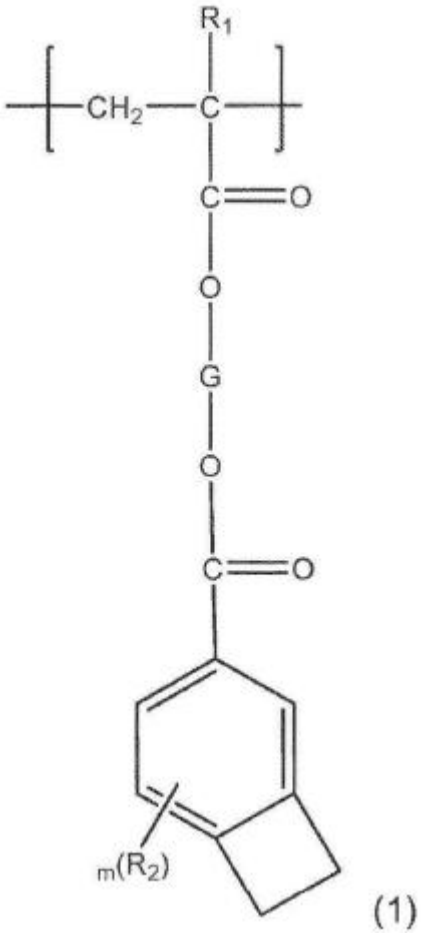
Claims

1. A composition comprising at least one random copolymer having at least one repeat unit of structure (1),

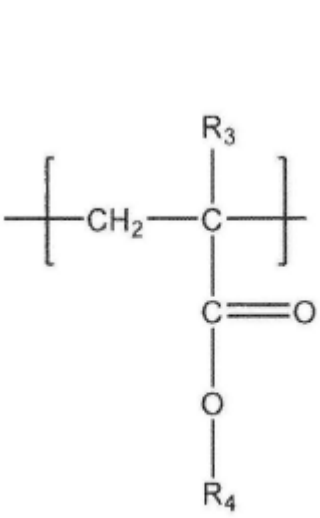


(1)

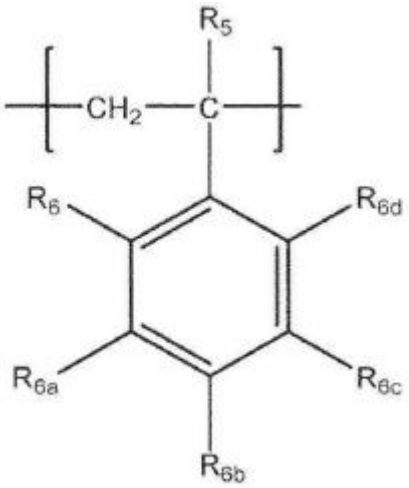
where R_1 is selected from a group consisting of H, C-1 to C-4 alkyl, a C-1 to C-4 fluoroalkyl, and a halide; and R_2 is selected from the group consisting of H, F, C-1 to C-8 alkyl and a C-1 to C-8 fluoroalkyl and m ranges from 1 to 3 and G is a C-2 to C-10 alkylene moiety.

2. The composition of claim 1 which is capable of forming a crosslinked layer on a coated substrate upon heating at a temperature between 220°C and 300°C and is insoluble in both organic solvents and aqueous bases and capable of affecting self-assembly of the block domains of a block copolymer cast on top of it and annealed.

3. The composition of claim 1 or 2, where said random copolymer further comprises at least one repeat units of structure (2) and at least one repeat unit of structure (3),



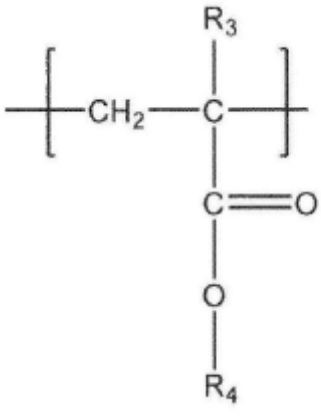
(2)



(3)

where R_3 is hydrogen, a C-1 to C-4 fluoroalkyl or a C-1 to C-4 alkyl, R_4 is a C-1 to C-20 alkyl, a halide, a C-1 to C-10 fluoroalkyl group, or a (trialkylsilyl)alkylene group, R_5 is hydrogen, a C-1 to C-4 alkyl, or a C-1 to C-4 fluoroalkyl, R_6, R_{6a}, R_{6b}, R_{6c} and R_{6d} are independently selected from the group consisting of hydrogen, a C-1 to C-20 alkyl, a C-1 to C-20 alkoxy, a C-1 to C-10 fluoroalkyl, a C-1 to C-10 fluoroalkoxy, a trialkylsilyl group, a (trialkylsilyl)alkylene group, and a (trialkylsilyl)alkyleneoxy group.

