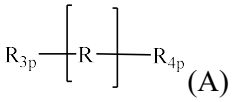
CLAIMS

What is claimed is:

1. A polymer of structure (A),



(A)

comprising two end groups R_{3p} and R_{4p}, and a polymer chain (R) comprising either a repeat unit of structure (Ip) or a repeat unit of structure (IIp), wherein

end group R_{3p}, which is derived from an anionic initiator, is either a C-1 to C-8 alkyl, a moiety of structure (IIIp), or a moiety of structure (IIIp1), but where **R_{3p}** can only be selected from a C-1 to C-8 alkyl if the in the polymer chain (R) the repeat unit is (IIp), and further where **R_{3p}** can only be selected from a moiety of structure (IIIp) or structure (IIIp1) if in the polymer chain (R) the repeat unit is of structure (Ip),

end group R_{4p} is either a moiety 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 dialkysilyl ((alkyl)$_2$HSi-), a C-1 to C-8 monoalkylsilyl ((alkyl)H$_2$Si-), silane (H$_3$Si-), and a benzylic moiety, a moiety of structure (IVp), a moiety of structure (IVp1) or a moiety of structure (IVp2), further end groups R_{3p} and R_{4p} cannot respectively, both simultaneously be moieties of structure (IIIp) and (IVp), both simultaneously be moieties of structure (IIIp) and (IVp1), or both simultaneously be moieties of structure (IIIp) and (IVp2), but where said polymer of structure (A) must contain one end group moiety selected from structures (IIIp), (IVp), (IVp1) or (IVp2),

in said repeat unit of structure (Ip) R_{m1} is a C-1 to C-8 alkyl, R_{1p} is a C-1 to C-8 alkyl, and n1 is the number of this repeat units in polymer chain (R);

in said repeat unit of structure (IIp) R_{m2} is H or a C-1 to C-8 alkyl, R_{2p} is H or a C-1 to C-8 alkyl, n2 is the number of this repeat unit polymer chain (R); and

in structure (IIIp),

R_1 is a chelating group, located at the para or meta position, selected from a phosphinothioic moiety of structure (Ia) an aminosulfonyl moiety of structure (Ib), a phosphonamide moiety of structure (Ic), where *** designates the attachment point of this end group moiety to the polymer of structure (A), wherein

in said phosphinothioic moiety of structure (Ia), 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 a dialkyl amino moiety, -N(R_9)(R_{10}), in which R_9 and R_{10} are independently selected from a C-1 to C-8 linear alkyl, a

C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, and ∗ designates the attachment point of this moiety to an end group moiety of structure of (IIIp),

in said aminosulfonyl moiety of structure (Ib), R_5 and R_6, are independently a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, and said dialkyl amino moiety, -$N(R_9)(R_{10})$, and ∗ designates the attachment point of this moiety to an end group moiety of structure of (IIIp),

in said phosphonamide moiety of structure (Ic), R_7 is said dialkyl amino moiety, -$N(R_9)(R_{10})$, and R_8 is selected from the group consisting of 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 ∗ designates the attachment point of this moiety to an end group moiety of structure of (IIIp),

R_2 is selected from the group consisting of H, 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, a C-3 to C-8 cyclic alkyloxy; a phosphinothioic moiety of structure (Ia), an aminosulfonyl of structure (Ib), and a phosphonamide of structure (Ic), and

R_{15} 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,

in structure (IIIp1),

R_{e1} and R_{e2} are individually selected from H, 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, a C-3 to C-8 cyclic alkyloxy, and R_{15} is a C-1 to C-8 alkyl, and *** designates the attachment point of this end group moiety to the polymer of structure (A),

in structure (IVp),

R_{12} is H or a C-1 to C-4 alkyl,

R_{11} is a phosphinothioic moiety of structure (IIa), wherein ∗ designates the attachment point of this phosphinothioic moiety to structure (IVp), wherein

R_{13} and R_{14} are independently selected from the group consisting of 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, a C-3 to C-8 cyclic alkyloxy; and a dialkyl amino moiety, -$N(R_9)(R_{10})$, in which R_9 and R_{10} are independently selected from a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl,

