CLAIMS

What is claimed is:

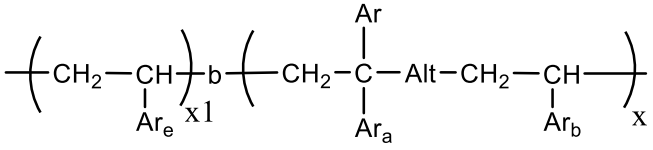
1. A block copolymer comprising structure (1)

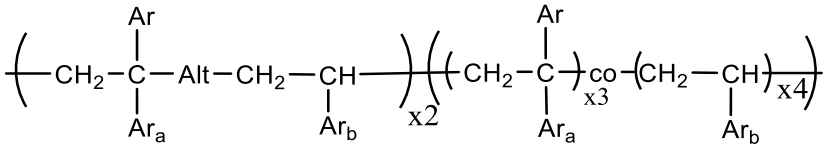
(A)-(C)-(B) (1);

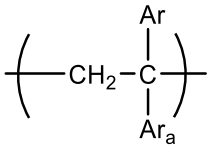
wherein (A) is a first polymer block segment comprising a copolymer block segment selected from structure (1a), structure (1b), and a mixture of structures (1a) and (1b), wherein Ar, Ar_a, Ar_b and Ar_e are each independently unsubstituted aryl moieties or aryl moieties with at least one substituent selected from the group consisting of a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, x, x1, x2 and x3 and x4 are independently the number of repeat units;

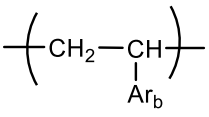
wherein the structures (1a1), (1a2) and (1a3), which are present in structure (1a), structure (1b) or a mixture of structures (1a) and (1b), are present in amounts such that the mole % of structure (1a1) ranges from ~~about~~ 3 mole % to ~~about~~ 40 mole %, as measured against to sum of structures (1a1), (1a2) and (1a3); and,

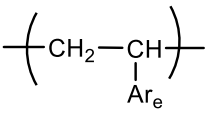
wherein the M_w of (A) ranges from ~~about~~ 5,000 to ~~about~~ 100,000 g/mole,


(1a),

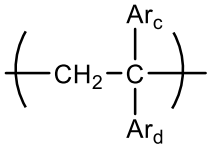

(1b),


(1a1)


(1a2)


(1a3);

wherein (C) is a spacer moiety comprising structure (1c), wherein Ar_c and Ar_d are independently unsubstituted aryl moieties or aryl moieties with at least one substituent selected from the group consisting of a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage,


(1c);

wherein (B) is a second polymer block segment comprising repeat units derived from either an alkyl 2-methylenealkanoate (alkyl-O-(C=O)-C(alkyl)=CH_2), a lactone; a cyclic carbonate, an oxirane, or an oxetane, wherein the Mw of (B) ranges from ~~about~~ 5,000 g/mol to ~~about~~ 100,000 g/mol; and

said block copolymer comprising structure (1) has a M_w ranging from ~~about~~ 10,000 g/mol to ~~about~~ 200,000 g/mol and has a polydispersity of 1.00 to ~~about~~ 1.20.

2. The block copolymer of claim 1, which has a polydispersity ranging from 1.00 to ~~about~~ 1.12.

~~3. The block copolymer of claim 1 or 2, which has a polydispersity ranging from 1.00 to about 1.10.~~

~~4~~3. The block copolymer of any one of claims 1 to ~~3~~2, wherein (A) comprises a block copolymer segment of structure (1a).

~~5~~4. The block copolymer of any one of claims 1 to ~~4~~3, wherein (A) comprises a diblock copolymer segment of structure (1b).

~~6~~5. The block copolymer of any one of claims 1 to ~~5~~4, wherein (A) comprises a mixture of diblock copolymer segment of structures (1a) and (1b).

~~7. The block copolymer of any one of claims 1 to 6, wherein said block copolymer undergoes self-assembly and forms a fingerprint pattern on a conventional neutral layer covered substrate.~~

~~8. The block copolymer of any one of claims 1 to 6, wherein said block copolymer forms L/S directed self-assembly and affects either line multiplication or line rectification, using either graphoepitaxy or chemoepitaxy and wherein the L/S directly patterns on a substrate containing, as part of the this L/S pattern, conventional neutral layer surface areas.~~

~~9. The block copolymer of claims 7 or 8, wherein said conventional neutral layer is one derived from a brush random copolymer of styrene and methyl methacrylate.~~

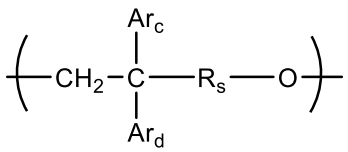
~~10~~6. The block copolymer of anyone of claims 1 to ~~9~~5, wherein (A) consists of structure (1a).

~~11~~7. The block copolymer of anyone of claims 1 to ~~9~~5, wherein (A) consists of structure (1b).

~~12~~8. The block copolymer of anyone of claims 1 to ~~9~~5, wherein (A) consists of a mixture of structure (1a) and (1b).

~~13~~9. The block copolymer of anyone of claims 1 to ~~12~~8, wherein (C) consists of structure (1c).

~~14~~10. The block copolymer of any one of claim 1 to ~~12~~8, wherein (C) comprises structure (1c1) wherein Rs is an unsubstituted C-1 to C-3 alkylene moiety or C-1 to C-3 alkylene moiety substituted with at least one substituent selected from the group consisting of a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, Ar_c, and Ar_d are independently unsubstituted aryl moieties or aryl moieties with at least one substituent selected from the group consisting of a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage;



(1c1).

~~15. The block copolymer of any one of claim 1 to 12 and 14, wherein (C) consists of structure (1c1).~~

~~16. The block copolymer of any one of claims 1 to 15, wherein at least one of Ar_e or Ar_d is substituted with at least one moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~17. The block copolymer of any one of claims 1 to 15, wherein Ar_e and Ar_d are not substituted with a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~18. The block copolymer of any one of claims 1 to 15, wherein Ar_e and Ar_d are each unsubstituted.~~

~~19. The block copolymer of any one of claims 1 to 15, wherein at least one Ar_e or Ar_d are is unsubstituted.~~

~~20. The block copolymer of any one of claims 1 to 15, wherein at least one of Ar_e is substituted with a C-1 to C-8 alkyl.~~

~~21~~11. The block copolymer of any one of claims 1 to ~~20~~10, wherein (B) is a polymer block segment whose repeat units are derived from an alkyl 2-methylenealkanoate.

