CLAIMS

1. A functional polymer comprising either acrylic repeat units, styrenic repeat units or a mixture of these having a polydispersity from 1 to 1.12, determined by gel permeation chromatography, calibrated to polystyrene standards, comprising at least one reactive moiety selected from

a moiety comprising at least one N-coordinative functional group having at least one lone pair of electrons,

a moiety comprising a dialkylsilyl group, or

a mixture of both groups,

wherein said reactive moiety is present in said functional polymer either on a repeat unit, on an end group or on both, and

said N-coordinative functional group is either

a monodentate N-coordinative functional group,

a polydendate N-coordinative group or a mixture thereof, and

said monodentate N-coordinative functional group is an azide moiety ($-N_3$), or a cyano moiety (-CN) and

said polydendate N-coordinative functional group is either

a moiety comprising 2 or 3 monocyclic heteroaryl moieties, wherein each said heteroaryl individually contains 1 to 3 nitrogen hetero atoms, or

a polycyclic fused ring heteroaryl moiety containing 2 to 4 nitrogen heteroatoms,

wherein the functional polymer is obtained by anionic polymerization.

2. The functional polymer of claim 1 comprising styrenic repeat units.

3. The functional polymer of claim 1 comprising acrylic repeat units.

4. The functional polymer of claim 1 comprising a mixture of acrylic and styrenic repeat units.

5. The functional polymer of any one of claims 1 to 4, wherein said reactive moiety is said monodentate N-coordinative functional group.

6. The functional polymer of any one of claims 1 to 4, wherein said reactive moiety is said polydentate N-coordinative functional group.

7. The functional polymer of any one of claims 1 to 4, wherein said reactive moiety is a mixture of said monodentate and polydentate N-coordinative functional groups.

8. The functional polymer of any one of claims 1 to 4, wherein said reactive moiety is said dialkylsilyl group.

9. The functional polymer of any one of claims 1, 2 and 5 having structure (I); wherein

n is the number of repeating units in the polymer;

R_1 is H or a C-1 to C-4 linear alkyl;

R_2 is selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_s is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_3 is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

a dialkylsilyl moiety [(R_{si})(R_{sia}) SiH-] wherein R_{si} and R_{sia} are independently selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

X and X_a are independently selected from

a direct valence bond,

a C-1 to C-8 linear alkylene moiety,

a C-3 to C-8 branched alkylene moiety,

a C-3 to C-8 cyclic alkylene moiety, and

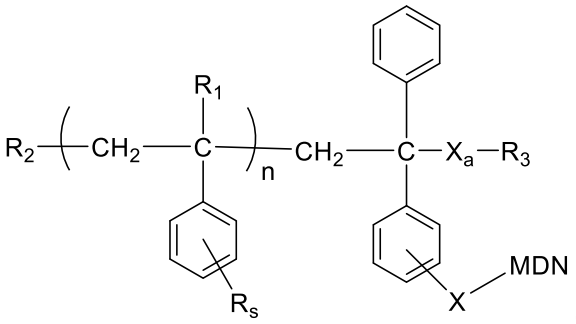
a -X_1-O-X_2- (-alkyleneoxyalkylene-) moiety wherein X_1 and X_2 are independently selected from

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene and

a C-3 to C-8 cyclic alkylene; and

MDN is an azide moiety (-N_3), or a cyano moiety (-CN);



(I).

10. The functional polymer of any one of claims 1, 2, and 5 having structure (II); wherein

na is the number of repeating units in the polymer;

R_{1a} is H or a C-1 to C-4 linear alkyl;

R_s is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{2a} is selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

X_b is selected from

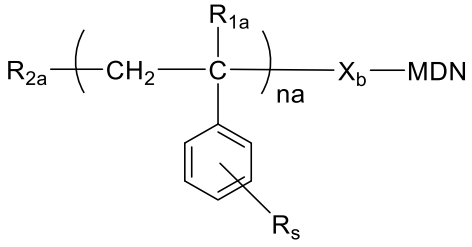
a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene,

a C-3 to C-8 cyclic alkylene and

a -X_{1a}-O-X_{2a}- (-alkyleneoxyalkylene-) moiety wherein X_{1a} and X_{2a} are independently selected from a C-1 to C-8 linear alkylene, a C-3 to C-8 branched alkylene and a C-3 to C-8 cyclic alkylene

MDN is an azide moiety (-N_3), or a cyano moiety (CN);



(II).

