CLAIMS

1. A composition comprising components a), b) and c), wherein

a) is a block copolymer component or blend of at least two block copolymers,

b) is a low T_g additive selected from the group consisting of

an oligo random copolymer b-1),

an oligo diblock copolymer b-2),

an oligo diblock copolymer b-3) and

mixture thereof, wherein;

b-1) is an oligo random copolymer, of two repeat units, which have structure (Ib) and structure (IIb), wherein R_{1b} and R_{3b} are independently selected from H or a C-1 to C-4 alkyl, R_{2b} is H or a C-1 to C-8 alkyl, R_{4b} is a C-1 to C-8 alkyl, and

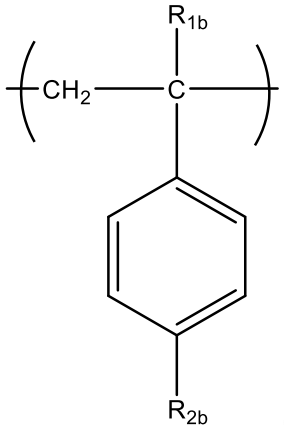
the mole % values, based on the total moles of repeat units of structures (Ib) and (IIb), are for the repeat units of structure (Ib) from 40 mole % to 80 mole % and for the repeat units of structure (IIb) from 20 mole % to 60 mole %, and

wherein the individual values of the mole % for the repeat units of structures (Ib) and (IIb) are selected from their respective ranges to add up to 100 mole % of the total moles of repeat units of structures (Ib) and (IIb); and further

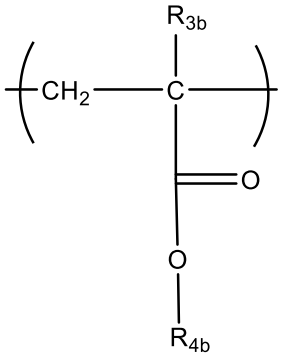
said oligo random copolymer b-1) has a T_g which is from 0°C to 90°C, and

has an M_n which is from 1000 g/mole to 5,000 g/mole, and

has a polydispersity from 1.3 to 1.8,



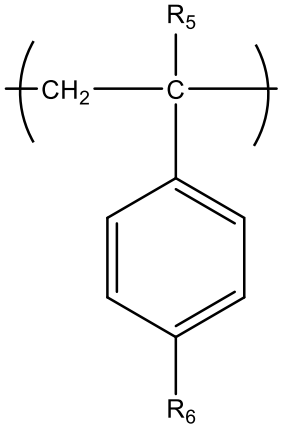
(Ib)



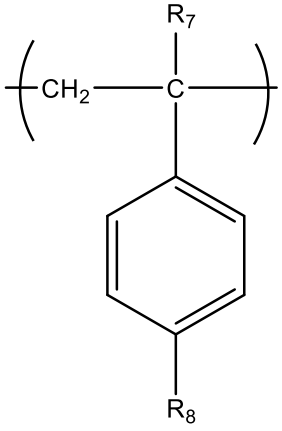
(IIb);

b-2) is an oligo diblock copolymer of block A-b) and block B-b), having an M_n from 1,000 to 35,000, and a polydispersity from 1.0 to 1.1, wherein

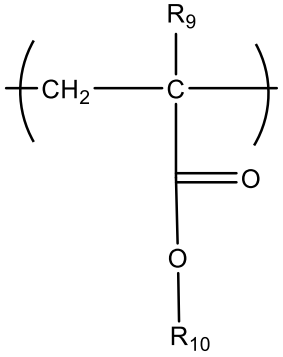
block A-b) is a random copolymer of repeat units having structures (III), and (IV), and block B-b) is a random copolymer of repeat units having structures (V), and (VI), and R_5, R_7, R_9, and R_{11}, are independently selected from H or a C-1 to C-4 alkyl, R_6 is a C-7 to C-10 linear alkyl, R_8 is H or a C-1 to C-4 alkyl, R_{10} is a C-1 to C-4 alkyl, R_{12} and R_{13} are individually selected from a C-2 to C-5 alkylene, and R_{14} is a C-1 to C-4 alkyl, and said oligo diblock copolymer b-2) has a T_g which has a value from 0°C to 95°C,



