CLAIMS

1. A block copolymer having structure (1), wherein

A segment is a polar block copolymer segment comprised of either alkyl 2-methylenealkanoate derived repeating units, lactone derived repeat units, oxirane derived repeat units, oxetane derived repeating units, or cyclic carbonate derived repeat units;

L is either a direct valence bond or a linking moiety derived from a 1,1-diarylethene;

B segment is a non-polar block copolymer segment comprised of styrenic repeat units,

E are end groups selected from H, an alkyl, a carbonylalkyl (-C=O-alkyl), a carbonyloxyalkyl (-C=O-O-alkyl, and an alkyl 2-arylacrylate derived end group (-CH_2-CH(Aryl)(C(=O))-O-alkyl); and further,

said block copolymer of structure (1) is multi-tethered with oligo flexible tethered groups which are selected from oligo linear alkylene tethered group, oligo ether tethered groups, and oligo dialkyl siloxane tethered groups, and these oligo flexible tethered groups are multi-tethered at positions selected from the following placements in the polymer block copolymer of structure (1):

said oligo flexible tethered groups are only present on segments A and are either randomly located along this segment on some of its repeat units or present on each of its repeat units.

said oligo flexible tethered groups are only present on segment B and are either randomly located along this segment on some of its repeat units or present on each of its repeat units,

said oligo flexible tethered groups are present on both segments A and segments B and are either randomly located along these segments on only some of its repeat units or present on each of their repeat units,

said oligo flexible tethered group are present on both E end groups, when these are an alkyl or an alkyl 2-arylacrylate derived end group (-CH_2-CH(Aryl)(C(=O))-O-alkyl),

said oligo flexible tethered groups are present on both L when L is a linking moiety derived from a 1,1-diarylethene,

said oligo flexible tethered groups are present in the center of the B segment; and

said oligo flexible tethered groups are present on at least one of A segments, B segments, L (when L is said linking moiety), and end groups E, and further wherein,

said block copolymer has a polydispersity ranging from 1 to 1.09:

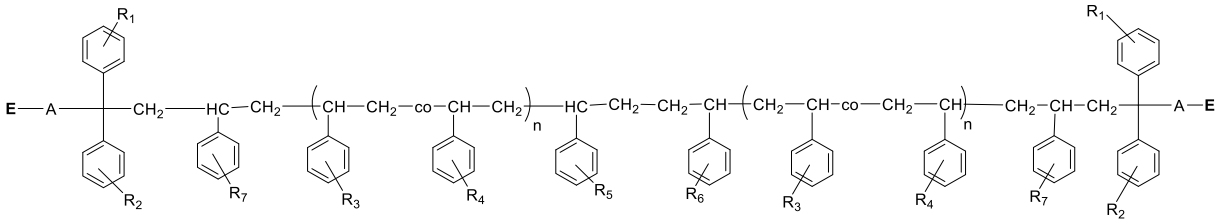
E-A-L-B-L-A-E (1).

2. The block copolymer of claim 1 wherein said polar block copolymer segment A is comprised of repeat units derived from a lactone.

3. The block copolymer of claim 1 wherein said polar block copolymer segment A is comprised of repeat units derived from an alkyl 2-methylenealkanoate.

4. The block copolymer of any one of claims 1 to 3, wherein said polar block copolymer segment A segment has a Mw between 20,000 and 200,000, and said non-polar styrenic block copolymer segment B has a Mw between 20,000 and 200,000.

5. The block copolymer of claims 1 or 4, having structure (2) wherein R_1, R_2, R_3, R_4, R_5, R_6, and R_7, are individually selected from H, a C-1 to C-5 alkyl, a halide, a C-1 to C-5 alkyloxy and said oligo flexible tethered groups wherein further at least one R_1, R_2, R_3, R_4, R_5, R_6, and R_7, is selected from said oligo flexible tethered groups and n is the number of repeat units;



(2).