~~22~~12. The block copolymer of any one of claims 1 to ~~21~~11, wherein (B) is a polymer block segment whose repeat units are derived from an alkyl methacrylate.

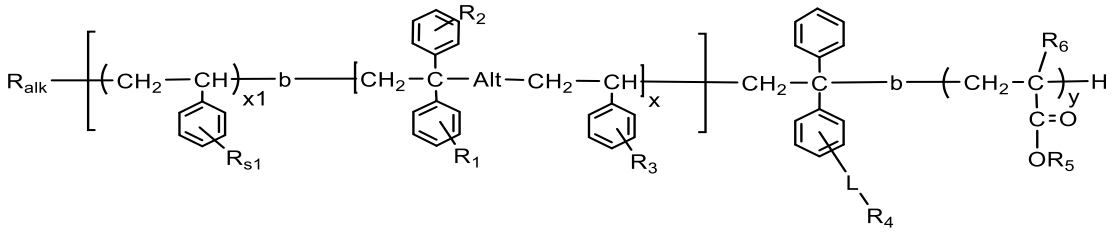
~~23~~13. The block copolymer of any one of claims 1 to ~~20~~10, wherein (B) is a polymer block segment whose repeat units are derived from a lactone.

~~24~~14. The block copolymer of any one of claims 1 to ~~20~~10, wherein (B) is a polymer block segment whose repeat units are derived from a cyclic carbonate.

~~25~~15. The block copolymer of any one of claims 1 to ~~20~~10, wherein (B) is a polymer block segment whose repeat units are derived from an oxirane.

~~26~~16. The block copolymer of any one of claims 1 to ~~20~~10, wherein (B) is a polymer block segment whose repeat units are derived from an oxetane.

~~27~~17. The block copolymer of any one of claims 1 to ~~4~~3, ~~7 to 9, 10~~6, ~~13~~ 9 to ~~22~~12, which has structure (2), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1} R_1, R_2, and R_3, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_5 is a C-1 to C-8 alkyl, R_6 is a C-1 to C-4 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, and x1, x, and y are independently the number of the respective repeat unit, L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



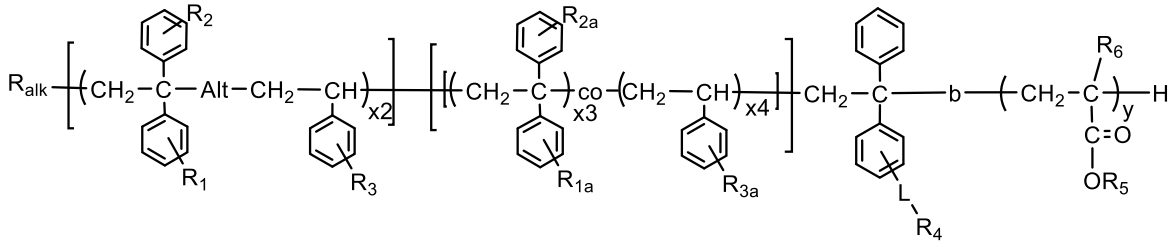
(2).

~~28. The block copolymer of claim 27, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~29. The block copolymer of claim 27, wherein R_4 is H.~~

~~30. The block copolymer of claim 27, wherein R_4 is a C-1 to C-8 alkyl.~~

~~31~~18. The polymer of any one of claims 1 to ~~3~~2, ~~5~~4, ~~7 to 9~~, ~~11~~7, ~~13~~9, 11~~16~~ to 12~~22~~, which has structure (3), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_5 is a C-1 to C-8 alkyl, R_6 is a C-1 to C-4 alkyl, x2, x3, x4 and y are independently the number of the respective repeat units, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



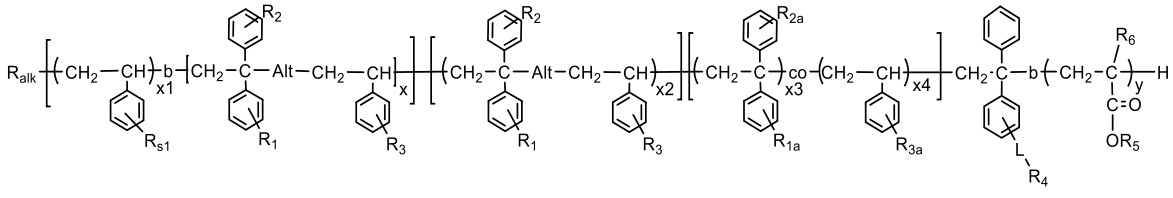
(3).

~~32. The block copolymer of claim 31, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~33. The block copolymer of claim 31, wherein R_4 is H.~~

~~34. The block copolymer of claim 31, wherein R_4 is a C-1 to C-8 alkyl.~~

~~35~~19. The polymer of any one of claims 1 to ~~4~~3, ~~5, 6~~4 to 5, ~~12, 13~~8 to 9, ~~16~~ 11 to ~~22~~12, which has structure (4), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_5 is a C-1 to C-8 alkyl, R_6 is a C-1 to C-4 alkyl, x, x1, x2, x3, x4 and y are independently the number of the respective repeat units, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



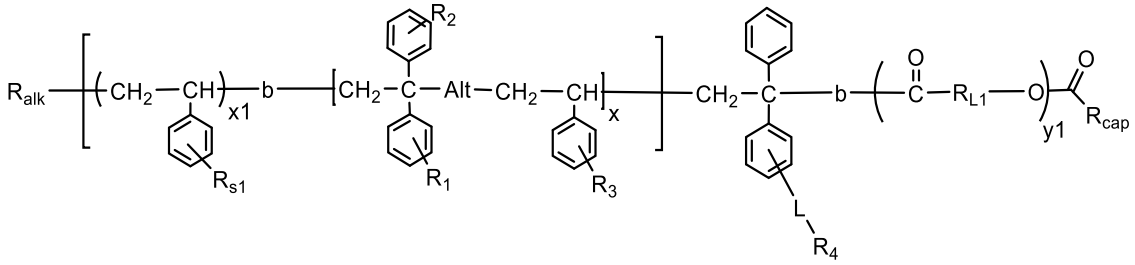
(4).

