CLAIMS

1. A block copolymer having structure **(I)**:

E'-A-L-B-E'' (I),

wherein

A segment is a non-polar block copolymer segment comprising styrenic repeat units,

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

B segment is a polar block copolymer segment comprising 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 a C-1 to C-12 alkyl end group,

E'' is and end group 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 groups, oligo ether tethered groups, and oligo dialkyl siloxane tethered groups, and these oligo flexible tethered groups are multi-tethered on at least one of either the A segments, B segments, and L, if L is a linking moiety derived from a 1,1-diarylethene, and said block copolymer has a polydispersity ranging from 1 to about 1.09, and a Mn of at least 40,000**.**

2. The block copolymer of claim 1, wherein said oligo flexible tethered groups are oligo linear alkylene tethered groups.

3. The block copolymer of claim 1, wherein said oligo flexible tethered groups are oligo linear alkylene tethered group having the general structure -X1-$(CH_2)_a$-CH_3, wherein n is 6 to 19 and X1 is and X1 is selected from a direct valence bond, a linear C-1 to C-4 alkylene spacer, -O- ,-CH_2-O- , -O-(C=O)-, -C=O-O-, C=O, -CH_2-O-(C=O)-, -S-, -SO_2-, and -SO-.

4. The block copolymer of claim 1, wherein said oligo flexible tethered groups are oligo ether tethered groups.

5. The block copolymer of claim 1, wherein said oligo flexible tethered groups are oligo ether tethered groups, which have the formulas: -O-[$(CH_2)_e$-O-]$_{e2}$-$(CH_2)_{e3}$-H, or -$(CH_2)_{e4}$-O-[$(CH_2)_e$-O-]$_{e2}$-$(CH_2)_{e3}$-H, wherein independently e is from 2 to 8, e2 is from 2 to 8, e3 is from 1 to 8, and e4 is from 1 to 8.

6. The block copolymer of claim 1, wherein said oligo flexible tethered groups are oligo dialkyl siloxane tethered groups.

7. The composition of claim 1, wherein said oligo flexible tethered groups are oligo dialkyl siloxane tethered groups which have the formula -X2-$[Si(alkyl)_2-O]_s$-$Si(alkyl)_3$, where s is from 6 to 18 and the alkyl moiety is a C-1 to C-8 alkyl and X2 is a direct valence bond, or a C-1 to C-8 linear alkylene spacer, or -O-.

8. The block copolymer of claim 1, wherein said polar block copolymer segment B comprises repeat units derived from a lactone.

9. The block copolymer of claim 1, wherein said polar block copolymer segment B comprises repeat units derived from an alkyl 2-methylenealkanoate.

10. The block copolymer of claim 1, wherein said polar block copolymer segment B segment has a Mw between about 20,000 and about 200,000 and said non-polar styrenic block copolymer segment A has a Mw between 20,000 and about 200,000.

11. The block copolymer of claim 1, wherein L is a direct valence bond.

12. The block copolymer of claim 1, wherein L is a linking group derived from a 1,1-diarylethene.

13. The block copolymer of claim 1, wherein E'' is H.

14. The block copolymer of claim 1, wherein oligo flexible tethered groups are located on the A segments and are either randomly located along this segment on some of its repeat units or present on each of its repeat units.

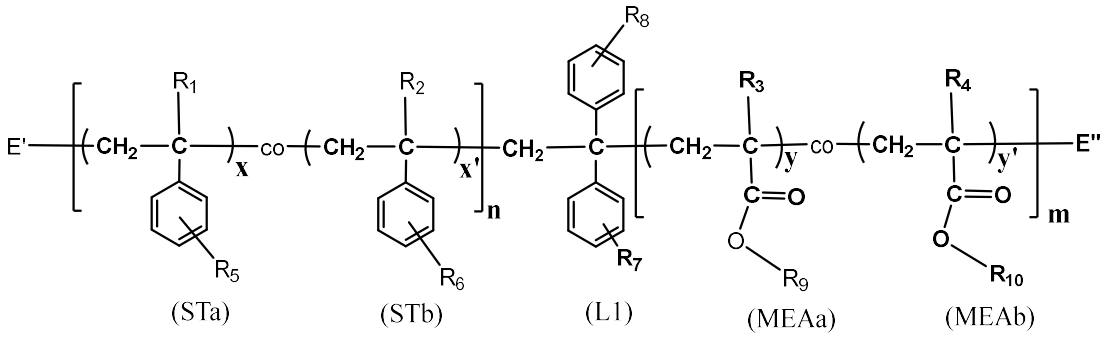
15. The block copolymer of claim 1, wherein said oligo flexible tethered groups are located on the B segment and are either randomly located along this segment on some of its repeat units or present on each of its repeat units.