11. The functional styrenic polymer of any one of claims 1, 2 and 7 having structure (III); wherein,

nb is the number of repeating units in the polymer;

R_{1b} is H or a C-1 to C-4 linear alkyl;

R_s is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{2b} is selected from

a C-1 to C-8 linear alkyl

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

X_c is selected from

a direct valence bond,

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene,

a C-3 to C-8 cyclic alkylene, and

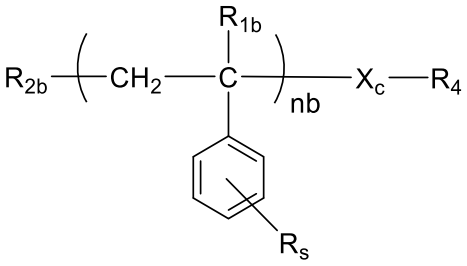
a -X_{1b}-O-X_{2b}- (-alkyleneoxyalkylene-) moiety wherein X_{1b} and X_{2b} are independently selected from

a C-1 to C-8 linear alkylene,

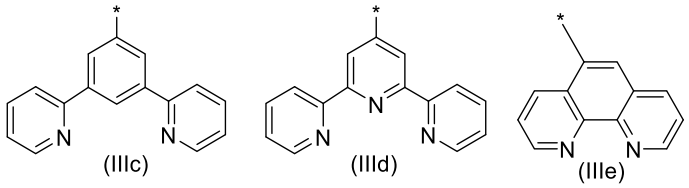
a C-3 to C-8 branched alkylene and

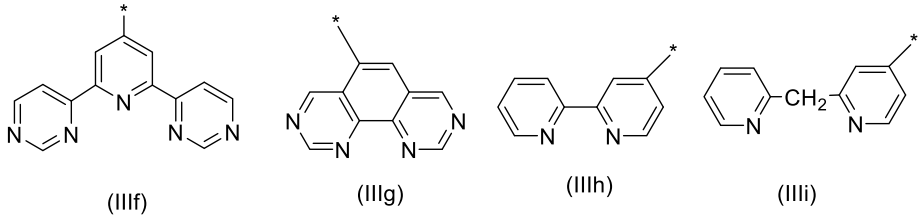
a C-3 to C-8 cyclic alkylene;

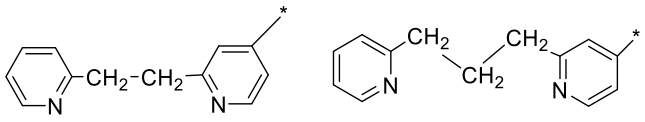
R_4 is a polydentate N-coordinative functional group having a structure selected from moieties (IIIc), (IIId), (IIIe), (IIIf), (IIIg), (IIIh), (IIIi), (IIIj), and (IIIk), wherein * designate the attachment point of these polydentate moieties to structure (III);



(III);


(IIIc) (IIId) (IIIe)


(IIIf) (IIIg) (IIIh) (IIIi)


(IIIj) (IIIk)

12. The functional polymer of any one of claims 1, 2, 5 and 8 which is a diblock copolymer having structure (IV); wherein

nc is the number of repeating units in a first block and

nd is the number of repeat units in a second block;

R_{1c} is H or a C-1 to C-4 linear alkyl;

R_s is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{2c} is selected from

a C-1 to C-8 linear alkyl

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

X_d and X_e are independently selected from

a direct valence bond,

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene,

a C-3 to C-8 cyclic alkylene, and

a $-X_{1c}-O-X_{2c}-$ (-alkyleneoxyalkylene-) moiety wherein X_{1c} and X_{2c} are independently selected from

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene and

a C-3 to C-8 cyclic alkylene;