~~36. The block copolymer of claim 35, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~37. The block copolymer of claim 35, wherein R_4 is H.~~

~~38. The block copolymer of claim 35, wherein R_4 is a C-1 to C-8 alkyl.~~

~~39~~20. The block polymer of any one of claims 1 to ~~4~~3, ~~7 to 9, 10~~6, ~~13~~ 9 to ~~20~~10, and ~~23~~ 13 which has structure (5), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1} R_1, R_2, and R_3, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, ~~R_5 is a C-1 to C-8 alkyl,~~ R_{L1} is an unsubstituted C-1 to C-4 alkylene or a C-1 to C-4 alkylene moiety substituted with at least one C-1 to C-8 alkyl, R_{cap} is a C-1 to C-8 alkyl, and x1, x, and y1 are independently the number of the respective repeat unit, L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



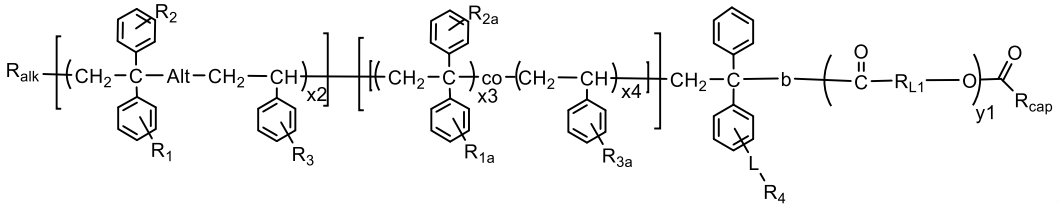
(5).

~~40. The block copolymer of claim 39, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~41. The block copolymer of claim 39, wherein R_4 is H.~~

~~42. The block copolymer of claim 39, wherein R_4 is a C-1 to C-8 alkyl.~~

~~43~~21. The block polymer of any one of claims 1 to ~~3~~2, ~~5~~4, ~~7 to 9, 11~~7, ~~13~~9, ~~16 to 20,~~ and ~~23~~ 13 which has structure (6), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_{L1} is an unsubstituted C-1 to C-4 alkylene or a C-1 to C-4 alkylene moiety substituted with at least one C-1 to C-8 alkyl, R_{cap} is a C-1 to C-8 alkyl, x2, x3, x4, and y1 are independently the number of the respective repeat units, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



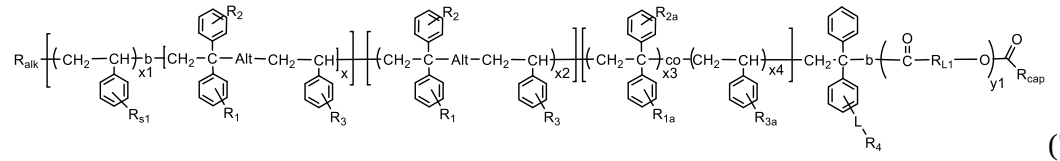
(6).

~~44. The block copolymer of claim 43, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~45. The block copolymer of claim 43, wherein R_4 is H.~~

~~46. The block copolymer of claim 43, wherein R_4 is a C-1 to C-8 alkyl.~~

~~47~~22. The block polymer of any one of claims 1 to ~~4~~3, ~~5~~4, ~~6~~5, ~~12~~8, ~~13~~9, ~~16 to 20,~~ and ~~23~~13, which has structure (7), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H, and a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_{L1} is an unsubstituted C-1 to C-4 alkylene or a C-1 to C-4 alkylene moiety substituted with at least one C-1 to C-4 alkyl, x1, x, x2, x3, x4 and y1 are independently the number of the respective repeat unit, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-8 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety and a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene);



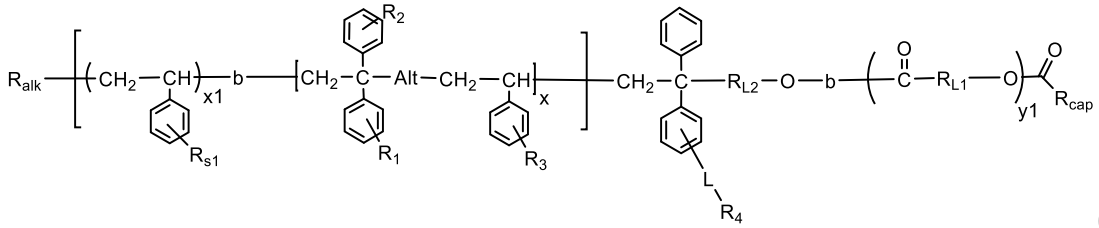
(7).

~~48. The block copolymer of claim 47, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~49. The block copolymer of claim 47, wherein R_4 is H.~~

~~50. The block copolymer of claim 47, wherein R_4 is a C-1 to C-8 alkyl~~

~~51~~23. The block polymer of any one of claims 1 to ~~4~~3, ~~7 to 9~~, ~~7~~11 to ~~20~~ 10 and ~~23~~ 13 which has structure (8), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1}, R_1, R_2, and R_3, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_{L1} and R_{l2} are independently an unsubstituted C-1 to C-4 alkylene or a C-1 to C-4 alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap} is a C-1 to C-8 alkyl, and x1, x, and y1 are independently the number of the respective repeat unit, L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy).



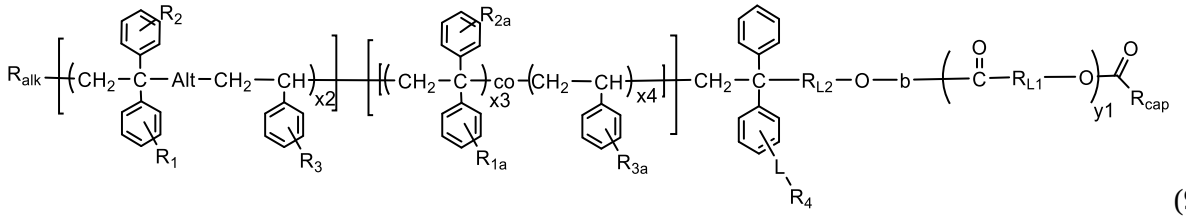
(8).

