CLAIMS

What is claimed is:

1. A polymer of structure (II), wherein

R_1 is H, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, an aryl, or an alkylenearyl;

R_2 is H, a halide, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy, a C-3 to C-8 cyclic alkyloxy, or -P(=O)(R_3)(R_4);

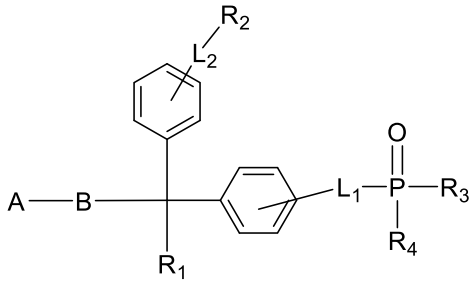
R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy;

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group;

B is a direct valence bond, or a methylene spacer (-CH_2-)

A is a styrenic polymer chain, or an acrylic polymer chain; and

said polymer has a polydispersity ranging from 1 to 1.1;



(II).

2. The polymer of claim 1, wherein

R_1 is H;

R_2 is H, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy, a C-3 to C-8 cyclic alkyloxy, or -P(=O)(R_3)(R_4);

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy;

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group; and

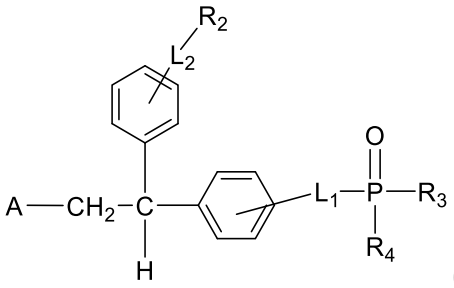
A is a styrenic polymer chain.

3. The polymer of claims 1 or 2, having structure (IIa), wherein

R_2 is H, or -P(=O)(R_3)(R_4);

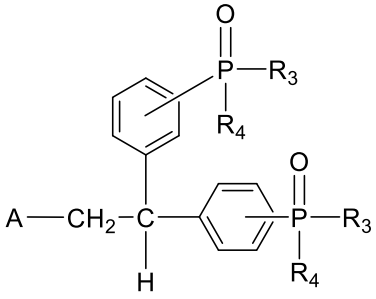
R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group;



(IIa).

4. The polymer of claim 3 which has structure (IIb);

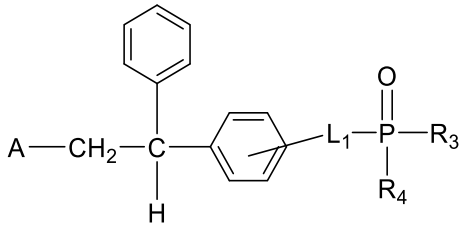


(IIb).

5. The polymer of claims 1 or 2, wherein it has structure (IIc), wherein

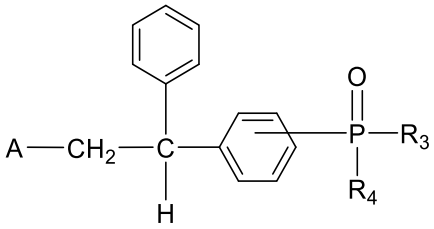
R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 is a direct valence bond, or a C-1 to C-8 alkylene spacer group;



(IIc).

6. The polymer of claim 5, which has structure (IId);



(IId).

7. The polymer of claim 1, wherein

R_1 is a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl or a C-3 to C-8 cyclic alkyl, an aryl, an alkylenearyl;

R_2 is H, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy, a C-3 to C-8 cyclic alkyloxy, or $-P(=O)(R_3)(R_4)$;

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy;

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group; and

A is an acrylic polymer chain.

8. The polymer of claims 1 or 7, wherein it has structure (IIf), wherein

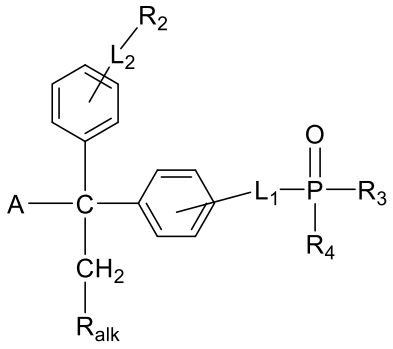
R_{alk} is a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl;

R_2 is H, or $-P(=O)(R_3)(R_4)$;

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic

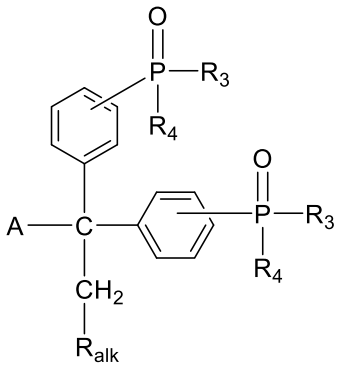
alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group;



(IIf).

