CLAIMS

1. A positive working chemically amplified photosensitive composition comprising:

Component a) at least one random copolymer, having structure (A), wherein

the repeat unit of structure (I) ranges from 17 mole % to 70 mole %,

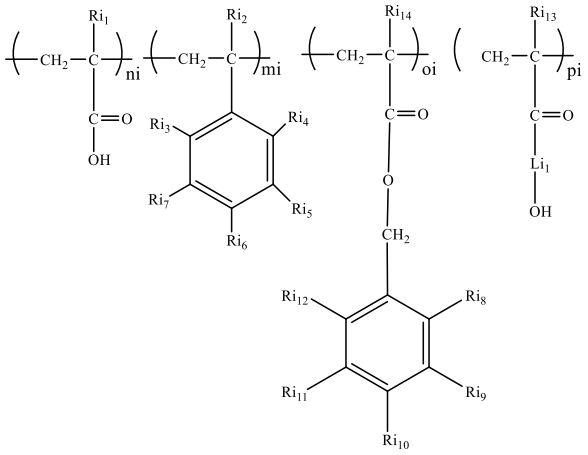
the repeat unit of structure (II) ranges from 0 to 70 mole %,

the repeat unit of structure (III) ranges from 0 to 70 mole %,

the sum of the repeat unit of structures (II) and (III) ranges from 30 mole % to 70 mole %,

the repeat unit of structure (IV) ranges from 0 mole % to 35 mole %, wherein the sum of the mole % of the repeat units of structure (I), (II), (III), and (IV) either does not exceed 100 mole % or is equal to 100 mole %, if other types of repeat units are not present, Ri_1, Ri_2, Ri_{14} and Ri_{13} are individually selected from H or a C-1 to C-4 alkyl, Ri_3, Ri_4, Ri_5, Ri_6, R_7, Ri_8, Ri_9, Ri_{10}, Ri_{11}, and Ri_{12}, are individually selected from H, a C-1 to C-8 alkyl, a C-1 to C-4 alkoxy, a phenyl, a substituted phenyl, and mixtures thereof, Li_1 is a C-2 to C-6 alkylene moiety, ni, mi, oi and pi are respectively the number of repeat units of structure (I), (II), (III) and (IV), and further wherein,

the copolymer of structure (A) has a minimum dissolution rate of 500 Å/sec in 0.26 N tetramethylammonium hydroxide at 23°C, and does not comprise any repeat units which have acid cleavable groups;



(I) (II) (III) (IV) **(A),**

component b) at least one acrylic copolymer component of structure (B) comprising repeat units selected from ones having structure (1), (2), (3), (4), (5), (6), and (7): wherein

R_1, R_2, R_3, R_4, R_5, R_6, and R_7 are individually selected from either H, F, a C-1 to C-4 perfluoroalkyl, or a C-1 to C-4 alkyl,

R_8 and R_9 are individually selected from H, a C-1 to C-4 alkyl, a C-1 to C-4 alkyloxy alkyl, and a halogen,

R_{10} is selected from the group consisting of a C-1 to C-8 primary alkyl, a C-3 to C-8 secondary alkyl, a C-3 to C-8 cyclic secondary alkyl, and a C-7 to C-14 secondary alicyclic alkyl,

R_{11} is a C-2 to C-8 (hydroxy)alkylene moiety,

R_{12} is a tertiary alkyl acid cleavable group, and

R_{13} is a C-3 to C-12, (alkyloxy)alkylene moiety; and further

these repeat units in total constitute 100 mole % of the repeat units in said functionalized acrylic copolymer, wherein,

the repeat unit of structure (1) ranges from 0 mole % to 20 mole % of the acrylic copolymer,

the repeat unit of structure (2) ranges from 0 mole % to 20 mole % of the acrylic copolymer,

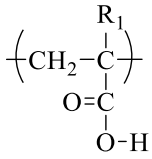
wherein the repeat unit of structure (3) ranges from 5 mole % to 55 mole % of the acrylic copolymer,

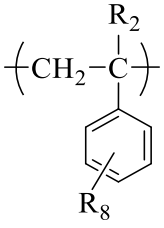
wherein the repeat unit of structure (4) ranges from 0 mole % to 30 mole % of the acrylic copolymer,

