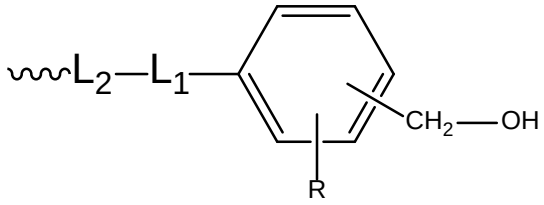
Claims

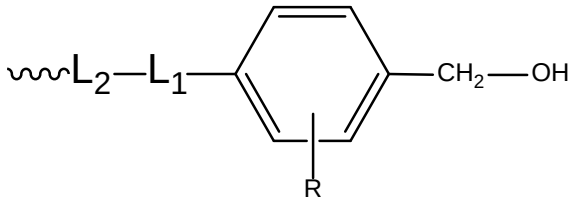
We claim:

1. A styrenic polymer having a polydispersity of 1 to 1.1, and further wherein each polymer chain of the styrenic polymer is capped with one end group of structure 1a) wherein L_1 is a linking group selected from the group consisting of oxy (-O-), carbonyloxy (-(C=O)-O-), and carbonate (-O-(C=O)-O-); and L_2 is a C-1 to C-20 substituted or unsubstituted alkylene spacer, and R is selected from the group consisting of hydrogen, a halide, a C-1 to C-20 alkyl moiety, and a C-1 to C-20 alkyloxy moiety;



1a).

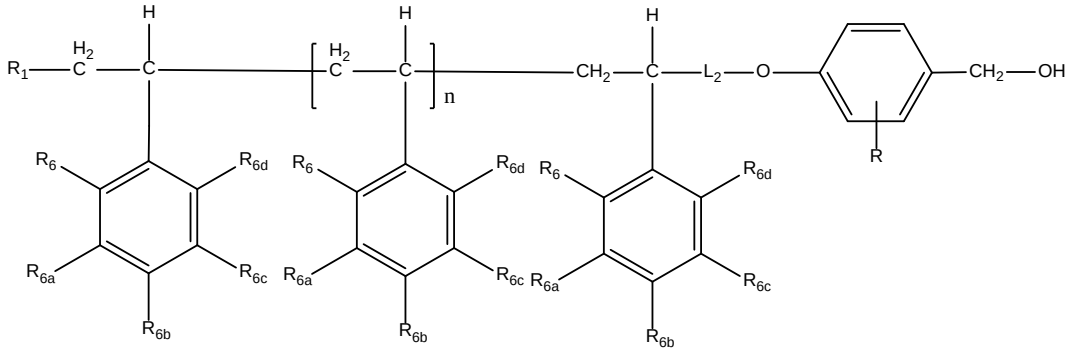
2. The styrenic polymer of claims 1 wherein the end group has structure 1b)



1b).

3. The styrenic polymer according to claim 1 or 2 where the styrenic polymer has structure 3c), wherein R_6, R_{6a}, R_{6b}, R_{6c} and R_{6d} are independently selected from the group consisting of hydrogen, a C-1 to C-20 alkyl, a C-1 to C-20 alkyloxy, a C-1 to C-10 fluoroalkyl, a C-1 to C-10 fluoroalkyloxy, a trialkylsilyl group, a (trialkylsilyl)alkylene group, and a (trialkylsilyl)alkyleneoxy group, R is selected from the group consisting

of hydrogen, a halide, a C-1 to C-20 alkyl moiety, and a C-1 to C-20 alkyloxy moiety, L_2 is a C-1 to C-20 substituted or unsubstituted alkylene spacer, n is the number of repeat unit in a polymer chain, and R is selected from the group consisting of hydrogen and a C-1 to C-20 alkyl,



3c).

4. The styrenic polymer according to claim 3 wherein R_6, R_{6a}, R_{6b}, R_{6c} and R_{6d} are hydrogen.

5. A composition which is comprised of a styrenic polymer of one of claims 1 to 4 and a solvent.

6. The composition of claim 5 further comprising a thermal acid generator.

7. A process of grafting a pinning layer on a substrate comprised of steps:

a) coating the substrate with the composition of claims 5 or 6 to form a coated layer;

b) heating the coated layer at a temperature from 140ºC to 170° to affect grafting; and

c) treating the heated coated layer with an organic solvent to remove ungrafted polymer, leaving an insoluble grafted pinning layer on the substrate.