9. The polymer of claim 8, which has structure (IIg);

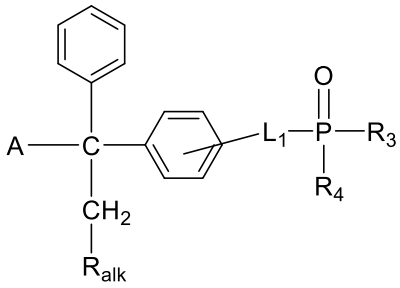


(IIg).

10. The polymer of claims 1 or 7, wherein it has structure (IIh), wherein

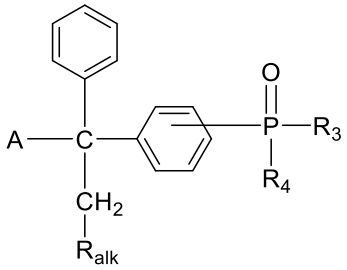
R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 is a direct valence bond, or a C-1 to C-8 alkylene spacer group;



(IIh).

11. The polymer of claim 10, wherein L_1 and L_2 are both a direct valence bond and the polymer of structure (II) has structure (IIi);



(IIi).

12. The polymer of any one of claims 1 to 6, wherein said polymer is a styrenic polymer having structure (III), wherein

R_{e1} is H, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, an aryl, or an alkylenearyl;

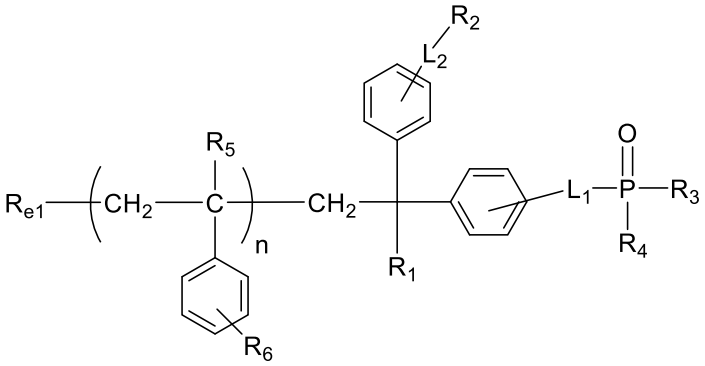
R_2 is H, a halide, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy, a C-3 to C-8 cyclic alkyloxy, or -P(=O)(R_3)(R_4);

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy;

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group;

R_5 is H, a C-1 to C-4 linear alkyl; R_6 is H, a halide, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy ; n is the number of repeat units; and

said styrenic polymer has a polydispersity ranging from 1 to 1.1;



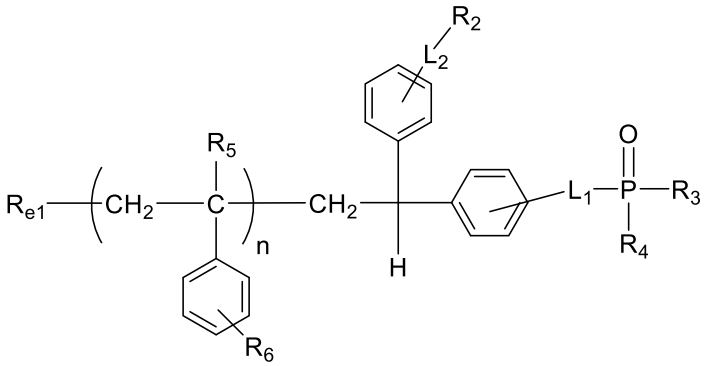
(III).