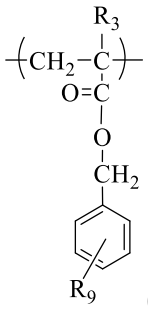
the repeat unit of structure (5) ranges from 15 mole % to 55 mole % of the acrylic copolymer,

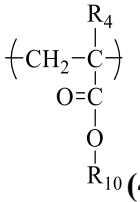
the repeat unit of structure (6) ranges from 18 mole % to 40 mole % of the acrylic copolymer

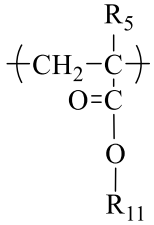
the repeat unit of structure (7) ranges from 0 mole % to 40 mole % of the acrylic copolymer

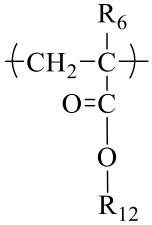

(1)

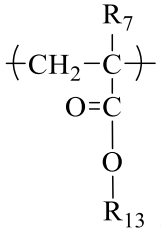

(2)


(3)


(4)


(5)


(6)


(7), (B)

component c) at least one Novolak polymer,

component d) at least one photoacid generator (PAG),
component e) at least one base additive,
component f) at least one heterocyclic thiol compound,
component g) an organic spin casting solvent.

2. The composition of claim 1, wherein component a) is a copolymer consisting of repeat units of structure (I) and (II).

3. The composition of claim 1, wherein component a) is a copolymer consisting of repeat units of structure (I), and (III).

4. The composition of claim 1, wherein component a) is a copolymer consisting of the repeat units of structure (I), (II), and (III).

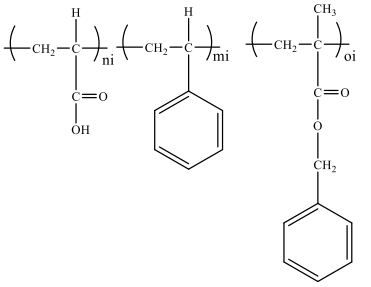
5. The composition of claim 1, wherein component a) is a copolymer consisting of repeat units of structure (I), (II) and (IV).

6. The composition of claim 1, wherein component a) is a copolymer consisting of repeat units of structure (I), (III) and (IV).

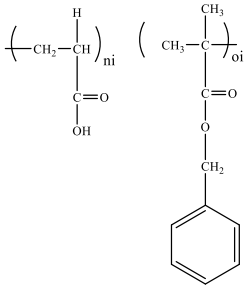
7. The composition of claim 1, wherein component a) is a copolymer consisting of the repeat units of structure (I), (II), (III) and (IV).

8. The composition of any one of claims 1 to 7, wherein the repeat units of structure (I) ranges from 20 mole % to 65 mole %, of the total repeat units in the copolymer.

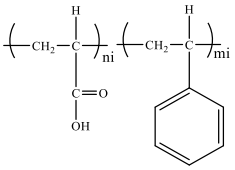
9. The composition of any one of claims 1, 4, and 8, wherein component a) has a structure selected from the group consisting of structure (A-1), structure (A-2), structure (A-3), structure (A-4), structure (A-5), structure (A-6), structure (A-7), structure (A-8), and structure (A-9),