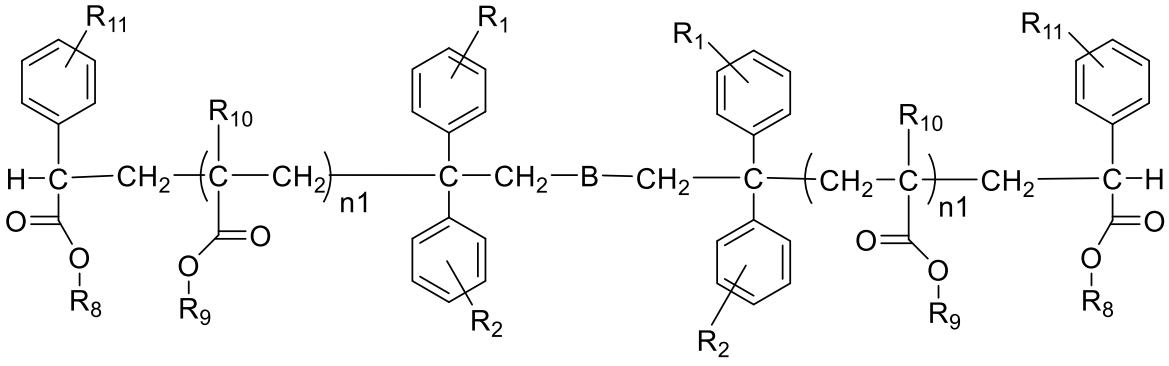
6. The block copolymer of any one of claims 1, 4, and 6 having structure (3), wherein

R_1, and R_2, are individually selected from H, a C-1 to C-5 alkyl, a halide, a C-1 to C-5 alkyloxy and said oligo flexible tethered groups,

R_8, and R_9, are individually selected from a C-1 to C-5 alkyl, and said oligo flexible tethered groups,

R_{10} is H or a C-1 to C-5 alkyl,

R_{11} is H, C-1 to C-5 alkyl, a halide or a C-1 to C-5 alkyloxy; wherein further at least one R_1, R_2, R_8, and R_9, is selected from said oligo flexible tethered groups, and n1 is the number of repeat units;



(3).

7. The block copolymer of claim 1 having structure (4), wherein

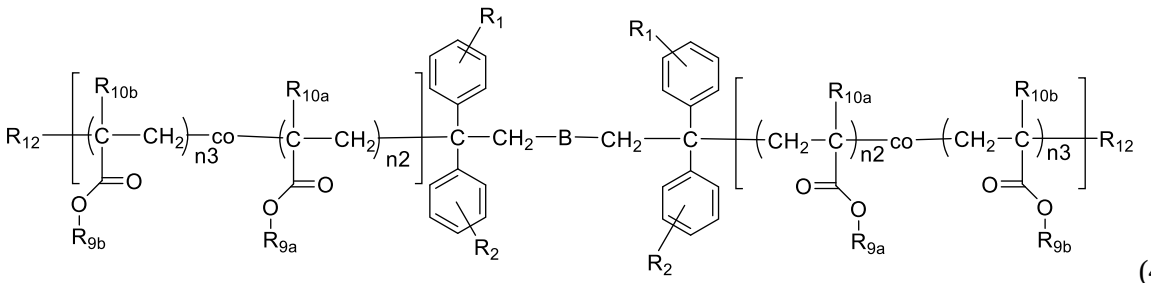
R_1, and R_2, are individually selected from H, a C-1 to C-5 alkyl, a halide, a C-1 to C-5 alkyloxy and said oligo flexible tethered groups,

R_{9a} and R_{9b} are individually selected from a C-1 to C-5 alkyl, and said oligo flexible tethered groups,

R_{10a} and R_{10b} are individually selected from H or a C-1 to C-5 alkyl,

R_{12} is H or a C-1 to C-5 alkyl, wherein further,

at least one of R_1, R_2, R_{9a} and R_{9b} is selected from said oligo flexible tethered groups and n2 and n3 are the number of repeat units;