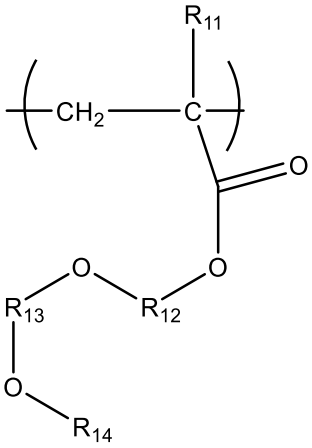
(III)



(IV);



(V)



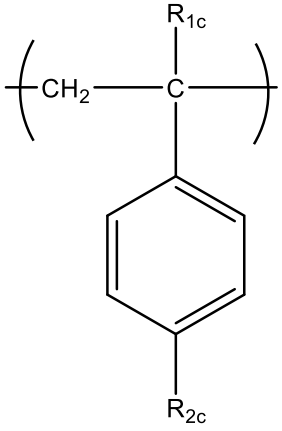
(VI); and

b-3) is an oligo diblock copolymer of block A-c), with repeat units having structure (Ic), and a block B-c), with repeat units having structure (IIc), wherein R_{1c} and R_{3c} are independently selected from H or a C-1 to C-4 alkyl, R_{2c} is H or a C-1 to C-8 alkyl, R_{4c} is a C-1 to C-8 alkyl, and

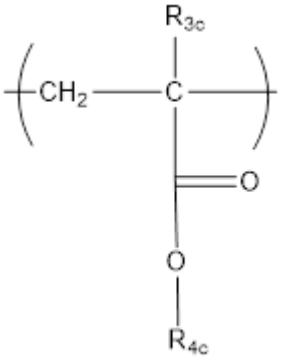
the mole % values, based on the total moles of repeat units of structures (Ic) and (IIc), are for the repeat units of structure (Ic) from 36 mole % to 74 mole % and for the repeat units of structure (IIc) from 26 mole % to 64 mole %, and the individual values of the mole % for the repeat units of structures (Ic) and (IIc) are selected

from their respective ranges to add up to 100 mole % of the total moles of repeat units of structures (Ic) and (IIc), and

said oligo diblock copolymer b-3) has an M_n from 1000 g/mole to 30,000 g/mole, a polydispersity from 1.0 to 1.1, and a T_g from 0°C to 90°C,



(Ic)



(IIc);

c) is a spin casting organic solvent,

the glass transition temperature (T_g) being determined by DSC measurement under nitrogen with a heating rate of 10 °C/min and measuring T_g in first heating scan from 0 to 300 °C as the midpoint of endothermic transition, and

M_n and polydispersity being determined by gel permeation chromatography equipped with 100Å, 500 Å, 103 Å, 105 Å and 106 Å µ-ultrastyragel columns using THF solvent as an eluent and polystyrene polymer standards for calibration.

2. The composition of claim 1, wherein said component a) is selected from either
a single triblock copolymer and blends of at least two triblock copolymers, or
a single diblock copolymer and blends of at least two diblock copolymers.

3. The composition of claims 1 or 2, wherein either said component a) is an ABA triblock copolymer component selected from the group consisting of ABA triblock copolymer a-1t), an ABA triblock copolymer a-2t) and a blend of ABA triblock polymer a-1t) and ABA triblock copolymer a-2t), wherein

a-1t) is an ABA triblock copolymer, comprising a middle B) styrenic block segment of repeat units having styrenic structure (I), and two end acrylic block A) segments of equal

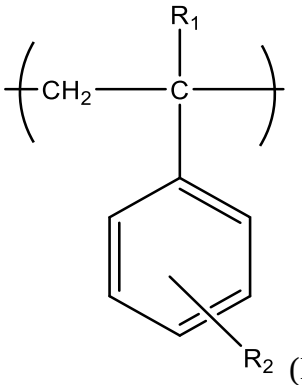
length having structure (II), wherein R_1 and R_3 are independently selected from H and C-1 to C-4 alkyl, R_2 is H or a C-1 to C-8 alkyl, R_4 is a C-1 to C-8 alkyl, and

the mole % values, based on the total moles of repeat units of structures (I) and (II), are for the repeat units of structure (I) from 40 mole % to 80 mole % and for the repeat units of structure (II) from 20 mole % to 60 mole %,

