxide
~~and the like.~~ In particular, tetramethylammonium hydroxide
25 among them can be preferably used.

The photoresist composition may further include additives such as a surfactant and a water-soluble alcohol,

according to necessity.

The copolymer of the present invention is rapidly dissolved in a common solvent, and is easily soluble in most of solvents. The copolymer can be produced into a resin
5 having a desired molecular weight by adjusting the amount of olefin introduced therein, and thus can be produced without using a molecular weight controlling agent.

The photoresist composition of the present invention is a chemically amplified type photoresist composition that is
10 sensitized by KrF excimer laser, ArF excimer laser, EUV, X-rays, electron beam or the like, which is less dependent on substrates, has excellent transparency in the far-ultraviolet wavelength region, and has excellent contrast, sensitivity, resolution and developability.

15 The photoresist composition can improve a decrease in the residual film ratio that occurs when a top coat substance is used in the liquid immersion exposure method, and can also enhance the resolution power by facilitating the fluidity and diffusion of acid at the time of
20 irradiation with ArF laser radiation. The photoresist composition also enhances the development properties manifested by developer solutions, and the adhesive power to substrates.

25 EXAMPLES

Hereinafter, the present invention will be specifically described with reference to Synthesis Examples and Examples,

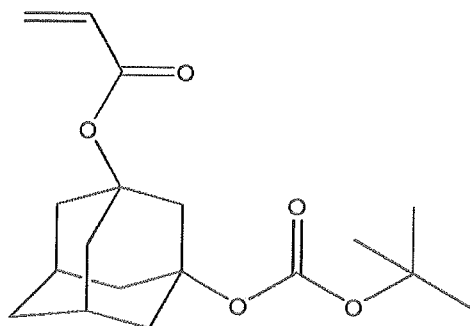
so that those having ordinary skill in the art to which the present invention pertains can easily carry out the invention. However, the present invention is not intended to be limited to the Synthesis Examples and Examples described herein.

Synthesis of monomers and copolymers

(Monomer Synthesis Example 1)

In a two-necked round-bottom flask equipped with a stirrer and a reflux cooling tube, 200 g of 3-hydroxyadamantane acrylate, 107 g of pyridine, 33 g of dimethylaminopyridine, and 0.6 g of Irganox 1010® were dissolved in 800 ml of ethyl acetate, and then a solution prepared by dissolving 295 g of di-t-butyl dicarbonate in 500 ml of ethyl acetate was slowly added dropwise to the flask at normal temperature under a nitrogen gas stream. After completion of the dropwise addition, the solution was refluxed for 4 hours at 70°C, and then was cooled to normal temperature. The solution was subjected to an acid treatment and an alkali treatment, and then was washed with distilled water. Subsequently, the organic layer was isolated, and the solvent was removed. The residue was recrystallized from hexane, to obtain 239 g of an acrylic acid 3-tert-butoxycarbonyloxy-adamantan-1-yl ester (BOC-HAA) monomer represented by the following general formula 3a.

[General Formula 3a]



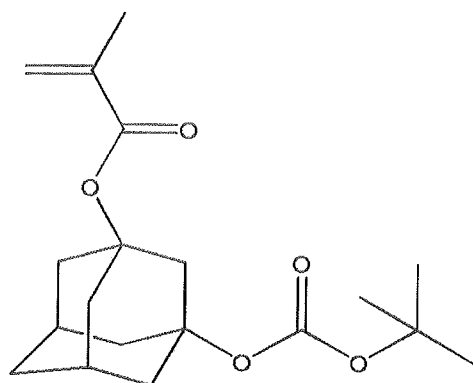
(Monomer Synthesis Example 2)

In a two-necked round-bottom flask equipped with a stirrer and a reflux cooling tube, 200 g of 3-hydroxyadamantane methacrylate, 100 g of pyridine, 31 g of dimethylaminopyridine, and 0.57 g of Irganox 1010® were dissolved in 800 ml of ethyl acetate, and then a solution prepared by dissolving 277 g of di-*t*-butyl dicarbonate in 500 ml of ethyl acetate was slowly added dropwise to the flask at normal temperature under a nitrogen gas stream. After completion of the dropwise addition, the solution was refluxed for 4 hours at 70°C, and then was cooled to normal temperature. The solution was subjected to an acid treatment and an alkali treatment, and then was washed with distilled water. Subsequently, the organic layer was isolated, and the solvent was removed. The residue was recrystallized from hexane, to obtain 212 g of a 2-methylacrylic acid 3-*tert*-butoxycarbonyloxy-adamantan-1-yl ester (BOC-HAMA) monomer represented by the following general formula 3b.

The nuclear magnetic resonance (NMR) data of the monomer synthesized as described above are presented in Fig.

1.

[Formula 3b]



(Copolymer Synthesis Example 1)

- 5 6.4 g of norbornene as a monomer for polymerization,
and 7.6 g of BOC-HAMA were added, together with 115 g of
1,4-dioxane, to a flask and were dissolved therein. The
inside of the flask was purged with nitrogen gas, and then
the internal temperature of the flask was raised to 70°C.
- 10 When the temperature reached 70°C, 20 g of methyladamantane
acrylate and 12 g of γ -butyrolactyl methacrylate were
dissolved in 25 g of 1,4-dioxane, together with 3 g of
dimethyl azobisisobutyrate as a polymerization initiator,
and the solution was slowly added dropwise to the flask
- 15 using a syringe pump over 2 hours. The mixture was allowed
to react for another 5 hours at this temperature, and then
the solution obtained after completion of polymerization was
cooled to normal temperature. The reaction solution cooled
to normal temperature was subjected to precipitation using
- 20 an excess amount of n-hexane, and the precipitate was
filtered. The precipitate was washed with the same solvent

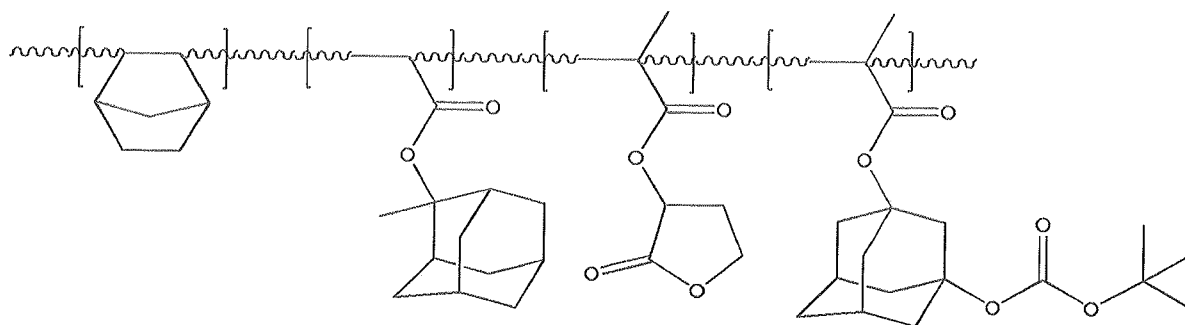
during filtration, and then was dried under reduced pressure, to yield 30 g of a copolymer represented by formula 53.

The nuclear magnetic resonance (NMR) data of the copolymer synthesized as described above are presented in Fig. 2, and the results of gel permeation chromatography measurement carried out under the conditions indicated in the following Table 1 are presented in Fig. 3. The weight average molecular weight (M_w) of this copolymer converted relative to polystyrene standards was 6180, and the ratio of the weight average molecular weight to the number average molecular weight, M_w/M_n , was 1.94.