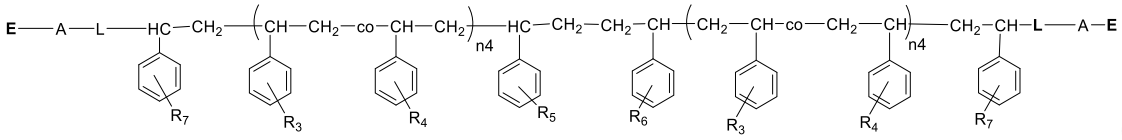
(4).

8. The block copolymer of claim 1 having structure (5), wherein R_3, R_4, R_5, R_6, and R_7, are individually selected from H, a C-1 to C-5 alkyl, a halide, a C-1 to C-5 alkyloxy and said oligo flexible tethered groups, wherein further at least one of R_3, R_4, R_5, R_6, and R_7, is selected from said oligo flexible tethered groups, unless the moiety E-A-L in structure (5) contains at least one said oligo flexible tethered group,

L is either a direct valence bond or a linking moiety derived from a 1,1-diarylethene;

A segment is said polar block copolymer segment comprised either alkyl 2-methylenealkanoate derived repeating units, lactone derived repeat units, oxirane derived repeat units, oxetane derived repeating units, or cyclic carbonate derived repeat units;

E is said end groups selected from H, an alkyl, a carbonylalkyl (-C=O-alkyl), a carbonyloxyalkyl (-C=O-O-alkyl), and an alkyl 2-arylacrylate derived end group (-CH_2-CH(Aryl)(C(=O))-O-alkyl) and n4 is the number of repeat units;



(5).

9. The block copolymer of claim 8, wherein in structure (5) E-A-L has structure (3a), wherein;

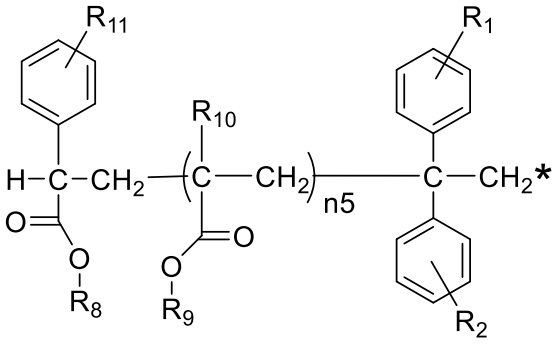
* represents the attachment point of the E-A-L moiety to B,

R_1, and R_2, are individually selected from H, a C-1 to C-5 alkyl, a halide, a C-1 to C-5 alkyloxy and said oligo flexible tethered groups,

R_8, and R_9, are individually selected from a C-1 to C-5 alkyl, and said oligo flexible tethered groups,

R_{10} is H or a C-1 to C-5 alkyl,

R_{11} is H, C-1 to C-5 alkyl, a halide or a C-1 to C-5 alkyloxy; wherein further at least one of R_1, R_2, R_8, and R_9, is selected from said oligo flexible tethered groups, unless said B has at least one said oligo flexible tethered group, and n5 is the number of repeat units;



(3a).

10. The block copolymer of claim 8, wherein in structure (5) E-A-L has structure (4a), wherein * represents the attachment point of the E-A-L moiety to B,

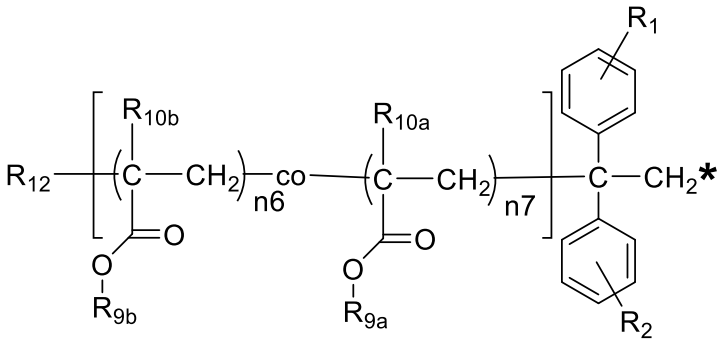
R_1, and R_2, are individually selected from H, a C-1 to C-5 alkyl, a halide, a C-1 to C-5 alkyloxy and said oligo flexible tethered groups,

