CLAIMS

What is claimed is:

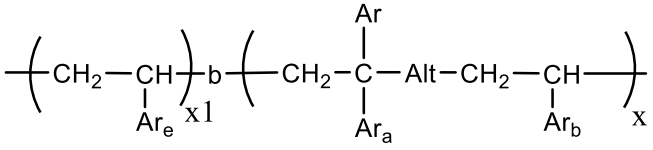
1. A block copolymer comprising structure (1)

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

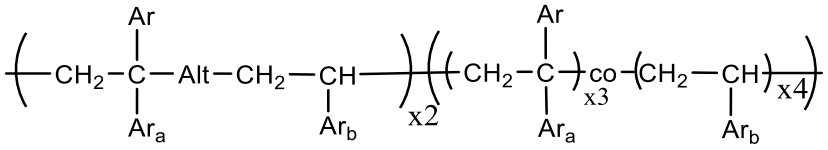
wherein (A) is a first polymer block segment comprising a copolymer block segment selected from structure (1a), structure (1b), and a mixture of structures (1a) and (1b), wherein Ar, Ar_a, Ar_b and Ar_e are each independently unsubstituted aryl moieties or aryl moieties with at least one substituent 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 3 mole % to 40 mole %, as measured against to sum of structures (1a1), (1a2) and (1a3); and,

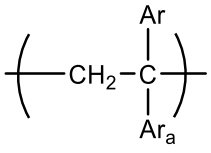
wherein the M_w of (A) ranges from 5,000 to 100,000 g/mole,



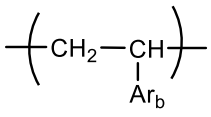
(1a),



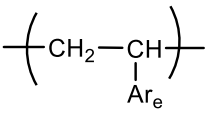
(1b),



(1a1)

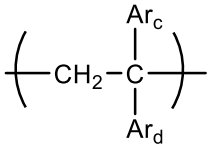


(1a2)



(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 5,000 g/mol to 100,000 g/mol; and

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

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

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

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

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

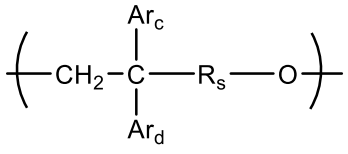
6. The block copolymer of anyone of claims 1 to 5, wherein (A) consists of structure (1a).

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

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

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

10. The block copolymer of any one of claim 1 to 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).

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

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

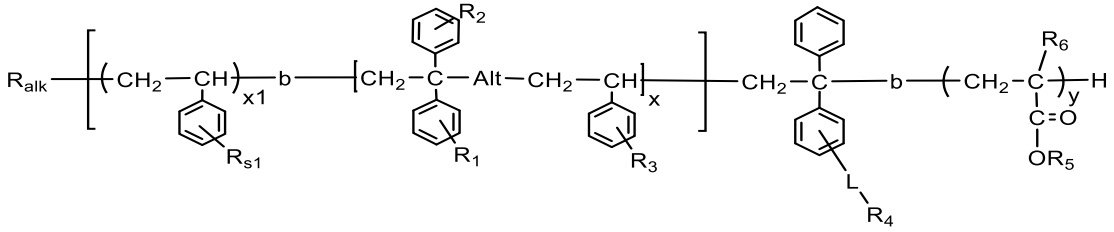
13. The block copolymer of any one of claims 1 to 10, wherein (B) is a polymer block segment whose repeat units are derived from a lactone.

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

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

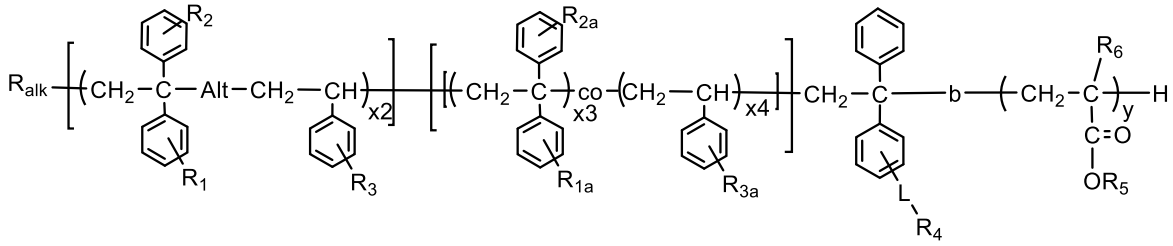
16. The block copolymer of any one of claims 1 to 10, wherein (B) is a polymer block segment whose repeat units are derived from an oxetane.