[Table 1]

System	DM400 + External RI
Columns	G4000Hhr + G2500Hhr
Solvent	THF
Flow rate	1.000 mL/min
Concentration	0.000 mg/mL
Injection Volume	100.0 μ L

[Formula 53]



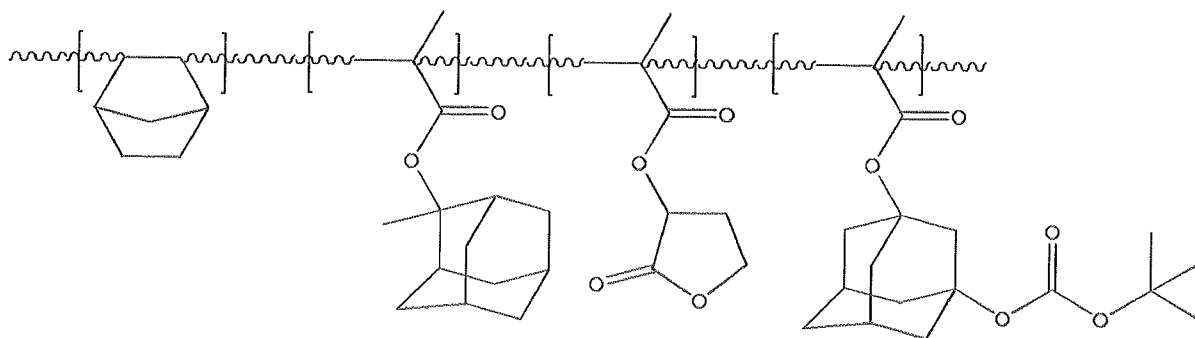
15 (Copolymer Synthesis Example 2)

7.5 g of norbornene as a monomer for polymerization, and 9 g of BOC-HAMA were added, together with 140 g of 1,4-dioxane, to a flask and were dissolved therein. The inside

of the flask was purged with nitrogen gas, and then the internal temperature of the flask was raised to 70°C. When the temperature reached 70°C, 25 g of methyladamantane methacrylate and 14 g of γ -butyrolactyl methacrylate were dissolved in 30 g of 1,4-dioxane, together with 3.5 g of dimethyl azobisisobutyrate as a polymerization initiator, and the solution was slowly added dropwise to the flask using a syringe pump over 2 hours. The mixture was allowed to react for another 5 hours at this temperature, and then the solution obtained after completion of polymerization was cooled to normal temperature. The reaction solution cooled to normal temperature was subjected to precipitation using an excess amount of n-hexane, and the precipitate was filtered. The precipitate was washed with the same solvent during filtration, and then was dried under reduced pressure, to yield 35 g of a copolymer represented by formula 54.

The nuclear magnetic resonance (NMR) data of the copolymer synthesized as described above are presented in Fig. 4, and the results of gel permeation chromatography measurement carried out under the conditions indicated in the Table 1 above are presented in Fig. 5. The weight average molecular weight (M_w) of this copolymer converted relative to polystyrene standards was 6460, and the ratio of the weight average molecular weight to the number average molecular weight, M_w/M_n , was 1.96.

[Formula 54]

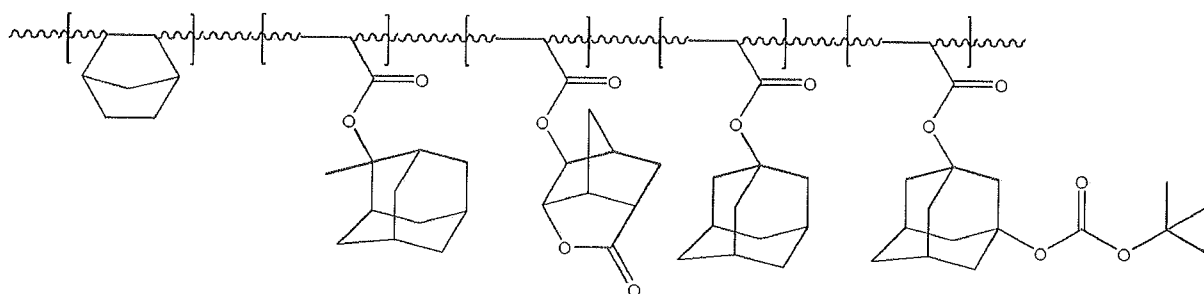


(Copolymer Synthesis Example 3)

6.4 g of norbornene as a monomer for polymerization, and 11 g of BOC-HAMA were added, together with 85 g of 1,4-dioxane, to a flask and were dissolved therein. The inside of the flask was purged with nitrogen gas, and then the internal temperature of the flask was raised to 70°C. When the temperature reached 70°C, 20 g of methyladamantane acrylate, 15 g of norbornane carbolactone methacrylate, and 5 g of adamantane methacrylate were dissolved in 25 g of 1,4-dioxane, together with 7 g of dimethyl azobisisobutyrate as a polymerization initiator, and the solution was slowly added dropwise to the flask using a syringe pump over 2 hours. The mixture was allowed to react for another 5 hours at this temperature, and then the solution obtained after completion of polymerization was cooled to normal temperature. The reaction solution cooled to normal temperature was subjected to precipitation using an excess amount of n-hexane, and the precipitate was filtered. The precipitate was washed with the same solvent during filtration, and then was dried under reduced pressure, to yield 38 g of a copolymer represented by formula 55.

The nuclear magnetic resonance (NMR) data of the copolymer synthesized as described above are presented in Fig. 6, and the results of gel permeation chromatography measurement carried out under the conditions indicated in the Table 1 above are presented in Fig. 7. The weight average molecular weight (M_w) of this copolymer converted relative to polystyrene standards was 5880, and the ratio of the weight average molecular weight to the number average molecular weight, M_w/M_n , was 1.95.

[Formula 55]

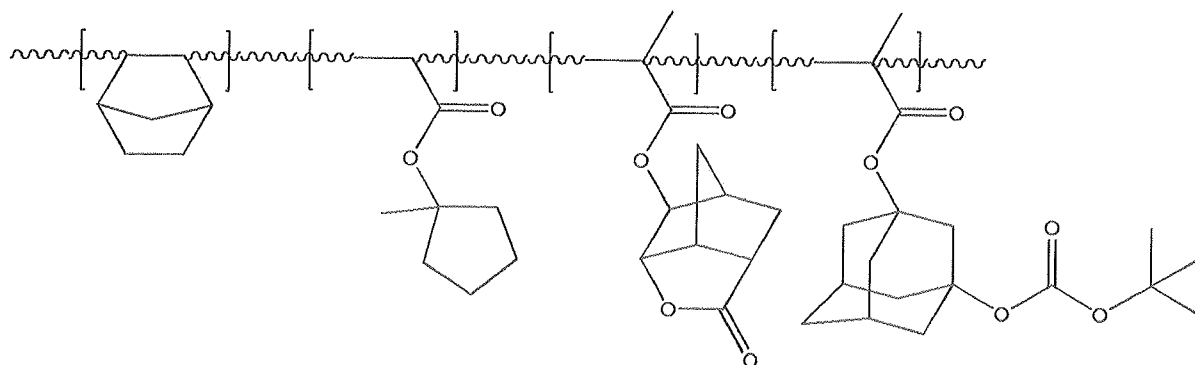


(Copolymer Synthesis Example 4)

8 g of norbornene as a monomer for polymerization, and 9.5 g of BOC-HAMA were added, together with 180 g of 1,4-dioxane, to a flask and were dissolved therein. The inside of the flask was purged with nitrogen gas, and then the internal temperature of the flask was raised to 70°C. When the temperature reached 70°C, 25 g of 2-methylcyclopentyl acrylate, and 17 g of norbornane carbolactone methacrylate were dissolved in 30 g of 1,4-dioxane, together with 4 g of dimethyl azobisisobutyrate as a polymerization initiator, and the solution was slowly added dropwise to the flask

using a syringe pump over 2 hours. The mixture was allowed to react for another 5 hours at this temperature, and then the solution obtained after completion of polymerization was cooled to normal temperature. The reaction solution cooled to normal temperature was subjected to precipitation using an excess amount of n-hexane, and the precipitate was filtered. The precipitate was washed with the same solvent during filtration, and then was dried under reduced pressure, to yield 40 g of a copolymer represented by formula 56. The weight average molecular weight (M_w) of this copolymer converted relative to polystyrene standards was 4550, and the ratio of the weight average molecular weight to the number average molecular weight, M_w/M_n , was 1.98.