R_{9a} and R_{9b} are individually selected from a C-1 to C-5 alkyl, and said oligo flexible tethered groups,

R_{10a} and R_{10b} are individually selected from H or a C-1 to C-5 alkyl,

R_{12} is H or a C-1 to C-5 alkyl, wherein further

at least one of R_1, R_2, R_{9a} and R_{9b} is selected from said oligo flexible tethered groups, unless said B has at least one said oligo flexible tethered group, wherein n6 and n7 are the number of repeat units;



(4a).

11. A block copolymer having structure (6), wherein

A_1 is a polar block copolymer segment, which has a T_g of 50°C to 100°C, comprised of either alkyl 2-methylenealkanoate derived repeating units, lactone derived repeat units, oxirane derived repeat units, oxetane derived repeating units, or cyclic carbonate derived repeat units;

B_1 is a styrenic block copolymer segment, which has a T_g from 50°C and to 100°C

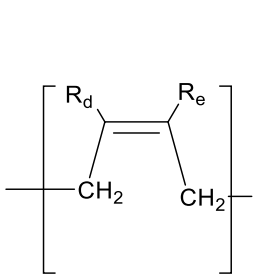
B_2 is block copolymer segment with a T_g ranging from -5°C to -50°C, which comprises repeat units derived from either an olefin selected from the group consisting of an alkene, an alkadiene, and an alkatriene, or a from mixture of at two different olefins selected from this group;

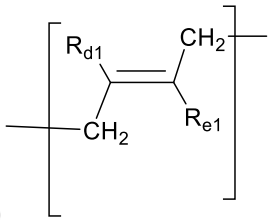
L_1 is either a direct valence bond or a linking moiety derived from a 1,1-diarylethene; wherein

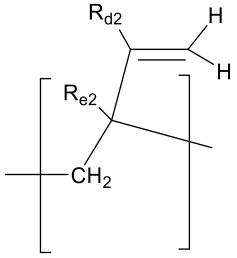
E_1 are end groups selected from H, an alkyl, a carbonylalkyl (-C=O-alkyl), a carbonyloxyalkyl (-C=O-O-alkyl, and an alkyl 2-arylacrylate derived end group (-CH_2-CH(Aryl)(C(=O))-O-alkyl), and further wherein said block copolymer has a polydispersity ranging from 1 to 1.09;

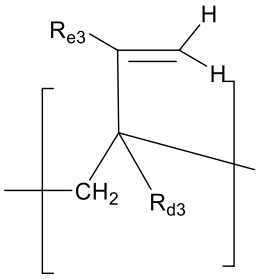
$$E_1\text{-}A_1\text{-}L_1\text{-}B_2\text{-}B_1\text{-}B_2\text{-}L_1\text{-}A_1\text{-}E_1 \quad (6).$$

12. The block copolymer of claim 11, wherein said B_2 is comprised of a mixture of at least two different olefinic repeat units having structures (7a), (7b), (7c), and (7d), derived from an alkadiene; wherein R_d, R_{d1}, R_{d2}, R_{d3}, R_e, R_{e1}, R_{e2}, and $R_{e3,}$ are individually selected from the group consisting of a H, and a C-1 to C-8 alkyl, and further wherein the total mole% of these olefinic repeat units in said block copolymer ranges from 3 mole% to 50 mole%;



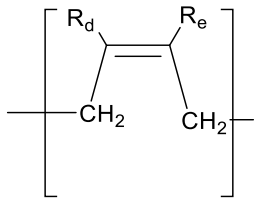
(7a)