17. The block copolymer of any one of claims 1 to 3, 6, 9 to 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).

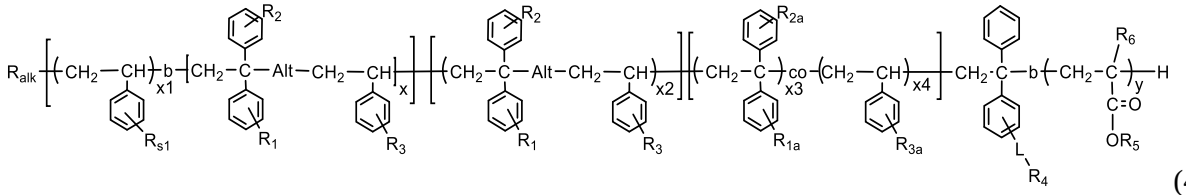
18. The polymer of any one of claims 1 to 2, 4, 7, 9, 11 to 12, which has structure (3), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a 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).

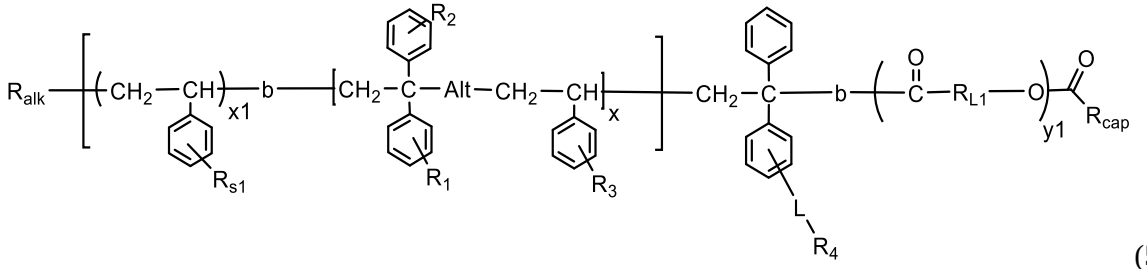
19. The polymer of any one of claims 1 to 3, 4 to 5, 8 to 9, 11 to 12, which has structure (4), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, 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);



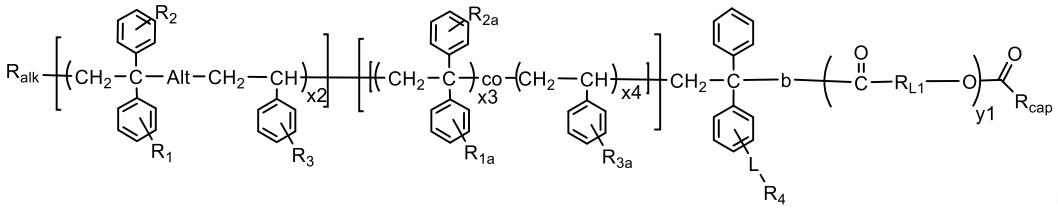
(4).

20. The block polymer of any one of claims 1 to 3, 6, 9 to 10, and 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_{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);



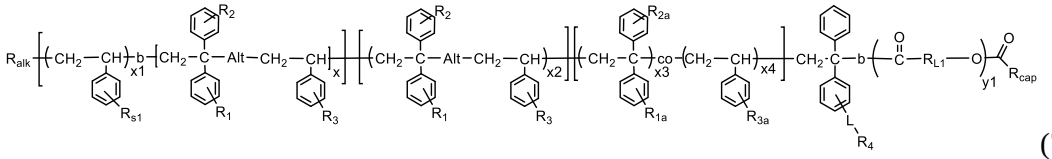
(5).

