CLAIMS

1. A random copolymer of structure (A), comprising

a repeat unit of structure (I), where R_{m1} is a C-1 to C-8 alkyl, R_1 is a benzylic comprising moiety of structure (V) wherein R_{benz} is a substituent individually selected from H, a C-1 to C-4 alkyl, and a C-1 to C-4 alkoxy, L_3 is a C-1 to C-4 alkylene, and "∗" designates the attachment point of this substituent to this repeat unit, and n1 designates the number of this repeating unit in the copolymer, and further where the mole % of this repeat unit is from 40 mole % to 100 mole %,

a repeat unit of structure (II), wherein, R_{m2} is a C-1 to C-8 alkyl, R_2 is a moiety selected from a C-1 to C-20 linear alkyl, a C-3 to C-20 branched alkyl, and a C-5 to C-20 cyclic alkyl, a cyclohexylalkylene moiety of structure (VI), an anthracenylalkylene moiety of structure (VII), a naphthalenylalkylene moiety of structure (VIII), and a biphenyl moiety of structure (VIV), wherein L_4 and L_5 are independently selected from a C-1 to C-4 alkylene, L_6 and L_7 are independently selected from a direct valence bond or a C-1 to C-4 alkylene moiety, $R_{cycl,}$ R_{anth}, R_{naph}, R_{biph}, are substituents individually selected from H, a C-1 to C-4 alkyl, and a C-1 to C-4 alkoxy, n2 designates the number of this repeating unit in the copolymer, and further where the mole % of this repeat unit is from 0 mole % to 60 mole %, and further wherein the total mole % of the repeat units in said copolymer of repeat units of structures (I) and (II) is 100 mole %;