R_{3a} is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl

a C-1 to C-8 cyclic alkyl and

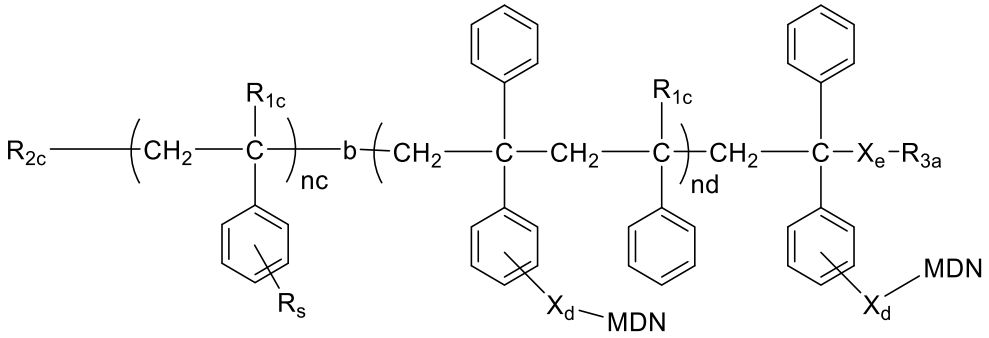
a dialkylsilyl moiety [(R_{sib})(R_{sic}) SiH-] wherein R_{sib} and R_{sic} are independently selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

MDN is an azide moiety (-N_3), or a cyano moiety (-CN);



(IV).

13. The functional polymer of any one of claims 1, 2, 5, 6 and 7, which is a diblock copolymer having structure (V); wherein

ne is the number of repeating units in a first block and

nf is the number of repeat units in a second block;

R_{1d} is H or a C-1 to C-4 linear alkyl;

R_s is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{2d} is selected from

a C-1 to C-8 linear alkyl

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

X_f and X_g are independently selected from

a direct valence bond,

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene,

a C-3 to C-8 cyclic alkylene, and

a -X_{1d}-O-X_{2d}- (-alkyleneoxyalkylene-) moiety wherein X_{1d} and X_{2d} are independently selected from

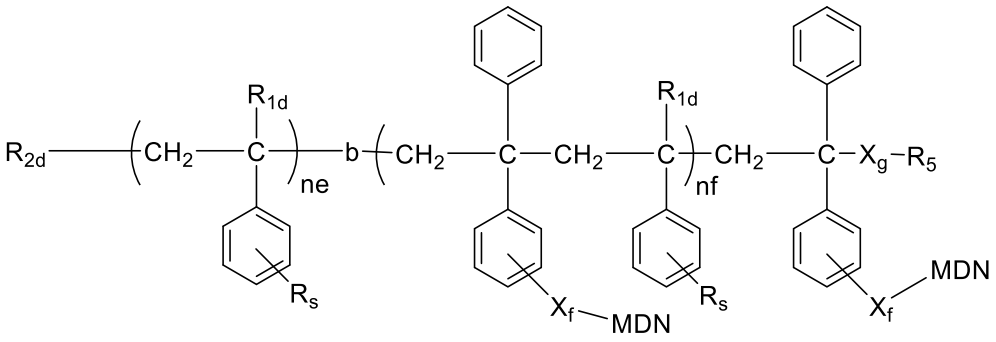
a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene, and

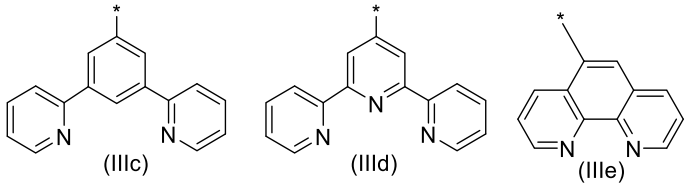
a C-3 to C-8 cyclic alkylene;

R_5 is a polydentate N-coordinative functional group having a structure selected from moieties (IIIc), (IIId), (IIIe), (IIIf), (IIIg), (IIIh), (IIIi), (IIIj), and (IIIk), wherein * designate the attachment point of these polydentate moieties to structure (V); and