21. The block polymer of any one of claims 1 to 2, 4, 7, 9, and 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);



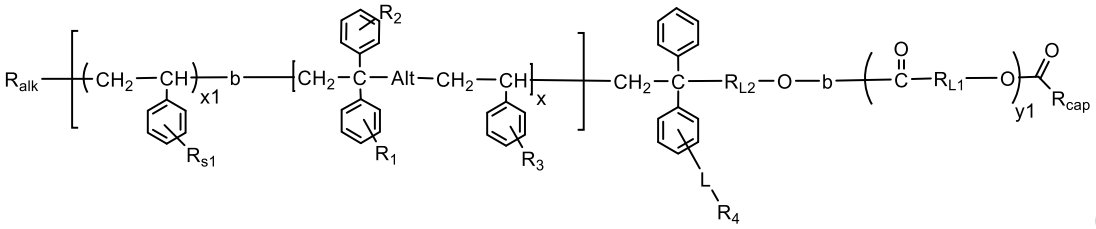
(6).

22. The block polymer of any one of claims 1 to 3, 4, 5, 8, 9, and 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).

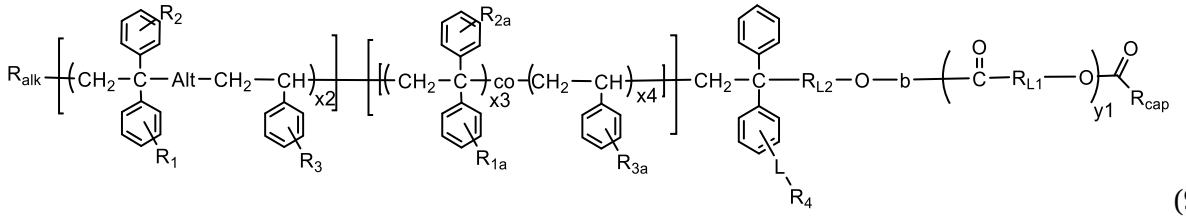
23. The block polymer of any one of claims 1 to 3, 7 to 10 and 13 which has structure (8), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1}, R_1, $R_{2,}$ and R_3, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety comprising 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).

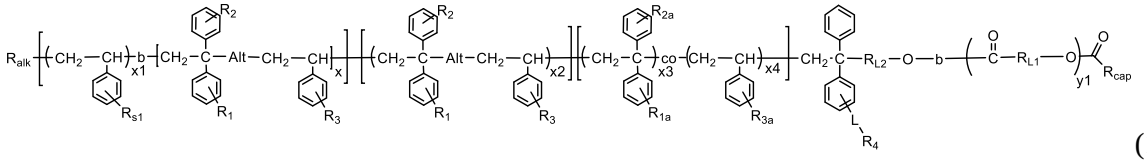
24. The block polymer of any one of claims 1 to 3, 4, 5, 7 to 10, and 13, which has structure (9), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, $R_{2,}$ $R_{2a,}$ R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is a C-5 to C-18 perfluoroalkyl pendant group comprising 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);



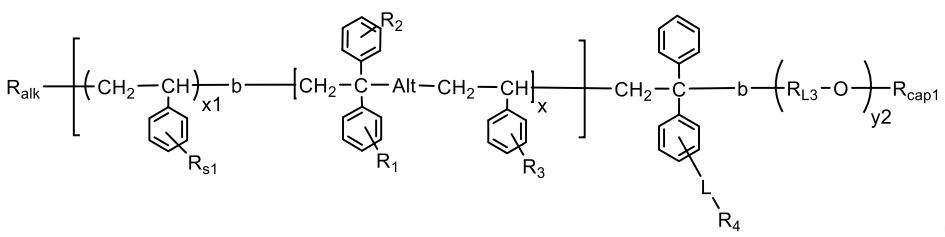
(9).

