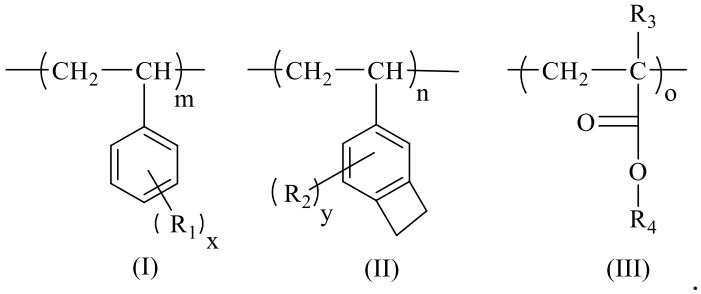
Claims

1. A random copolymer whose repeat units comprise repeat units of structure (I), (II) and (III), wherein R_1 and R_2 are independently a C-1 to C-4 alkyl, x and y are independently the number of R_1 and R_2 which independently range from an integer from 0 to 3, R_3 is a C-1 to C-4 alkyl, and R_4 is selected from a C-2 to C-10 primary alkyl, or a moiety comprising an arene selected from the group consisting of a substituted or unsubstituted biphenyl moiety, a substituted or unsubstituted phenyl moiety, and a substituted or unsubstituted benzylic moiety and m, n, and o are respectively the number of repeat units of structures (I), (II) and (III), where the mole % of the repeat unit of structure (I) ranges from 60 mole % to 95 mole %, the mole % of repeat unit of structure (II) ranges from 5 mole % to 25 mole %, the mole % of repeat unit of structure (III) ranges from 2 mole % to 18 mole %, where the sum of the mole % of these repeat units either is less than 100 mole %, if other different repeat units are present, or equals 100 mole % if only the repeat units of structures (I), (II) and (III) are present, and further where said random copolymer has a polydispersity ranging from 1.25 to 1.80 and has an Mw which ranges from 30,000 to 45,000 daltons, and said random copolymer is free of reactive end groups comprising a benzylic alcohol comprising moiety,



(I) (II) (III)

2. The random copolymer of claim 1, whose repeat units consist essentially of repeat units of structure (I), (II) and (III).

3. The random copolymer of claim 1 or 2, whose repeat units consist of repeat units of structure (I), (II) and (III), where the sum of the mole % of repeat units (I), (II) and (III) equals 100 mole %.

4. The random copolymer of any one of claims 1 to 3, wherein the repeat unit of structure (III) ranges from 2.5 mole % to 16 mole %.

5. The random copolymer of any one of claims 1 to 4, wherein the repeat unit of structures (II) ranges from 6 mole % to 23 mole %.

6. The random copolymer of any one of claims 1 to 5, wherein the repeat unit of structure (I) ranges from 62 mole % to 93 mole %.

7. The random copolymer of any one of claims 1 to 6, wherein the repeat unit of structure (I) ranges from 60 mole % to 90 mole %, the repeat unit of structure (II) ranges from 7 mole % to 20 mole% and the repeat unit of structure (III) ranges from 3 mole % to 15 mole%.

8. The random copolymer of any one of claims 1 to 7, wherein x is 0.

9. The random copolymer of any one of claim 1 to 8, wherein y is 0.

10. The random copolymer of any one of claims 1 to 9, wherein x and y are 0.

11. The random copolymer of any one of claims 1 to 10, wherein R_3 is CH_3.

12. The random copolymer of any one of claims 1 to 11, wherein R_4 is a C-2 to C-10 primary alkyl.

13. The random copolymer of any one of claims 1 to 11, wherein R_4 is a C-3 to C-7 primary alkyl.

14. The random copolymer of any one of claims 1 to 13, wherein R_4 is n-butyl.

15. The random copolymer of any one of claims 1 to 11, wherein R_4 is a C-2 to C-6 primary alkyl.

16. The random copolymer of any one of claims 1 to 11, wherein R_4 is n-propyl.

17. The random copolymer of any one of claims 1 to 11, wherein R_4 is an ethyl.

18. The random copolymer of any one of claims 1 to 11, wherein R_4 is a benzylic moiety.

19. The random copolymer of any one of claims 1 to 11, wherein R_4 is benzyl.

20. The random copolymer of any one of claims 1 to 11, wherein R_4 is a substituted phenyl moiety.

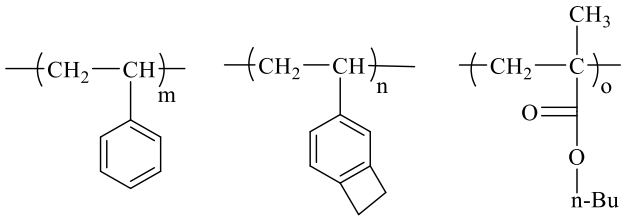
21. The random copolymer of any one of claims 1 to 11, and 24, wherein R_4 is phenyl.