L_1 is a linking moiety selected from the group consisting of a direct valence bond, a C-2 to C-8 alkylene moiety(-alkylene-), an arylene moiety (-aryl-), an alkyleneoxyaryl moiety (*-alkylene-O-aryl-**), an alkylenearyl moiety (*-alkylene-aryl-**), wherein ** designates the attachment points of the L_1 organic linking moiety to the phosphorous in structure (IIa), and * designates where L_1 within the moiety R_{11} is attached to carbonyloxy of structure (IVp),

R_{17} 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 dialkysilyl ((alkyl)$_2$HSi-), a C-1 to C-8 monoalkylsilyl ((alkyl)H$_2$Si-), silane (H$_3$Si-), and a benzylic moiety, and *** designates the attachment point of this end group moiety to the polymer of structure (A),

in structure (IVp1),

L is either a direct valence bond or a linking group selected from a C-1 to C-8 linear alkylene, C-3 to C-8 branched alkylene, and a C-5 to C-8 cyclic alkylene, an alkyleneoxyaryl moiety (*-alkylene-O-aryl-**), and an alkylenearyl moiety (*-alkylene-aryl-**), wherein ** designates the attachment points of the L linking moiety to the phosphorous in structure (IVp1), and * designates where L is attached to said polymer of structure (A), and Rs and Rs1 are individually selected from a C-1 to C-8 alkoxy or a C-1 to C-8 alkyl, and where *** designates the attachment point of this end group moiety to the polymer of structure (A),

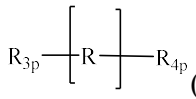
in structure (IVp2),

R_1 is a chelating group, located at the para or meta position, selected from said phosphinothioic moiety of structure (Ia) said aminosulfonyl moiety of structure (Ib), and said phosphonamide moiety of structure (Ic),

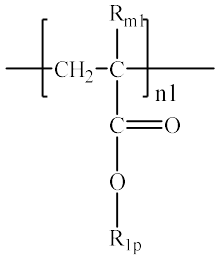
R_2 is selected from the group consisting of H, an aryl, an alkylenearyl, a C-2 to C-8 alkyleneoxyalkyl, a C-2 to C-8 haloalkyl, a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, a C-1 to C-8 linear alkyloxy, a C-3 to C-8 branched alkyloxy, a C-3 to C-8 cyclic alkyloxy; a phosphinothioic moiety of structure (Ia), an aminosulfonyl of structure (Ib), and a phosphonamide of structure (Ic), R_{18} 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 dialkysilyl ((alkyl)$_2$HSi-), a C-1 to C-8 monoalkylsilyl ((alkyl)H$_2$Si-), silane (H$_3$Si-), and a benzylic moiety,

and where *** designates the attachment point of this end group moiety to the polymer of structure (A),

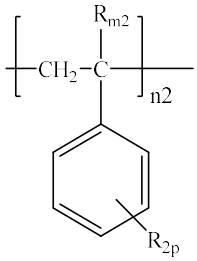
further, said polymer of structure (A) has a M_n ranging from about 4000 to about 7000, and has a polydispersity ranging from 1 to about 1.15;



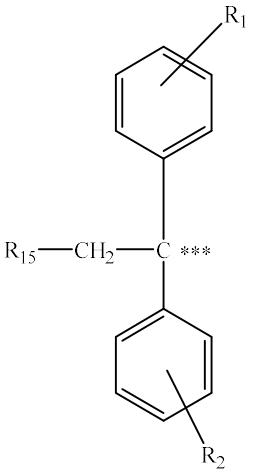
(A)



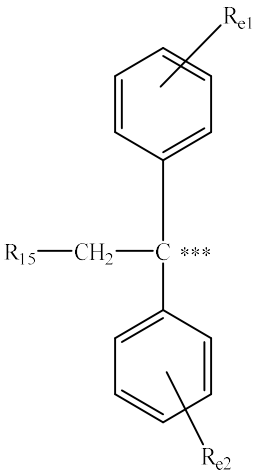
(Ip)