~~52. The block copolymer of claim 51, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~53. The block copolymer of claim 51, wherein R_4 is H.~~

~~54. The block copolymer of claim 51, wherein R_4 is a C-1 to C-8 alkyl.~~

~~55~~24. The block polymer of any one of claims 1 to ~~4~~3, ~~5~~4, ~~6~~5, ~~11~~ 7 to ~~20~~10, and ~~23~~13, which has structure (9), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is a C-5 to C-18 perfluoroalkyl pendant group comprising at least one ether linkage, R_{L1} and R_{L2} are independently an unsubstituted C-1 to C-4 alkylene or a C-1 to C-4 alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap} is a C-1 to C-8 alkyl,and x, x1, x2, and y1 are independently the number of the respective repeat units, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



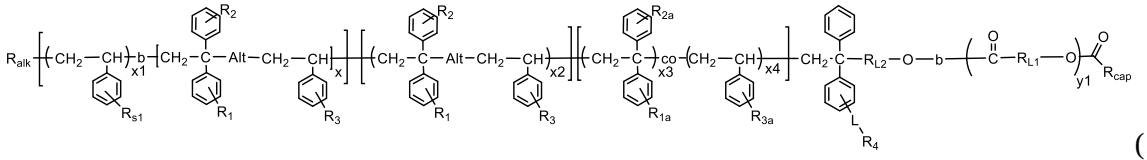
(9).

~~56. The block copolymer of claim 55, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~57. The block copolymer of claim 55, wherein R_4 is H.~~

~~58. The block copolymer of claim 55, wherein R_4 is a C-1 to C-8 alkyl.~~

~~59~~25. The block polymer of any one of claims 1 to ~~4~~3, ~~5~~4, ~~6~~5, ~~11~~ 7 to ~~20~~10, and ~~23~~13, which has structure (10), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1},R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H, and a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_{L1} and R_{L2} are independently an unsubstituted C-1 to C-4 alkylene or a C-1 to C-4 alkylene moiety substituted with at least one C-1 to C-4 alkyl, x1, x, x2, x3, x4 and y1 are independently the number of the respective repeat unit, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-8 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety and a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene);



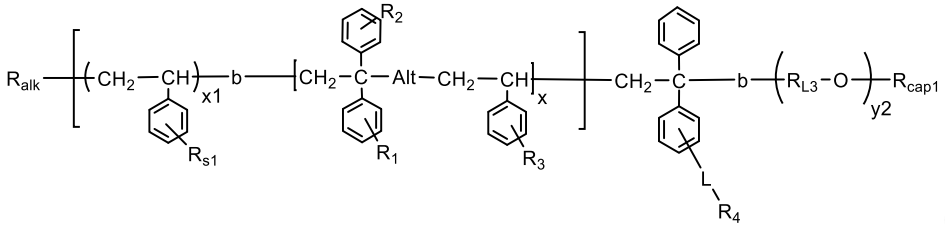
(10).

~~60. The block copolymer of claim 59, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~61. The block copolymer of claim 59, wherein R_4 is H.~~

~~62. The block copolymer of claim 59, wherein R_4 is a C-1 to C-8 alkyl.~~

~~63~~26. The block copolymer of any one of claims 1 to ~~4~~3, ~~7 to 9, 10~~6, ~~13~~ 9 to ~~20~~10, ~~22~~ 12 and ~~23~~13, which has structure (11), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1}, R_1, R_2, and R_3, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_{L3} is an unsubstituted C-2 to C-3 linear alkylene or a C-2 to C-3 linear alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap1} is a C-1 to C-8 alkyl or a C-2 to C-8 carbonylalkyl, and x1, x, and y2 are independently the number of the respective repeat unit, L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



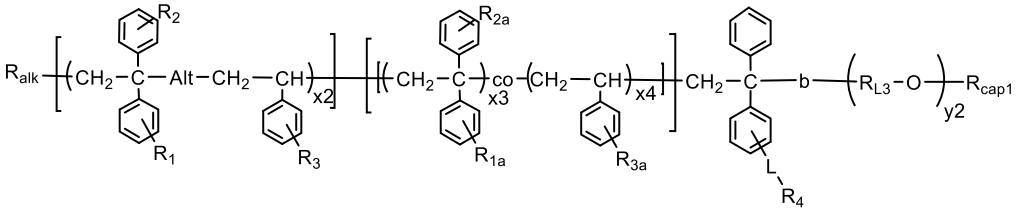
(11).

~~64. The block copolymer of claim 63, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~65. The block copolymer of claim 63, wherein R_4 is H.~~

~~66. The block copolymer of claim 63, wherein R_4 is a C-1 to C-8 alkyl.~~

~~67~~27. The block copolymer of any one of claims 1 to ~~3~~2, ~~5~~4, ~~7 to 9, 11~~7, ~~13~~9, ~~16 to 20, 22~~ 12 and ~~23~~13,~~,~~ which has structure (12), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is a C-5 to C-18 perfluoroalkyl pendant group comprising at least one ether linkage, R_{L3} is an unsubstituted C-2 to C-3 linear alkylene or a C-2 to C-3 linear alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap1} is a C-1 to C-8 alkyl or a C-2 to C-8 carbonylalkyl, and x, x1, x2, and y2 are independently the number of the respective repeat units, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



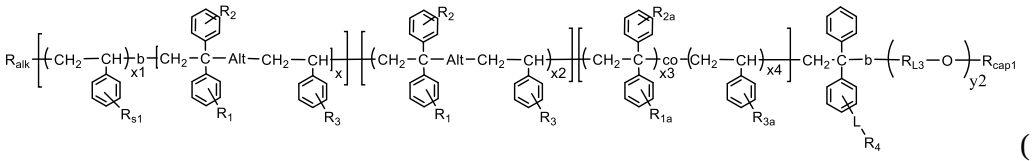
(12).