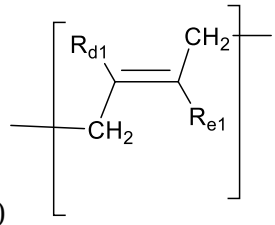
(7b)


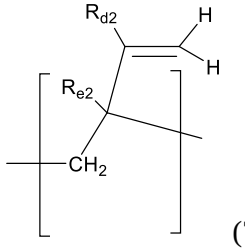
(7c)


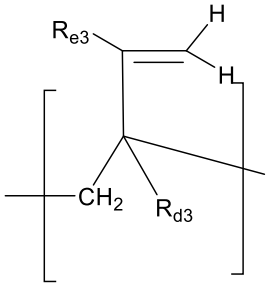
(7d).

13. The block copolymer of claim 11, wherein R_d, R_{d1}, R_{d2}, and R_{d3} are the same and are selected from a H, or a C-1 to C-8 alkyl, and R_e, R_{e1}, R_{e2}, and R_{e3}, are selected from a H, or a C-1 to C-8 alkyl,



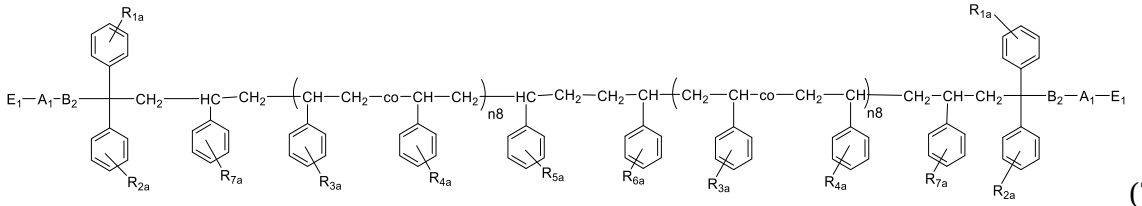
(7a)


(7b)


(7c)


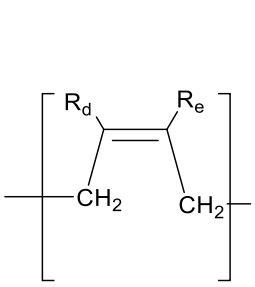
(7d).

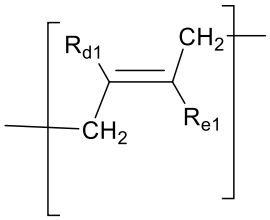
14. The block copolymer of any one of claims 11 to 13, having structure (7) which comprises a central non-polar styrenic block copolymer segment attached at either end to the moiety -B_2-A_1-E_1 wherein R_{1a}, R_{2a}, R_{3a}, R_{4a}, $R_{5a,}$ R_{6a}, and R_{7a}, are individually selected from H, a C-1 to C-5 alkyl, a halide, a C-1 to C-5 alkyloxy, n8 is the number of repeat units;

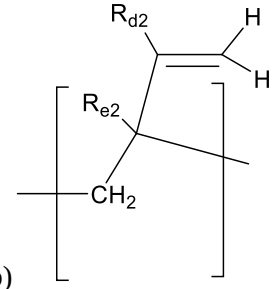


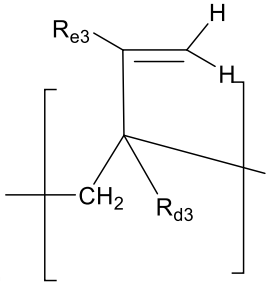
(7).