13. The polymer of claim 12, wherein it has structure (IIIa), wherein

R_2 is H, or -P(=O)(R_3)(R_4);

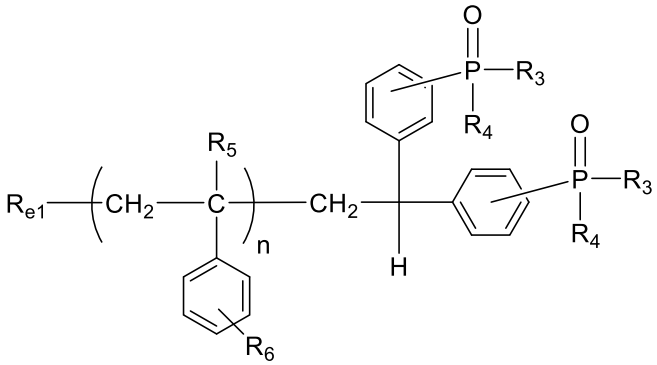
R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group;



(IIIa).

14. The polymer of claim 13, which has structure (IIIb);

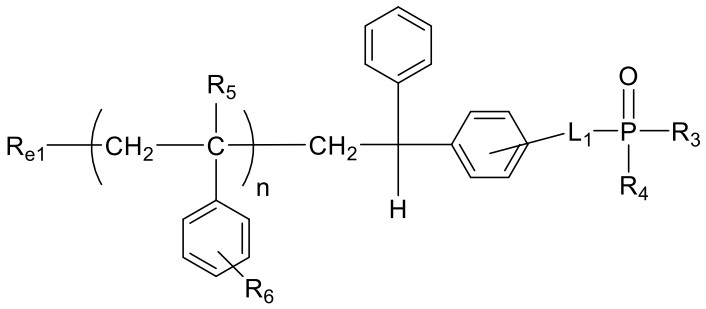


(IIIb).

15. The polymer of claim 12 or 13, wherein it has structure (IIIc), wherein

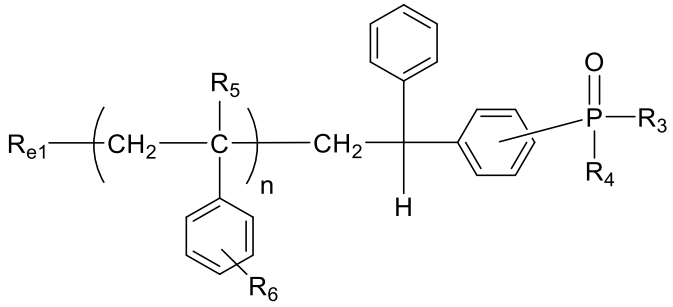
R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 is a direct valence bond, or a C-1 to C-8 alkylene spacer group;



(IIIc).

16. The polymer of claim 15, wherein L_1 is a direct valence bond and has structure (IIId);



(IIId).

17. The polymer of any one of claims 1 or 7 to 11 wherein said polymer is an acrylic polymer having structure (IV), wherein

R_{alk} is a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl or a C-3 to C-8 cyclic alkyl;

R_2 is H, a halide, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy, a C-3 to C-8 cyclic alkyloxy, or $-P(=O)(R_3)(R_4)$;

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy;

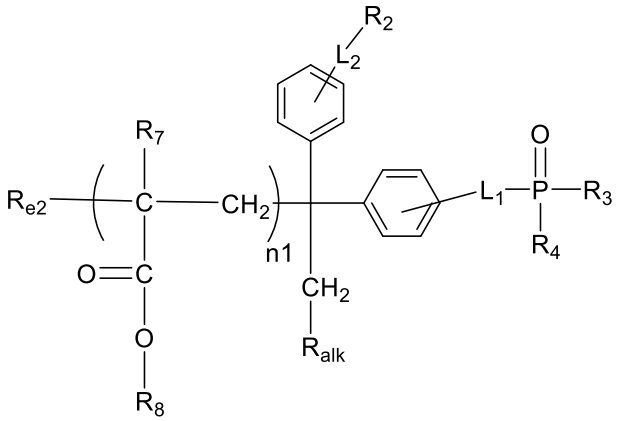
L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group;

R_7 is H or a C-1 to C-4 linear alkyl;

R_8 is a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl or a C-3 to C-8 cyclic alkyl;

R_{e2} is and end group selected from H, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, or a C-3 to C-8 cyclic alkyl;

n1 is the number of repeat units in said acrylate polymer of structure (IV); and said acrylic polymer has a polydispersity ranging from 1 to 1.1;



(IV).