two end groups R_3 and R_4, wherein

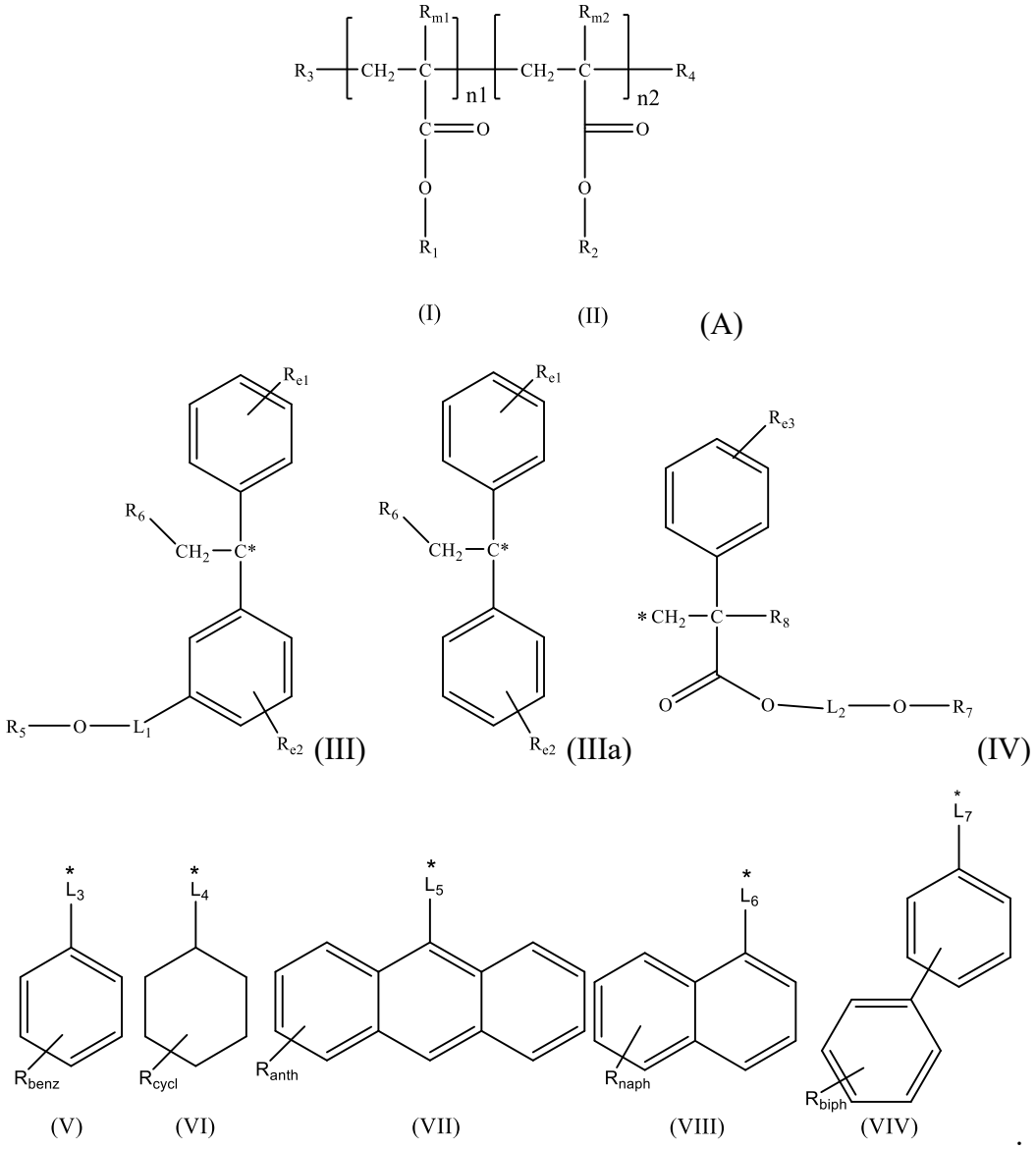
end group R_3, which is derived from an anionic initiator, wherein R_3 is either a moiety of structure (IIIa), or is a moiety of structure (III), wherein L_1 is a C-1 to C-8 alkylene, and R_5 is H, an acetal protecting group, or a trialkylsilyl protecting group, R_6 is a C-1 to C-8 alkyl, and R_{e1} and R_{e2} are individually selected from H, a C-1 to C-8 alkyl, and a C-1 to C-8 alkoxy, and "∗" designates the attachment point of this end group to said copolymer of structure (A), and

wherein R_4 is either selected from the group consisting of H, a C-1 to C-8 alkyl, C-1 to C-8 alkylcarbonyl (alkyl-C(=O)-), a C-1 to C-8 trialkylsilyl ($(alkyl)_3Si$), a C-1 to C-8 dialkylsilyl ($(alkyl)_2HSi$), a C-1 to C-8 monoalkylsilyl- ($(alkyl)H_2Si$-), silane (-H_3Si-), and a benzylic moiety, or is a moiety of structure (IV), wherein L_2 is a C-2 to C-8 alkylene, and R_7 is H, an acetal protecting group, or a trialkylsilyl protecting group, R_8 is selected from the group consisting of H, a C-1 to C-8 alkyl, C-1 to C-8 alkylcarbonyl (alkyl-C(=O)-), a C-1 to C-8 trialkylsilyl ($(alkyl)_3Si$), a C-1 to C-8 dialkylsilyl ($(alkyl)_2HSi$), a C-1 to C-8 monoalkylsilyl- ($(alkyl)H_2Si$-), silane (-H_3Si-

), and a benzylic moiety and R_{e3} is selected from H, a C-1 to C-8 alkyl, and a C-1 to C-8 alkoxy, and "*" designates the attachment point of the end group to said copolymer of structure (A), and further, wherein