15. The block copolymer of claim 14, wherein said B_2 is comprised of a mixture of at least two different olefinic repeat units having structures (7a), (7b), (7c), and (7d); wherein R_d, R_{d1}, R_{d2}, R_{d3}, R_e, R_{e1}, R_{e2}, and R_{e3}, are individually selected from the group consisting of a H, and a C-1 to C-8 alkyl, and further wherein the total mole% of these olefinic repeat units in said block copolymer ranges from 3 mole% to 50 mole%;



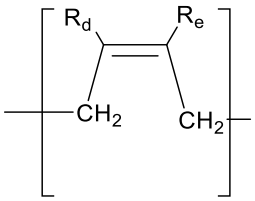
(7a)


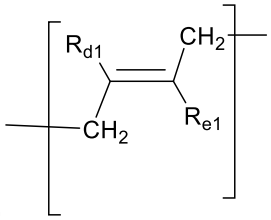
(7b)


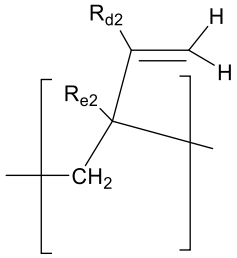
(7c)


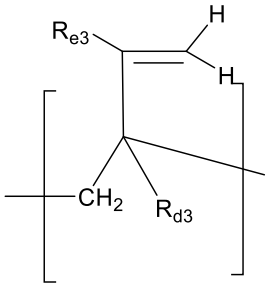
(7d).

16. The block copolymer of claim 14, wherein R_d, R_{d1}, R_{d2}, and R_{d3} are the same and are selected from a H, or a C-1 to C-8 alkyl, and R_e, R_{e1}, R_{e2}, and R_{e3}, are selected from a H, or a C-1 to C-8 alkyl.



(7a)


(7b)


(7c)


(7d).

17. A composition comprising a least one block copolymer of any one of claims 1 to 10 and a spin casting solvent.

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

a) forming a coating layer of a block copolymer from the composition of claim 17 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.

19. 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 17 on said first topographical substrate, wherein the thickness of 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.

20. 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 Lo, 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 17 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 of the topographical pattern.

21. 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:

a) forming a coating layer of a block copolymer with the composition of claim 17 on the substrate having a surface chemical prepattern; and,

b) 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.

22. A composition comprising the block copolymer of any one of claims 11 to 16 and a solvent.

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

a) forming a coating layer of a block copolymer from the composition of claim 22 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.

24. 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 22 on said first topographical substrate, wherein the thickness of 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.

25. 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 22 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,

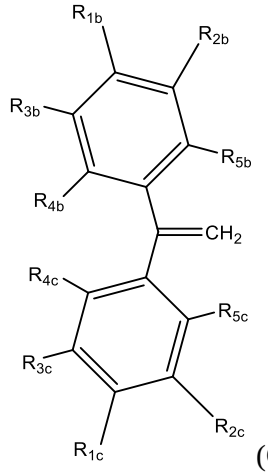
b2) annealing the block copolymer layer to generate a non-zero positive integer number of first and second block copolymer domains vertically oriented on said second patterned substrate and aligning them to the second patterned substrate where the sum of vertically oriented domains is equal or larger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

26. 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:

a) forming a coating layer of a block copolymer with the composition of claim 22 on the substrate having a surface chemical prepattern; and,

b) 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.

27. A compound of structure (C1), wherein R_{1b}, R_{1c}, R_{2b} and R_{2c} are individually selected from H, a halide, a C-1 to C-4 alkyl, a C-1 to C-4 alkyloxy and an oligo flexible tethered groups, wherein at least one of $R_{1b,}$ $R_{2b,}$ R_{1c} and R_{2c} is an oligo flexible tethered group and R_{3b}, R_{3c}, R_{4b}, R_{4c}, R_{5b} and R_{5c} are individually selected from H, a halide, a C-1 to C-4 alkyl, and a C-1 to C-4 alkyloxy; wherein said oligo flexible tethered group is an oligo ether tethered group or an oligo dialkyl siloxane tethered group,

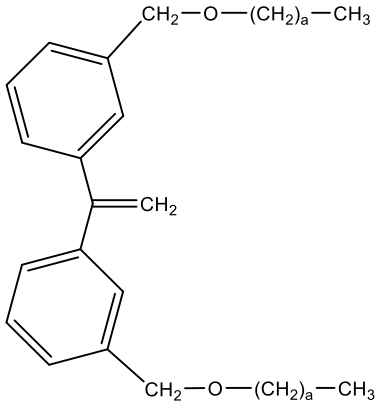


(C1).