25. The block polymer of any one of claims 1 to 3, 4, 5, 7 to 10, and 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);



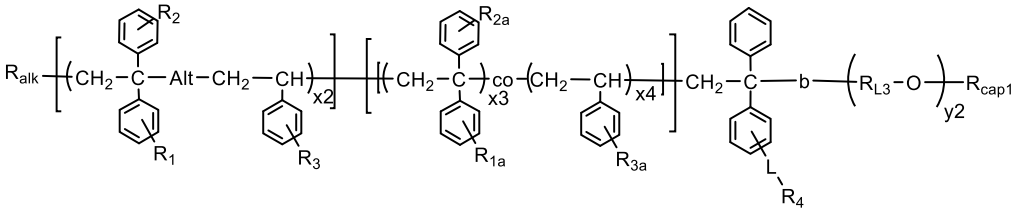
(10).

26. The block copolymer of any one of claims 1 to 3, 6, 9 to 10, 12 and 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);



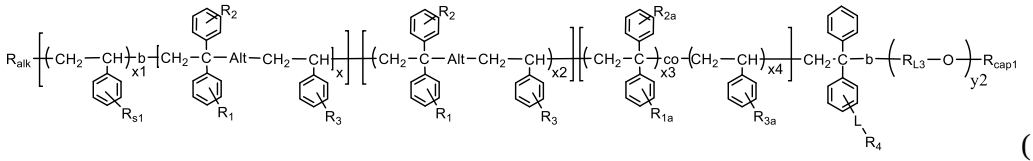
(11).

27. The block copolymer of any one of claims 1 to 2, 4, 7, 9, 12 and 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).

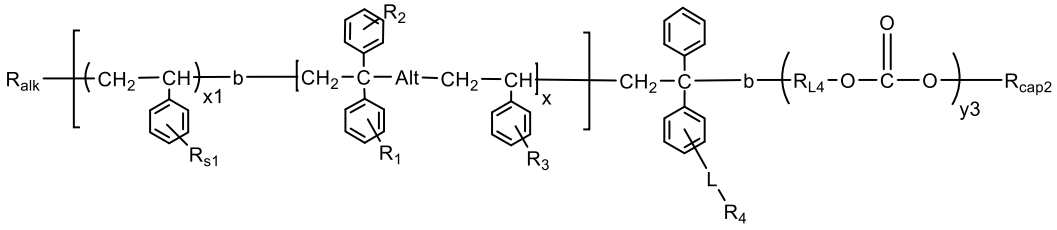
28. The block copolymer of any one of claims 1 to 3, 4, 5, 8, 9, 12 and 13, which has structure (13), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1}, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H, and a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a 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).

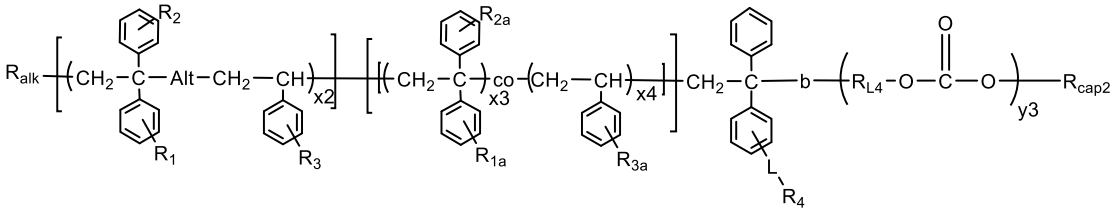
29. The block copolymer of any one of claims 1 to 3, 6, 9 to 10 and 14, which has structure (14), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1} R_1, R_2, and R_3, are independently selected from H or a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to C-8 alkyl, and a moiety 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);



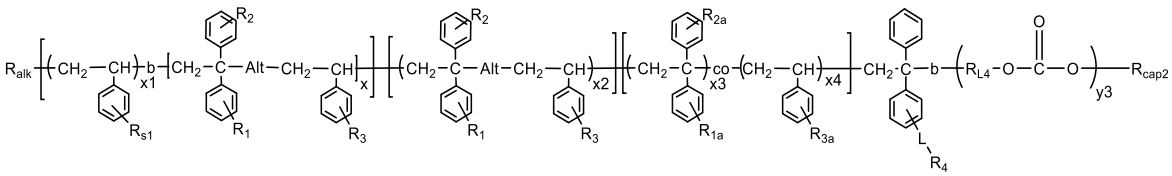
(14).