22. The random copolymer of any one of claims 1 to 11, wherein R_4 is a substituted biphenyl.

23. The random copolymer of any one of claims 1 to 11, wherein R_4 is an unsubstituted biphenyl moiety.

24. The random copolymer of any one of claims 1 to 11, wherein R_4 is [1.1'-biphenyl-4-yl].

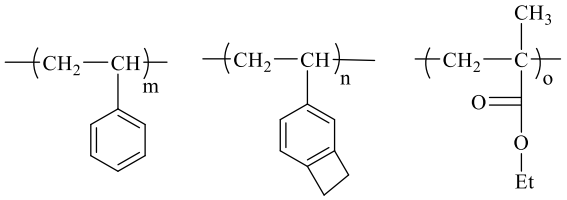
25. The random copolymer of any one of claims 1 to 11, wherein the repeat units have structures (Ia), (IIa) and (IIIa);



(Ia) (IIa) (IIIa)

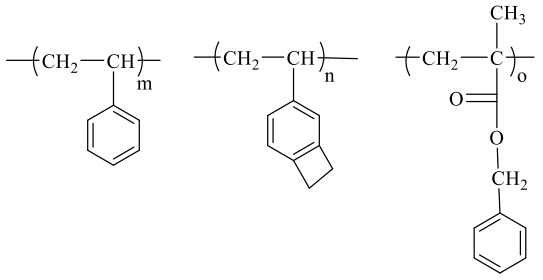
26. The random copolymer of any one of claims 1 to 11, wherein the repeat units have

structures (Ia), (IIa) and (IIIa-1);



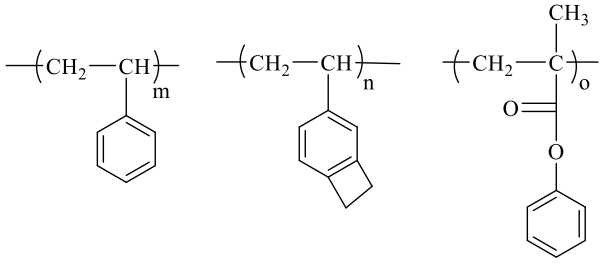
(Ia) (IIa) (IIIa-1)

27. The random copolymer of any one of claims 1 to 11, wherein the repeat units have structures (Ia), (IIa) and (IIIb);



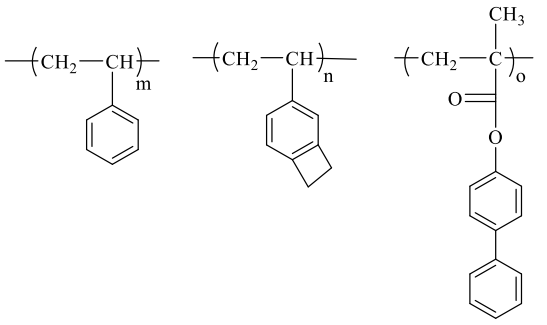
(Ia) (IIa) (IIIb).

28. The random copolymer of any one of claims 1 to 11, wherein the repeat units have structure (Ia), (IIa) and (IIIc);



(Ia) (IIa) (IIIc).

29. The random copolymer of any one of claims 1 to 11, wherein the repeat units have structure (Ia), (IIa) and (IIId);



(Ia) (IIa) (IIId) .

30. A composition comprising the random copolymer of any one of claims 1 to 29, and an organic spin casting solvent.

31. A process of forming a crosslinked layer of a copolymer on a substrate comprising the steps:

a) forming a coating of the composition of claim 42 on a substrate;

b) heating the coating at a temperature ranging from 90°C to 180°C to remove solvent;

c) heating the coating at a temperature ranging from 200°C to 350°C to form a crosslinked copolymer coating layer.

32. A process of chemoepitaxy, directed self-assembly of a block copolymer layer used to form an image comprised of the steps:

a-1) coating a substrate with a graftable neutral layer polymer precursor to form a coated layer 1;

b-1) heating coated layer 1 at a temperature from 90°C to 180°C to remove solvent;

c-1) heating the coated layer 1 after step b-1) at a temperature from 200°C to 350°C to affect grafting;

d-1) treating the coated layer 1 after step c-1) with an organic solvent to remove ungrafted neutral layer polymer, leaving an insoluble grafted neutral layer on the substrate;

e-1) coating a negative photoresist layer over the grafted neutral layer;

f-1) forming a negative pattern in the photoresist layer, thereby forming regions in which the grafted neutral layer is covered or uncovered by the photoresist, where the pattern in the photoresist is comprised of both small nanometer sized repeating patterns and also large areas of

photoresist removed during the imaging process containing no repeating nanometer sized patterns;

g-1) etching to remove the neutral layer regions uncovered in step f-1) leaving bare substrate in these regions;

h-1) stripping the photoresist away from the substrate after step g-1), leaving a patterned substrate in which regions of substrate left uncovered by photoresist in step f-1) are free of a grafted neutral layer and the regions covered by photoresist in step f-1) retain the grafted neutral layer;

i-1) coating the patterned substrate with the composition of claim 42 to form a coated layer 2;

j-1) heating the coated layer 2 a temperature of 90°C to 180°C remove solvent;