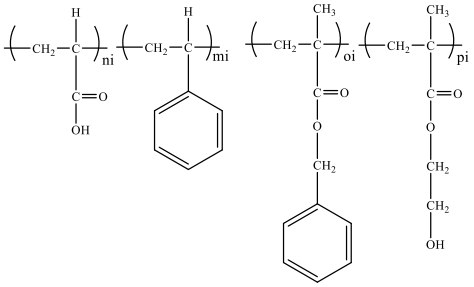
(Ia) (IIa) (IIIa) **(A-1),**



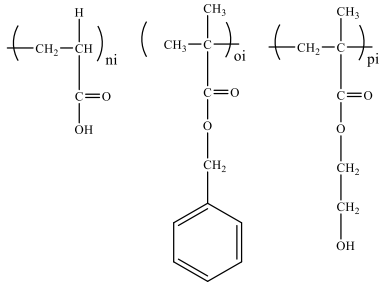
(Ia) (IIIa) **(A-2),**



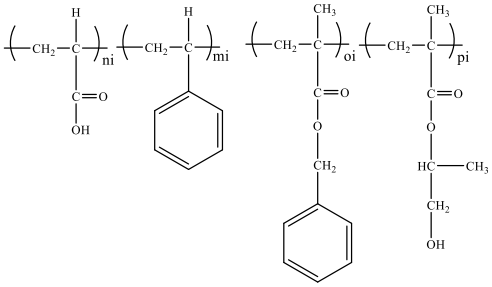
(Ia) (IIa) **(A-3),**



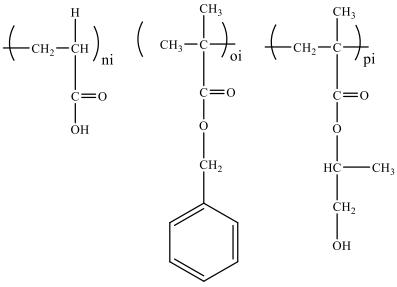
(Ia) (IIa) (IIIa) (IVa) **(A-4),**



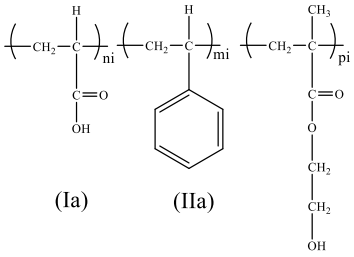
(Ia) (IIIa) (IVa) **(A-5),**



(Ia) (IIa) (IIIa) (IVb) **(A-6),**

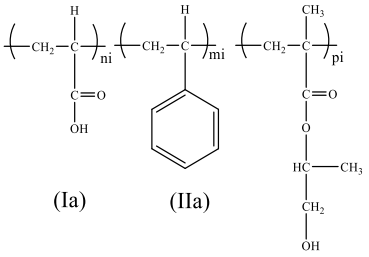


(Ia) (IIIa) (IVb) **(A-7),**



(Ia) (IIa)

(IVa) **(A-8),**



(Ia) (IIa)

(IVb) **(A-9).**

10. The composition of any one of claim 1 to 9, wherein component a) ranges from 10 wt. % to 25 wt. % of total solid components.

11. The composition of anyone of claims 1 to 10, wherein component b) ranges from 20 wt. % to 65 wt. % of total solid components.

12. The composition of any one of claims 1 to 11, wherein component b) comprises at least one copolymer of structure (B) which comprises from 5 mole % to 20 mole % of the repeat unit of structure (1).

13. The composition of any one of claims 1 to 12, wherein component b) comprises at least one copolymer of structure (B) which comprises from 5 mole % to 20 mole % of the repeat unit of structure (7).

14. The composition of any one of claim 1 to 13, wherein component b) comprises at least one copolymer of structure (B) in which the repeat unit of structure (1) ranges from 5 mole % to 20 mole % and the repeat unit of structure (7) ranges from 5 mole % to 20 mole %.

15. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists of from 5 mole % to 15 mole % of the repeat unit of structure (1), from 15 mole % to 25 mole % of the repeat unit of structure (3), from 35 mole % to 45 mole % of the repeat unit of structure (5), and from 25 mole % to 35 mole % of the repeat unit of structure (6).

16. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), which consist from 5 mole % to 10 mole % of the repeat unit of structure (1), from 18 mole % to 25 mole % of the repeat unit of structure (3), from 45 mole % to 55 mole % of the repeat unit of structure (5), from 15 mole % to 25 mole % of the repeat unit of structure (6).

17. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 5 mole % to 10 mole % of the repeat unit of structure (1), from 12 mole % to 22 mole % of the repeat unit of structure (3), from 20 mole % to 35 mole % of the repeat unit of structure (5), 25 mole % to 40 mole % of the repeat unit of structure (6) and from 5 mole % to 15 mole % of the repeat unit of structure (7).

18. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 12 mole % to 22 mole % of the repeat unit of structure (3), from 30 mole % to 40 mole % of the repeat unit of structure (5), from 25 mole % to 40 mole % of the repeat unit of structure (6), and from 5 mole % to 15 mole % of the repeat unit of structure (7).

19. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 5 mole % to 8 mole % of the repeat unit of structure (1), from 10 mole % to 17 mole % of the repeat unit of structure (3), from 30 mole % to 40 mole % of the repeat unit of structure (5), from 25 mole % to 40 mole % of the repeat unit of structure (6), and from 5 mole % to 15 mole % of the repeat unit of structure (7).

20. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 5 mole % to 7.5 mole % of the repeat unit of structure (1), from 10 mole % to 17 mole % of the repeat unit of structure (3), from 30 mole % to 40 mole % of the repeat unit of structure (5), from 25 mole % to 40 mole % of the repeat unit of structure (6), and from 5 mole % to 15 mole % of the repeat unit of structure (7).

21. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 5 mole % to 15 mole % of the repeat unit of structure (1), from 5 mole % to 15 mole % of the repeat unit of structure (3), from 30 mole % to 40 mole % of the repeat unit of structure (5), from 25 mole % to 40 mole % of the repeat unit of structure (6), and from 5 mole % to 15 mole % of the repeat unit of structure (7).

22. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 5 mole % to 15 mole % of the repeat unit of structure (1), from 20 mole % to 35 mole % of the repeat unit of structure (3), from 30 mole % to 40 mole % of the repeat unit of structure (5), from 18 mole % to 25 mole

% of the repeat unit of structure (6), and from 5 mole % to 15 mole % of the repeat unit of structure (7).

23. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 5 mole % to 15 mole % of the repeat unit of structure (1), from 20 mole % to 30 mole % of the repeat unit of structure (3), from 35 mole % to 45 mole % of the repeat unit of structure (5), from 18 mole % to 25 mole % of the repeat unit of structure (6), and from 5 mole % to 15 mole % of the repeat unit of structure (7).

24. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 7 mole % to 18 mole % of the repeat unit of structure (1), from 15 mole % to 25 mole % of the repeat unit of structure (3), from 25 mole % to 35 mole % of the repeat unit of structure (5), from 18 mole % to 25 mole % of the repeat unit of structure (6), and from 5 mole % to 15 mole % of the repeat unit of structure (7).

25. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 7 mole % to 15 mole % of the repeat unit of structure (1), from 25 mole % to 35 mole % of the repeat unit of structure (3), from 25 mole % to 35 mole % of the repeat unit of structure (5), from 25 mole % to 35 mole % of the repeat unit of structure (6).

26. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 7 mole % to 15 mole % of the repeat unit of structure (1), from 27 mole % to 45 mole % of the repeat unit of structure (3), from 30 mole % to 40 mole % of the repeat unit of structure (5), from 18 mole % to 25 mole % of the repeat unit of structure (6).

27. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 7 mole % to 15 mole

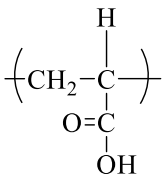
% of the repeat unit of structure (1), from 15 mole % to 25 mole % of the repeat unit of structure (3), from 35 mole % to 45 mole % of the repeat unit of structure (5), from 25 mole % to 35 mole % of the repeat unit of structure (6).

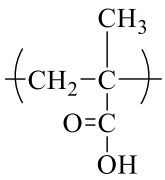
28. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 7 mole % to 15 mole % of the repeat unit of structure (1), from 20 mole % to 37 mole % of the repeat unit of structure (3), from 30 mole % to 45 mole % of the repeat unit of structure (5), from 20 mole % to 30 mole % of the repeat unit of structure (6).

29. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 7 mole % to 15 mole % of the repeat unit of structure (1), from 20 mole % to 30 mole % of the repeat unit of structure (3), from 30 mole % to 45 mole % of the repeat unit of structure (5), from 20 mole % to 35 mole % of the repeat unit of structure (6).

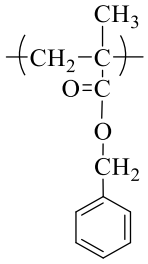
30. The composition of any one of claim 1 to 11, wherein component b) comprises at least one copolymer of structure (B), where at least one said copolymer consists from 10 mole % to 20 mole % of the repeat unit of structure (1), from 20 mole % to 30 mole % of the repeat unit of structure (3), from 30 mole % to 45 mole % of the repeat unit of structure (5), from 20 mole % to 35 mole % of the repeat unit of structure (6).