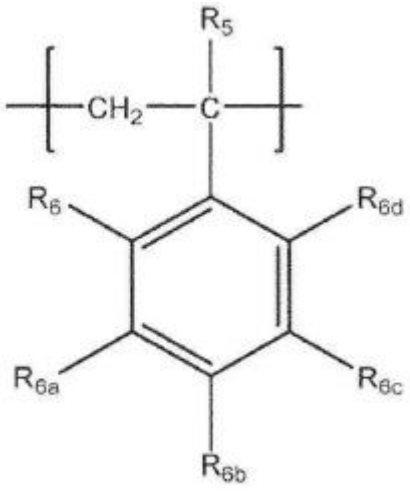
4. The composition of claim 1 or 2 where said random copolymer further comprises at least one repeat unit having structure (2),



(2)

where R_3 is hydrogen, a C-1 to C-4 fluoroalkyl or a C-1 to C-4 alkyl, R4 is a C-1 to C-20 alkyl, a halide, a C-1 to C-10 fluoroalkyl group, or a (trialkylsilyl)alkylene group.

5. The composition of claim 1 or 2 where said random copolymer further comprises at least one styrenic repeat having structure (3),



(3)

where R_5 is hydrogen, a C-1 to C-4 alkyl, or a C-1 to C-4 fluoroalkyl, R_6, R_{6a}, R_{6b}, R_{6c} and R_{6d} are independently selected from the group consisting of hydrogen, a C-1 to C-20 alkyl, a C-1 to C-20 alkoxy, a C-1 to C-10 fluoroalkyl, a C-1 to C-10 fluoroalkoxy, a trialkylsilyl group, a (trialkylsilyl)alkylene group, and a (trialkylsilyl)alkyleneoxy group.

6. The composition of claims 1 or 2 where R_1 is selected from a group consisting of H and methyl, and R_2 is H and G is a C-2 to C-5 alkylene moiety.

7. The composition of claims 1 or 2 where R_1 is H.

8. The composition of claims 1 or 2 where R_1 is methyl.

9. The composition of claims 1 or 2 where R_2 is H.

10. The composition of claims 1 or 2 where G is a C-2 to C-5 alkylene moiety.

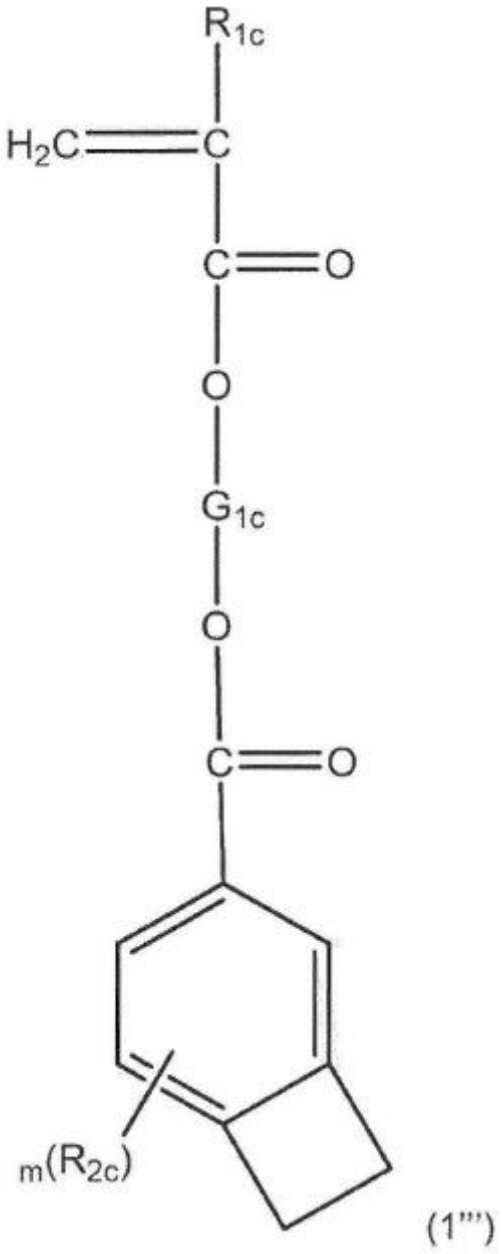
11. A pinning directing layer for polar aliphatic polymer block domains of a block copolymer overlying the directing layer formed by coating a composition of claim 1 on a substrate and cross-linking it, where this pinning layer has a total mole % of structure (1) and other (meth)acrylate derived repeat units equal or greater than 60 mole %, and further where the total mole % composition of repeat units in the random copolymer does not exceed 100 mole %.

