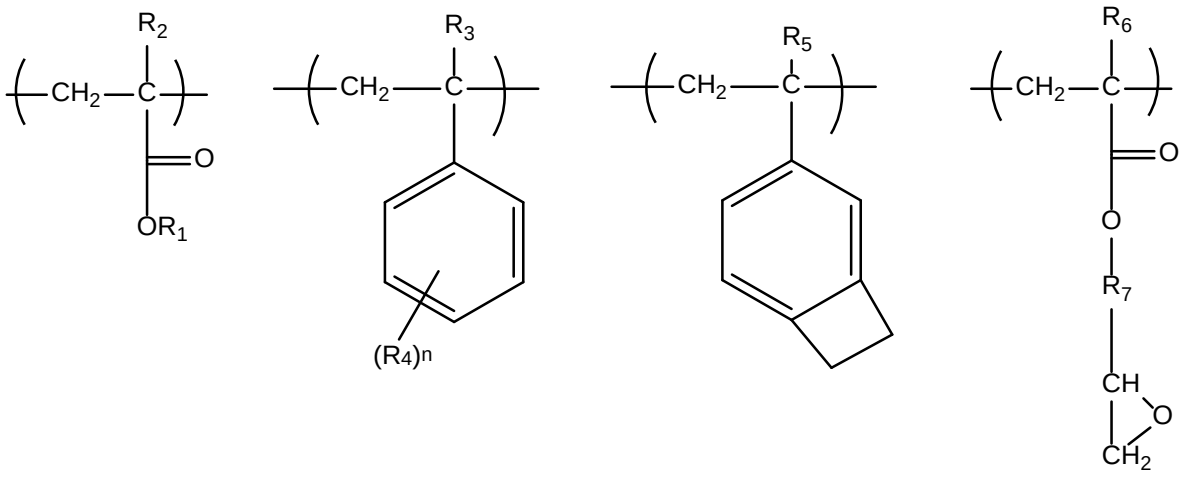
Claims

1. A random polymer comprising, preferably essentially consisting of, the following repeat units of structure (I), (II), (III), and (IV)



(I) (II) (III) (IV)

wherein,

R_1 is selected from the group consisting of a C-1 to C-4 alkyl,

R_2, R_3, R_5, and R_6 are independently selected from the group consisting of H, and a C-1 to C-4 alkyl,

R_4 is a C-1 to C-4 alkyl, and n is an integer from 0 to 5, and

R_7 is an alkylene is selected from a C-1 to C-4 alkylene.

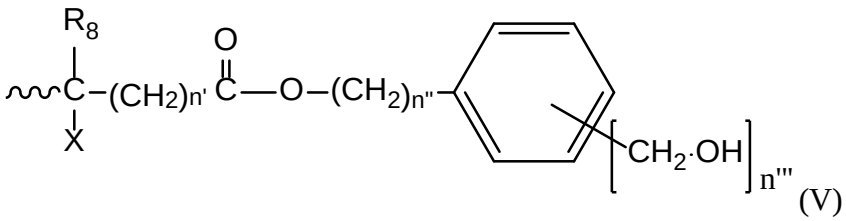
~~2. The random copolymer according to claim 1 consisting essentially of repeat units of structures (I), (II), (III), and (IV).~~

~~3~~2. The random copolymer according to claims 1 or 2, wherein each polymer chain of said random copolymer further comprises a first end group, which is a benzylic alcohol comprising moiety of structure (V), preferably (Va), more preferably (Vb), more preferably (Vc), more preferably (Vd), wherein

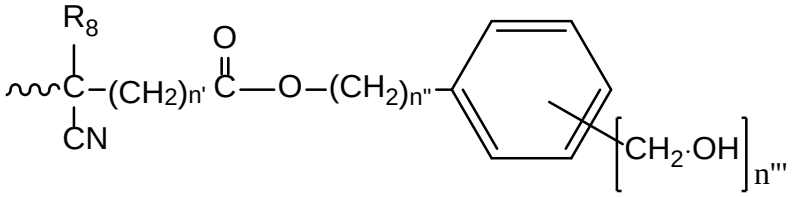
n' is an integer and ranges from 1 to 5; n'' is an integer and ranges from 1 to 5;

n''' is an integer and ranges from 1 to 5;