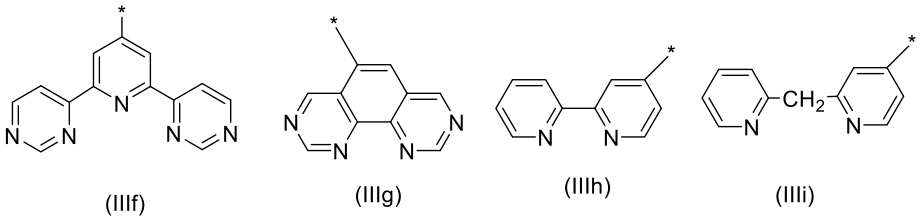
MDN is an azide moiety (-N_3), or a cyano moiety (-CN);



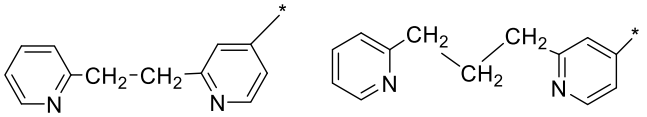
(V);



(IIIc) (IIId) (IIIe)



(IIIf) (IIIg) (IIIh) (IIIi)



(IIIj) (IIIk)

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14. The functional polymer of any one of claims 1, 2, and 5 having structure (VI); wherein

n is the number of repeating units in the polymeric segment;

nos is the number of repeating units in the oligomeric segment and ranges from 1 to 10,

R_1 is H or a C-1 to C-4 linear alkyl;

R_s is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{dp} is H or a C-1 to C-4 linear alkyl;

R_2 is selected from a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{CN} is selected from

H

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

a dialkylsilyl moiety [(R_{si})(R_{sia}) SiH-] wherein R_{si} and R_{sia} are independently selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

X_a is selected from

a direct valence bond,

a C-1 to C-8 linear alkylene moiety,

a C-3 to C-8 branched alkylene moiety,

a C-3 to C-8 cyclic alkylene moiety, and

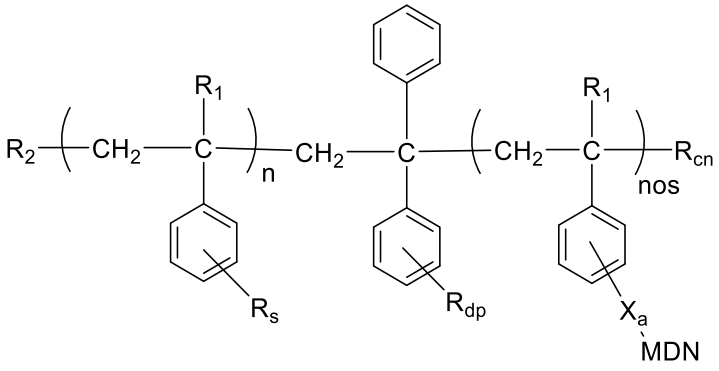
a -X_1-O-X_2- (-alkyleneoxyalkylene-) moiety wherein X_1 and X_2 are independently selected from

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene, and

a C-3 to C-8 cyclic alkylene; and

MDN is an azide moiety (-N_3), or a cyano moiety (-CN);



(VI).

15. The functional polymer of any one of claims 1 to 4, and 5 having structure (VII); wherein

n is the number of repeating units in the styrenic polymer segment;

nacr is the number of repeating units in the acrylic polymer segment;

nos is the number of repeat units in the oligomeric styrenic segment and ranges from 1 to 10,

R_1 is H or a C-1 to C-4 linear alkyl;

R_s is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{1ac} is H or a C-1 to C-4 linear alkyl;

R_{3ac} is selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{4ac} is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

a dialkylsilyl moiety [$(R_{si})(R_{sia})SiH$-] wherein Rsi and Rsia are independently selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

R_{dp} is H or a C-1 to C-4 linear alkyl;