[Formula 56]



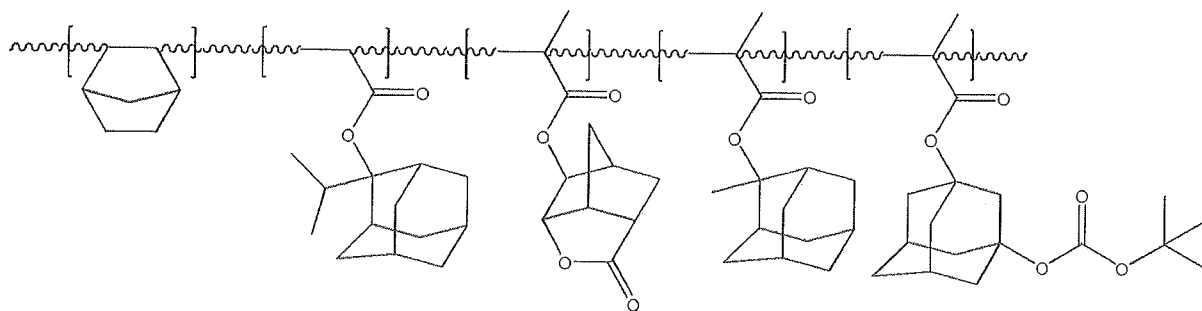
(Copolymer Synthesis Example 5)

7 g of norbornene as a monomer for polymerization, and 4 g of BOC-HAMA were added, together with 120 g of 1,4-dioxane, to a flask and were dissolved therein. The inside of the flask was purged with nitrogen gas, and then the internal temperature of the flask was raised to 70°C. When the temperature reached 70°C, 15 g of isopropyladamantane

acrylate, 21 g of norbornane carbolactone methacrylate, and 14 g of methyladamantane methacrylate were dissolved in 60 g of 1,4-dioxane, together with 3.5 g of dimethyl azobisisobutyrate as a polymerization initiator, and the
5 solution was slowly added dropwise to the flask using a syringe pump over 2 hours. The mixture was allowed to react for another 5 hours at this temperature, and then the solution obtained after completion of polymerization was cooled to normal temperature. The reaction solution cooled
10 to normal temperature was subjected to precipitation using an excess amount of n-hexane, and the precipitate was filtered. The precipitate was washed with the same solvent during filtration, and then was dried under reduced pressure, to yield 42 g of a copolymer represented by formula 57.

15 The nuclear magnetic resonance (NMR) data of the copolymer synthesized as described above are presented in Fig. 8, and the results of gel permeation chromatography measurement carried out under the conditions indicated in the Table 1 above are presented in Fig. 9. The weight
20 average molecular weight (M_w) of this copolymer converted relative to polystyrene standards was 6810, and the ratio of the weight average molecular weight to the number average molecular weight, M_w/M_n , was 2.37.

[Formula 57]

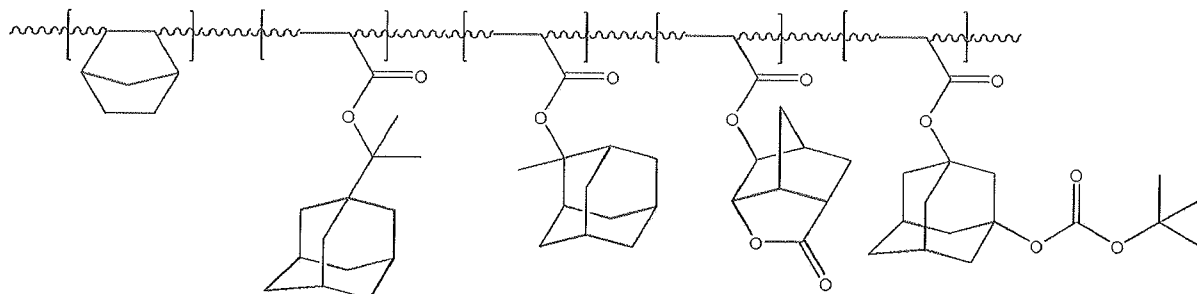


(Copolymer Synthesis Example 6)

7 g of norbornene as a monomer for polymerization, and
 4 g of BOC-HAMA were added, together with 120 g of 1,4-
 5 dioxane, to a flask and were dissolved therein. The inside
 of the flask was purged with nitrogen gas, and then the
 internal temperature of the flask was raised to 70°C. When
 the temperature reached 70°C, 16 g of isopropyladamantane
 acrylate, 21 g of norbornane carbolactone methacrylate, and
 10 13 g of methyladamantane acrylate were dissolved in 60 g of
 1,4-dioxane, together with 3.5 g of dimethyl
 azobisisobutyrate as a polymerization initiator, and the
 solution was slowly added dropwise to the flask using a
 syringe pump over 2 hours. The mixture was allowed to react
 15 for another 5 hours at this temperature, and then the
 solution obtained after completion of polymerization was
 cooled to normal temperature. The reaction solution cooled
 to normal temperature was subjected to precipitation using
 an excess amount of n-hexane, and the precipitate was
 20 filtered. The precipitate was washed with the same solvent
 during filtration, and then was dried under reduced pressure,
 to yield 40 g of a copolymer represented by formula 58. The
 weight average molecular weight (Mw) of this copolymer

converted relative to polystyrene standards was 6470, and the ratio of the weight average molecular weight to the number average molecular weight, M_w/M_n , was 2.19.

[Formula 58]



5

Preparation and evaluation of photoresist composition

(Example 1)

4 parts by weight of triphenylsulfonium nonaflate as an acid generator, and 0.2 parts by weight of tetramethylammonium hydroxide as a basic additive per 100 parts by weight of the copolymer obtained in Copolymer Synthesis Example 1 (formula 53) were dissolved in 1,000 parts by weight of propylene glycol methyl ether acetate, and then the solution was filtered through a 0.2- μm membrane filter, to prepare a photoresist composition.

The obtained photoresist composition was applied to a substrate using a spinner, and was dried at 110°C for 90 seconds to form a film having a thickness of 0.2 μm . The formed film was exposed using an ArF excimer laser stepper (numerical aperture of the lens: 0.78), and then was heat treated at 110°C for 90 seconds. Subsequently, the film was developed with a 2.38 wt% aqueous solution of

tetramethylammonium hydroxide for 40 seconds, and the film was washed and dried to form a resist pattern.

The development properties in connection with the aqueous solution of tetramethylammonium hydroxide, and the adhesiveness of the formed resist pattern to the substrate were satisfactory. The resolution was 0.09 μm , and the sensitivity was 15 mJ/cm^2 . The results are summarized in the following Table 1.

Here, the adhesiveness was determined from the results obtained by observing the state of pattern adhesion for a 0.09- μm line-and-space (L/S) pattern formed after development, and the sensitivity was determined from the optimum exposure level, which is defined as a dose of exposure that forms a 0.09- μm line-and-space (L/S) pattern formed after development, at a line-to-space ratio of 1:1. The minimum pattern dimension resolved at this sensitivity was defined as resolution.

(Examples 2 to 8)

Each of the copolymers obtained in the Copolymer Synthesis Examples 1, 4 and 5 (formulas 53, 56 and 57) was dissolved, together with an acid generator and a basic additive at each of the contents indicated in the following Table 2, in 1,000 parts by weight of propylene glycol methyl ether acetate. The solution was filtered through a 0.2- μm membrane filter, and thus a photoresist composition was prepared. Subsequently, a positive photoresist pattern was formed in the same manner as in Example 1, and then various

evaluations were performed. The evaluation results are presented in the Table 2.