~~68. The block copolymer of claim 67, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~69. The block copolymer of claim 67, wherein R_4 is H.~~

~~70. The block copolymer of claim 67, wherein R_4 is a C-1 to C-8 alkyl.~~

~~71~~28. The block copolymer of any one of claims 1 to ~~4~~3, ~~5~~4, ~~6~~5, ~~12~~8, ~~13~~9, ~~16 to 20, 22~~ 12 and ~~23~~13, which has structure (13), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1}, R_1, R_{1a}, R_2, $R_{2a,}$ R_3, and R_{3a}, are independently selected from H, and a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, is an unsubstituted C-2 to C-3 linear alkylene or a C-2 to C-3 linear alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{L3} is an unsubstituted C-2 to C-3 linear alkylene or a C-2 to C-3 linear alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap1} is a C-1 to C-8 alkyl or a C-2 to C-8 carbonylalkyl, x1, x, x2, x3, x4 and y2 are independently the number of the respective repeat unit, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-8 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety and a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene);



(13).

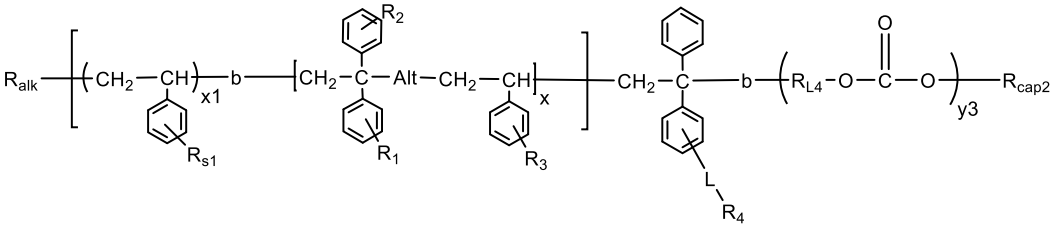
~~72. The block copolymer of claim 71, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~73. The block copolymer of claim 71, wherein R_4 is H.~~

~~74. The block copolymer of claim 71, wherein R_4 is a C-1 to C-8 alkyl.~~

~~75~~29. The block copolymer of any one of claims 1 to ~~4~~3, ~~7 to 9, 10~~6, ~~13~~ 9 to ~~20~~ 10 and ~~24~~14, which has structure (14), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1} R_1, $R_{2,}$ and R_3, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_{L4} is an unsubstituted C-2 to C-3 linear alkylene or a C-2 to C-3 linear alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap2} is a C-1 to C-8 alkyl, R_{cap1} is a C-1 to C-8 alkyl or a C-2 to C-8 carbonylalkyl, x1, x, and y3 are independently the number of the respective repeat unit, L is a linking group selected from the group consisting of a direct valence bond, a C-1

to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



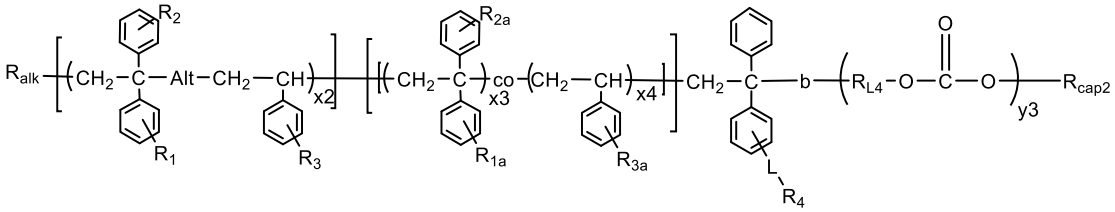
(14).

~~76. The block copolymer of claim 75, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~77. The block copolymer of claim 75, wherein R_4 is H.~~

~~78. The block copolymer of claim 75, wherein R_4 is a C-1 to C-8 alkyl.~~

~~79~~30. The block copolymer of any one claims 1 to ~~3~~2, ~~5~~4, ~~7 to 9, 11~~7, ~~13~~9, ~~16 to 20,~~ and ~~24~~ 14 which has structure (15), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is a C-5 to C-18 perfluoroalkyl pendant group comprising at least one ether linkage, R_{L4} is a C-2 to C-4 alkylene or a C-1 to C-4 alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap2} is a C-1 to C-8 alkyl or a C-2 to C-8 carbonylalkyl, x2, x3, x4 and y3 are independently the number of the respective repeat units, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



(15).

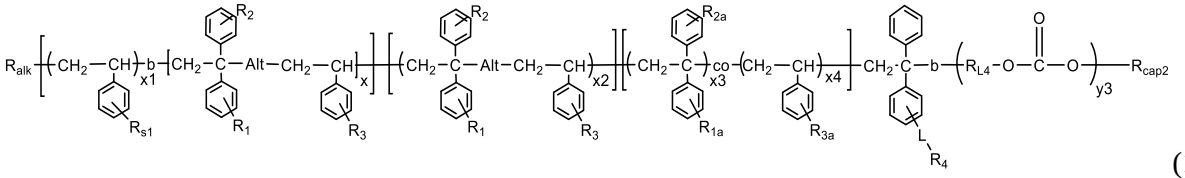
~~80. The block copolymer of claim 79, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~81. The block copolymer of claim 79, wherein R_4 is H.~~

~~82. The block copolymer of claim 79, wherein R_4 is a C-1 to C-8 alkyl.~~

~~83~~31. The block copolymer of any one of claims 1 to ~~4~~3, ~~5~~4, ~~6~~5, ~~12~~8, ~~13~~9, ~~16 to 20~~ and ~~24~~ 14 which has structure (16), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1}, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H, and a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_{L4} is an unsubstituted C-2 to C-4 alkylene or a C-2 to C-4 alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap2} is a C-1 to C-8 alkyl or a C-2 to C-8 carbonylalkyl, x1, x, x2, x3, x4 and y3 are independently the number of the respective repeat unit, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-8

alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety and a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene);



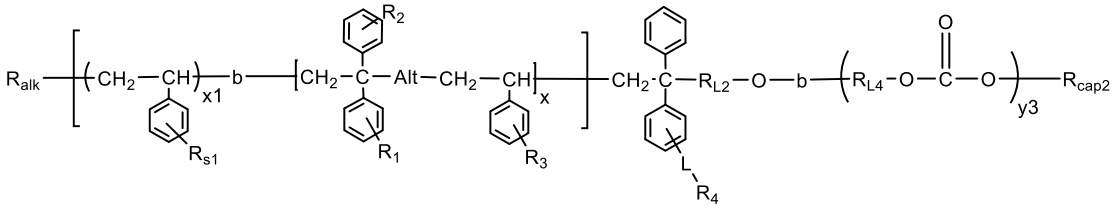
(16).