X_a and X_{aac} are independently selected from

a direct valence bond,

a C-1 to C-8 linear alkylene moiety,

a C-3 to C-8 branched alkylene moiety,

a C-3 to C-8 cyclic alkylene moiety, and

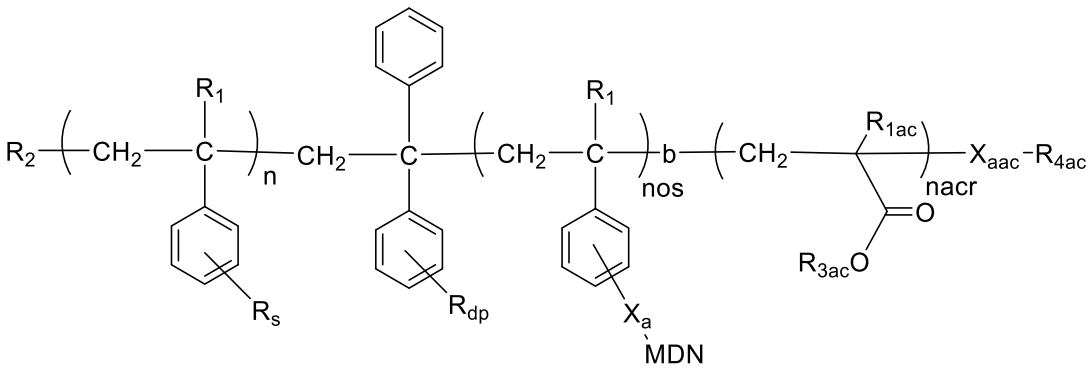
a -X_1-O-X_2- (-alkyleneoxyalkylene-) moiety wherein X_1 and X_2 are independently selected from

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene and

a C-3 to C-8 cyclic alkylene; and

MDN is an azide moiety (-N_3), or a cyano moiety (CN);



(VII).

16. The functional polymer of any one of claims 1 to 4, 8, 9, 12, 14, and 15 which contain a dialkylsilyl end group.

17. The functional polymer of any one of claims 1, 3, 5 and 8 having structure (VIII), where,

nh is the number of repeating units in the polymer;

R_{1f} is H or a C-1 to C-4 linear alkyl;

R_s is selected from

H,

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{2f} is selected from

a C-1 to C-8 linear alkyl

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

X_e is selected from

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene,

a C-3 to C-8 cyclic alkylene, and

a -X_{1f}-O-X_{2f}- (-alkyleneoxyalkylene-) moiety wherein X_{1f} and X_{2f} are independently selected from

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene and

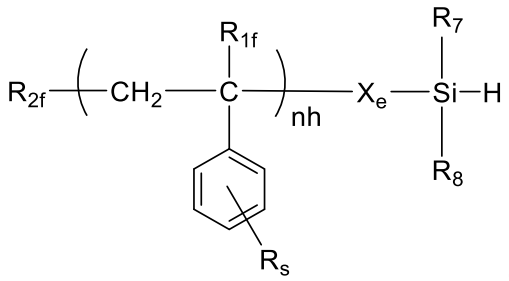
a C-3 to C-8 cyclic alkylene;

R_7 and R_8 are independently selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;



(VIII**).**

18. The functional polymer of any one of claims 1, 3, 5, and 8 having structure (VIV); wherein nacr is the number of repeating units in the acrylic polymer segment;

R_{1ac} is H or a C-1 to C-4 linear alkyl;

R_{2ac} is selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{3ac} is 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

R_{4ac} is selected from

H

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

a dialkylsilyl moiety [(R_{si})(R_{sia})SiH-] wherein R_{si} and R_{sia} are independently selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