[Table 2]

	Type of copolymer	Proportion of copolymer (parts by weight)	*PAG (parts by weight)	*Base (parts by weight)	Sensitivity (mJ/cm ²)	Resolution (μm)
Example 2	Formula 53	100	4	0.2	15	90
Example 3	Formula 56	100	4	0.2	15	80
Example 4	Formula 57	100	4	0.2	15	100
Example 5	Formula 53	100	5	0.2	13	90
Example 6	Formula 56	100	5	0.2	13	80
Example 7	Formula 57	100	5	0.2	12	80
Example 8	Formula 53	100	5	0.3	16	100
Example 9	Formula 56	100	5	0.3	16	90
Example 10	Formula 57	100	5	0.3	15	100

(*PAG: Triphenylsulfonium nonaflate,

5 *Base: Tetramethylammonium hydroxide)

(Comparative Examples 1 to 3)

A COMA® resin represented by the following formula 59 (product of Kumho Petrochemical Co., Ltd.) was dissolved, together with an acid generator and a basic additive at each of the contents indicated in the following Table 3, in 1,000 parts by weight of propylene glycol methyl ether acetate. The solution was filtered through a 0.2-μm membrane filter, and thus a photoresist composition was prepared. Each of

the composition solutions was used to form a positive photoresist pattern in the same manner as in Example 1, except that an ArF excimer laser exposure apparatus (numerical aperture of the lens 0.78) was used, and the copolymer used was the copolymer represented by formula 59. Then, various evaluations were performed. The evaluation results are presented in the following Table 3.

[Table 3]

	Type of copolymer	Proportion of copolymer (parts by weight)	PAG (parts by weight)	Base (parts by weight)	Sensitivity (mJ/cm ²)	Resolution (μm)
Comparative Example 1	Formula 59	100	2.5	0.02	15	120
Comparative Example 2	Formula 59	100	3.0	0.02	14	110
Comparative Example 3	Formula 59	100	3.0	0.03	16.5	120

By referring to the Table 1 and Table 2, it can be seen that in the case of the photoresist compositions of the Examples 2 to 10, the resolution was from 80 to 100 μm, that is, less than or equal to 100 μm, while in the case of the Comparative Examples 1 to 3, the resolution was from 110 to 120 μm.

Test for generation of t-BOC from BOC-HAMA under action of acid

The copolymer according to an embodiment of the present invention includes a monomer in which a BOC-substituent is

introduced into hydroxyadamantane methacrylate. Therefore,
when a photoresist composition containing the copolymer is
exposed to light, the acid-labile group of the copolymer is
cleaved under the action of the strong acid generated by the
5 acid generator, and at the same time, the BOC-substituent is
also cleaved.

The isoprene and hydroxy structure that are generated
as the BOC-substituent is cleaved, allows the fluidity of
the acid to be enhanced, and therefore, the resolution is
10 increased.

Fig. 10 presents the results obtained by analyzing BOC-
HAMA itself produced in the Monomer Synthesis Example 2,
using a thermal analyzer (NETZSCH TG 209®) while raising the
temperature up to 250°C. Fig. 11 presents the results
15 obtained by analyzing a mixture of 92 parts by weight of
BOC-HAMA and 8 parts by weight of toluenesulfonic acid,
using a thermal analyzer (NETZSCH TG 209®) while raising the
temperature up to 250°C.

The purpose of this experiment is to verify whether the
20 BOC-substituent will be detached from BOC-HAMA when
toluenesulfonic acid, which is a weaker acid than the acid
generated from PAG, is used together with BOC-HAMA, and to
verify thereby whether the BOC-substituent will be detached
from BOC-HAMA even when BOC-HAMA is used together with PAG.

25 When reference is made to Fig. 10 and Fig. 11, it can
be confirmed that when used together with toluenesulfonic
acid, the BOC-substituent is detached from BOC-HAMA from a

temperature as low as 50°C, and therefore, it is understood that the BOC substituent would be detached by the acid generated by PAG.

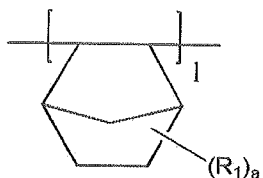
It is known from the results obtained as described
5 above that the photoresist composition using the copolymer according to embodiments of the present invention has an effect of aiding the fluidity of acid and improving the resolution because of the isoprene and hydroxy structure generated when t-BOC is decomposed by the acid generated
10 after exposure.

As such, preferred embodiments of the present invention have been explained in detail. However, the scope of rights to the present invention is not intended to be limited to the embodiments, and various modifications and improvements
15 made by those skilled in the art by using the fundamental concept of the present invention defined in the following claims, also belong to the scope of rights to the present invention.

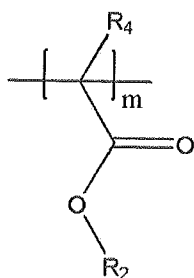
WHAT IS CLAIMED IS:

1. A copolymer comprising monomers represented by the following formulas 1 to 4:

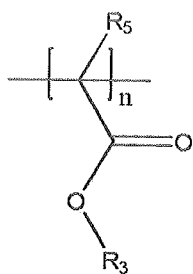
5 [Formula 1]



[Formula 2]

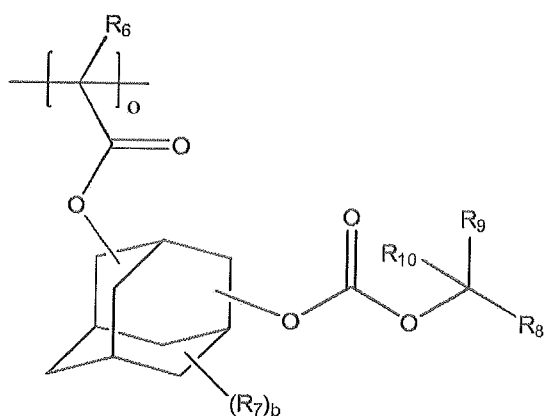


[Formula 3]



10

[Formula 4]



wherein in the formulas 1 to 4,

R_1 to R_{10} each independently represent any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy group, an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group;

a is an integer from 0 to 10;

b is an integer from 0 to 14; and

l , m , n and o are integers satisfying the relationships such as that $l+m+n+o=1$, $0.01 < l/(l+m+n+o) < 0.4$, $0 < m/(l+m+n+o) < 0.6$, $0 \leq n/(l+m+n+o) < 0.6$, and $0 < o/(l+m+n+o) < 0.4$.

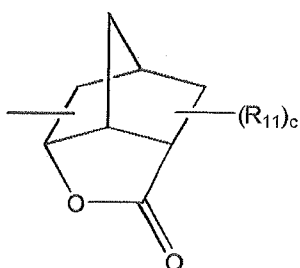
2. The copolymer according to claim 1, wherein

any one selected from the group consisting of R_1 to R_3 and combinations thereof is any one selected from the group consisting of an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group, each of which comprises any one selected from the group

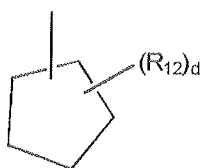
consisting of an ether group, an ester group, a carbonyl group, an acetal group, an amine group and combinations thereof, in the middle of the carbon chain.