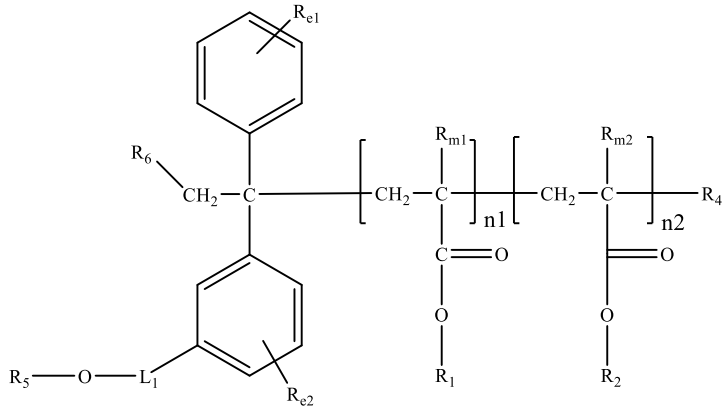
both R_3 and R_4 cannot, simultaneously, be respectively selected from a moiety of structure (III), and a moiety of structure (IV), and

either R_3 is a moiety of structure (III) or R_4 is a moiety of structure (IV):



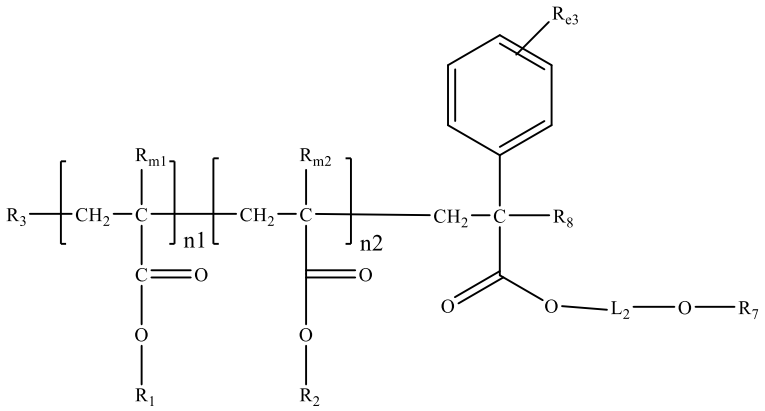
2. The copolymer of claim 1, wherein said copolymer has structure (A-1), wherein R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, C-1 to C-8 alkylcarbonyl (alkyl-C(=O)-

), a C-1 to C-8 trialkylsilyl ((alkyl)$_3$Si), a C-1 to C-8 dialkylsilyl ((alkyl)$_2$HSi), a C-1 to C-8 monoalkylsilyl- ((alkyl)H$_2$Si-), silane (-H$_3$Si-), and a benzylic moiety:



(I) (II) (A-1).

3. The copolymer of claim 1, wherein said copolymer has structure (A-2), wherein R$_8$ is selected from the group consisting of H, a C-1 to C-8 alkyl, C-1 to C-8 alkylcarbonyl (alkyl-C(=O)-), a C-1 to C-8 trialkylsilyl ((alkyl)$_3$Si), a C-1 to C-8 dialkylsilyl ((alkyl)$_2$HSi), a C-1 to C-8 monoalkylsilyl- ((alkyl)H$_2$Si-), silane (-H$_3$Si-), and a benzylic moiety:



(I) (II) (A-2).

4. The copolymer of claim 1, wherein said repeat unit of structure (I) is 100 mole % of the repeat units and said repeat unit of structure (II) is 0 mole %.

5. The copolymer of claim 1, wherein said repeat unit of structure (II) is present.

6. The copolymer of claim 1, wherein said repeat unit of structure (II) is one wherein R$_2$ is a cyclohexylalkylene moiety of structure (VI).

