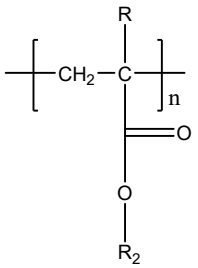
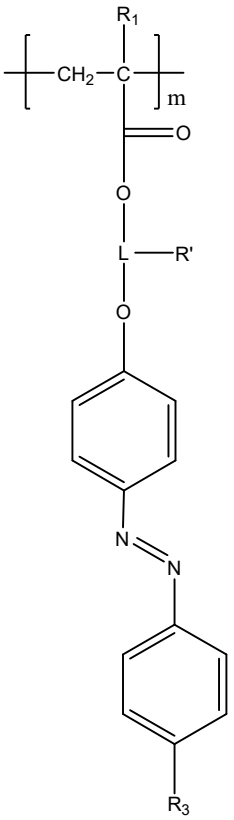
What is claimed is:

1. A block copolymer, which is an AB diblock copolymer with a first block A of structure (I) and a second block B of structure (II), wherein R and R_1 are individually selected from a C-1 to C-4 alkyl, n is the number of repeat units in structure (I), m is the number of repeat units in structure (II), and the mole % of repeat units of structure (I) ranges from 35 mole % to 94 mole %, and the mole % of repeat units of structure (II) ranges from 6 mole % to 65 mole % of the total moles of repeat units of structures (I) and (II), and the sum of the mole % of repeat units of structure (I) and (II) equals 100 mole %;

R_2 is selected from a C-1 to C-11 alkyl, L is a C-5 to C-12 linear alkylene, R_3 is selected from a C-3 to C-8 linear alkyl, and R' is H or a C-3 to C-8 linear alkyl, and further wherein said block copolymer has a polydispersity of 1 to 1.13, where said block copolymer is made by either RAFT polymerization of anionic polymerization, and has an M_n ranging from 8 kDa to 25 kDa;

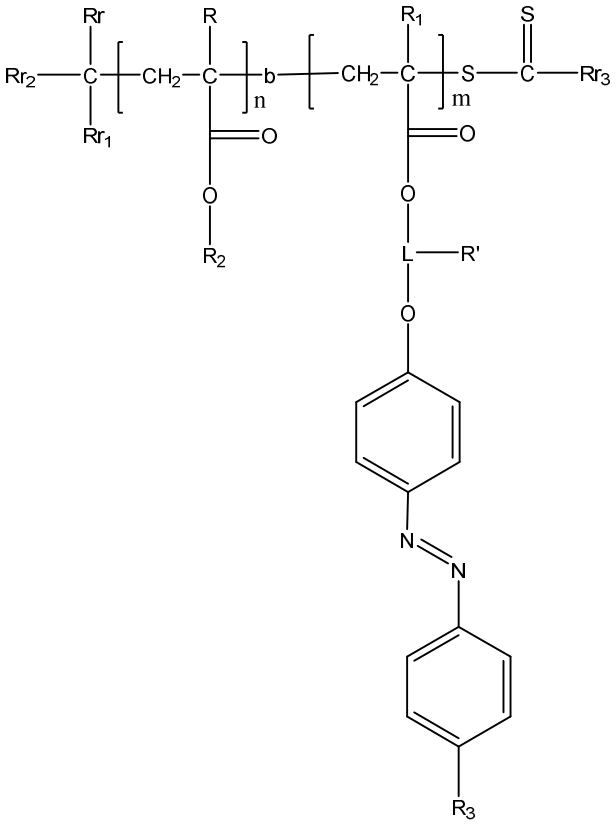


(I)