~~84. The block copolymer of claim 83, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~85. The block copolymer of claim 83, wherein R_4 is H.~~

~~86. The block copolymer of claim 83, wherein R_4 is a C-1 to C-8 alkyl.~~

~~87~~32. The block copolymer of any one of claims 1 to ~~4~~3, ~~7 to 9, 11~~7 to ~~20~~ 10 and ~~24~~14, which has structure (17), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1} R_1, R_2, and R_3, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_{l2} and R_{L4} are independently an unsubstituted C-1 to C-4 alkylene or a C-1 to C-4 alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap2} is a C-1 to C-8 alkyl or a C-2 to C-8 carbonylalkyl, x1, x, and y3 are independently the number of the respective repeat unit, L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



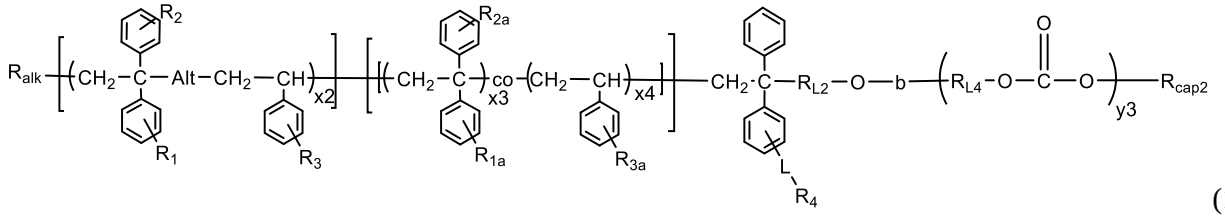
(17).

~~88. The block copolymer of claim 87, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~89. The block copolymer of claim 87, wherein R_4 is H.~~

~~90. The block copolymer of claim 87, wherein R_4 is a C-1 to C-8 alkyl.~~

~~91~~33. The block copolymer of any one of claims 1 to ~~4~~3, ~~5~~4, ~~6~~5, ~~11~~ 7 to ~~20~~10~~,~~ and ~~24~~14, which has structure (18), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is a C-5 to C-18 perfluoroalkyl pendant group comprising at least one ether linkage, R_{l2} and R_{L4} are independently an unsubstituted C-1 to C-4 alkylene or a C-1 to C-4 alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap2} is a C-1 to C-8 alkyl or a C-2 to C-8 carbonylalkyl, x2, x3, x4 and y3 are independently the number of the respective repeat units, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-4 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety, a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene), and a C-1 to C-4 (alkylene-oxy);



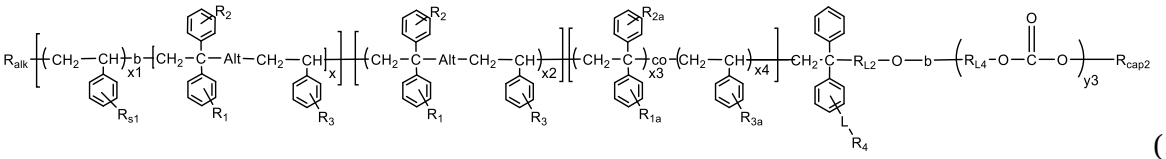
(18).

~~92. The block copolymer of claim 91, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~93. The block copolymer of claim 91, wherein R_4 is H.~~

~~94. The block copolymer of claim 91, wherein R_4 is a C-1 to C-8 alkyl.~~

~~95~~34. The block copolymer of any one of claims 1 to ~~4~~3, ~~5~~4, ~~6~~5, ~~11~~ 7 to ~~20~~10~~,~~ and ~~24~~14, which has structure (19), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, $R_{2a,}$ R_3, and R_{3a}, are independently selected from H, and a C-1 to C-8 alkyl, R_{l2} and R_{L4} are independently an unsubstituted C-1 to C-4 alkylene or a C-1 to C-4 alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, R_{L4} is an unsubstituted C-2 to C-4 alkylene or a C-2 to C-4 alkylene moiety substituted with at least one C-1 to C-4 alkyl, R_{cap2} is a C-1 to C-8 alkyl or a C-2 to C-8 carbonylalkyl, x1, x, x2, x3, x4 and y3 are independently the number of the respective repeat unit, and L is a linking group selected from the group consisting of a direct valence bond, a C-1 to C-8 alkylene spacer, a C-1 to C-4 alkyleneoxycarbonyl-alkylene (alkylene-oxy-C(=O)-alkylene) moiety and a C-2 to C-4 alkyleneoxyalkylene spacer (-alkylene-oxy-alkylene);



(19).

~~96. The block copolymer of claim 95, wherein R_4 is a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.~~

~~97. The block copolymer of claim 95, wherein R_4 is H.~~

~~98. The block copolymer of claim 95, wherein R_4 is a C-1 to C-8 alkyl.~~

~~99~~35. A composition comprising at least one block copolymer of any one of claims 1 to ~~98~~ 34 and a solvent.

~~100. The composition of claim 99 further comprising a second different block copolymer.~~

~~101. The composition of any one of claims 99 to 100, wherein said second different block copolymer has a polydispersity ranging from 1.0 to about 1.1, and a Mw ranging from about 30,000 g/mole to about 100,000 g/mole.~~

~~102. The composition of any one of claims 99 to 101, wherein said second block copolymer is a block copolymer of styrene or a substituted styrene monomer, with a comonomer selected from the group consisting~~

of an alkyl 2-methylenealkanoate (alkyl-O-(C=O)-C(alkyl)=CH_2) , a lactone; a cyclic carbonate, an oxirane, and an oxetane.