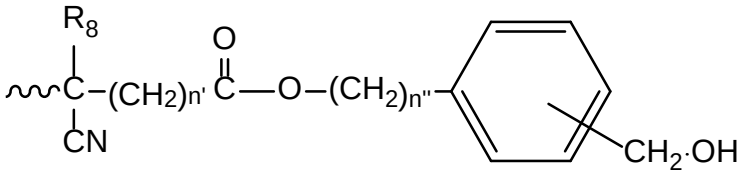
R_8 is a C-1 to C-8 alkyl; X is -CN or an alkyloxycarbonyl moiety R_9-O-(C=O)- where R_9 is a C-1 to C-8 alkyl; and ∿∿∿ represent the attachment point of said end group to said random copolymer,



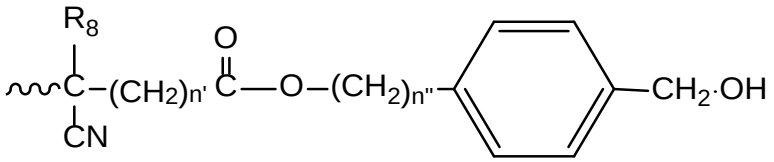
(V)



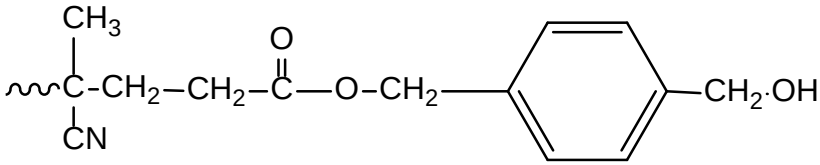
(Va)



(Vb)



(Vc)



(Vd).

3. The random copolymer according to any one of claims 3 to 15, wherein said random copolymer further comprises in each polymer chain further a second end group selected from H and a C-1 to C-4 alkyl moiety.

4. The random copolymer polymer according to any one of claims 1 to 3 wherein,

n is 0,

R_2 and R_6 are independently selected from the group consisting of CH_3, and H,

R_3 and R_5 are H, and
R_7 is a C-1 to C-3 alkylene.

5. The random copolymer according to any one of claims 1 to 4 wherein R_1 is methyl and/or ~~.~~

~~6. The random copolymer according to any one of claims 1 to 5, wherein~~ R_2 is methyl and/or ~~.~~

~~7. The random copolymer according to any one of claims 1 to 6, wherein~~ R_3 is H and/or ~~.~~

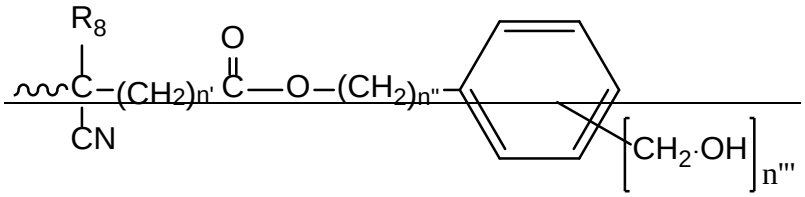
~~8. The random copolymer according to any one of claims 1 to 7, wherein~~ R_5 is H and/or ~~.~~

~~9. The random copolymer according to any one of claims 1 to 8, wherein~~ R_6 is methyl and/or ~~.~~

~~10. The random copolymer according to any one of claims 1 to 9, wherein~~ R_7 is methylene, preferably ~~.~~

~~11. The random copolymer according to any one of claims 1 to 10,~~ wherein R_1, R_2, and R_6 are methyl, R_3 and R_5 are H, R_7 is methylene and n=0.

12. The random copolymer according to any one of claims 3 to 11, wherein said first end group has structure (Va):



(Va).

13. The random copolymer according to any one of claims 3 to 12, wherein said first end group has structure (Vb):

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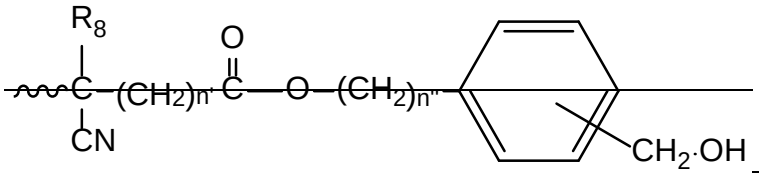
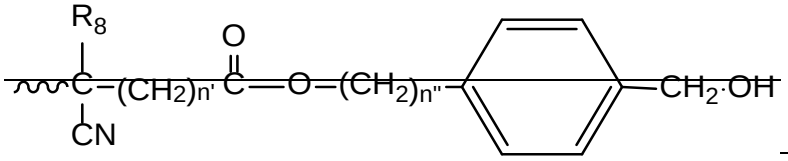


(Vb).