16. The block copolymer of claim 1, wherein said oligo flexible tethered groups are located on the linking group L, when it is derived from a 1,1-diarylethene.

17. The block copolymer of claim 1, wherein said oligo flexible tethered groups are located on the A segment, the B segment, and the linking group L, if L is derived from a 1,1-diarylethene and are either

randomly located along A segment or B Segment on some of their respective repeat units or present on each of their respective repeat units.

18. The block copolymer of claim 1, wherein said copolymer has structure **(II)**:



(II),

comprising

a styrenic block consisting of the randomly copolymerized styrenic repeat units of structures (STa) and (STb) wherein R_1 and R_2 are individually selected from H or a C-1 to C-4 alkyl, R_5 and R_6 are individually selected from H or a C-1 to C-4 alkyl, and an oligo flexible tethered group which are selected from an oligo linear alkylene tethered group, an oligo ether tethered groups, and an oligo dialkyl siloxane tethered groups;

a linking moiety of structure (L_1), wherein R_7 and R_8 are individually selected from H, a C-1 to C-4 alkyl and a is multi-tethered with oligo flexible tethered group which is selected from an oligo linear alkylene tethered group, an oligo ether tethered groups, and an oligo dialkyl siloxane tethered groups;

a 2-methylenealkanoate derived block consisting of the randomly copolymerized 2-methylenealkanoate repeat units of structures (MEAa) and (MEAb), wherein R_3 and R_4 and individually selected from a C-1 to C-4 alkyl and R_9 and R_{10} are individually selected from a C-1 to C-4 alkyl and is multi-tethered with oligo flexible tethered group which is selected from an oligo linear alkylene tethered group, an oligo ether tethered groups, and an oligo dialkyl siloxane tethered groups;

E' is a C-1 to C-10 alkyl end group,

E'' is 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);

x and x' designate respectively the number of repeat units of structures (STa) and (STb) in said styrenic block having a Mw from about 20,000 to about 200,000, and in this non-polar block segment it is delineated by the parenthesis designated by n,

y and y' designate respectively the number of repeat units of structures (MEAa) and (MEAb) in said 2-methylenealkanoate derived block having a Mw from about 20,000 to about 200,000, and in this polar block segment it is delineated by the parenthesis designated by m, and further wherein at least one of

structures (STa), (STb), (L_1), (MEAa) and (MEAb) respectively have R_5, R_6, R_7, R_8, R_9 or R_{10} is selected from said oligo flexible tethered group.

19. The block copolymer of claim 18, wherein R_5 is an oligo flexible tethered group, R_6 is H or a C-1 to C-4 alkyl, R_7 and R_8 are individually selected from H and a C-1 to C-4 alkyl, R_9 and R_{10} are individually selected from a C-1 to C-4 alkyl.

20. The block copolymer of claim 18, wherein R_5 and R_6 are multi-tethered with oligo flexible tethered groups, R_7 and R_8 are individually selected from H and a C-1 to C-4 alkyl, R_9 and R_{10} are individually selected from a C-1 to C-4 alkyl.

21. The block copolymer of claim 18, wherein R_5 and R_6 are individually selected from H and a C-1 to C-4 alkyl, at least one of R_8 and R_7 is an oligo flexible tethered group and R_9 and R_{10} are individually selected from a C-1 to C-4 alkyl.

22. The block copolymer of claim 18, wherein R_5 and R_6 are individually selected from H and a C-1 to C-4 alkyl, R_8 and R_7 are individually selected from H and a C-1 to C-4 alkyl, and at least one of R_9 and R_{10} is an oligo flexible tethered group.