X_{ac} and X_{aac} are independently selected from

a direct valence bond,

a C-1 to C-8 linear alkylene moiety,

a C-3 to C-8 branched alkylene moiety,

a C-3 to C-8 cyclic alkylene moiety, and

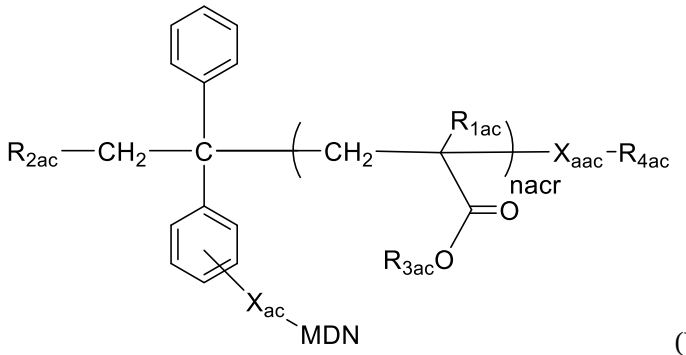
a -X_1-O-X_2- (-alkyleneoxyalkylene-) moiety wherein X_1 and X_2 are independently selected from

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene and

a C-3 to C-8 cyclic alkylene; and

MDN is an azide moiety (-N_3), or a cyano moiety (-CN);



(VIV).

19. The functional polymer of any one of claims 1, 3, 5 and 8 having structure (VV); wherein

nacr is the number of repeating units in the acrylic polymer segment;

noac is the number of repeating units in the acrylic oligomer segment and ranges from 1 to 10;

R_{1ac} is H or a C-1 to C-4 linear alkyl;

R_{2ac} is selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{3ac} is 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

R_{4ac} is selected from

H

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

a dialkylsilyl moiety [(R_{siac})(R_{siaac})SiH-] wherein R_{siac} and R_{siaac} are independently selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

R_{5ac} is H or a C-1 to C-4 linear alkyl;

R_{6ac} is selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

X_{ac} and X_{aac} are independently selected from

a direct valence bond,

a C-1 to C-8 linear alkylene moiety,

a C-3 to C-8 branched alkylene moiety,

a C-3 to C-8 cyclic alkylene moiety, and

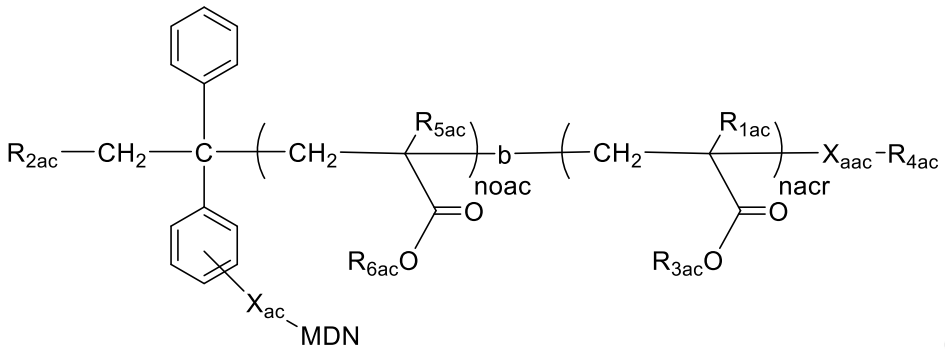
a -X_1-O-X_2- (-alkyleneoxyalkylene-) moiety wherein X_1 and X_2 are independently selected from

a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene and

a C-3 to C-8 cyclic alkylene; and

MDN is an azide moiety (-N_3), or a cyano moiety (-CN);



(VV).

20. The functional styrenic polymer of any one of claims 1, 3, 5 and 8 having structure (VVI); wherein

nacr is the number of repeating units in the acrylic polymer segment;

noca is the number of repeating units in the acrylic oligomeric segment and ranges from 1 to 10;

R_{1ac} is H or a C-1 to C-4 linear alkyl;

R_{2ac} is selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl;

R_{3ac} is selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl

and a C-3 to C-8 cyclic alkyl;

R_{dp} is H or a C-1 to C-4 linear alkyl;

R_{4ac} is selected from

H

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

a dialkylsilyl moiety [(R_{si})(R_{sia})SiH-] wherein R_{si} and R_{sia} are independently selected from

a C-1 to C-8 linear alkyl,

a C-3 to C-8 branched alkyl and

a C-3 to C-8 cyclic alkyl; and

R_{cna} is H or a C-1 to C-4 linear alkyl;