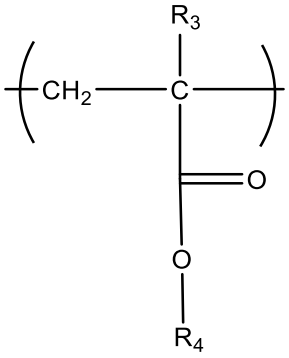
wherein the individual values of the mole % for the repeat units of structures (I) and (II) are selected from their respective ranges to add up to 100 mole % of the total moles of repeat units of structures (I) and (II), and

said triblock copolymer a-1t) has a polydispersity from 1.0 to 1.1 and

has an M_n from 70,000 g/mole to 350,000 g/mole,



(I)



(II);

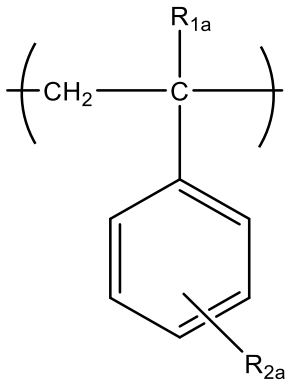
a-2t) is an ABA triblock copolymer, comprising a middle B) block segment of repeat units having styrenic structure (Ia), and two end block B) segments of equal length having acrylic structure (IIa), wherein R_{1a} and R_{3a} are independently selected from H and C-1 to C-4 alkyl, R_{2a} is H or a C-1 to C-8 alkyl, R_{4a} is a C-1 to C-8 alkyl,

the mole % values, based on the total moles of repeat units of structures (Ia) and (IIa), are for the repeat units of structure (Ia) from 40 mole % to 80 mole % and for the repeat units of structure (IIa) from 20 mole % to 60 mole %, and

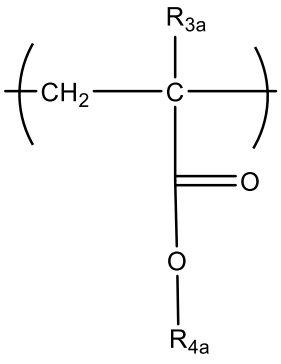
wherein the individual values of the mole % for the repeat units of structures (Ia) and (IIa) are selected from their respective ranges to add up to 100 mole % of the total moles of repeat units of structures (Ia) and (IIa), and