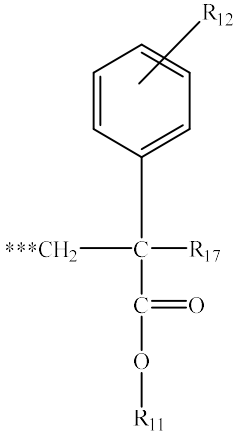
(IIp)



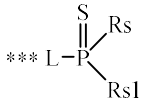
(IIIp)



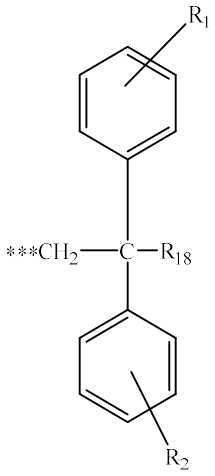
(IIIp1)



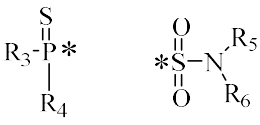
(IVp)



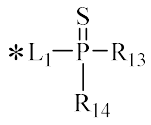
(IVp1)



(IVp2)

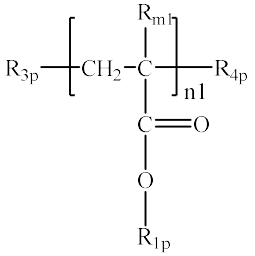


(Ia) (Ib) (Ic)



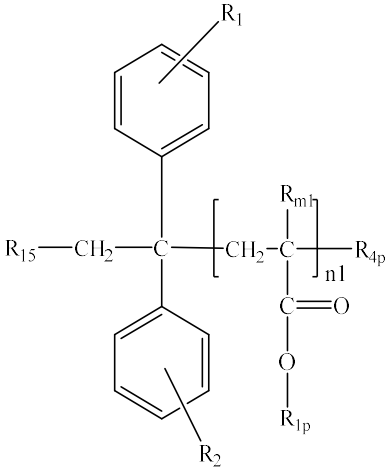
(IIa)

2. The polymer of claim 1, which has structure (A-1),



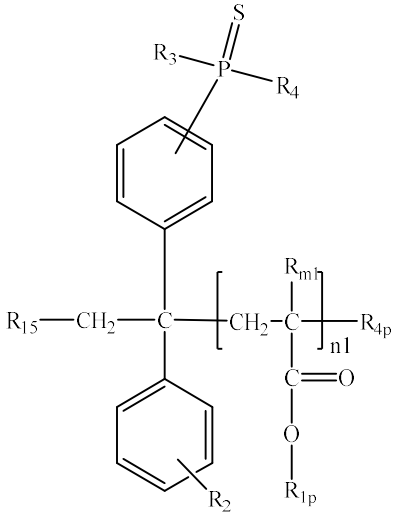
(Ip) (A-1).

3. The polymer of claim 1, which has structure (A-2),



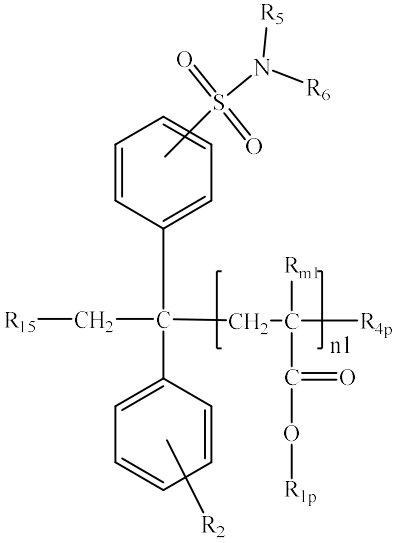
(IIIp) (Ip) (A-2).

4. The polymer of claim 1, which has structure (A-2a)



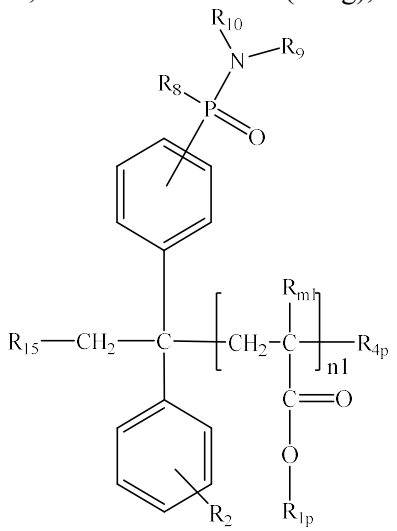
(IIIpa) (Ip) (A-2a).