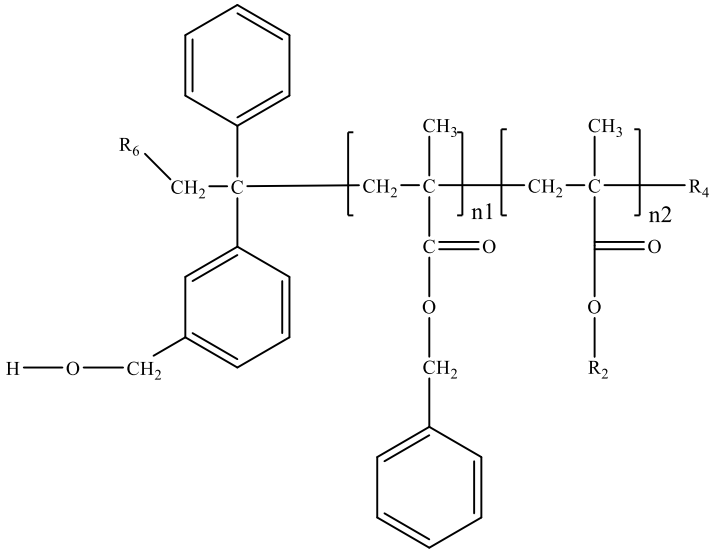
7. The copolymer of claim 1, wherein said repeat unit of structure (II) is one wherein R_2 is an anthracenylalkylene moiety of structure (VII).

8. The copolymer of claim 1, wherein said repeat unit of structure (II) is one wherein R_2 is a naphthalenylalkylene moiety of structure (VIII).

9. The copolymer of claim 1, wherein said repeat unit of structure (II) is one wherein R_2 is a biphenyl moiety of structure (VIV).

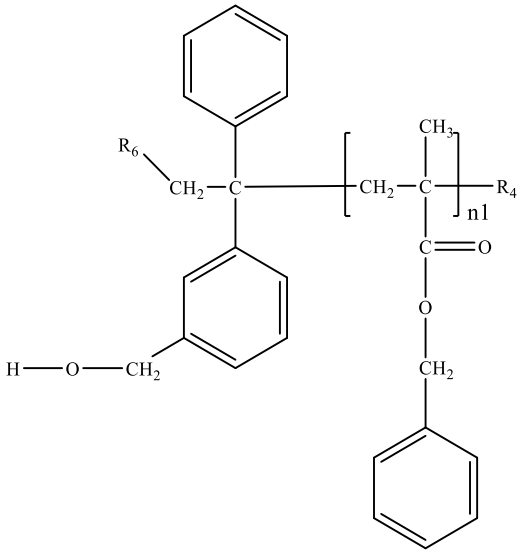
10. The copolymer of claim 1, wherein R_3 has structure (III) and L_1 is a C-1 to C-2 alkylene.

11. The copolymer of claim 1, wherein said copolymer has structure (A-3):



(Ia) (II) (A-3).

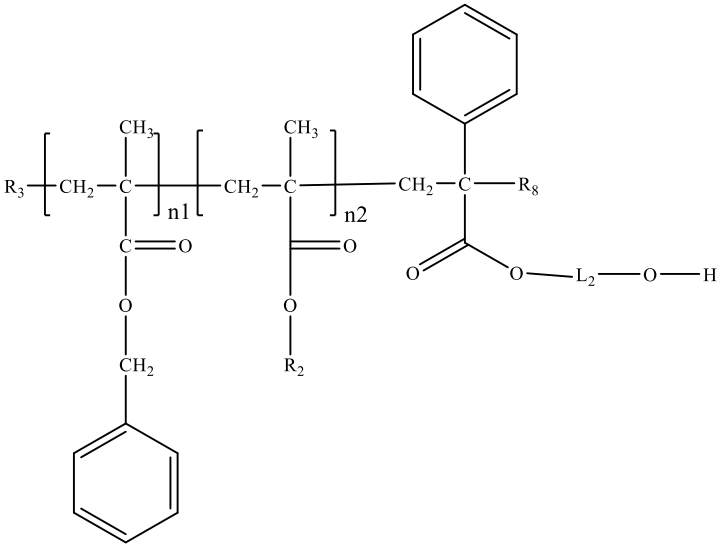
12. The copolymer of claim 1, wherein said copolymer has structure (A-6):



(Ia) (A-6).