- 5 3. The copolymer according to claim 1, wherein
any one selected from the group consisting of R_1 to R_3
and combinations thereof is represented by any one chemical
formulas selected from the group consisting of the following
formulas 5 to 11:

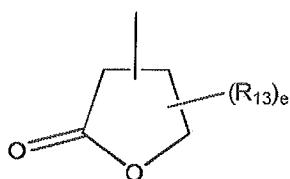
10 [Formula 5]



[Formula 6]

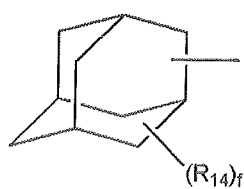


[Formula 7]

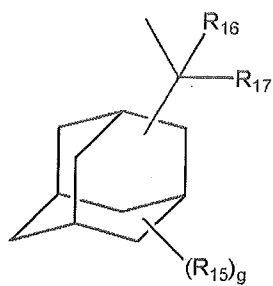


15

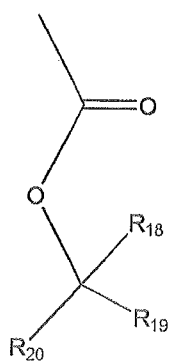
[Formula 8]



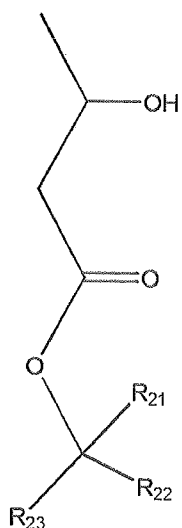
[Formula 9]



[Formula 10]



[Formula 11]



wherein in the formulas 5 to 11,

R₁₁ to R₂₃ each independently represent any one selected from the group consisting of a halogen atom, a hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy group, an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroalkyl group;

c is an integer from 0 to 9;

d is an integer from 0 to 4;

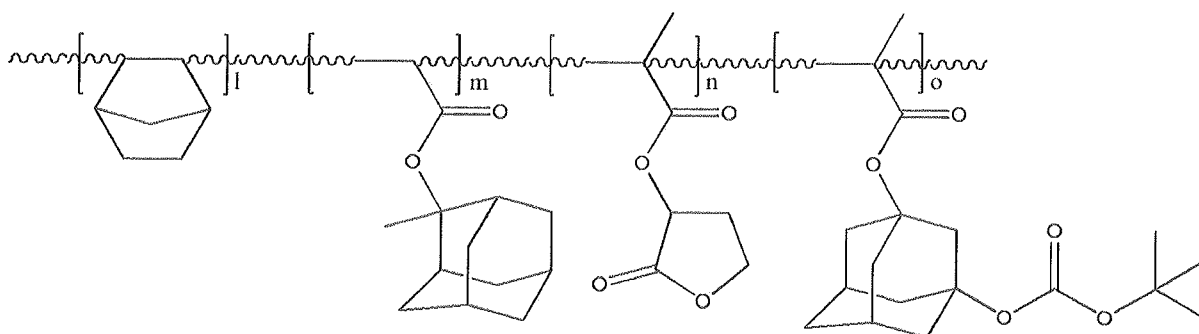
e is an integer from 0 to 4;

f is an integer from 0 to 14; and

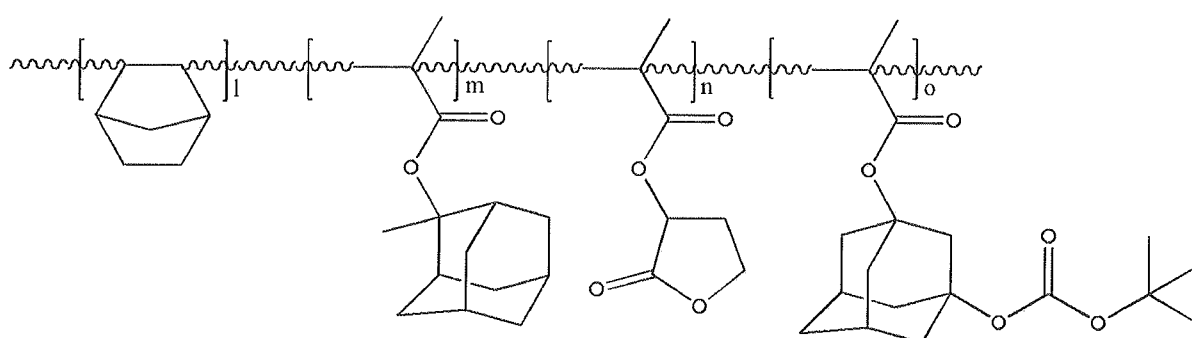
g is an integer from 0 to 14.

4. The copolymer according to claim 1, wherein the copolymer comprising the monomers represented by the formulas 1 to 4 is represented by any one formula selected from the group consisting of the following formulas 12 to 21:

[Formula 12]

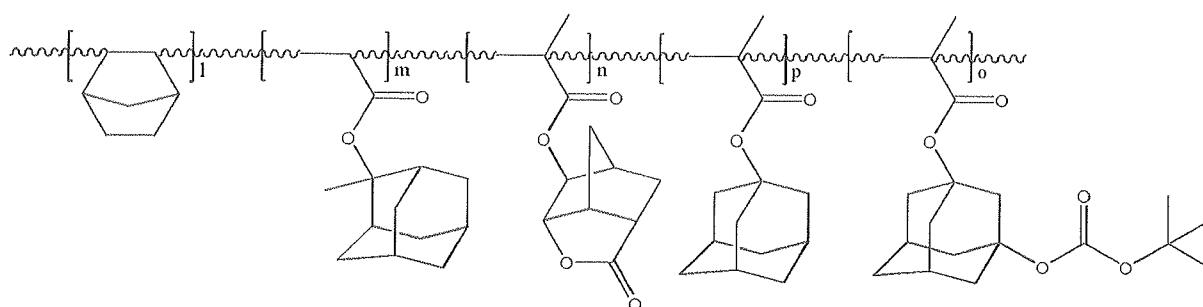


[Formula 13]

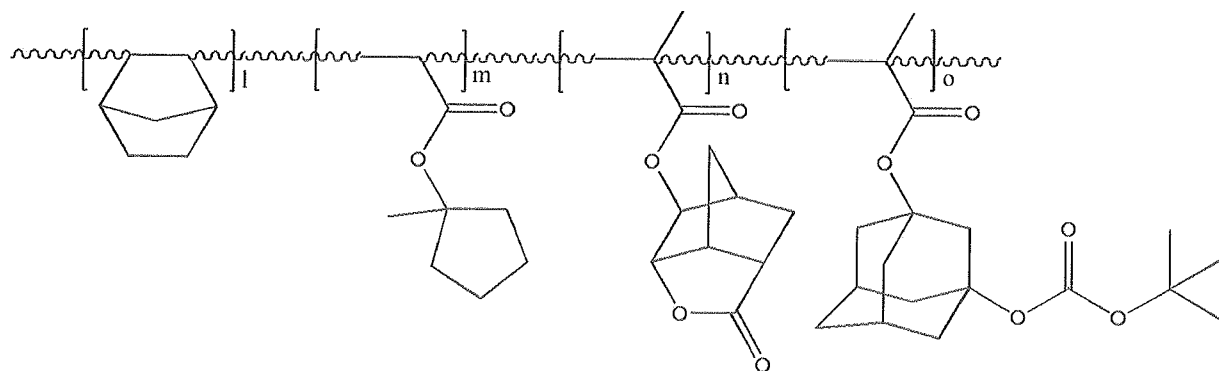


5

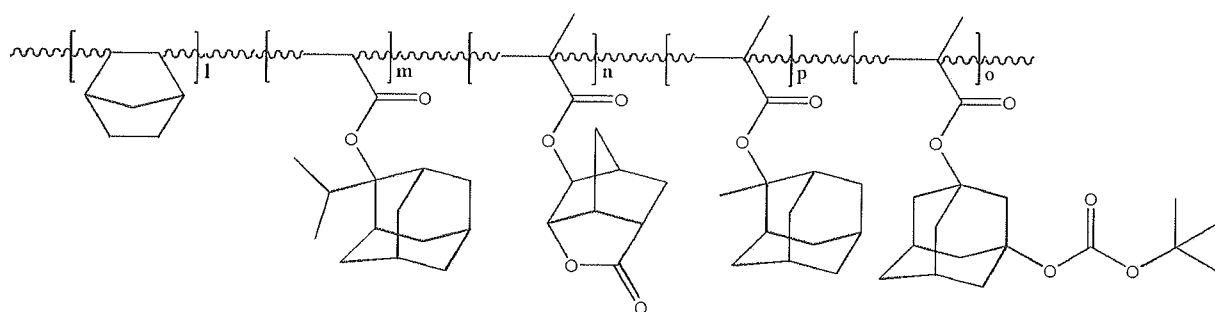
[Formula 14]