30. The block copolymer of any one claims 1 to 2, 4, 7, 9 and 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).

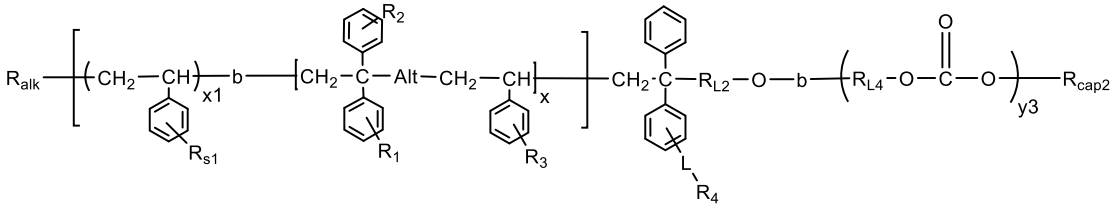
31. The block copolymer of any one of claims 1 to 3, 4, 5, 8, 9 and 14 which has structure (16), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1}, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H, and a C-1 to C-8 alkyl, R_4 is selected from the group consisting of H, a C-1 to 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).

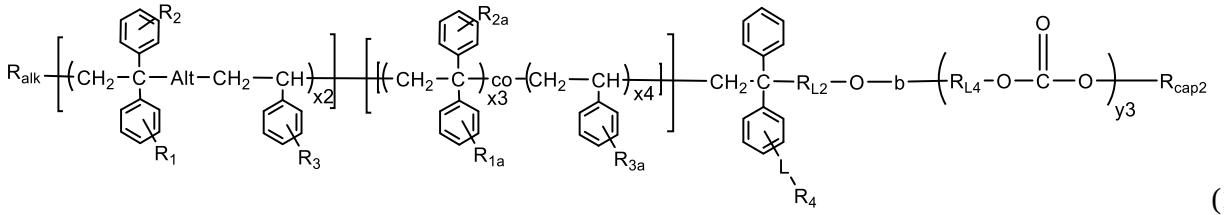
32. The block copolymer of any one of claims 1 to 3, 7 to 10 and 14, which has structure (17), wherein R_{alk} is a C-1 to C-8 alkyl, R_{s1} R_1, R_2, and R_3, are independently selected from H or a C-1 to C-8 alkyl, R_4 is

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).

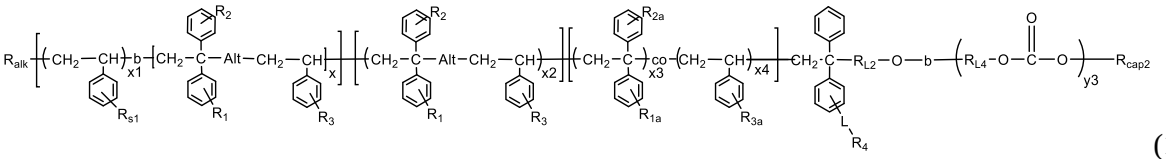
33. The block copolymer of any one of claims 1 to 3, 4, 5, 7 to 10 and 14, which has structure (18), wherein R_{alk} is a C-1 to C-8 alkyl, R_1, R_{1a}, R_2, R_{2a}, R_3, and R_{3a}, are independently selected from H or a C-1 to C-8 alkyl, R_4 is a C-5 to C-18 perfluoroalkyl pendant group comprising 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).

34. The block copolymer of any one of claims 1 to 3, 4, 5, 7 to 10 and 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).

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

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 claim 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.

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 claim 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.

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 claim 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.

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 claim 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.