said triblock copolymer a-2t) has a polydispersity from 1.0 to 1.1,

has an M_n from 70,000 g/mole to 350,000 g/mol,

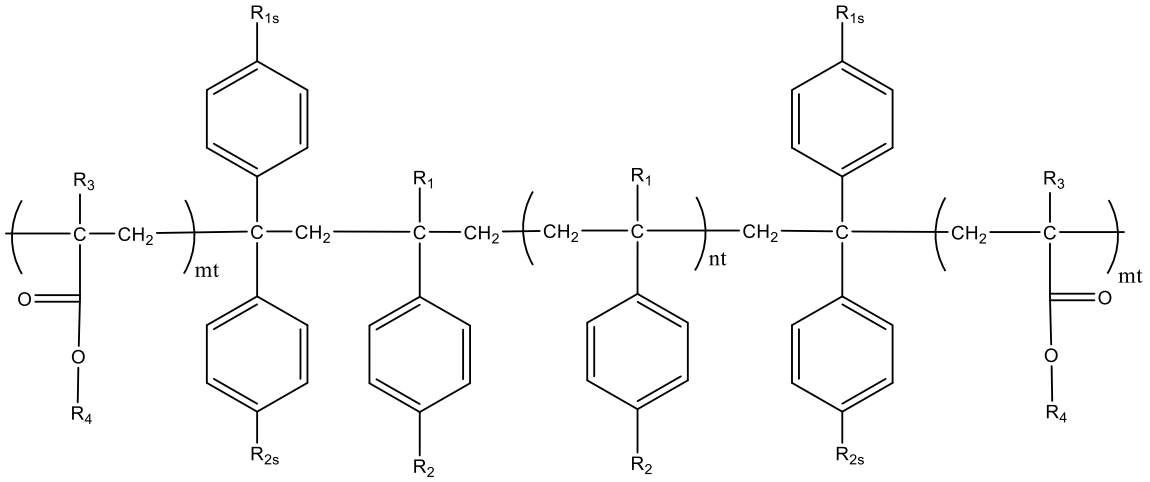


(Ia)

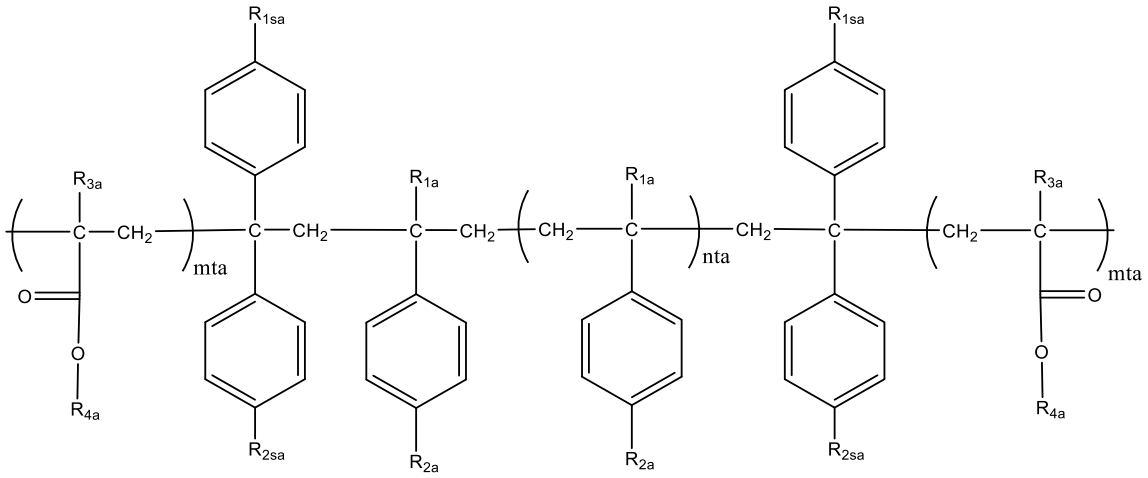


(IIa),

preferably wherein component a) is a triblock copolymer selected from a triblock copolymer of structure (ABA-1), a triblock copolymer of structure (ABA-2) and a mixture of these two block copolymers, wherein mt, mta, nt and nta are the number of repeat units, R_{1s}, R_{1sa}, R_{2s}, and R_{2sa} are independently selected from hydrogen, a C-1 to C-8 alkyl, $-N(R_{3s})_2$, $-OR_{4s}$, and $Si(R_{5s})_3$, wherein R_{3s}, R_{4s} and R_{5s} are independently selected from a C-1 to C-4 alkyl,



(ABA-1)



(ABA-2),

and wherein preferably R_1, R_{1a}, R_2, R_{2a} and R_{1s} and R_{2s} are H and R_3, R_{3a}, R_4, and R_{4a} are methyl, or wherein

a) is a diblock copolymer component selected from the group consisting of diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), wherein

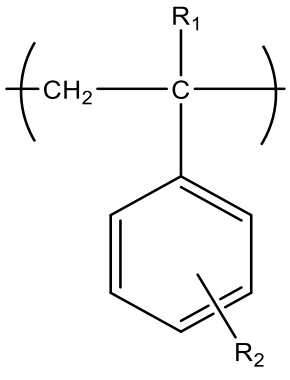
a-1) is a diblock copolymer of block A), with styrenic repeat units having styrenic structure (I), and block B), having acrylic structure (II), wherein R_1 and R_3 are independently selected from H and C-1 to C-4 alkyl, R_2 is H or a C-1 to C-8 alkyl, R_4 is a C-1 to C-8 alkyl, and