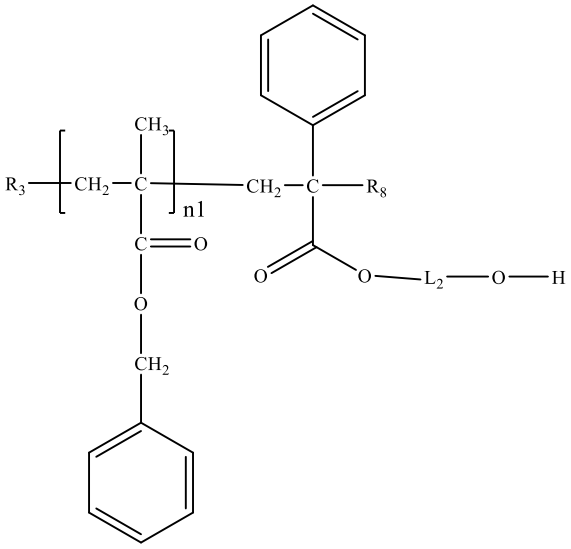
13. The copolymer of claim 1, wherein R_4 has structure (IV) and L_2 is a C-2 to C-4 alkylene.

14. The copolymer of claim 1, wherein said copolymer has structure (A-9):



(Ia) (II) (A-9).

15. The copolymer of claim 1, wherein said copolymer has structure (A-12):



(Ia) (A-12).

16. The copolymer of claim 1, which comprises both repeat units of structures (I) and (II), wherein said repeat unit of structure (II) ranges from 1 mole % to 60 mole % of the total repeat units of structure (I) and (II).

17. The copolymer of claim 1, which comprises both repeat units of structures (I) and (II), wherein said repeat unit of structure (II) ranges from 5 mole % to 50 mole % of the total repeat units of structure (I) and (II).

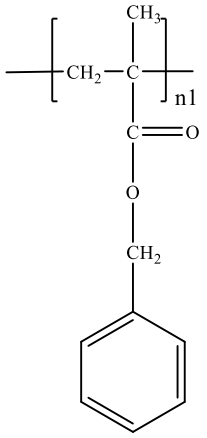
18. The copolymer of claim 1, which comprises both repeat units of structures (I) and (II), wherein said repeat unit of structure (II) ranges from 7 mole % to 40 mole % of the total repeat units of structure (I) and (II).

19. The copolymer of claim 1, which comprises both repeat units of structures (I) and (II), wherein said repeat unit of structure (II) ranges from 9 mole % to 40 mole % of the total repeat units of structure (I) and (II).

20. The copolymer of claim 1, which comprises both repeat units of structures (I) and (II), wherein said repeat unit of structure (II) ranges from 10 mole % to 30 mole % of the total repeat units of structure (I) and (II).

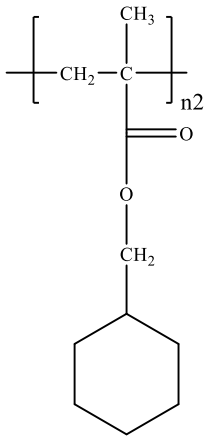
21. The copolymer of claim 1, which comprises both repeat units of structures (I) and (II), wherein said repeat unit of structure (II) ranges from 10 mole % to 25 mole % of the total repeat units of structure (I) and (II).