14. The random copolymer according to any one of claims 3 to 13, wherein said first end group has structure (Vc):

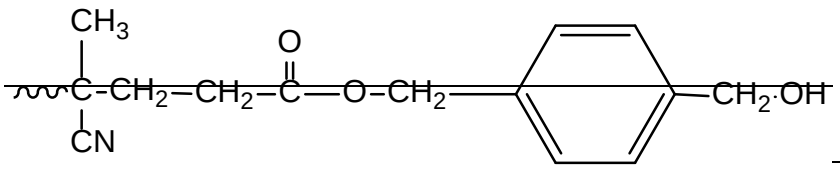
÷



(Vc).

15. The random copolymer according to any one of claims 3 to 14, wherein said first end group has structure (Vd):

÷



(Vd).

16. The random copolymer according to any one of claims 3 to 15, wherein said random copolymer further comprises in each polymer chain further a second end group selected from H and a C-1 to C-4 alkyl moiety.

17. The random copolymer according to any one of claims 3 to 16, wherein said second end group is H.

186. The random copolymer according to any one of claims 1 to 17 5, wherein, based on the total moles of all repeat units,

the repeat unit of structure (I) is present in a range from about 28 mole % to about 78 mole %,

the repeat unit of structure (II) is present in a range from about 5 mole % to about 70 mole %,

the repeat unit of structure (III) is present in a range from about 15 mole % to about 25 mole %,

the repeat unit of structure (IV) is present in a range from about 0.5 mole % to about 3 mole %,

and

each mole % for these repeat units are individually selected such that the sum of all the repeat units mole % values for the repeat units present in said random copolymer equals 100 mole %.

197. The random copolymer according to any one of claims 1 to 18 6, wherein, based on the total moles of all repeat units,

the repeat unit of structure (I) is present in a range from about 28 mole % to about 58 mole %,

the repeat unit of structure (II) is present in a range from ~~about~~ 20 mole % to ~~about~~ 40 mole %,

the repeat unit of structure (III) is present in a range from ~~about~~ 15 mole % to ~~about~~ 25 mole %,

the repeat unit of structure (IV) is present in a range from ~~about~~ 0.5 mole % to ~~about~~ 3 mole %, and

the mole % sum of repeat unit of structure (II) and (III) ranges from ~~about~~ 40 mole % to ~~about~~ 65 mole %, and

each mole % for these repeat units are individually selected such that the sum of all the repeat units mole % values for the repeat units present in said random copolymer equals 100 mole %.

~~20. The random copolymer according to any one of claims 1 to 19, wherein, based on the total moles of all repeat units,~~preferably wherein

the repeat unit of structure (I) is present in a range from ~~about~~ 35 mole % to ~~about~~ 55 mole %,

the repeat unit of structure (II) is present in a range from ~~about~~ 25 mole % to ~~about~~ 35 mole %,

the repeat unit of structure (III) is present in a range from ~~about~~ 18 mole % to ~~about~~ 22 mole %,

the repeat unit of structure (IV) is present in a range from ~~about~~ 1 mole % to ~~about~~ 2.5 mole %,

the mole % sum of repeat unit of structure (II) and (III) is present in a range from ~~about~~ 40 mole % to ~~about~~ 60 mole %, and

each mole % for these repeat units are individually selected such that the sum of all the repeat units mole % values for the repeat units present in said random copolymer equals 100 mole %.

~~21~~18. The random copolymer according to any one of claims 1 to ~~20~~ 6, wherein, based on the total moles of all repeat units,

the repeat unit of structure (I) is present in a range from ~~about~~ 48 mole % to ~~about~~ 78 mole %,

the repeat unit of structure (II) is present in a range from ~~about~~ 5 mole % to ~~about~~ 20 mole %,

the repeat unit of structure (III) is present in a range from ~~about~~ 15 mole % to ~~about~~ 25 mole %,

the repeat unit of structure (IV) is present in a range from ~~about~~ 0.5 mole % to ~~about~~ 3 mole %,

the mole % sum of repeat unit of structure (II) and (III) is present in a range from ~~about~~ 20 mole % to ~~about~~ 45 mole %, and

each mole % for these repeat units are individually selected such that the sum of all the repeat units mole % values for the repeat units present in said random copolymer equals 100 mole %~~.~~.

~~22. The random copolymer according to any one of claims 1 to 21, wherein, based on the total moles of all repeat units,~~preferably wherein

the repeat unit of structure (I) is present in a range from ~~about~~ 50 mole % to ~~about~~ 70 mole %,

the repeat unit of structure (II) is present in a range from ~~about~~ 7 mole % to ~~about~~ 15 mole %,

the repeat unit of structure (III) is present in a range from ~~about~~ 18 mole % to ~~about~~ 22 mole %,

the repeat unit of structure (IV) is present in a range from ~~about~~ 1 mole % to ~~about~~ 2.5 mole %,

the mole % sum of repeat unit of structure (II) and (III) ranges from ~~about~~ 25 mole % to ~~about~~ 35 mole %, and

each mole % for these repeat units are individually selected such that the sum of all the repeat units mole % values for the repeat units present in said random copolymer equals 100 mole %.