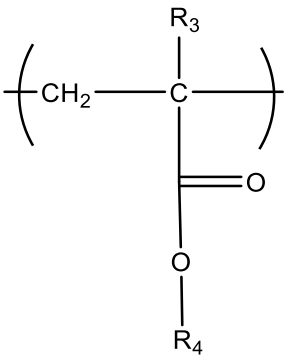
the mole % values, based on the total moles of repeat units of structures (I) and (II), are for the repeat units of structure (I) from 40 mole % to 80 mole % and for the repeat units of structure (II) from 20 mole % to 60 mole %,

wherein the individual values of the mole % for the repeat units of structures (I) and (II) are selected from their respective ranges to add up to 100 mole % of the total moles of repeat units of structures (I) and (II), and

said diblock copolymer a-1) has a polydispersity from 1.0 to 1.1

has an M_n from 50,000 g/mole to 150,000 g/mole,



(I)


(II);

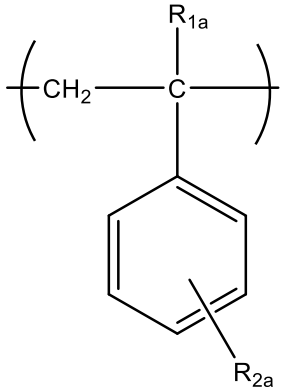
a-2) is a di-block copolymer of a block A-a), with repeat units having styrenic structure (Ia), and block B-a), with repeat units having acrylic structure (IIa), wherein R_{1a} and R_{3a} are independently selected from H or a C-1 to C-4 alkyl, R_{2a} is H or a C-1 to C-8 alkyl, C_{4a} is a C-1 to C-8 alkyl and,

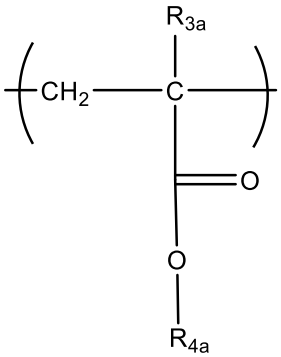
the mole % values, based on the total moles of repeat units of structures (Ia) and (IIa), are for the repeat units of structure (Ia) from 40 mole % to 80 mole % and for the repeat units of structure (IIa) from 20 mole % to 60 mole %, and

wherein the individual values of the mole % for the repeat units of structures (Ia) and (IIa) are selected from their respective ranges to add up to 100 mole % of the total moles of repeat units of structures (Ia) and (IIa), and

said diblock copolymer a-2) has a polydispersity from 1.0 to 1.1,

has an M_n from 30,000 g/mole to 90,000 g/mole,

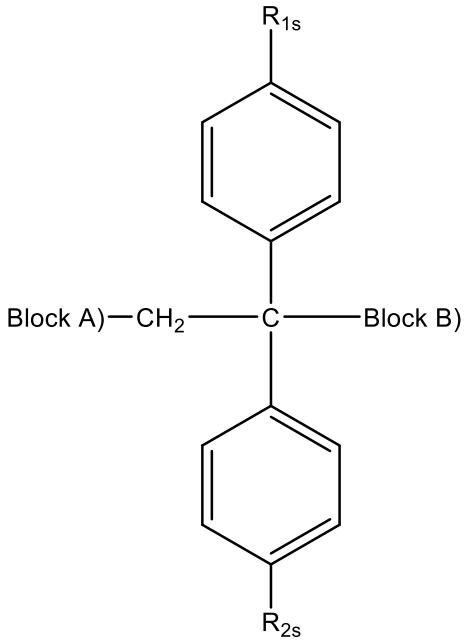


(Ia)