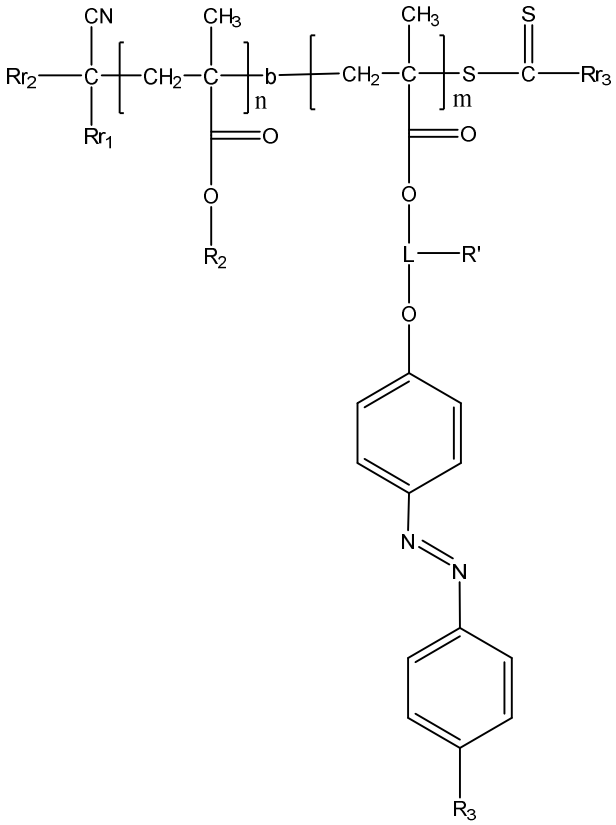
(II)

2. The block copolymer of claim 1, made by RAFT polymerization, which has structure (III), wherein Rr_1, is a C-1 to C-8 alkyl, Rr_2 is a C-1 to C-8 alkyl, and Rr is a cyano moiety (-CN) or a carbonylalkyl moiety (-C(=O)-Ri), wherein Ri is a C-1 to C-8 alkyl or an aryl moiety, and Rr_3 is an unsubstituted or substituted aryl moiety;



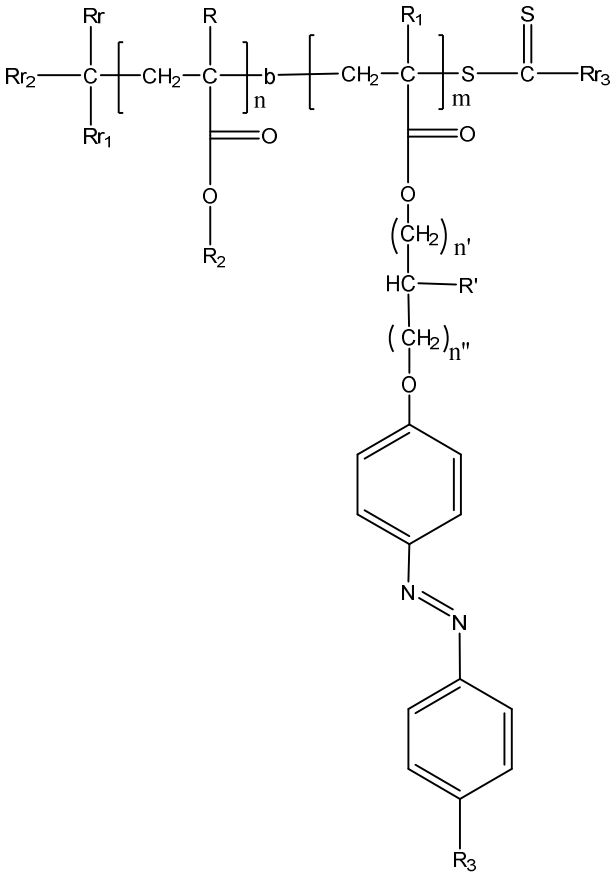
(I) (II) (III).