28. The compound of claim 27, wherein said flexible oligo flexible tethered group is an oligo ether tethered group.

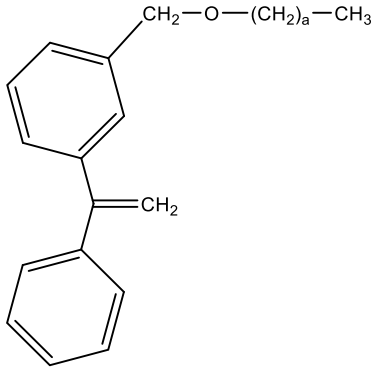
29. The compound of claim 27, wherein said flexible oligo flexible tethered groups is an oligo dialkyl siloxane tethered group.

30. The compound of claim 27, which has structure (C1-A), wherein a is 7 to 19;



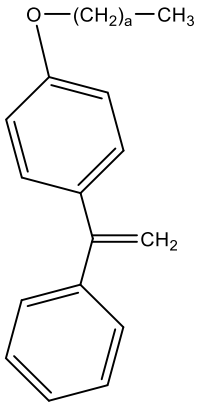
(C1- A).

31. The compound of claim 27, which has structure (C1-B), wherein a is 7 to 19;



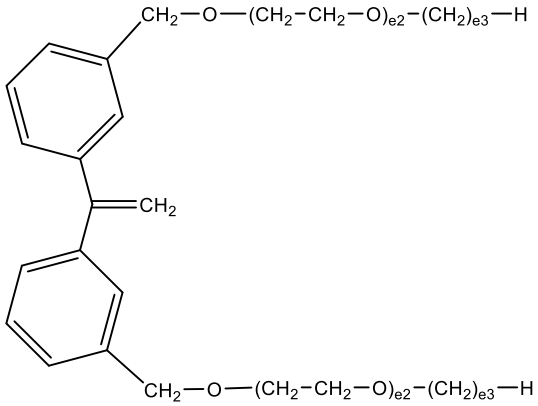
(C1-B).

32. The compound of claim 27, which has structure (C1-D), wherein a is 7 to 19;



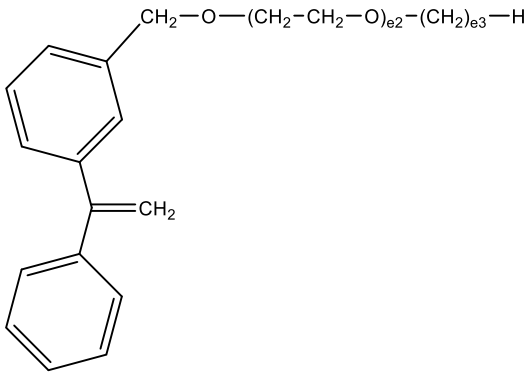
(C1-D).

33. The compound of any one of claims 27 and 28, which has structure (C1-E), wherein e2 is 2 to 8, and e3 is 1 to 8.



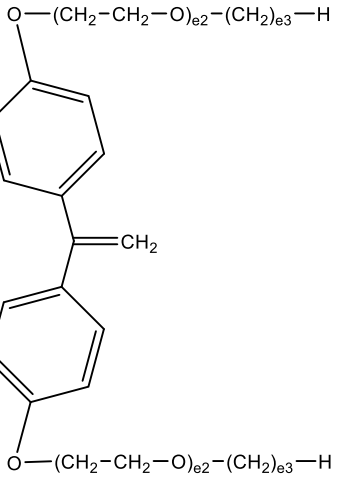
(C1-E).