X_b is selected from

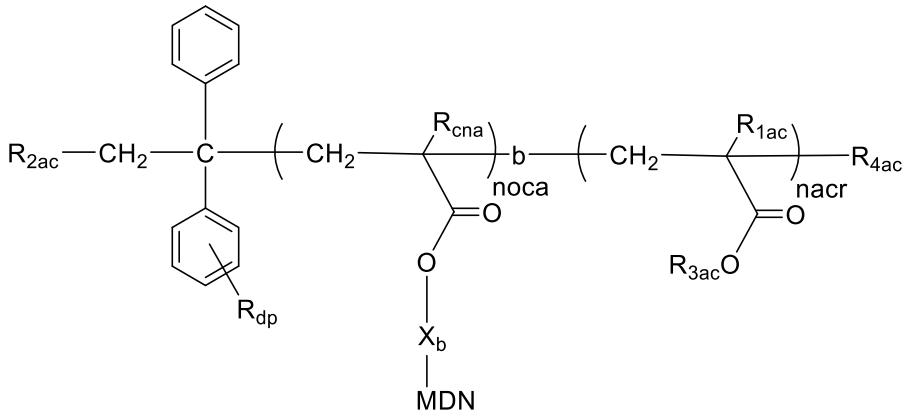
a C-1 to C-8 linear alkylene,

a C-3 to C-8 branched alkylene,

a C-3 to C-8 cyclic alkylene and

a $-X_{1a}-O-X_{2a}-$ (-alkyleneoxyalkylene-) moiety wherein X_{1a} and X_{2a} are independently selected from a C-1 to C-8 linear alkylene, a C-3 to C-8 branched alkylene and a C-3 to C-8 cyclic alkylene; and

MDN is an azide moiety ($-N_3$), or a cyano moiety (-CN);



(VVI).

21. A composition comprising the functional polymer of any one of claims 1 to 20, and a spin casting solvent.

22. A process of coating a pinning layer comprising the step of

i) coating the compositions of claim 16 on a substrate which contains only metallic surfaces, or which contains a mixture of metallic and non-metallic surfaces forming a coating on said substrate.

23. The process of claim 22 wherein said substrate is one which contains both metallic and non-metallic surfaces selected from the group consisting of

a substrate having metallic surfaces and Si surfaces,

a substrate having metallic surfaces and GaAs surfaces,

a substrate having metallic surfaces and Ge surfaces,

a substrate having metallic and silicon oxide surfaces,

a substrate having metallic and silicon nitride surfaces,

a substrate having metallic and silicon oxynitride surfaces,

a substrate having metallic and neutral layer surfaces,

a substrate having metallic and photoresist surfaces, and

a substrate having metallic and spin on carbon surfaces.

24. The process of claims 22 or 23 wherein comprises additional step ii) and iii):

ii) baking said coating to form a baked coating,

iii) rinsing said baked coating, with an organic solvent, leaving a brush film attached to the metallic surface.

25. The process of any one of claims 22 to 24, wherein said non-metallic surfaces, are Si surfaces, SiO_2 surfaces or a mixture of these two types of surfaces.

26. The process of any one of claims 22 to 25, wherein said metallic surfaces are surfaces which are selected for at least one of a Cu, W, Mo, Al, Zr, Ti, Hf, Ag and Au surfaces.

27. The process of forming a patterned substrate by directed self-assembly comprising steps ib) to vib),

ib) coating the composition of claim 21 on a substrate containing both metallic surfaces and non-metallic neutral layer surfaces,

iib) baking said coating to form a baked coating,

iiib) rinsing said baked coating, leaving a brush layer selectively attached to said metal surfaces, forming a patterned pinning layer,

ivb) coating a block copolymer layer on top of said patterned pinning layer,

vb) forming a directed self-assembly film of the overlying block copolymer

vib) etching said directed self-assembled block copolymer forming a pattern in said substrate.

28. The use of the functional polymer according to any one of claims 1 to 20 or of the composition according to claim 21 for forming an attached film selectively on a metal substrate.