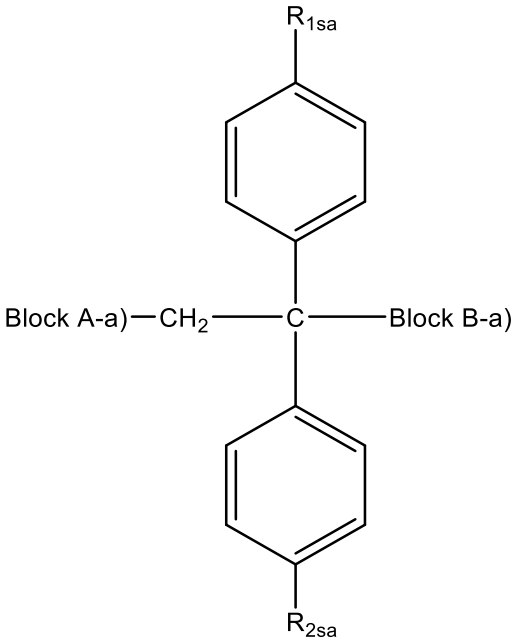
(IIa),

preferably wherein R_1, R_{1a}, R_2 and R_{2a} are H and R_3, R_{3a}, R_4, and R_{4a} are methyl.

4. The composition of claim 3, wherein the diblock copolymers a-1) and a-2), respectively, have structure (I-S), and structure (I-S-a), wherein R_{1s}, R_{1sa}, R_{2s}, and R_{2sa} are independently selected from hydrogen, a C-1 to C-8 alkyl, $-N(R_{3s})_2$, $-OR_{4s}$, and $Si(R_{5s})_3$, wherein R_{3s}, R_{4s} and R_{5s} are independently selected from a C-1 to C-4 alkyl,



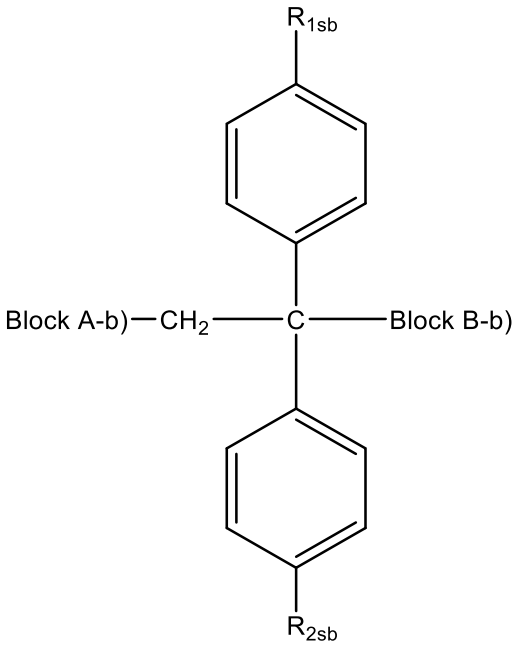
(I-S)



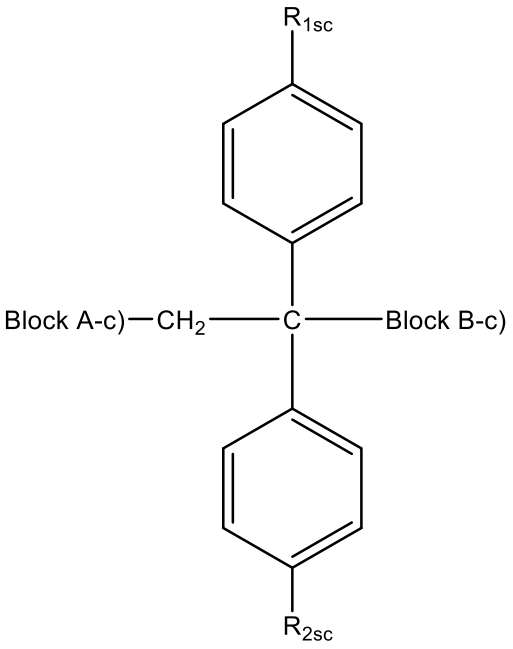
(I-S-a),

preferably wherein R_{1s}, R_{2s}, R_{1sa}, and R_{2sa} are hydrogen.