12. A pinning directing layer for polar aliphatic polymer block domains of a block copolymer overlying the directing layer formed by coating a composition of claim 4 on a substrate and cross-linking it, where this pinning layer has a total mole % of structure (1), and structure (2) equal or greater than 60 mole %, and further where the total mole % composition of repeat units in the random copolymer does not exceed 100 mole %.

13. A pinning directing layer for aromatic polymer block domains of a block copolymer overlying the directing layer formed by coating a composition of claim 5 on a substrate and cross-linking it, where this pinning layer has a total mole % of structure (3) equal or greater than 60 mole %, and further where the total mole % composition of repeat units in the random copolymer does not exceed 100 mole %.

14. A neutral directing layer for a block copolymer comprised of aromatic polymer block domains and polar aliphatic block domains overlying the directing layer formed by coating a composition of claim 5 on a substrate and cross-linking it, where this neutral directing layer has a total mole % of structure (1) and structure (2) which ranges from 45 mole % to 55 mole % and where structure (3) ranges from 45 mole % to 55 mole %, and further where the total mole % composition of repeat units in the random copolymer does not exceed 100 mole %.

15. A monomer of structure (1’’’)



(1’’’)

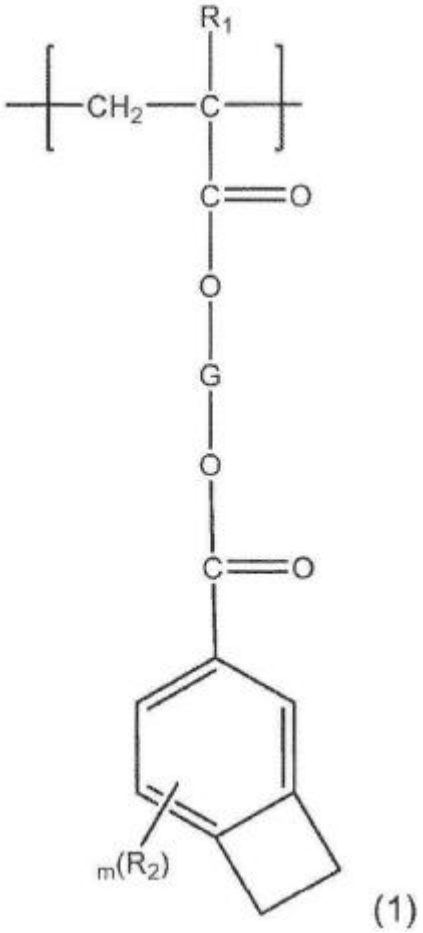
where R_{1c} is selected from a group consisting of H, C-1 to C-4 alkyl, a C-1 to C-4 fluoroalkyl, and a halide; and R_{2c} is selected from the group consisting of H, F, C-1 to C-8 alkyl and a C-1 to C-8 fluoroalkyl and m ranges from 1 to 3 and G_{1c} is a C-2 to C-10 alkylene moiety.

16. The monomer of claim 15 where R_{1c} is selected from H or a C-1 to C-4 alkyl.

17. The monomer of claim 15 where R_{2c} is selected from H or a C-1 to C-8 alkyl.

18. The monomer of claim 15 where G_{1c} is a C-2 to C-10 alkylene moiety.

19. A random copolymer having at least one repeat unit of structure (1),



(1)

where R_1 is selected from a group consisting of H, C-1 to C-4 alkyl, a C-1 to C-4 fluoroalkyl, and a halide; and R2 is selected from the group consisting of H, F, C-1 to C-8 alkyl and a C-1 to C-8 fluoroalkyl and m ranges from 1 to 3 and G is a C-2 to C-10 alkylene moiety.

20. The copolymer of claim 19 where R_1 is selected from H or a C-1 to C-4 alkyl.

21. The copolymer of claim 19 or 20 where R_2 is selected from H or a C-1 to C-8 alkyl.

22. A process for forming a crosslinked layer on a substrate comprised of steps a) to b)

a) coating the composition of claim 1 on a substrate to form a layer;

b) heating the layer at a temperature between 220°C and 350°C to form a crosslinked layer.

23. The process of claim 22 where between steps and a) and b) the layer is heated at a temperature between 80°C and 180°C to remove solvent.

24. A process for forming a self-assembly block copolymer comprised of steps a) to d)

a) coating of the composition of claim 1 on a substrate to form a layer;
b) heating the layer at a temperature between 220°C and 350°C to form a crosslinked directing layer;
c) applying a block copolymer layer over the crosslinked directing layer;
d) annealing the block copolymer layer.