34. The compound of any one of claims 27 and 28 which has structure (C1-F), wherein e2 is 2 to 8 and e3 is 1 to 8;



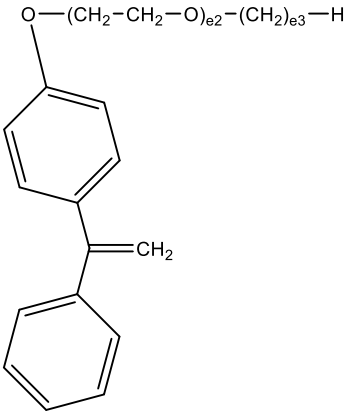
(C1-F).

35. The compound of any one of claims 27 and 28, which has structure (C1-G), wherein e2 is 2 to 8, and e3 is 1 to 8.



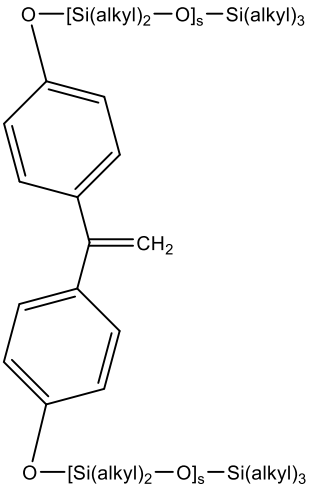
(C1-G).

36. The compound of claim 27, which, has structure (C1-H), wherein e2 is 2 to 8, and e3 is 1 to 8;



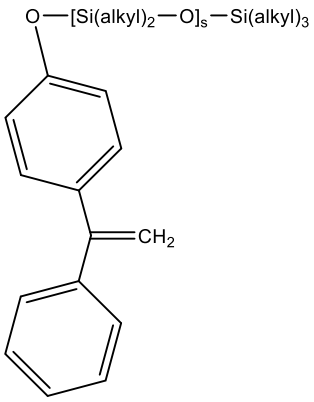
(C1-H).

37. The compound of any one of claims 27 and 29, which has structure (C1-I), wherein s is 6 to 18, and the alkyl moiety is a C-1 to C-8 alkyl;



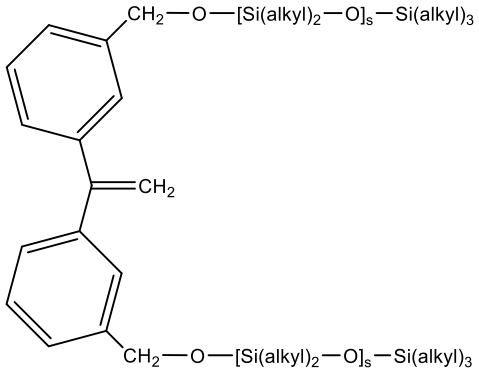
(C1-I).

38. The compound of any one of claims 27 and 29, which, has structure (C1-J), wherein s is 6 to 18, and the alkyl moiety is a C-1 to C-8 alkyl;



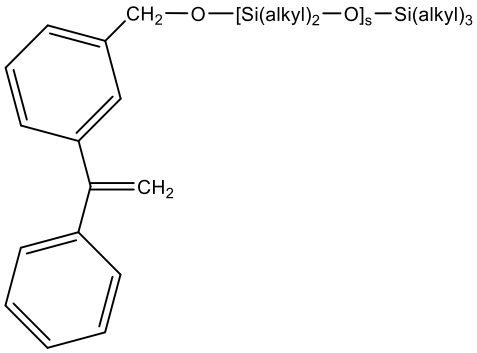
(C1-J).

39. The compound of any one of claims 27 and 29, which has structure (C1-K), wherein s is 6 to 18, and the alkyl moiety is a C-1 to C-8 alkyl;



(C1-K).

40. The compound of any one of claims 27 and 29 which has structure (C1-L), wherein s is 6 to 18, and the alkyl moiety is a C-1 to C-8 alkyl;



(C1-L).