3. The block copolymer of claim 1 or 2, wherein said block copolymer has structure (IIIa)



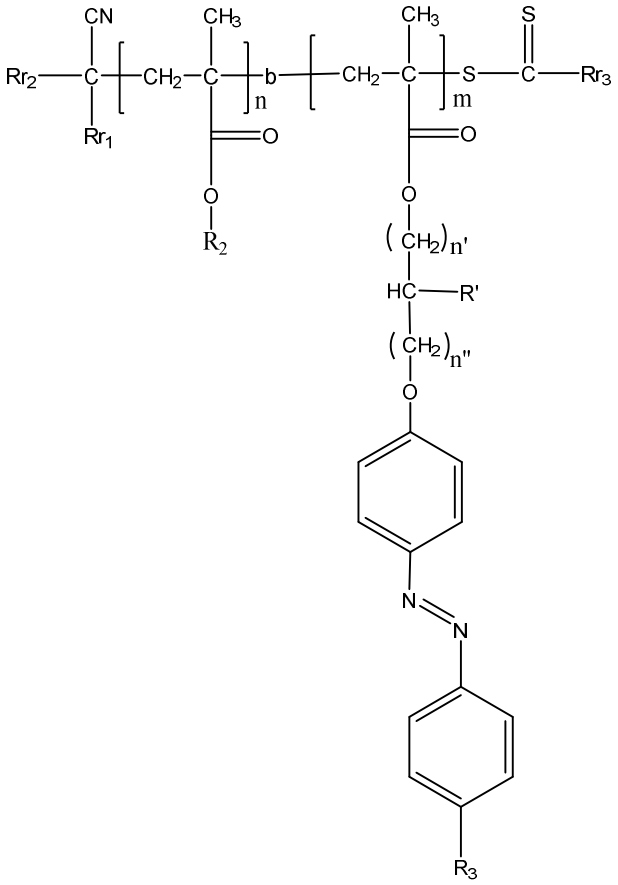
(Ia) (IIa) (IIIa).

4. The block copolymer of any of claims 1 to 3, wherein said block copolymer is one of structure (IIIb), wherein n' and n'' are integers ranging independently from 0 to 11 and further where the sum of n' and n'' ranges from 4 to 11.



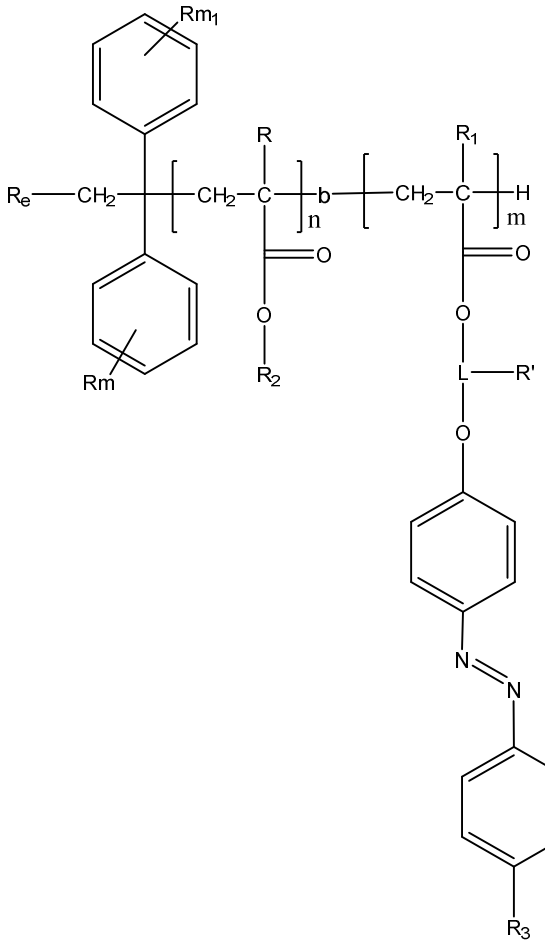
(I) (IIb) (IIIb).

5. The block copolymer of claim 4, which has structure (IIIc)



(Ia) (IIc) (IIIc).