25. The process of claim 24 where between steps and a) and b) the layer is heated at a temperature between 80°C and 180°C to remove solvent.

26. A process for forming an image using graphoepitaxy comprised of step a) to f)

a) coating the composition of claim 3 on a substrate to form a layer;
b) heating the layer at a temperature between 220°C and 350°C to form a crosslinked neutral layer;
c) providing a coating of a photoresist layer over the crosslinked neutral layer;
d) forming a pattern in the photoresist;
e) applying a block copolymer comprising an etch resistant block and highly etchable block over the photoresist pattern and annealing until directed self-assembly occurs; and,
f) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a pattern.

27. The process of claim 26 where between steps a) and b) the layer is heated at a temperature between 80°C and 180°C to remove solvent.

28. A process for forming an image using graphoepitaxy comprised of step a) to h)

a) forming a coating of a crosslinked neutral layer;

b) providing a coating of a negative tone photoresist layer over the crosslinked neutral layer;

c) forming a pattern in the photoresist;

d) coating the composition of claim 4 on a patterned photoresist film to form a layer where this layer is of a thickness which just fills the voids in the photoresist pattern;

e) heating the layer at a temperature between 200°C and 350°C to form a crosslinked pinning layer;

f) removing the photoresist;

g) applying a layer of a block copolymer comprising an etch resistant block and highly etchable block and annealing until directed self-assembly occurs;

h) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a pattern.

29. The process of claim 28 where between steps d) and e) the layer is heated at a temperature between 80°C to 180°C to remove solvent.

30. A process for forming an image by chemoepitaxy comprising steps a) to h):

a) coating the composition of claim 1 on a substrate to form a layer;

b) heating neutral layer at a temperature between 220°C-350°C to form a crosslinked neutral layer;

c) providing a coating of a photoresist layer over the crosslinked neutral layer;

d) forming a pattern in the photoresist layer to remove the unexposed photoresist, thereby forming an uncovered crosslinked neutral layer region;

e) treating the uncovered crosslinked neutral layer,

f) removing the photoresist,

g) applying a block copolymer comprising an etch resistant block and highly etchable block over the neutral layer and annealing until directed self-assembly occurs; and,

h) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a pattern.

31. The process of claim 30 where between steps a) and b) the layer is heated at a temperature between 80°C and 180°C to remove solvent.

32. A process for forming an image by chemoepitaxy comprising steps a) to i):

a) coating the composition of claim 3, on a substrate to form a layer;

b) heating the layer at a temperature between 220°C and 350°C to form a crosslinked neutral layer;

c) providing a coating of a photoresist layer over a crosslinked pinning layer;

d) forming a pattern in the photoresist layer;

e) etching, to remove pinning later in the area without photoresist;

f) removing the photoresist;

g) forming a brush neutral layer at the area of non-pinning layer;

h) applying a block copolymer comprising an etch resistant block and highly etchable block over the neutral layer and annealing until directed self-assembly a) occurs; and,

i) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a pattern.

33. The process of claim 32 where between steps a) and b) the layer is heated at a temperature between 80°C and 180°C to remove solvent.

34. A process for forming an image by chemoepitaxy comprising steps a) to i):

a) coating the composition of claim 4 on a substrate to form a layer;

b) heating the layer at a temperature between 220°C and 350°C to form a crosslinked pinning layer;

c) providing a coating of a photoresist layer over the crosslinked pinning layer;

d) forming a pattern in the photoresist layer;

e) etching, to remove pinning later in the area without photoresist;

f) removing the photoresist;

g) forming a brush neutral layer at the area of non-pinning layer;

h) applying a block copolymer comprising an etch resistant block and highly etchable block over the neutral layer and annealing until directed self-assembly occurs; and,

i) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a pattern.

35. The process of claim 34 where between steps a) and b) the layer is heated at a temperature between 80°C and 180°C to remove solvent.

36. A process for forming an image by chemoepitaxy comprising:

a) forming a layer by coating the composition of claim 5 on a substrate;

b) optionally heating the layer at a temperature between 80°C-180°C to remove solvent;

c) heating the layer at a temperature between 220°C and 350°C to form a crosslinked pinning layer;

d) providing a coating of a photoresist layer over the crosslinked pinning layer;

e) forming a pattern in the photoresist layer;

f) etching, to remove pinning later in the area without photoresist;

g) removing the photoresist;

h) forming a brush neutral layer at the area of non-pinning layer;

i) applying a block copolymer comprising an etch resistant block and highly etchable block over the neutral layer and annealing until directed self-assembly occurs; and,

j) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a pattern.