~~23~~9. A composition comprising said random copolymer according to any one of claims 1 to ~~22~~ 8, and a spin casting solvent, preferably ~~.~~

~~24. The composition of claim 23 wherein said composition comprises a mixture of~~ at least two said random copolymers according to any one of claims 1 to ~~22~~ 8, and a spin casting solvent.

~~25~~10. A composition according to claim 9 comprising said random copolymer according to claim 7~~s 19 or 20~~ and a spin casting solvent, preferably a said single random copolymer according to claim 7 and a spin casting solvent, or a mixture of at least two said random copolymers of claim 7~~,~~ and a spin casting solvent.

~~26. The composition of claim 25 wherein said composition comprises a mixture of at least two said random copolymers.~~

~~27. The composition of claim 25 wherein said composition comprises a single said random copolymer.~~

~~28~~11. A composition according to claim 9 comprising a blend of at least two random copolymers of any one of claims 1 to ~~22~~ 8, and a spin casting solvent, wherein, based on the total moles of repeat units present in the said blend,

the repeat unit of structure (I) is present in a range from ~~about~~ 28 mole % to ~~about~~ 58 mole %,

the repeat unit of structure (II) is present in a range from ~~about~~ 20 mole % to ~~about~~ 40 mole %,

the repeat unit of structure (III) is present in a range from ~~about~~ 15 mole % to ~~about~~ 25 mole %,

the repeat unit of structure (IV) is present in a range from ~~about~~ 0.5 mole % to ~~about~~ 3 mole %,

the mole % sum of repeat unit of structure (II) and (III) is present in a range from ~~about~~ 40 mole % to ~~about~~ 65 mole %, and

each mole % for these repeat units are individually selected such that the sum of all the repeat units mole % values for the repeat units present in said blend of random copolymers equals 100 mole %.~~.~~

~~29. A composition comprising a blend of at least two random copolymers of any one of claims 1 to 22, and a spin casting solvent, wherein, based on the total moles of repeat units present in the said blend,~~preferably wherein

the repeat unit of structure (I) is present in a range from ~~about~~ 35 mole % to ~~about~~ 55 mole %,

the repeat unit of structure (II) is present in a range from ~~about~~ 25 mole % to ~~about~~ 35 mole %,

the repeat unit of structure (III) is present in a range from ~~about~~ 18 mole % to ~~about~~ 22 mole %,

the repeat unit of structure (IV) is present in a range from ~~about~~ 1 mole % to ~~about~~ 2.5 mole %,

the mole % sum of repeat unit of structure (II) and (III) is present in a range from ~~about~~ 40 mole % to ~~about~~ 60 mole %, and

each mole % for these repeat units are individually selected such that the sum of all the repeat units mole % values for the repeat units present in said blend of random copolymers equals 100 mole %.

~~30~~12. A composition according to claim 9 comprising said random copolymer according to claim 8~~s 21 or 22,~~ and a spin casting solvent, preferably a single said random copolymer according to claim 8 and a spin casting solvent, or a mixture of at least two said random copolymers of claim 8 and a spin casting solvent.

~~31. The composition of claim 30 wherein said composition comprises a mixture of at least two different said random copolymers.~~

~~32. The composition of claim 30 wherein said composition comprises a single said random copolymer.~~

~~33~~13. A composition according to claim 9 comprising a blend of at least two random copolymers of any one of claims 1 to ~~22~~ 8, and a spin casting solvent, wherein, based on the total moles of repeat units present in the said blend,

the repeat unit of structure (I) is present in a range from ~~about~~ 48 mole % to ~~about~~ 78 mole %,

the repeat unit of structure (II) is present in a range from ~~about~~ 5 mole % to ~~about~~ 20 mole %,

the repeat unit of structure (III) is present in a range from ~~about~~ 15 mole % to ~~about~~ 25 mole %,

the repeat unit of structure (IV) is present in a range from ~~about~~ 0.5 mole % to ~~about~~ 3 mole %,

the mole % sum of repeat unit of structure (II) and (III) is present in a range from ~~about~~ 20 mole % to ~~about~~ 45 mole %, and

each mole % for these repeat units are individually selected such that the sum of all the repeat units mole % values for the repeat units present in said blend of random copolymers equals 100 mole %~~.~~.