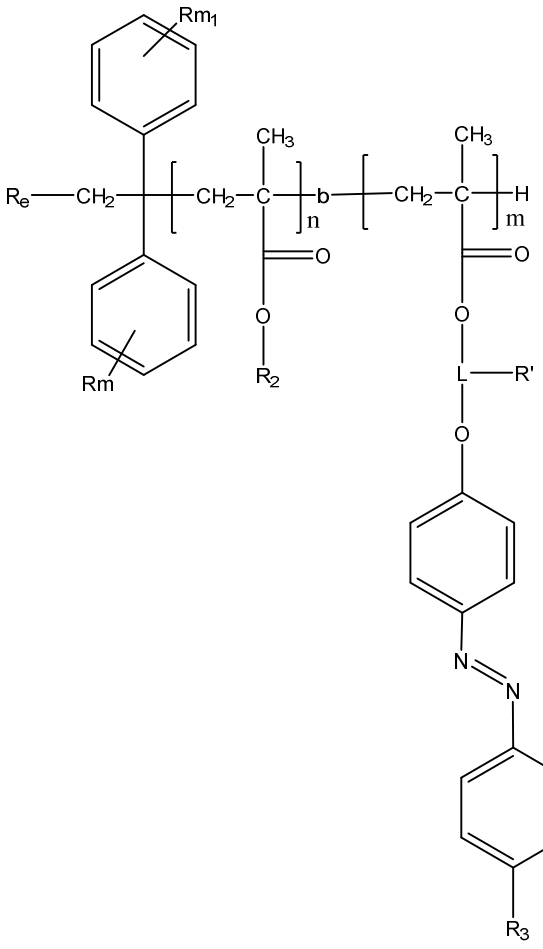
6. The block copolymer of claim 1, which is made by anionic polymerization, and which has structure (IV), wherein R_e is a C-1 to C-8 alkyl, Rm and Rm_1 are individually selected from H, a C-1 to C-8 alkyl, a C-1 to C-8 alkoxy;



(I) (II) (IV).

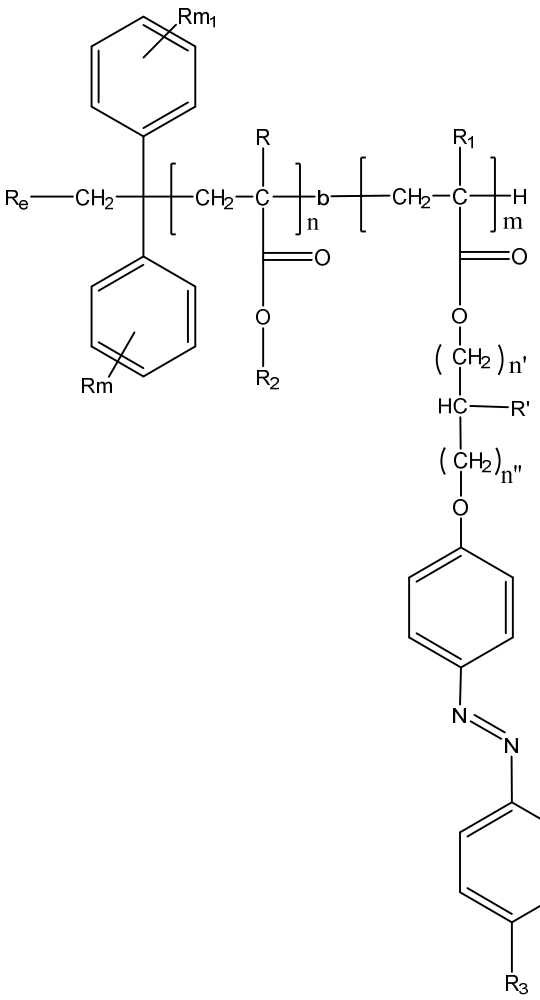
7. The block copolymer of any one of claims 1 to 3, and 6, wherein L is a C-5, C-6, C-7, C-8, C-9, C-10, C-11 or C-12 linear alkylene.