5. The polymer of claim 1, which has structure (A-2d),



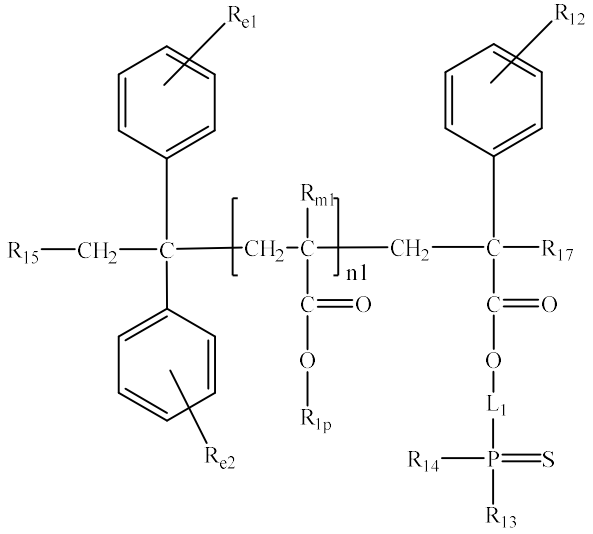
(IIIpd) (Ip) (A-2d).

6. The polymer of claim 1, which has structure (A-2g),



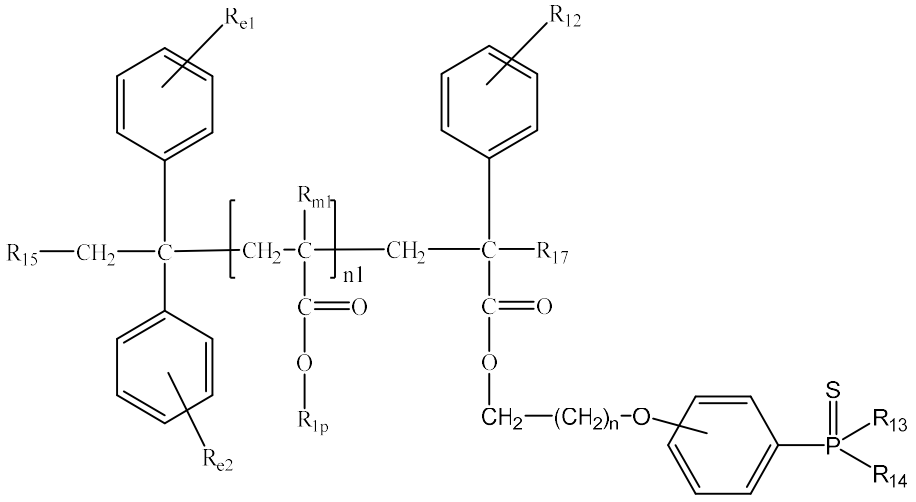
(IIIpg) (Ip) (A-2g).

7. The polymer of claim 1, which has structure (A-3)



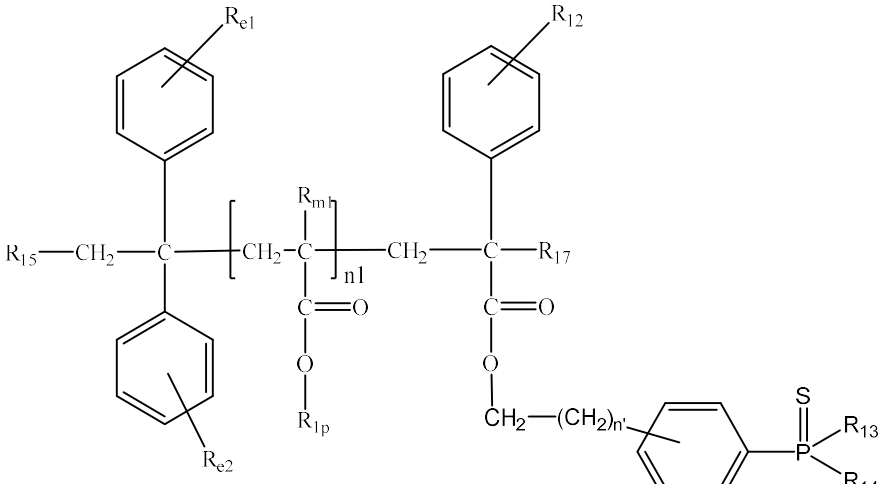
(IIIpa) (Ip) (IVpa) (A-3).