22. The copolymer of claim 17, wherein said repeat unit of structure (I) has the more specific structure (Ia),



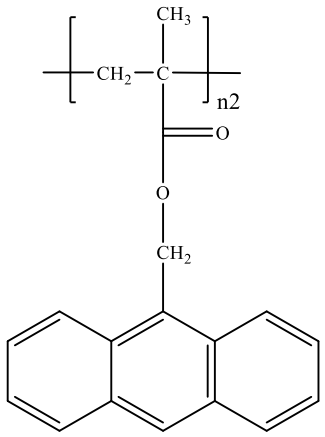
(Ia)

23. The copolymer of claim 17, wherein said repeat unit of structure (II) has the more specific structure (IIa),



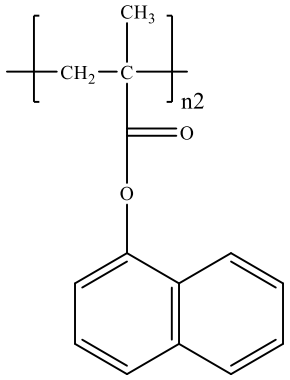
(IIa)

24. The copolymer of claim 17, wherein said repeat unit of structure (II) has the more specific structure (IIb)



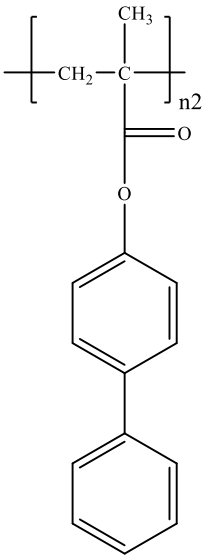
(IIb) .

25. The copolymer of claim 17, wherein said repeat unit of structure (II) has the more specific structure (IIc)



(IIc) .

26. The copolymer of claim 17, wherein said repeat unit of structure (II) has the more specific structure (IId)



(IId)

27. A composition comprising:

a copolymer of claim 1, and an organic spin casting solvent, wherein said copolymer is one wherein either end group (III) is present and R_5 is H or end group (IV) is present and R_7 is H.

28. A process for forming a grafted coating of a copolymer on a substrate comprising the steps:

i) forming a coating of a composition of claim 27 on a substrate,

ii) heating the coating at a temperature from 90°C to 180°C to remove solvent and to form a grafted coating of the copolymer,

iii) heating the grafted coating of step ii) from 200°C to 250°C to form a fully cross-linked or fully crosslinked and grafted copolymer coating.

29. A process for forming a grafted neutral layer coating on a substrate comprising the steps:

ia) forming a coating of a composition of claim 27 on a substrate,

iia) heating the coating at a temperature from 90°C to 180°C to remove solvent and to form a grafted coating,

iiia) heating the grafted coating of step iia) at a temperature from 200°C to 250°C to form a fully grafted neutral layer coating.

30. A process for forming a self-assembled block copolymer coating on a neutral layer coating comprising the steps:

ij) forming neutral layer coating according to claim 29,

iij) applying a block copolymer over the neutral layer coating and annealing until directed self-assembly of the block copolymer coating occurs.

31. A process of graphoepitaxy, directed self-assembly of a block copolymer coating used to form an image comprising the steps:

ik) forming neutral layer coating according to claim 29,

iik) providing a coating of a photoresist coating over the neutral layer coating,

forming a pattern in the photoresist coating,

iiik) applying a block copolymer comprising an etch resistant block and a highly etchable block over the photoresist pattern and annealing until directed self-assembly occurs; and,

ivk) etching the block copolymer, thereby removing the highly etchable block of the copolymer overcoating areas of the substrate and simultaneously forming a pattern in the substrate selectively in these areas.

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

il) forming neutral layer coating on as substrate according claim 29,

iil) providing a coating of a photoresist coating over the neutral layer coating,

forming a pattern in the photoresist coating, thereby forming regions in which the neutral layer coating is uncovered by the resist,

iiil) treating the uncovered neutral layer coating to remove it, forming a pinning area,

ivl) removing the photoresist, uncovering the unaffected neutral layer coating forming a chemoepitaxy pattern containing neutral and pinning areas,

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

vil) etching the block copolymer, thereby removing the highly etchable block of the copolymer overcoating areas of the substrate and simultaneously forming a pattern in the substrate selectively in these areas.