8. The block copolymer of any one of claims 1, and 6 and 7, which has structure (IVa),



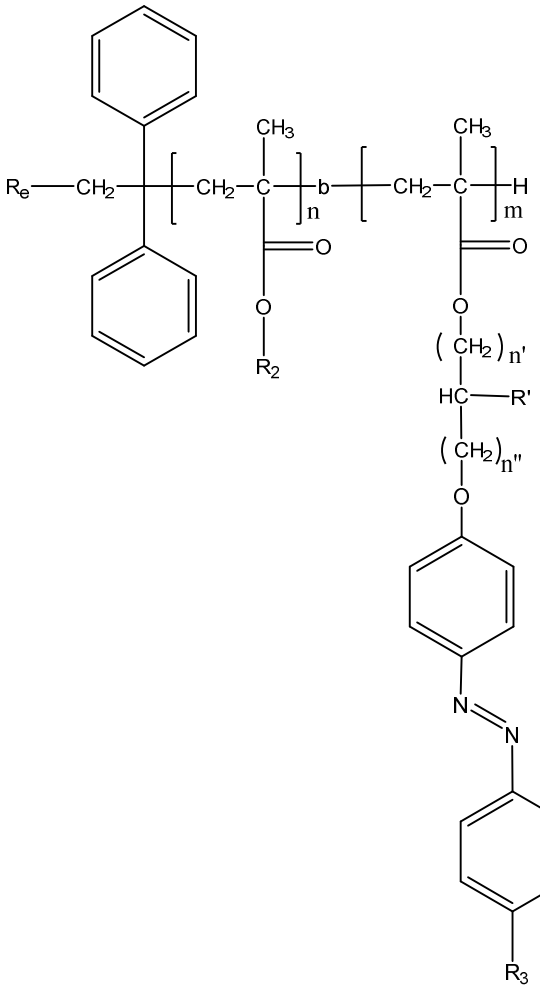
(Ia) (IIa) (IVa).

9. The block copolymer of claim 8, wherein R’ is a C-3 to C-8 linear alkyl and said block copolymer is one of structure (IVb), wherein n’ and n’’ are integers which independently range from 0 to 11 and further wherein the sum of n’ and n’’ ranges from 4 to 11,



(I) (IIb) (IVb).

10. The block copolymer of claim 9, wherein said block copolymer is one of structure (IVc),



(Ia) (IIc) (IVc).

11. A composition comprising the block copolymer of any one of claims 1 to 10 and an organic spin casting solvent.

12. 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 with the composition of claim 11 on said unpatterned substrate which is not a neutral layer; 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, which is selected from silicon, silicon dioxide, silicon nitride and silicon oxynitride.

13. 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:

a-1) forming a coating layer of the block copolymer with the composition of claim 11, 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,

b-1) 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, wherein said patterned substrate comprises a pattern of a crosslinked polar polymer on a silicon, silicon dioxide, silicon nitride or silicon oxynitride substrate.

14. 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 P_1 where the pitch P_1 is a non-zero positive integer multiplied by L_0, where further the bottom of the patterned substrate defined by said topography is not a neutral layer surface, and aligning the domains with the pattern comprising the steps of:

a-2) forming a coating layer of the block copolymer with the composition of claim11, 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,

b-2) 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 to or larger than the pitch the P_1 of the topographical pattern, wherein said patterned substrate comprises a pattern of a crosslinked polar polymer on a silicon, a silicon dioxide, silicon nitride or silicon oxynitride substrate.

15. The method of claims 13 or 14, wherein said pattern of a crosslinked polar polymer is formed by patterning with UV radiation a coating of a copolymer of methyl methacrylate and 2-(vinyloxy)ethyl methacrylate on said substrate.

16. A method of vertically orienting first and second block copolymer domains over a substrate having a surface chemical prepattern which does not include a neutral layer area, having a pitch P_2, where the pitch P_2 is a non-zero positive integer multiplied by L_0 and aligning the domains comprising the steps of:

a-3) forming a coating layer of the block copolymer with the composition of claim 11, on the substrate having a surface chemical prepattern; and,

b-3) 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 P_2, wherein said surface chemical prepattern comprises polar areas and areas of silicon, silicon dioxide, silicon nitride or silicon oxynitride.

17. The method of claim 16, wherein said surface chemical prepattern is formed by patterning with UV radiation a coating of a copolymer of methyl methacrylate and 2-(vinyloxy)ethyl methacrylate on said substrate.

18. The method of claim 16, where said surface chemical prepattern is a patterned polar brush formed by first grafting onto a substrate a polar brush layer using a poly(methyl methacrylate) polymer functionalized at one of the polymer chains with a hydroxy group and then forming said chemical and then selectively etching it away using an overlying patterned photoresist as an etch barrier and stripping the photoresist.

19. The use of the block copolymer of any one of claims 1 to 10 or the composition of claim 11 for self-assembly and directed self-assembly lithographic processing.