5. The composition of any one of claims 1 to 4, wherein the oligo diblock copolymer components b-2) and b-3) have a spacer moiety, respectively between block A-b) and block B-b) or between block A-c) and block B-c) as shown, respectively, in structure (I-S-b), and structure (I-S-c) wherein R1sb, R1sc, R2sb, and R2sc are independently selected from hydrogen, a C-1 to C-8 alkyl, -N(R3s)2, -OR4s, Si(R5s)3, wherein R3s, R4s and R5s are independently selected from a C-1 to C-4 alkyl,



(I-S-b)



(I-S-c),

preferably wherein R1sb, R2sb, R1sc, and R2sc are hydrogen.

6. The composition of any one of claims 1 to 5, wherein for component a) the diblock copolymer component a-2t1), has a polydispersity from 1.00 to 1.03, and/or an Mn from 93,000 g/mole to 105,300 g/mole.

7. The composition of any one of claims 1 to 6, wherein for component a) the diblock copolymer component a-1), either the mole % values, for the repeat units of structure (I) are from 40 mole % to 60 mole % and for the repeat units of structure (II) from 40 mole % to 60 mole %, or the mole % values, for the repeat units of structure (I) are from 60 mole % to 75 mole % and for the repeat units of structure (II) from 25 mole % to 40 mole %.

8. The composition of any one of claims 1 to 7, wherein for component a) the diblock copolymer component a-2), has a polydispersity from 1.00 to 1.03, and/or an Mn from 40,800 g/mole to 61,200 g/mole.

9. The composition of any one of claims 1 to 8, wherein either for component a) the total mole % values, for the repeat units of structures (I) and (Ia) is from 40 mole % to 60 mole % and the total mole % value, for the repeat units of structures (II) and (IIa) is from 40 mole % to 60

mole % in for either a single block copolymer a-1) or a-2) or in a blend of a-1) and a-2), or wherein for component a) the total mole % values, for the repeat units of structures (I) and (Ia) is from 60 mole % to 75 mole % and the total mole % value, for the repeat units of structures (II) and (IIa) is from 25 mole % to 40 mole % for either a single block copolymer a-1) or a-2) or in a blend of a-1) and a-2).

10. The composition of any one of claims 1 to 9, wherein component a) is from 0.5 wt. % to 2.0 wt. % of the total composition.

11. The composition of any one of claims 1 to 10, wherein, component b), the oligo random copolymer b-1), is one wherein R_{1b}, and R_{2b} are H and $R_{3b,}$ and R_{4b}, are methyl, and/or the oligo diblock copolymer b-2) it is one in which R_5, R_7 and R_8 are H, R_6 is n-octyl or n-nonyl, R_9 and R_{11} are methyl, R_{10} is methyl or ethyl, R_{12} and R_{13} are independently ethylene or propylene, and R_{14} is methyl or ethyl, preferably wherein R_6 is n-octyl, R_{10} is methyl, R_{12} and R_{13} are ethylene, and R_{14} is methyl, and/or the oligo diblock copolymer b-3), is one wherein R_{1c}, and R_{2c} are H and $R_{3c,}$ and R_{4c}, are methyl.

12. The composition of any one of claims 1 to 11, wherein for component b), the oligo random copolymer b-1), has a polydispersity from 1.3 to 1.5, and/or a T_g from 50°C to 90°C.

13. The composition of any one of claims 1 to 12, wherein for component b), the oligo diblock copolymer b-2) it is one wherein, said mole % for the repeat units of structure (IV) is from 25 mole % to 50 mole %, and said mole % for the repeat units of structure (V) is from 40 mole % to 60 mole %,

and/or wherein, said mole % for the repeat unit of structure (III) its mole % is from 20% to 30 % of the mole % of the repeat unit of structure (IV), and for the repeat unit of structure (VI) its mole % is from 12 % to 20 % of the mole % of the repeat unit of structure (V).

14. The composition of any one of claims 1 to 13, wherein for component b), the oligo diblock copolymer b-2), has a polydispersity from 1.03 to 1.08, and/or an Mn from 15000 g/mole to 32000 g/mole and/or a T_g from 50°C to 90°C.

15. The composition of any one of claims 1 to 14, wherein for component b), the oligo diblock copolymer b-3) has an Mn from 15,000 to 30,000 g/mole, and/or a polydispersity from 1.02 to 1.08, and/or a T_g from 50°C to 90°C.