8. A process of chemoepitaxy, directed self-assembly of a block copolymer layer used to form an image comprised of the steps:

a1) coating a substrate with a graftable neutral layer polymer precursor to form a coated layer 1;

b1) heating coated layer 1 at a temperature from 90ºC to 180ºC to remove solvent; c1) heating the coated layer 1 after step b1) at a temperature from 200ºC to 300ºC to affect grafting;

d1) treating the coated layer 1 after step c1) with an organic solvent to remove ungrafted neutral layer polymer, leaving an insoluble grafted neutral layer on the substrate;

e1) coating a photoresist layer over the grafted neutral layer;

f1) forming a negative pattern in the photoresist layer, thereby forming regions in which the grafted neutral layer is covered or uncovered by the resist, where the pattern in the resist is comprised of both small nanometer sized repeating patterns and also large areas of resist removed during the imaging process containing no repeating nanometer sized patterns;

g1) etching to remove the neutral layer regions uncovered in step f1) leaving bare substrate in these regions;

h1) stripping the resist away from the substrate after step g1), leaving a patterned substrate in which regions of substrate left uncovered by resist in step f1) are free of a grafted neutral layer and the regions covered by

resist in step f1) retain the grafted neutral layer;

i1) coating the patterned substrate with the composition of claims 5 or 6 to form a coated layer 2;

j1) heating the coated layer 2 a temperature from 120ºC to 190ºC;

k1) treating the coated layer 2 after heating step j1) with an organic solvent to remove ungrafted polymer, leaving an insoluble grafted pinning layer material on the substrate in the regions free of grafted neutral layer creating a substrate with both pinning layer areas and neutral layer areas;

l1) applying a coating of a block copolymer comprising an etch resistant styrenic block and a highly etchable aliphatic block over the substrate containing a patterned neutral layer and pinning layer, creating a substrate containing both a patterned neutral layer and a patterned pinning layer;

m1) annealing the block copolymer layer until directed self-assembly occurs in the small nanometer sized repeating patterns of the substrate, but where no perpendicular orientation of block polymer domains occurs in the large areas containing grafted pinning layer;

n1) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a repeating nanometer sized pattern in the areas where directed self-assembly of the block copolymer occurred on the substrate in step m1).

9. A process of chemoepitaxy, directed self-assembly of a block copolymer layer used to form an image comprised of the steps:

a2) forming a coating of a neutral layer polymer precursor which is crosslinkable or which is both crosslinkable and graftable on a substrate;

b2) heating the neutral polymer layer precursor coating which is crosslinkable or the precursor coating which is both crosslinkable and graftable at a temperature from 90ºC to 180ºC to remove solvent;

c2) heating the neutral layer polymer precursor coating which is crosslinkable or the precursor coating which is both crosslinkable and graftable at a temperature from 200ºC to 300ºC to form a crosslinked neutral layer or a crosslinked and grafted neutral layer;

d2) providing a coating of a photoresist layer over the crosslinked neutral layer or over the crosslinked and grafted neutral layer;

e2) forming a negative pattern in the photoresist layer, thereby forming regions in which the crosslinked or the crosslinked and grafted neutral layer is covered or uncovered by the resist, where the pattern in the resist is comprised of both small nanometer repeating patterns and also large areas of resist removed during the imaging process containing no repeating nanometer sized patterns;

f2) etching with a plasma to remove in the neutral layer regions uncovered in step e2) removing crosslinked or crosslinked and grafted neutral layer leaving bare substrate in the regions uncovered in step e2);

g2) stripping the resist away from the substrate after step f2), leaving a patterned substrate in which regions of substrate left uncovered by resist in step e2) are free of a crosslinked or crosslinked and grafted neutral layer and the regions covered by resist in step f2) retain the crosslinked or crosslinked and grafted neutral layer;

h2) coating the patterned substrate with the composition of claims 5 or 6 to form a coated layer;

i2) heating the coated layer at a temperature from 120ºC to 190ºC;

j2) treating the coated layer after heating step i2) with an organic solvent to remove ungrafted polymer, leaving an insoluble crosslinked or crosslinked and grafted pinning layer material on the substrate in the regions free of crosslinked neutral layer or free of crosslinked and grafted neutral layer, creating a substrate containing both a patterned neutral layer and a patterned pinning layer;

k2) applying a coating of a block copolymer comprising an etch resistant styrenic block and a highly etchable aliphatic block over the substrate containing a patterned neutral layer and pinning layer;

l2) annealing the block copolymer layer until directed self-assembly occurs in the small nanometer sized repeating patterns of the substrate, but where no perpendicular orientation of block polymer domains occurs in the large areas containing grafted pinning layer;

m2) etching the block copolymer, thereby removing the highly etchable block of the copolymer and forming a repeating nanometer sized pattern in the areas where directed self-assembly of the block copolymer occurred on the substrate in step l2).