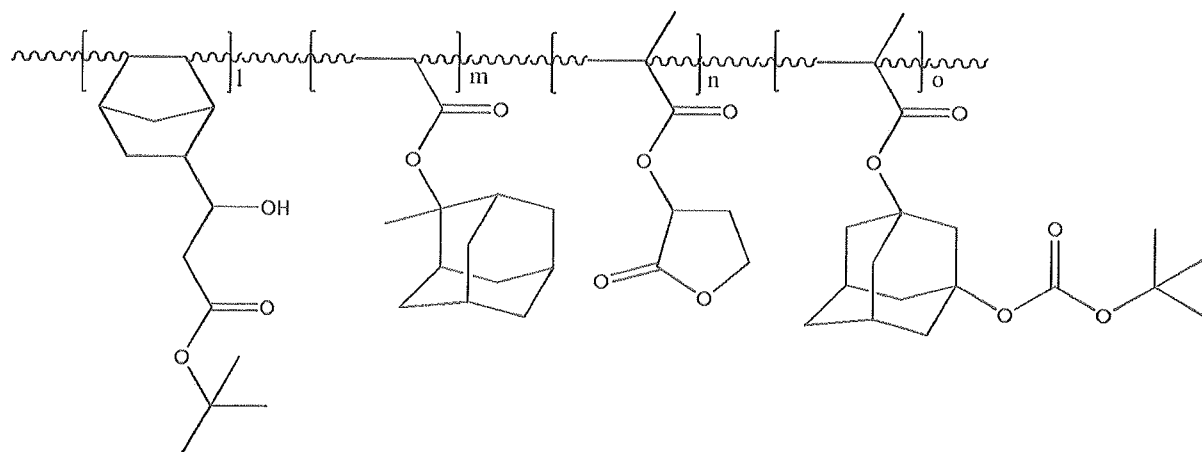
[Formula 15]



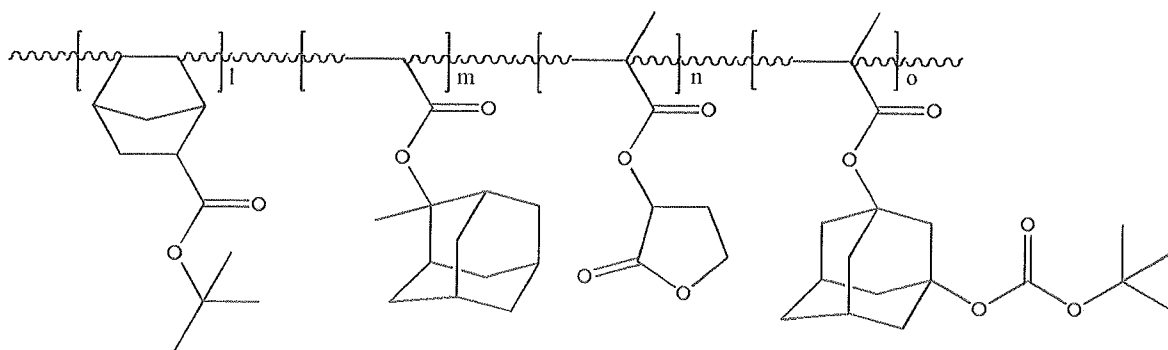
[Formula 16]



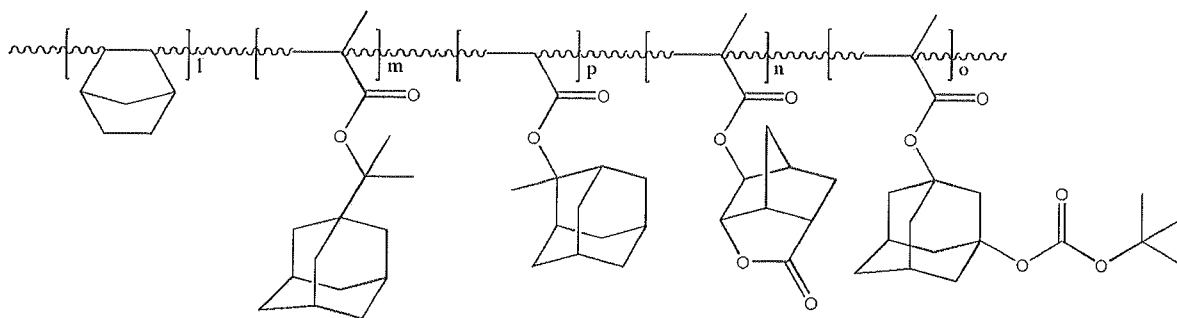
[Formula 17]



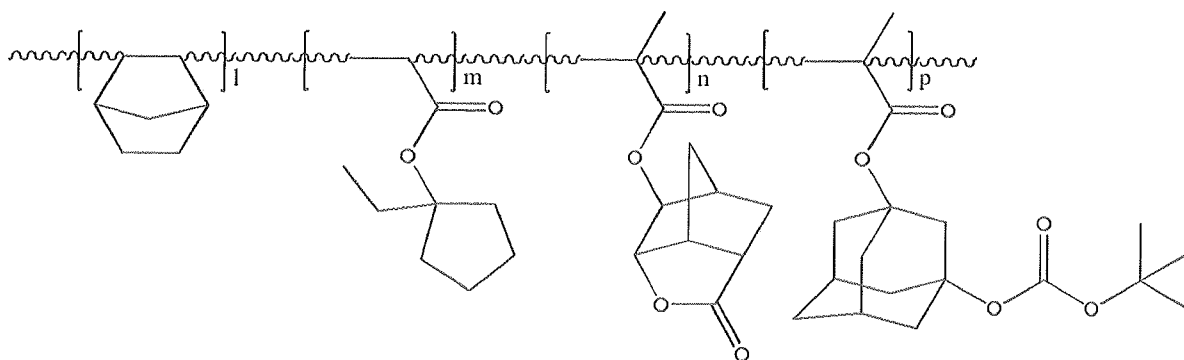
[Formula 18]



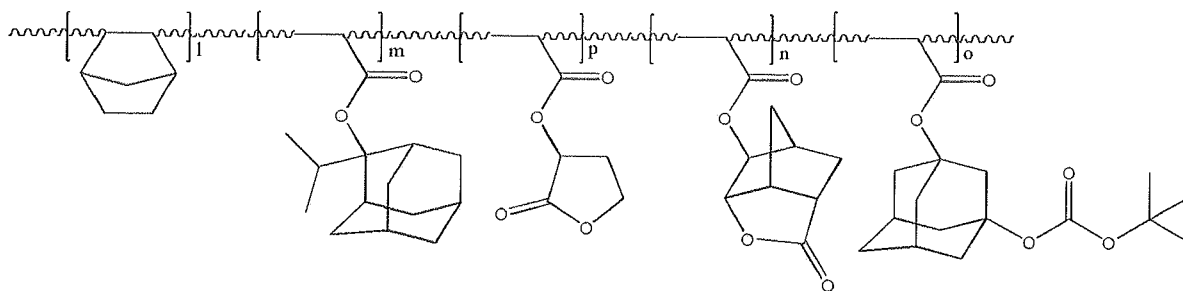
[Formula 19]



[Formula 20]



[Formula 21]



wherein in the formulas 12, 13, 15, 17, 18 and 20,

l, m, n and o are integers satisfying the relationships such as that $l+m+n+o=1$, $0.01 < l/(l+m+n+o) < 0.4$,

$0 < m/(l+m+n+o) < 0.6$, $0 \leq n/(l+m+n+o) < 0.6$, and $0 < o/(l+m+n+o) < 0.4$;

5 and in the formulas 14, 16, 19 and 21,

l, m, n, o and p are integers satisfying the relationships such as that $l+m+n+o+p=1$,

$0.01 < l/(l+m+n+o+p) < 0.4$, $0 < m/(l+m+n+o+p) < 0.6$,

$0 \leq n/(l+m+n+o+p) < 0.6$, $0 < o/(l+m+n+o+p) < 0.4$, and

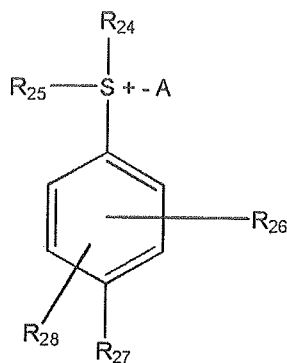
10 $0 \leq p/(l+m+n+o+p) < 0.6$.