16. The composition of any one of claims 1 to 15, wherein component b), is the oligo diblock copolymer b-3), and it is one wherein, said mole % for the repeat units of structure (Ic) is from 40 mole % to 70 mole %, and said mole % for the repeat units of structure (IIc) is from 40 mole % to 70 mole %.

17. The composition of any one of claims 1 to 16, wherein component a) is either a diblock copolymer component selected from the group consisting of diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), or a triblock copolymer component selected from the group consisting of triblock copolymer a-1t), triblock copolymer a-2t) and a blend of a-1t) and a-2t), whose total mole % of styrenic repeat units of structures (I) and (Ia) is from 60 mole % to 75 mole % and whose total mole % of acrylic repeat units of structure (II) and (IIa) is from 40 mole % to 60 mole %; and component b) is copolymer b-1), oligo diblock copolymer b-2) or copolymer b-3).

18. The composition of any one of claims 1 to 16, wherein component a) is either a diblock copolymer component selected from the group consisting of diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), or a triblock copolymer component selected from the group consisting of triblock copolymer a-1t), triblock copolymer a-2t) and a blend of a-1t) and a-2t), whose total mole % of styrenic repeat units of structure (I) and (Ia) is from 60 mole % to 75 mole % and further wherein the total mole % of the acrylic repeat units of structures (II) and (IIa) is from 25 mole % to 40 mole %; and component b) is oligo random copolymer b-1), oligo diblock copolymer b-2), or oligo diblock copolymer b-3).

19. A process comprising steps:

i) forming a coating of a neutral layer on a substrate,

ii) coating the composition of any one of claims 1 to 18, onto said neutral layer, to form a film

iii) baking said film, in an inert gas atmosphere, at a temperature selected from 240°C to 260°C, to form a self-assembled film, and

iv) etching said substrate with a plasma to pattern transfer said self-assembled film into the substrate.

20. A process for forming a line and space array comprising steps:

ia) forming a coating of a neutral layer on a substrate,

iia) coating the composition of claim 17, onto said neutral layer, to form a film

iiia) baking said film, in an inert gas atmosphere, at a temperature selected from 240°C to 260°C, to form a self-assembled film, and

iva) etching said substrate with a plasma to pattern transfer said self-assembled film into the substrate.

21. A process for forming a contact hole array comprising steps:

ib) forming a coating of a neutral layer on a substrate,

iib) coating the composition of claim 18 onto said neutral layer, to form a film,

iiib) baking said film, in an inert gas atmosphere, at a temperature selected from 240°C to 260°C, to form a self-assembled film, and

ivb) etching said substrate with a plasma to pattern transfer said self-assembled film into the substrate.

22. An oligo diblock copolymer b-2) as defined in any one of claims 1 to 18.

23. The oligo diblock copolymer of claim 22, wherein the mole % of the sum of the mole % for repeat units (III) and (IV), based on the total moles of repeating units having structures (III), (IV), (V) and (VI), is from 40 mole % to 80 mole % and the sum of the mole % for repeat unit (V) and (VI) ranges from 20 mole % to 60 mole %, and further wherein the mole % of repeat unit (III) ranges from 2 mole % to 80 mole % and the mole % of repeat unit (VI) ranges from 1 mole % to

80 mole %, and further wherein the individual values of the mole % for the repeat units of structures (III), (IV), (V), and (VI), are selected from their respective ranges to add up to 100 mole % of the total moles of repeat units of structures (III), (IV), (V), and (VI).

24. The oligo diblock copolymer of claim 22 or 23, wherein the mole % of repeat unit (III) is from 2 mole % to 64 mole % and/or wherein the mole % of (VI) ranges from 2 mole % to 48 mole %, and/or wherein,
said mole % for the repeat units of structure (IV) is from 25 mole % to 50 mole %, and
said mole % for the repeat units of structure (V) is from 40 mole % to 60 mole %.

25. The use of the composition according to any one of claims 1 to 18 or of the oligo diblock copolymer according to any one of claims 22 to 24 for preparing a self-assembled film on a substrate.