8. The polymer of claim 1, which has structure (A-3a) wherein R_{13} and R_{14} are independently selected from a C-1 to C-8 alkyl or alkoxy-and n is an integer ranging from 1 to 7,



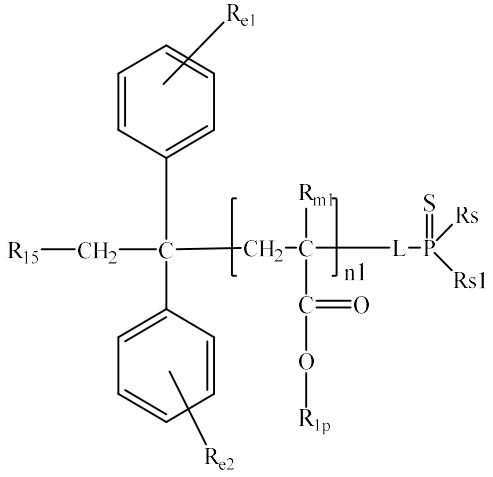
(IIIp1) (Ip) (IVpb) (A-3a).

9. The polymer of claim 1, which has structure (A-3c), wherein R_{13} and R_{14} are independently selected from a C-1 to C-8 alkyl or alkoxy, and n' is an integer ranging from 0 to 7,



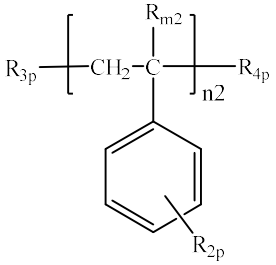
(IIIp1) (Ip) (IVpd) (A-3c).

10. The polymer of claim 1, which has structure (A-4),



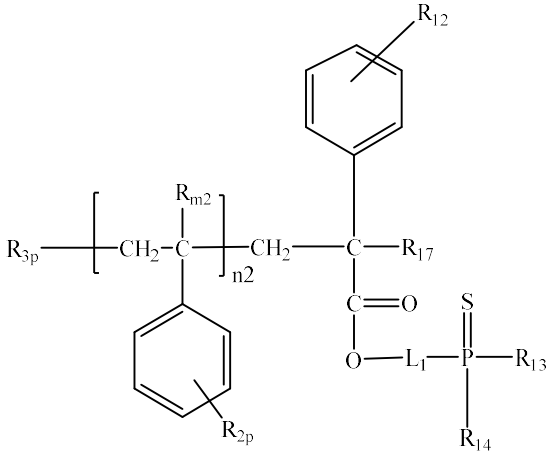
(IIIpa) (Ip) (IVp1) (A-4).

11. The polymer of claim 1, which has structure (B-1), wherein R_{3p} is a C-1 to C-8 alkyl,



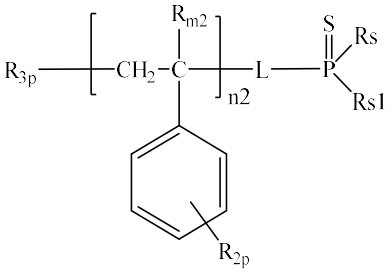
(IIp) (B-1).