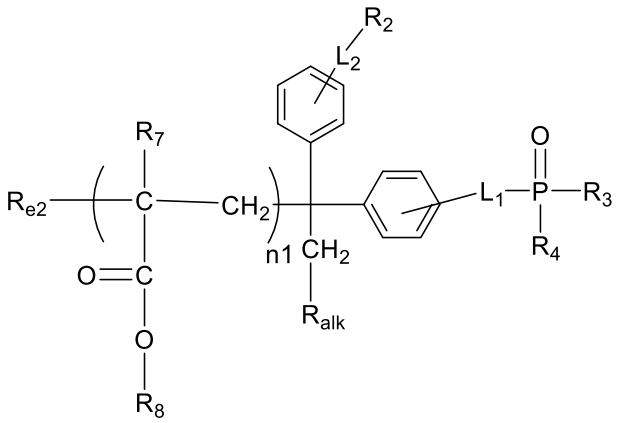
18. The polymer of claim 17, wherein it has structure (IVa), wherein

R_{alk} is a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl;

R_2 is H, or -P(=O)(R_3)(R_4);

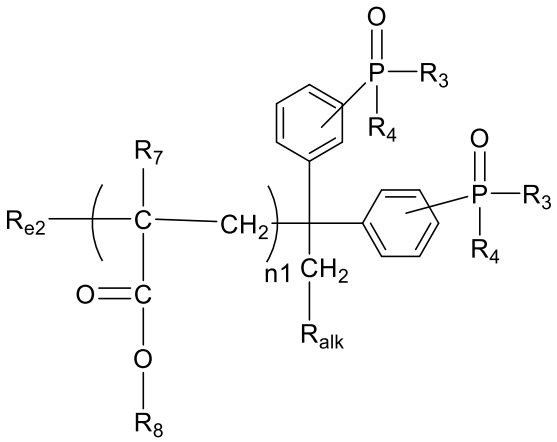
R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group;



(IVa).

19. The polymer of claim 18, which has structure (IVb);

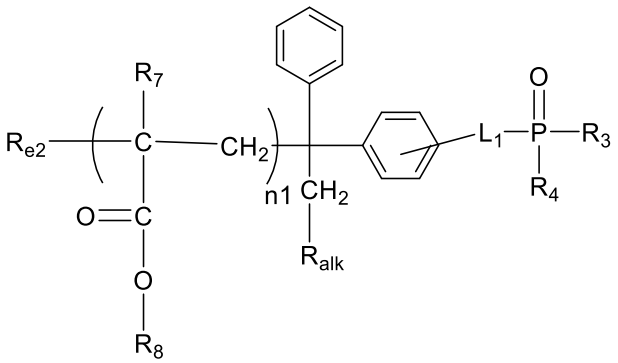


(IVb).

20. The polymer of claim 17, wherein it has structure (IVc), wherein

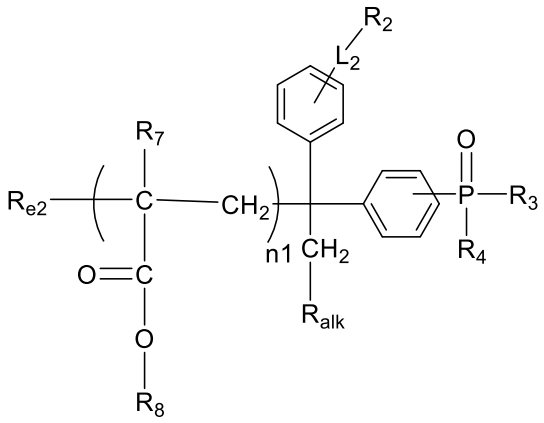
R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 is a direct valence bond, or a C-1 to C-8 alkylene spacer group;



(IVc).

21. The polymer of claims 17 to 20, wherein L_1 is a direct valence bond and the polymer has structure (IVd);



(IVd).

22. A composition comprising a polymer according to any one of claims 1 to 21 and a spin casting solvent.

23. A process of forming a pinning layer brush selectively on a substrate which comprises both metallic surface areas and a non-metallic surface area, comprising the steps;

i) coating said composition according to claim 22, on a said substrate, forming a film,

ii) baking said film at a temperature from 120°C to 250°C for 1 minute to 1 hour, to form a baked film,

iii) washing said baked film with a solvent to remove ungrafted polymer, forming a pinning layer brush only on said metallic surface areas of said substrate.