k-1) heating the coating layer 2 at a temperature ranging from 200°C to 350°C, leaving an insoluble crosslinked pinning MAT layer on the substrate in the regions free of grafted neutral layer creating a substrate with both pinning MAT layer areas and neutral layer areas;

l-1) applying a coating of a block copolymer comprising an etch resistant styrenic block and a highly etchable aliphatic block over the substrate containing a patterned neutral layer and pinning MAT layer, creating a substrate containing both a patterned neutral layer and a patterned pinning MAT layer;

m-1) annealing the block copolymer layer until directed self-assembly occurs in the small nanometer sized repeating patterns of the substrate, but where no perpendicular orientation of block polymer domains occurs in the large areas containing crosslinked pinning MAT layer;

o-1) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a repeating nanometer sized pattern in the areas where directed self-assembly of the block copolymer occurred on the substrate in step m-1).

33. A process of chemoepitaxy, directed self-assembly of a block copolymer layer used to form an image comprising the steps:

a-2) forming a coating of a neutral layer polymer precursor which is crosslinkable or which is both crosslinkable and graftable on a substrate;

b-2) heating the neutral polymer layer precursor coating which is crosslinkable or the precursor coating which is both crosslinkable and graftable at a temperature from 90°C to 180°C to remove solvent;

c-2) heating the neutral layer polymer precursor coating which is crosslinkable or the

coating precursor coating which is both crosslinkable and graftable at a temperature from 200°C to 330°C to form a crosslinked neutral layer or a crosslinked and grafted neutral layer;

d-2) providing a coating of a photoresist layer over the crosslinked neutral layer or over the crosslinked and grafted neutral layer;

e-2) forming a negative pattern in the photoresist layer, thereby forming regions in which the crosslinked or the crosslinked and grafted neutral layer is covered or uncovered by the photoresist, where the pattern in the photoresist is comprised of both small nanometer repeating patterns and also large areas of photoresist removed during the imaging process containing no repeating nanometer sized patterns;

f-2) etching with a plasma to remove in the neutral layer regions uncovered in step e-2) removing crosslinked or crosslinked and grafted neutral layer leaving bare substrate in the regions uncovered in step e-2);

g-2) stripping the photoresist away from the substrate after step f-2), leaving a patterned substrate in which regions of substrate left uncovered by photoresist in step e-2) are free of a crosslinked or crosslinked and grafted neutral layer and the regions covered by photoresist in step f2) retain the crosslinked or crosslinked and grafted neutral layer;

h-2) coating the patterned substrate with the composition of claim 42 to form a coated layer 3;

i-2) heating coated layer 3 at a temperature of 90°C to 180°C to remove solvent;

j-2) heating the coating layer 3 at a temperature ranging from 200°C to 350°C, leaving an insoluble crosslinked pinning MAT layer on the substrate in the regions free of grafted neutral layer, creating a substrate containing both pinning MAT layer areas and neutral layer areas;

k-2) applying a coating of a block copolymer comprising an etch resistant styrenic block and a highly etchable aliphatic block over the substrate containing a patterned neutral layer and pinning MAT layer;

l-2) annealing the block copolymer layer until directed self-assembly occurs in the small nanometer sized repeating patterns of the substrate, but where no perpendicular orientation of block polymer domains occurs in the large areas containing crosslinked pinning MAT layer;

m-2) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a repeating nanometer sized pattern in the areas where directed self-assembly of the block copolymer occurred on the substrate in step l-2).

34. A process of chemoepitaxy, directed self-assembly of a block copolymer layer used to form an image comprising the steps:

a-3) forming a coating of the composition of claim 42, on a substrate forming a film,

b-3) baking said film at a temperature from 200°C to 350°C for 1 to 10 minutes forming an insoluble crosslinked pinning MAT layer,

c-3) providing a coating of a positive or negative photoresist layer over the crosslinked pinning MAT layer,

d-3) forming a negative or positive image respectively in negative or positive photoresist layer, thereby forming regions in which the crosslinked pinning is covered or uncovered by the photoresist,

e-3) etching with a plasma to remove the crosslinked pinning MAT layer in the areas uncovered in step d-3) leaving bare substrate and leaving the crosslinked pinning MAT layer in the areas left covered in step d-3), forming a patterned crosslinked pinning MAT layer,

f-3) coating said patterned crosslinked pinning MAT layer with a neutral brush layer coating,

g-3) curing said neutral layer brush coating and washing away with a solvent ungrafted neutral layer forming in areas of said substrate not covered by said patterned crosslinked pinning MAT layer, a neutral brush directing layer forming on said substrate forming a chemoepitaxy directing layer,

h-3) coating on said chemoepitaxy directing layer a block copolymer solution forming a coating of block copolymer,

i-3) annealing said coating of block copolymer to form a directed self-assembled film of the block copolymer on said chemoepitaxy directing layer,

j-3) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a repeating nanometer sized pattern in the areas where directed self-assembly of the block copolymer occurred on the substrate in step h-3).

35. The use of the copolymer according to any one of claims 1 to 29 or the composition according to claim 42, for coating a substrate, preferably in a chemoepitaxy process.