103. The composition of claim 100, wherein said second different block copolymer is a block copolymer of unsubstituted styrene or a substituted styrene monomer, with an alkyl 2-methylenealkanoate.

104. The composition of claim 100 or 104, wherein said second different block copolymer is a block copolymer of styrene with methyl methacrylate.

105. The composition of Claim 99 further comprising a homopolymer.

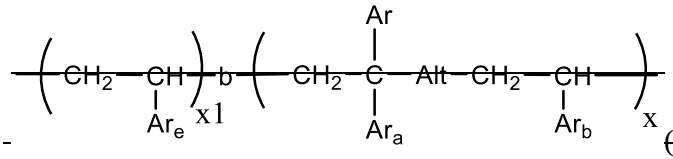
106. The composition of claim 99 wherein it comprises at least two different block copolymers having structure (1),

(A)-(C)-(B)-(1);

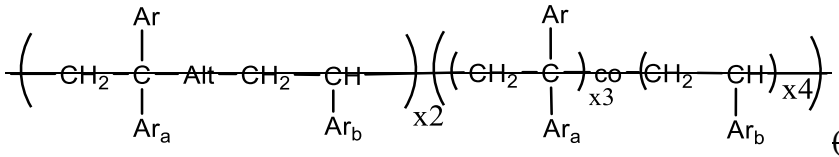
wherein (A) is a first polymer block segment comprising a copolymer block segment selected from structure (1a), structure (1b), and a mixture of structures (1a) an (1b), wherein Ar, Ar_a, Ar_b and Ar_e are independently unsubstituted aryl moieties or aryl moieties with at least one substituent selected from the group consisting of a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, x, x1, x2 and x3 and x4 are independently the number of repeat units;

wherein the structures (1a1), (1a2) and (1a3), which are present in structure (1a), structure (1b) or a mixture of structures (1a) and (1b), are present in amounts such that the mole % of structure (1a1) ranges from about 3 mole % to about 40 mole %, as measured against to sum of structures (1a1), (1a2) and (1a3); and,

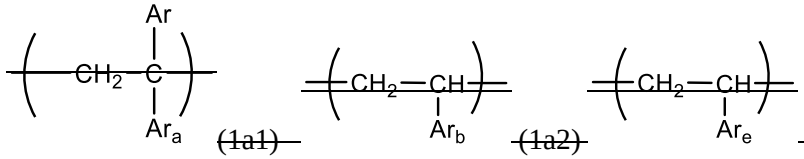
wherein the M_w of (A) ranges from about 5,000 to about 100,000 g/mole,



(1a),

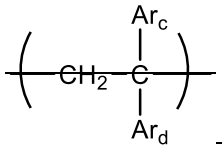


(1b),



(1a1) (1a2) (1a3);

wherein (C) is a spacer moiety comprising structure (1c), wherein Ar_c and Ar_d are independently unsubstituted aryl moieties or aryl moieties with at least one substituent selected from the group consisting of a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage,



(1c);

(B) is a second polymer block segment comprising repeat units derived from either an alkyl 2-methylenealkanoate, a lactone; a cyclic carbonate, an oxirane, or an oxetane, wherein the Mw of (B) ranges from about 5,000 g/mol to about 100,000 g/mol; wherein

said block copolymer comprising structure (1) has a M_w ranging from about 10,000 g/mol to about 200,000 g/mol and has a polydispersity of 1.00 to about 1.20;

wherein further said composition is one wherein,

at least one said block copolymer has either Ar_c, Ar_d, or both substituted with at least one moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, and

at least one said block copolymer in said composition in one in which neither Ar_c and Ar_d has as a substituent a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.

107. The composition of claim 106 wherein said mixture is one of a first and second block copolymer of structure (1), wherein

said first block copolymer has either Ar_c, Ar_d, or both substituted with at least one moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage and wherein (A) consist of either structure (1a), structure (1b) or a mixture of structure (1a) and (1b), and said second block copolymer is one in which (A) consist of structure (1b) and in which neither Ar_c, nor Ar_d, are substituted with a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage.

108. The composition of claim 107, wherein said first block copolymer is one wherein (A) consists of structure (1a).

109. The composition of claim 107, wherein said first block copolymer is one wherein (A) consists of structure (1b).

110. The composition of claim 107, wherein said first block copolymer is one wherein (A) consist of a mixture of structures (1a) and (1b).

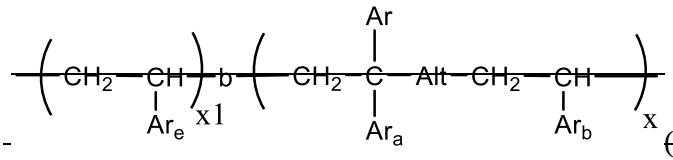
111. The composition of claim 99 comprising at least two different block copolymers having structure (1),

(A)-(C)-(B)-(1);

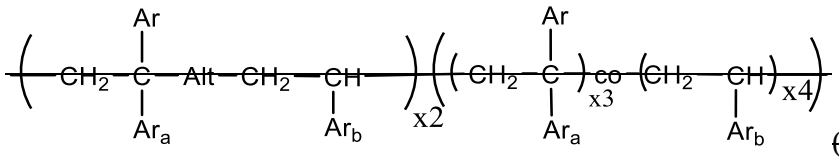
wherein (A) is a first polymer block segment comprising a copolymer block segment selected from structure (1a), structure (1b), and a mixture of structures (1a) an (1b), wherein Ar, Ar_a, Ar_b, and Ar_e are independently unsubstituted aryl moieties or aryl moieties with at least one substituent selected from the group consisting of a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage, x, x1, x2 and x3 and x4 are independently the number of repeat units;

wherein the structures (1a1), (1a2) and (1a3), which are present in structure (1a), structure (1b) or a mixture of structures (1a) and (1b), are present in amounts such that the mole % of structure (1a1) ranges from about 3 mole % to about 40 mole %, as measured against to sum of structures (1a1), (1a2) and (1a3); and,