24. A process comprising the steps;

ia) coating said composition according to claim 22, on a substrate which comprises both metallic surface areas and non-metallic surface areas, forming a film,

iia) baking said film at a temperature from 120°C to 250°C for 1 minute to 1 hour, to form a baked film,

iiia) washing said baked film with a solvent to remove ungrafted polymer, forming a grafted substrate wherein pinning layer brushes are only present on said metallic surface areas of said substrate,

iva) coating said grafted substrate with a neutral layer composition, forming a neutral layer coating,

va) curing said neutral layer coating,

via) washing away, with a solvent, uncured neutral layer, leaving in said non-metallic areas of said substrate a neutral directing brush forming on said substrate a chemoepitaxy directing layer,

viia) coating said chemoepitaxy directing layer with a block copolymer solution, forming a coating of block copolymer,

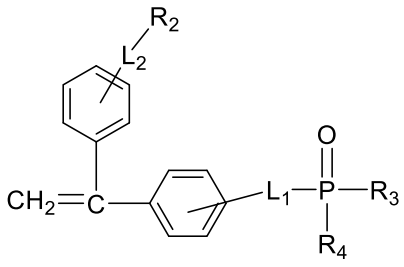
viiia) annealing said coating of block copolymer, to form a directed self-assembled film of the block copolymer on said chemoepitaxy directing layer.

25. The use of a compound of structure (I), wherein

R_2 is H, a halide, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy, a C-3 to C-8 cyclic alkyloxy, or -P(=O)(R_3)(R_4);

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group;



(I)

for the preparation of a polymer according to any one of claims 1 to 21.

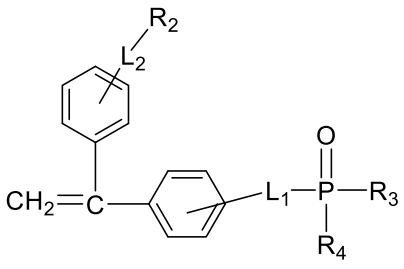
26. The use of a polymer according to any one of claims 1 to 21 or of the composition of claim 22 for forming a pinning layer brush on a substrate.

27. A compound of structure (I), wherein

R_2 is a halide, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy, a C-3 to C-8 cyclic alkyloxy, or -P(=O)(R_3)(R_4);

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group;



(I).

28. The compound of claim 27, wherein

R_2 is a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy, a C-3 to C-8 cyclic alkyloxy, or -P(=O)(R_3)(R_4);

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group.

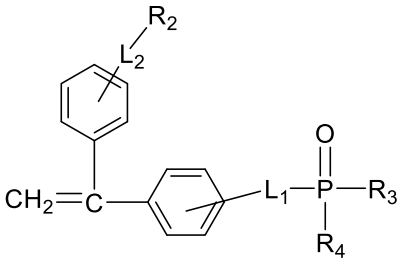
29. The compound of claims 27 or 28, wherein said compound has structure (Ia), wherein

R_2 is -P(=O)(R_3)(R_4);

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic

alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

L_1 and L_2 are independently a direct valence bond, or a C-1 to C-8 alkylene spacer group;

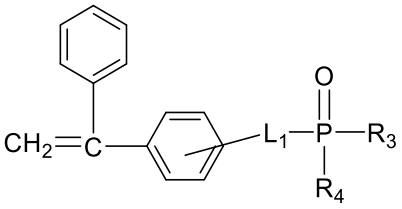


(Ia).

30. A compound of structure (Ib), wherein

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy; and

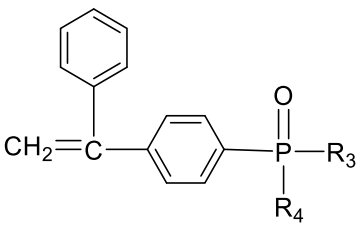
L_1 is a C-1 to C-8 alkylene spacer group;



(Ib).

31. A compound of structure (Id), wherein

R_3 and R_4 are independently an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy or a C-3 to C-8 cyclic alkyloxy;



(Id).