31. The composition of any one of claims 1 to 30, wherein:
the repeat unit of structure (1), if present, has either structures (1a) or (1b),

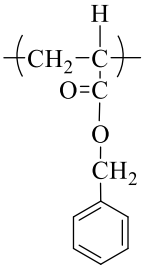

(1a)


(1b),

the repeat unit of structure (3) has either structures (3a) or (3b),

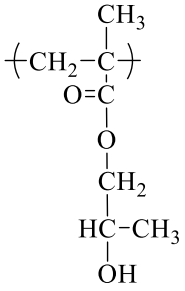


(3a)

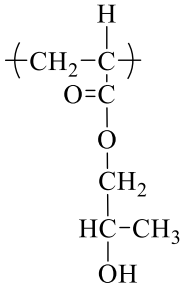


(3b),

the repeat unit of structure (5) has either structures (5a) or (5b),

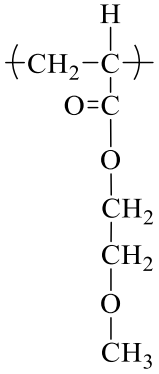


(5a)

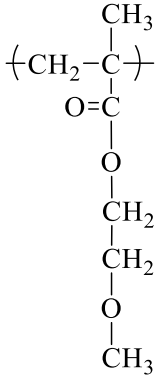


(5b),

the repeat unit of structure (7), if present, has either structure (7a) or (7b),

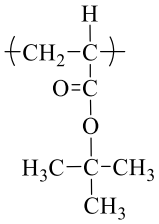


(7a)

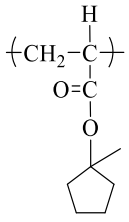


(7b),

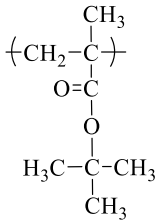
the repeat unit of structure (6), has either structures (6a), (6b), (6c) or (6d)



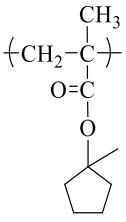
(6a),



(6b)



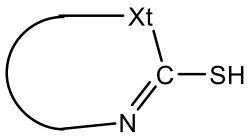
(6c),



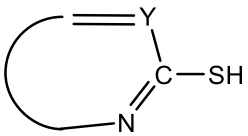
(6d).

32. The composition of claim 1, wherein, component d), the photo acid generator (PAG) is an aromatic imide N-oxysulfonate derivative of an organic sulfonic acid, an aromatic sulfonium salt of an organic sulfonic acid, a trihalotriazine derivative or a mixture thereof.

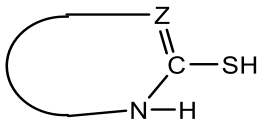
33. The composition of claim 1, wherein, component f), said heterocyclic thiol is chosen from the general formulas:



(H1)



(H2)



(H3)

in said structure (H1), Xt is selected from the group consisting of $N(Rt_3)$, $C(Rt_1)(Rt_2)$, O, S, Se, and Te;

in said structure (H2), Y is selected from the group consisting of $C(Rt_3)$ and N;

in said structure (H3), Z is selected from the group consisting of $C(Rt_3)$ and N; and

Rt_1, Rt_2, and Rt_3 are independently selected from the group consisting of H, a substituted alkyl group having 1 to 8 carbon atoms, an unsubstituted alkyl group having 1 to 8 carbon atoms, a substituted alkenyl group having 2 to 8 carbon atoms, unsubstituted alkenyl group having 2 to 8 carbon atoms, a substituted alkynyl group having 2 to 8 carbon atoms, unsubstituted alkynyl group having 2 to 8 carbon atoms, a substituted aromatic group having 6 to 20 carbon atoms, a substituted heteroaromatic group having 3 to 20 carbon atoms, unsubstituted aromatic group having 6 to 20 carbon atoms and unsubstituted heteroaromatic group having 3 to 20 carbon atoms.

34. A process for imaging a resist comprising the steps;

i) coating the composition of any one of claims 1 to 33 on a substrate to form a resist film;

ii) selectively exposing the resist film to UV light using a mask to form a selectively exposed resist film;

iii) developing the selectively exposed film to form a positively imaged resist film over the substrate.

35. The process of claim 34 for imaging a resist comprising the steps;

ia) coating the composition of any one of claims 1 to 33 on a substrate to form a resist film;

iia) selectively exposing the resist film to UV light using a mask to form a selectively exposed resist film;

iiia) baking the selectively exposed resist film to form a baked selectively exposed resist film;

iva) developing the selectively exposed and baked resist film to form a positively imaged resist film over the substrate.