5. A photoresist composition comprising the copolymer according to any one of claims 1 to 4, an acid generator, additives, and a solvent.

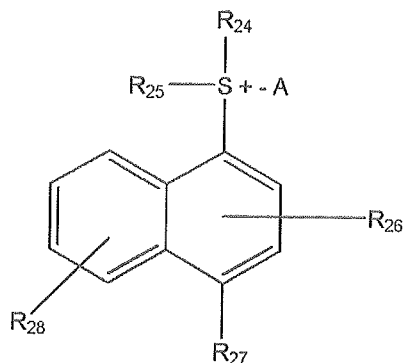
15

6. The photoresist composition according to claim 5, wherein the acid generator is represented by any one formula selected from the group consisting of the following formula 22, formula 23 and combinations thereof:

20 [Formula 22]



[Formula 23]



wherein in the formulas 22 and 23,

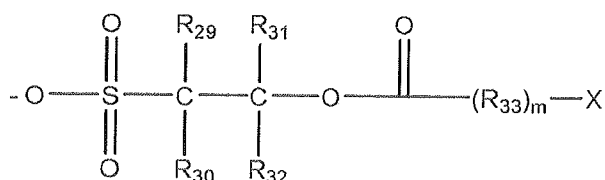
R₂₄ and R₂₅ each independently represent any one
 5 substituent selected from the group consisting of an alkyl
 group, an allyl group, a perfluoroalkyl group, a benzyl
 group and an aryl group;

R₂₆ to R₂₈ each independently represent any one
 substituent selected from the group consisting of a hydrogen
 10 atom, an alkyl group, a halogen group, an alkoxy group, an
 aryl group, a thiophenoxy group, a thioalkoxy group, and an
 alkoxycarbonylmethoxy group; and

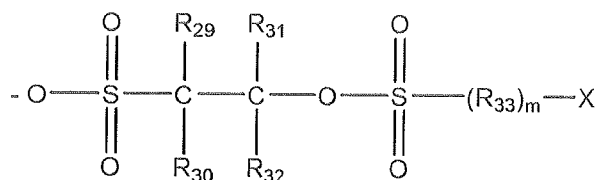
-A is an anion.

15 7. The photoresist composition according to claim 6,
 wherein the anion -A is 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, a compound
 represented by the following formula 24, and a compound
 20 represented by the following formula 25:

[Formula 24]



[Formula 25]



wherein in the formulas 24 and 25,

5 X is any one selected from the group consisting of an alkyl group, a perfluoroalkyl group, a cycloalkyl group, an allyl group, a benzyl group, an aryl group and a heteroaryl group;

10 R₃₃ is any one selected from the group consisting of an alkylene group, NR₃₄, S(R₃₅)₄, O and combinations thereof;

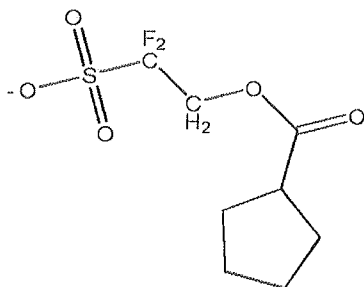
R₂₉ to R₃₂, R₃₄ and R₃₅ each independently represent any one selected from the group consisting of a hydrogen atom, a halogen atom, a hydroxyl group, a carboxyl group, a nitrile group, an aldehyde group, an epoxy group, an alkyl group, a cycloalkyl group, a heterocycloalkyl group, an aryl group and a heteroaryl group; and

m is an integer from 0 to 2.

8. The photoresist composition according to claim 7,
20 wherein the anion -A, which is any one selected from the group consisting of a compound represented by the formula 24

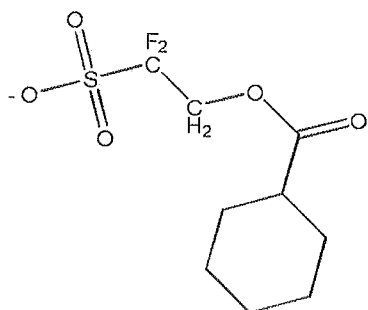
and a compound represented by the formula 25, is represented by any one formula selected from the group consisting of the following formulas 26 to 52:

[Formula 26]

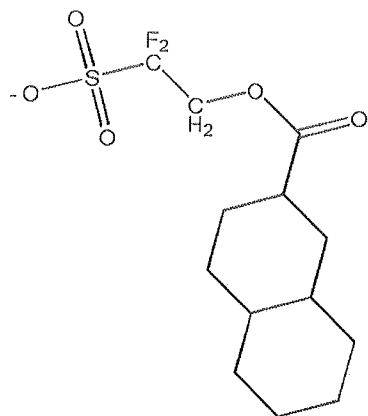


5

[Formula 27]

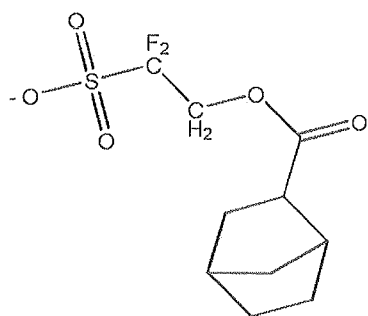


[Formula 28]

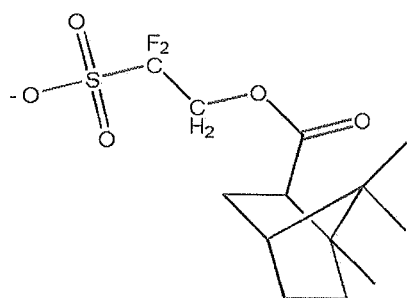


[Formula 29]

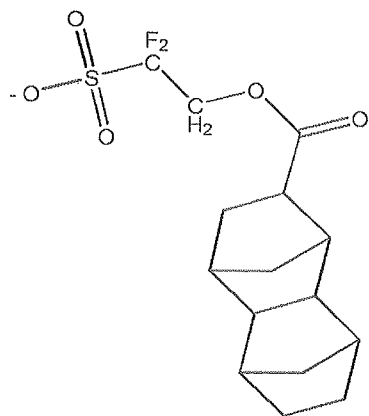
10



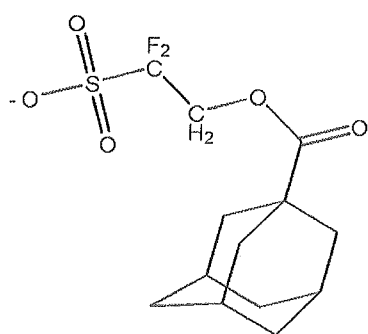
[Formula 30]