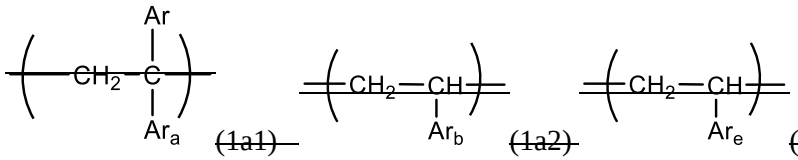
wherein the M_w of (A) ranges from about 5,000 to about 100,000 g/mole,



(1a),

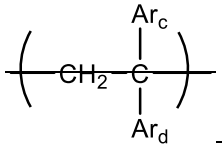


(1b),



(1a1) (1a2) (1a3);

wherein (C) is a spacer moiety comprising structure (1c), wherein Ar_c and Ar_d are independently unsubstituted aryl moieties or aryl moieties with at least one substituent selected from the group consisting of a C-1 to C-8 alkyl, and a moiety comprising a C-5 to C-18 perfluoroalkyl with at least one ether linkage,



(1c);

(B) is a second polymer block segment comprising repeat units derived from either an alkyl 2-methylenealkanoate, a lactone; a cyclic carbonate, an oxirane, or an oxetane, wherein the Mw of (B) ranges from about 5,000 g/mol to about 100,000 g/mol; wherein

said block copolymer comprising structure (1) has a M_w ranging from about 10,000 g/mol to about 200,000 g/mol and has a polydispersity of 1.00 to about 1.20;

and further wherein,

at least one said block copolymer in said composition is one wherein (A) consists of structure (1a),

at least one said block copolymer in said composition is one wherein (A) consists of either structure (1b), or a mixture of structures (1a) and (1b).

112. The composition of claim 111, wherein said composition is one wherein,

at least one said block copolymer in said composition is one wherein (A) consists of structure (1a),

at least one said block copolymer in said composition is one wherein (A) has structure (1b).

113. The composition of claim 111, wherein said composition is one wherein,

~~at least one said block copolymer in said composition is one wherein (A) has structure (1a), and~~

~~at least one said block copolymer in said composition is one wherein (A) has a mixture of structures (1a) and (1b).~~

~~114. The composition of claim 113 wherein said mixture is one of a first and second block copolymer, wherein~~

~~said first block copolymer is one wherein (A) consists of structure (1a) and said second block copolymer in said composition is one wherein (A) consist of either structure (1b), or a mixture of structures (1a) and (1b).~~

~~115. The composition of claim 114, wherein said composition is one wherein,~~

~~said first block copolymer is one wherein (A) has structure (1a), and said second block copolymer~~

~~is one wherein (A) has structure (1b).~~

~~116. The composition of claim 114, wherein said composition is one wherein,~~

~~said first block copolymer is one wherein (A) has structure (1a), and said second block copolymer~~

~~is one wherein (A) has is a mixture of structures (1a) and (1b).~~

~~117~~36. A method of vertically orienting first and second block copolymer domains over an unpatterned substrate using a layer of a block copolymer composition having a periodicity of L_0 comprising the steps of:

a) forming a coating layer of a block copolymer from the composition of ~~any one of~~ claim~~s~~ ~~99 to 116~~35 on said unpatterned substrate; and,

b) annealing the layer of the block copolymer to generate a non-zero positive integer number of first and second block copolymer domains, vertically oriented on said unpatterned substrate.

~~118. The method of claim 117, wherein said unpatterned substrate is one which is an unpatterned conventional neutral layer.~~

~~119~~37. A method of vertically orienting first and second block copolymer domains over a first patterned substrate where the height of topography of the pattern on the substrate is at least 0.7 times L_0 and aligning the domains with the pattern, using a coating comprised of a block copolymer having a periodicity of L_0 comprising the steps of:

a1) forming a coating layer of the composition of ~~any one of~~ claim~~s~~ ~~99 to 116~~35 on said first topographical substrate, wherein the average thickness of the coating layer of the block copolymer is less than the height of the topography of the first topographical substrate, wherein the block copolymer layer is laterally confined by the topography; and,

b1) annealing the block copolymer layer to generate first and second block copolymer domains, vertically oriented on said first patterned substrate, and confined within the recessed region.

~~120. The method of claim 119, wherein said first patterned substrate is one which has at the bottom of said recessed region a layer of a conventional neutral layer.~~

~~121~~38. A method of vertically orienting, first and second block copolymer domains with a periodicity of L_0 over a second patterned substrate having a topographical pattern with the height of topography larger than 0.7

times L_0 and a pitch P1 where the pitch P1 is a non-zero positive integer multiplied by L_0, and aligning the domains with the pattern comprising the steps of:

a2) forming a coating layer of a block copolymer with the composition of ~~any one of~~ claim~~s~~ ~~99 to 116~~35 on said second patterned substrate, where~~-~~ the thickness of the coating layer of the block copolymer is more~~-~~ than the height of the topography of the second patterned substrate; and,

b2) annealing the block copolymer layer to generate a non-zero positive integer number of first and second block copolymer domains vertically oriented on said second patterned substrate and aligning them to the second patterned substrate where the sum of vertically oriented domains is equal or larger than the pitch P1 the of topographical pattern.

~~122. The method of claim 121, wherein said second patterned substrate is one which has at the bottom of said recessed region a layer of a conventional neutral layer.~~

~~123~~39. A method of vertically orienting first and second block copolymer domains over a substrate having a surface chemical prepattern having a pitch P2, where the pitch P2 is a non-zero positive integer multiplied by L_0 and aligning the domains comprising the steps of:

a3) forming a coating layer of the composition of ~~any one of~~ claim~~s~~ ~~99 to 116~~35 on the substrate having a surface chemical prepattern; and,

b3) annealing the block copolymer layer to generate vertically oriented first and second block copolymer domains aligned with the substrate having a surface chemical prepattern having a pitch P2.

~~124. The method of claim 122, wherein said surface chemical prepattern having a pitch P2 is one in which one of the elements having pitch P2 is a region of conventional neutral layer.~~

~~125. The use of a block copolymer according to any one of claims 1 to 98 or a composition according to any one of claims 99 to 116 for forming patterns in processes comprising directed self-assembly of block copolymers.~~