12. The polymer of claim 1, which has structure (B-1a), wherein R_{3p} is a C-1 to C-8 alkyl,



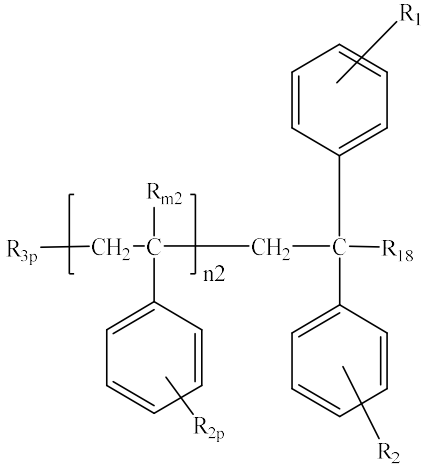
(IIp) (IVpa) (B-1a).

13. The polymer of claim 1, which has structure (B-2),



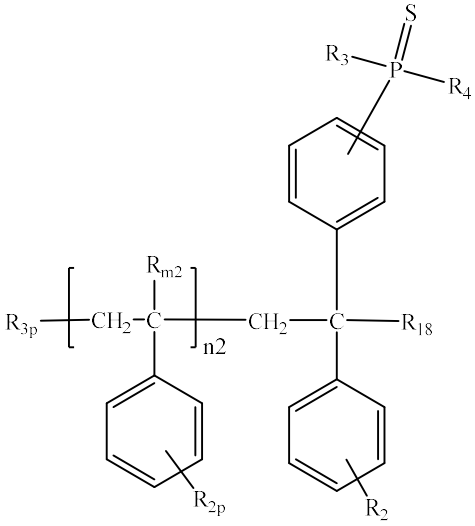
(IIp) (IVp1a) (B-2).

14. The polymer of claim 1, which has structure (B-3),



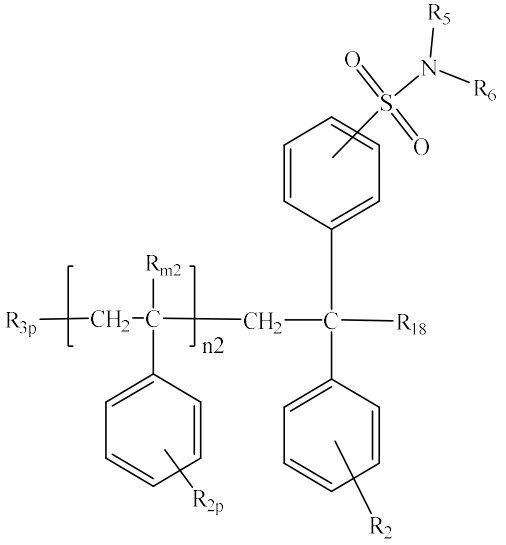
(IIp) (Vp) (B-3).

15. The polymer of claim 1, which has structure (B-3a)



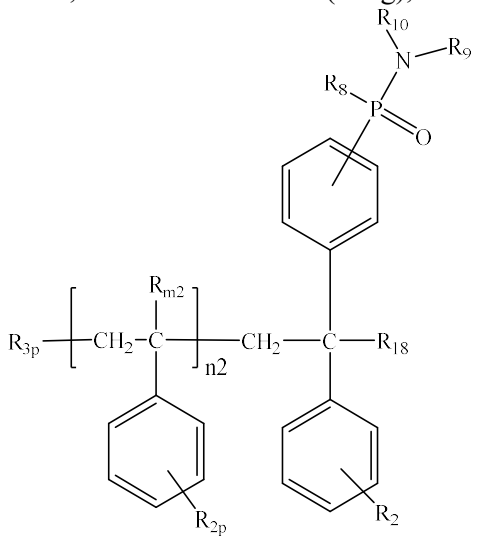
(IIp) (Vpa) (B-3a).

16. The polymer of claim 1, which has structure (B-3d),



(IIp) (Vpd) (B-3d).

17. The polymer of claim 1, which has structure (B-3g),



(IIp) (Vpg) (B-3g).

18. A composition comprising a polymer of claim 1 and an organic spin casting solvent.

19. A composition comprising a polymer of claim 2 and an organic spin casting solvent.

20. A composition comprising a polymer of claim 3and an organic spin casting solvent.

21. A composition comprising a polymer of claim 7 and an organic spin casting solvent.

22. A composition comprising a polymer of claim 10 and an organic spin casting solvent.

23. A composition comprising a polymer of claim 11, and an organic spin casting solvent.

24. A composition comprising a polymer of claim 12 and an organic spin casting solvent.

25. A composition comprising a polymer of claim 13 and an organic spin casting solvent.

26. A composition comprising a polymer of claim 14 and an organic spin casting solvent.

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

i) coating the composition of claim 18 on a said substrate forming a film,

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

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.