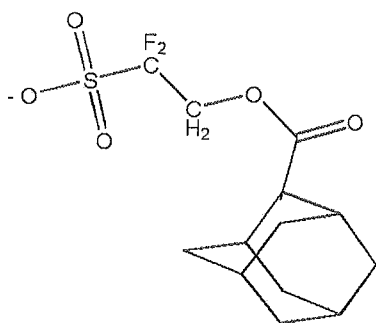
[Formula 31]



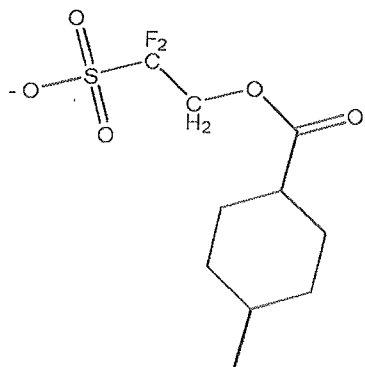
[Formula 32]



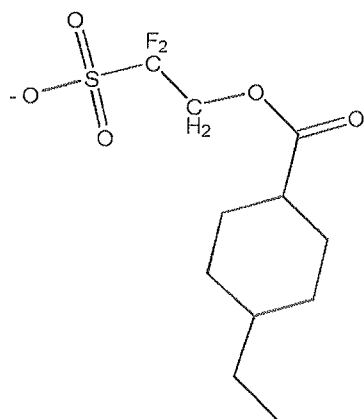
[Formula 33]



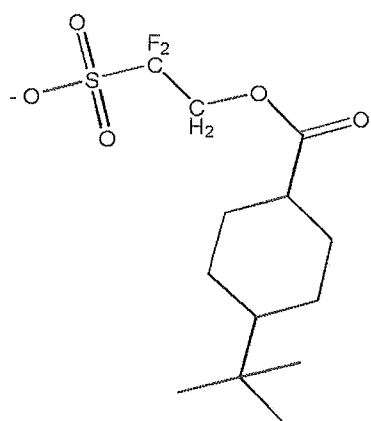
[Formula 34]



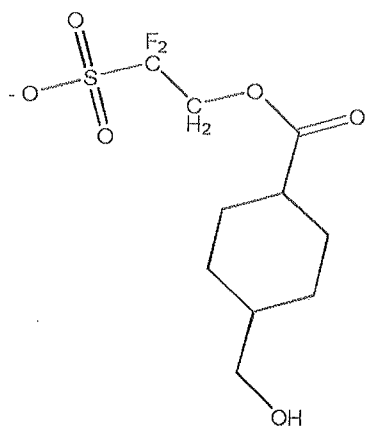
[Formula 35]



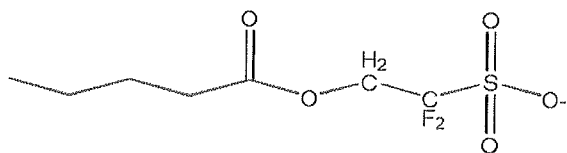
[Formula 36]



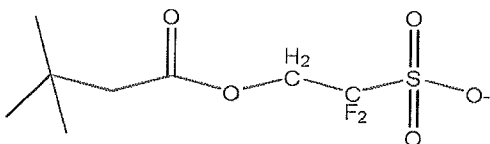
[Formula 37]



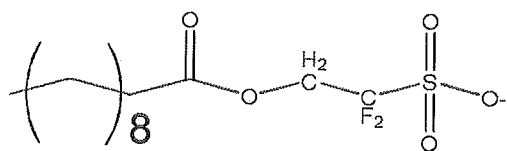
[Formula 38]



[Formula 39]

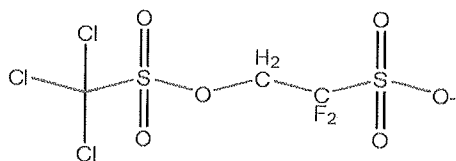


[Formula 40]

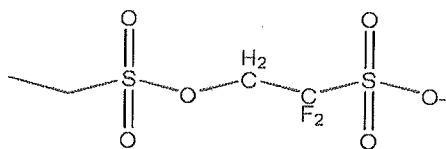


5

[Formula 41]

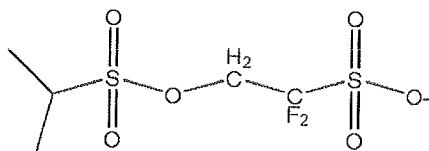


[Formula 42]

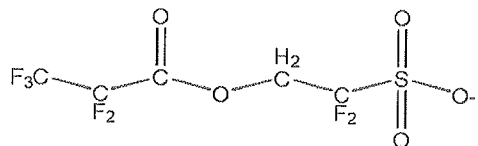


10

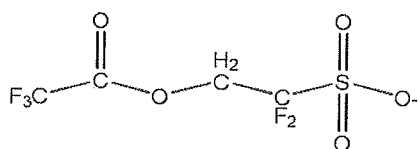
[Formula 43]



[Formula 44]

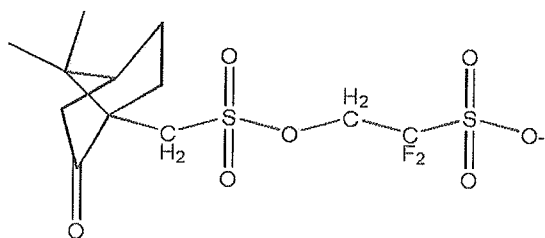


[Formula 45]

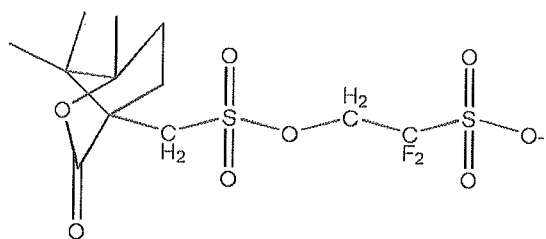


5

[Formula 46]

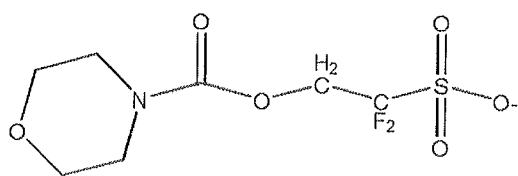


[Formula 47]

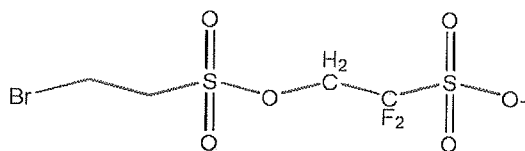


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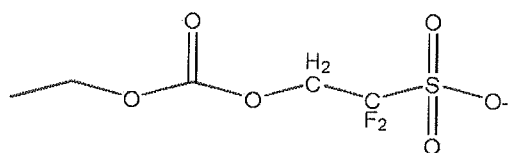
[Formula 48]



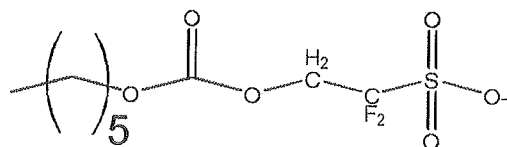
[Formula 49]



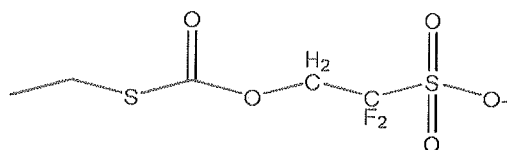
[Formula 50]



[Formula 51]



[Formula 52]



9. The photoresist composition according to claim 5,
 wherein the photoresist composition comprises the acid
 generator in an amount of 0.5 to 15 parts by weight relative
 to 100 parts by weight of the total solids content of the
 photoresist composition.

10. The photoresist composition according to claim 5, wherein the photoresist composition comprises the copolymer in an amount of 3 to 20% by weight relative to the total weight of the photoresist composition.

5