23. The block copolymer of claim 18, wherein both R_9 and R_{10} are oligo flexible tethered group.

24. A block copolymer having structure **(III)**:

$$\mathbf{E^3\text{-}A_1\text{-}A_2\text{-}L_1\text{-}B_1\text{-}E^4\ (III),}$$

wherein

A_1 is a styrenic block copolymer segment, which has a T_g from about 50°C to about 100°C

A_2 is block copolymer segment with a T_g ranging from about -5°C to about -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 least two different olefins selected from this group;

B_1 is a polar block copolymer segment, which has a T_g of about 50°C to about 100°C, comprising 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;

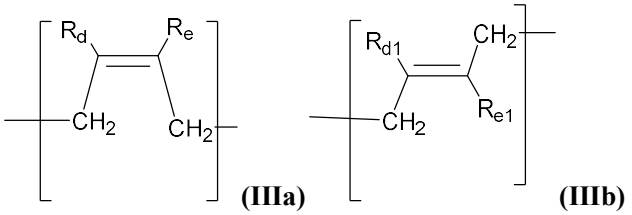
L_1 is either a direct valence bond or a linking moiety derived from a 1,1-diarylethene; wherein

E^3 is an alkyl,

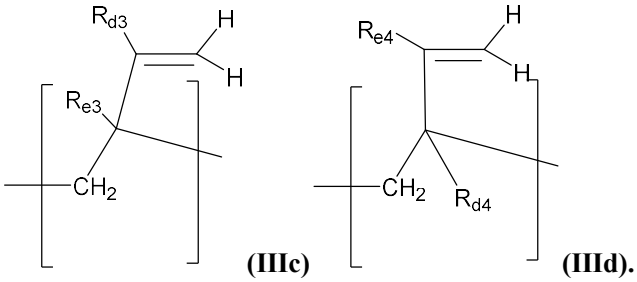
E^4 is an groups selected from H, an alkyl, a carbonylalkyl (-C=O-alkyl), a carbonyloxyalkyl (-C=O-O-alkyl, and an alkyl 2-arylacrylate derived end group (-CH_2-CH(Aryl)(C(=O))-O-alkyl), and further wherein

said block copolymer has a polydispersity ranging from 1 to about 1.09.

25. The block copolymer of claim 24, , wherein said A_2 comprises a mixture of at least two different repeat units having structures **(IIIa), (IIIb), (IIIc), and (IIId),** derived from an alkadiene; wherein R_d, R_{d1}, R_{d3}, R_{d4}, R_e, R_{e1}, R_{e3}, and R_{e4} 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 olefinic repeat units in said block copolymer ranges from about 3 mole% to about 50 mole%;

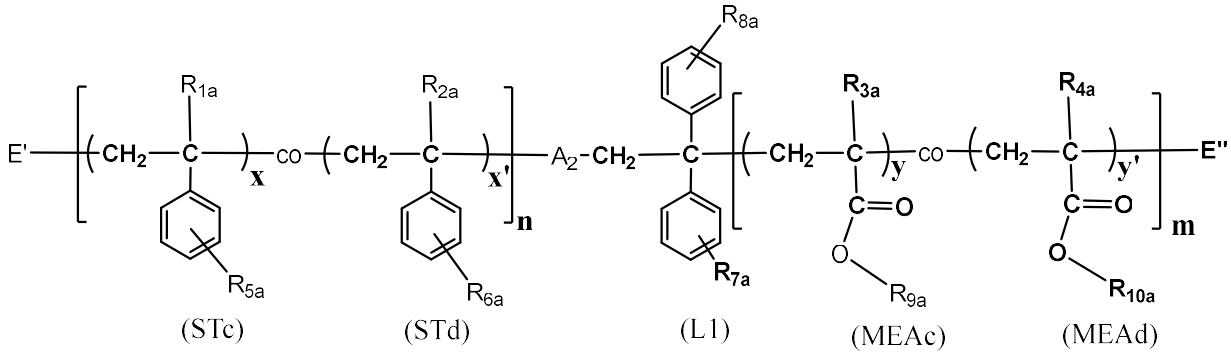


(IIIa) **(IIIb)**



(IIIc) **(IIId).**

26. The block copolymer of claim 24, having structure **(IIIe)**:



(IIIe),

comprising:

a styrenic block consisting of the randomly copolymerized styrenic repeat units of structures (STc) and (STc) wherein R_{1a} and R_{2a} are individually selected from H or a C-1 to C-4 alkyl, R_{5a} and R_{6a} are individually selected from H or a C-1 to C-4 alkyl,

a linking moiety of structure (L_1), wherein R_{7a} and R_{8a} are individually selected from H, and a C-1 to C-4 alkyl, wherein

E' is a C-1 to C-20 alkyl end group,

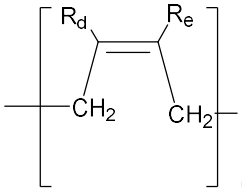
E'' is selected from H an alkyl, a carbonylalkyl (-C=O-alkyl), a carbonyloxyalkyl (-C=O-O-alkyl, and an alkyl 2-arylacrylate derived end group (-CH_2-CH(Aryl)(C(=O))-O-alkyl);

x and x' designate respectively the number of repeat units of structures (STc) and (STd) in said styrenic block having a Mw from about 20,000 to about 200,000, in this non-polar block segment it is delineated by the parenthesis designated by n,

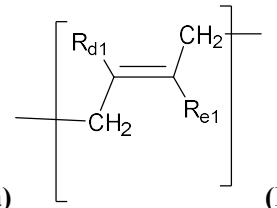
y and y' designate respectively the number of repeat units of structures (MEAc) and (MEAd) in said a 2-methylenealkanoate derived block having a Mw from about 20,000 to about 200,000, in this polar block segment delineated by the parathesis designated by m, wherein R_{3a} and $R_{4a,}$ R_{9a} and R_{10a} are individually selected from a C-1 to C-4 alkyl,

A_2 is block copolymer segment with a T_g ranging from about -5°C to about -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 from mixture of at two different olefins selected from this group.

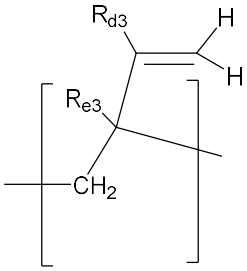
27. The block copolymer of claim 26, wherein said A_2 comprises a mixture of at least two different repeat units having structures (**IIIa), (IIIb), (IIIc), and (IIId**); wherein R_d, R_{d1}, R_{d3}, R_{d4}, R_e, R_{e1}, R_{e3}, and $R_{e4,}$ are individually selected from the group consisting of a H, and a C-1 to C-8 alkyl, and further wherein the total mole% of olefinic repeat units in said block copolymer ranges from about 3 mole% to about 50 mole%;



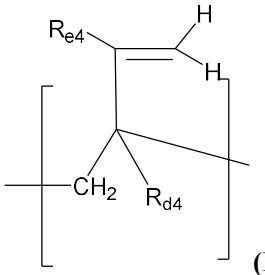
(IIIa)



(IIIb)



(IIIc)



(IIId).

28. A composition comprising a least one block copolymer of claim 1 and a spin casting organic solvent.

29. 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 claim28 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.

30. 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 comprising a block copolymer having a periodicity of L_0 comprising the steps of:

a1) forming a coating layer of the composition of claim 28 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.

31. 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 28 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.

32. 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 a block copolymer with the composition of claim 28 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.

33. A composition comprising the block copolymer of claim 24 and a solvent.

34. 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:

a4) forming a coating layer of a block copolymer from the composition of claim 33 on said unpatterned substrate; and

b4) 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.

35. 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 comprising a block copolymer having a periodicity of L_0 comprising the steps of:

a5) forming a coating layer of the composition of claim 33 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

b5) 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.

36. 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:

a6) forming a coating layer of a block copolymer with the composition of claim 33 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

b6) 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.

37. 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:

a7) forming a coating layer of a block copolymer with the composition of claim 33 on the substrate having a surface chemical prepattern; and

b7) 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.