28. A process comprising the steps;

ia) coating a composition according of claim 18, 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 about 120°C to about 250°C for about 1 minute to about 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 brush 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,

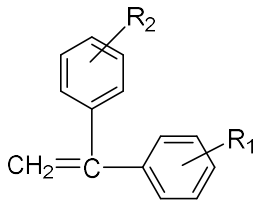
va) curing said neutral layer coating,

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

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

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

29. A compound of structure (I),



(I)

wherein

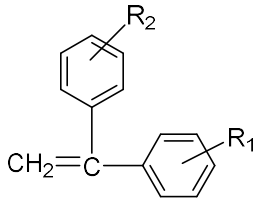
R_1 is a chelating group located at the meta or para position selected from a phosphinothioic moiety of structure (Ia) an aminosulfonyl moiety of structure (Ib), a phosphonamide moiety of structure (Ic) wherein ∗ designates the attachment point of these moieties to said compound of structure (I), wherein

in said phosphinothioic moiety of structure (Ia), 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 a dialkyl amino moiety, -$N(R_9)(R_{10})$, in which R_9 and R_{10} are independently selected from a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl,

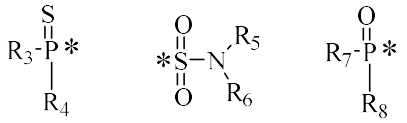
in said aminosulfonyl moiety of structure (Ib), R_5 and R_6, are independently a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl, and said dialkyl amino moiety, -$N(R_9)(R_{10})$,

in said phosphonamide moiety of structure (Ic), R_7 is said dialkyl amino moiety, -$N(R_9)(R_{10})$, and R_8 is selected from the group consisting of 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,

R_2 is a substituent, located at the meta or para positions which is selected from the group consisting of H, 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, a C-3 to C-8 cyclic alkyloxy; a phosphinothioic moiety of structure (Ia), an aminosulfonyl of structure (Ib), and a phosphonamide of structure (Ic)

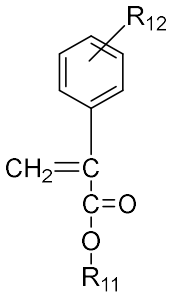


(I)



(Ia) (Ib) (Ic).

30. A compound of structure (II),



(II)

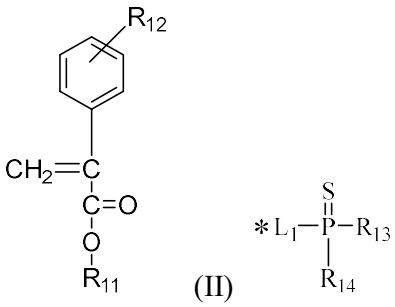
wherein

R_{11} is a phosphinothioic moiety of structure (IIa), wherein ∗ designates the attachment point of this moieties to said compound of structure (II), wherein

R_{13} and R_{14} are independently selected from the group consisting of 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, a C-3 to C-8 cyclic alkyloxy; and a dialkyl amino moiety, -N(R_9)(R_{10}), in which R_9 and R_{10} are independently selected from a C-1 to C-8 linear alkyl, a C-3 to C-8 branched alkyl, a C-3 to C-8 cyclic alkyl;

L_1 is a linking moiety selected from the group consisting of a direct valence bond, a C-2 to C-8 alkylene moiety(-alkylene-), an arylene moiety (-aryl-), an alkyleneoxyaryl moiety (*-alkylene-O-aryl-**), an alkylenearyl moiety (*-alkylene-aryl-**), wherein ** designates the attachment points of the L_1 organic linking moiety to the phosphorous in structure (IIa), and * designates where L_1 within the moiety R_{11} is attached to the carbonyloxy of compound (II),

R_{12} is H or a C-1 to C-4 alkyl,



(II)

(IIa).