~~34. A composition comprising a blend of at least two random copolymers of any one of claims 1 to 22, and a spin casting solvent, wherein, based on the total moles of repeat units present in the said blend,~~preferably wherein

the repeat unit of structure (I) is present in a range from ~~about~~ 50 mole % to ~~about~~ 70 mole %,

the repeat unit of structure (II) is present in a range from ~~about~~ 7 mole % to ~~about~~ 15 mole %,

the repeat unit of structure (III) is present in a range from ~~about~~ 18 mole % to ~~about~~ 22 mole %,

the repeat unit of structure (IV) is present in a range from ~~about~~ 1 mole % to ~~about~~ 2.5 mole %,

the mole % sum of repeat unit of structure (II) and (III) is present in a range from ~~about~~ 25 mole % to ~~about~~ 35 mole %, and

each mole % for these repeat units are individually selected such that the sum of all the repeat units mole % values for the repeat units present in said blend of random copolymers equals 100 mole%.

~~35~~14. A process for forming an array pattern comprising:

a) coating the composition of any one of claims ~~23~~ 9 to ~~34~~ 13, on a substrate, forming a neutral layer coating;

b) heating the neutral layer coating to form a crosslinked neutral layer;

c) applying a film of a block copolymer material, comprising an etch resistant block and highly etchable block, over said crosslinked neutral layer and annealing said film until a self-assembled film of block copolymer forms; and,

d) etching said self-assembled block copolymer film, thereby removing the highly etchable block of the copolymer and forming an array pattern, .

~~36. The process of claim 35,~~ more preferably wherein in step c) said block copolymer material is either a single block copolymer or a blend of at least two different block copolymers, wherein said blend block copolymers is one of different block copolymers, containing the same repeat units comprising the highly etchable block and the same type repeat units comprising the etch resistant block, but differ either in the proportions of these block, weight average molecular weight, number average molecular weight, polydispersity or a mixture of these properties, .

~~37. The process of claims 35 or 36~~ more preferably wherein in step c) said block copolymer material is either a single poly(styrene-b-methyl methacrylate) block copolymer or a blend of at least two different polystyrene-b-methyl methacrylate) block copolymers.

~~38~~15. A process for forming a contact hole array according to claim 14 comprising:

a') coating the composition of ~~any one of~~ claims ~~25 to 29~~ 10 or 11 on a substrate, forming a neutral layer coating;

b') heating said neutral layer coating to form a crosslinked neutral layer;

c') applying a film of a block copolymer material, comprising an etch resistant block and highly etchable block, over said crosslinked neutral layer, and annealing said film until a self-assembled film of block copolymer forms; and

wherein said block copolymer material is either a single polystyrene-b-poly(methyl methacrylate) block copolymer or a blend of at least two different polystyrene-b-poly(methyl methacrylate) block copolymers wherein in said block copolymer material

the mole % of the repeat units, as measure against the total moles of styrene derived repeat units and methyl methacrylate repeat units, for said polystyrene derived repeat unit is present in a range from ~~about~~ 60 mole % to ~~about~~ 75 mole %, and for said methyl methacrylate derived repeat units is present in a range from ~~about~~ 25 mole % to ~~about~~ 40 mole %,

d') etching said self-assembled block copolymer film, thereby removing the highly etchable block of the copolymer and forming a contact hole array.

~~39~~16. A process for forming a post array according to claim 14 comprising:

a'') coating the composition of ~~any one of~~ claims ~~30 to 34~~ 12 or 13, on a substrate, forming a neutral layer coating;

b'') heating said neutral layer coating to form a crosslinked neutral layer;

c'') applying a film of a block copolymer material, comprising an etch resistant block and highly etchable block, over said crosslinked neutral layer, and annealing said film until a self-assembled film of block copolymer forms; and

wherein said block copolymer material is either a single polystyrene-b-poly(methyl methacrylate) block copolymer or a blend of at least two different polystyrene-b-poly(methyl methacrylate) block copolymers wherein in said block copolymer material the mole % of the repeat units, as measure against the total moles of styrene derived repeat units and methyl methacrylate repeat units, for said polystyrene derived repeat unit is present in a range from ~~about~~ 25 mole % to ~~about~~ 40 mole %, and for said methyl methacrylate derived repeat units range from ~~about~~ 60 mole % to ~~about~~ 75 mole %,

d'') etching said self-assembled block copolymer film, thereby removing the highly etchable block of the copolymer and forming a post array.

~~40~~17. The use of the random copolymer according to any one of claims 1 to ~~22~~ 8 or of the composition according to any one of claims ~~23~~ 9 to ~~34~~ 13 for preparing a crosslinked neutral layer on a substrate.