BLOCK COPOLYMER FORMULATION FOR THE IMPROVEMENT OF SELF-ASSEMBLED MORPHOLOGY IN DIRECTED SELF-ASSEMBLY APPLICATION

FIELD OF THE INVENTION

[0001] The disclosed subject matter pertains to block copolymers compositions containing low T_g additives for use in DSA IC manufacturing processes.

BACKGROUND

[0002] Self-assembly of block copolymers is a method useful for generating smaller and smaller patterned features for the manufacture of microelectronic devices in which the critical dimensions (CD) of features on the order of nanoscale can be achieved. Self-assembly methods are desirable for extending the resolution capabilities of microlithographic technology for repeating features such as an array of contact holes or posts. In a conventional lithography approach, ultraviolet (UV) radiation may be used to expose through a mask onto a photoresist layer coated on a substrate or layered substrate. Positive or negative photoresists are useful, and these can also contain a refractory element such as silicon to enable dry development with conventional integrated circuit (IC) plasma processing. In a positive photoresist, UV radiation transmitted through a mask causes a photochemical reaction in the photoresist such that the exposed regions are removed with a developer solution or by conventional IC plasma processing. Conversely, in negative photoresists, UV radiation transmitted through a mask causes the regions exposed to radiation to become less removable with a developer solution or by conventional IC plasma processing. An integrated circuit feature, such as a gate, via or interconnect, is then etched into the substrate or layered substrate, and the remaining photoresist is removed. When using conventional lithographic exposure processes, the dimensions of features of the integrated circuit feature are limited. Further reduction in pattern dimensions is difficult to achieve with radiation exposure due to limitations related to aberrations, focus, proximity effects, minimum achievable exposure wavelengths and maximum achievable numerical apertures. The need for large-scale integration has led to a continued shrinking of the circuit dimensions and features in the devices. In the past, the final resolution of the features has been dependent upon the wavelength of light used to expose the photoresist, which has its own limitations. Directed (a.k.a. guided) self-assembly techniques, such as graphoepitaxy and chemoepitaxy using block copolymer imaging, which employ a patterned area on a substrate, are highly desirable techniques used to enhance resolution while reducing CD

variation. These techniques can be employed to either enhance conventional UV lithographic techniques or to enable even higher resolution and CD control in approaches employing EUV, e-beam, deep UV or immersion lithography. The directed self-assembly block copolymer comprises a block of etch resistant copolymeric unit and a block of highly etchable copolymeric unit, which when coated, aligned, and etched on a substrate give regions of very high-density patterns.

[0003] For directed (guided), or unguided self-assembly, of a block copolymer film, respectively, on a patterned or non-patterned substrate area, typically the self-assembly process of this block polymer layer occurs during annealing of this film overlying a neutral layer. This neutral layer over a semiconductor substrate may be an unpatterned neutral layer, or in chemoepitaxy or graphoepitaxy, this neutral layer may contain, respectively, graphoepitaxy or chemoepitaxy guiding features (formed through the above-described UV lithographic technique). During annealing of the block copolymer film, the underlying, neutral layer, directs the nano-phase separation of the block copolymer domains. One example is the formation phase separated domains which are lamellas or cylinders perpendicular to the underlying neutral layer surface. These nano-phase separated block copolymer domains, form a pre-pattern (e.g., line and space L/S) which may be transferred into the substrate through an etching process (e.g., plasma etching). In graphoepitaxy, or in chemoepitaxy, these guiding features may dictate both pattern rectification and pattern multiplication. In the case of an unpatterned neutral layer this produces a repeating array of for instance L/S or CH. For example, in a conventional block copolymer such as poly(styrene-b-methyl methacrylate (P(S-b-MMA)), in which both blocks have similar surface energies at the BCP-air interface, this can be achieved by coating and thermally annealing the block copolymer on a layer of non-preferential or neutral material that is grafted or cross-linked at the polymer-substrate interface.

[0004] In the graphoepitaxy directed self-assembly method, the block copolymers self organizes around a substrate that is pre-patterned with conventional lithography (Ultraviolet, Deep UV, e-beam, Extreme UV (EUV) exposure source) to form repeating topographical features such as a line/space (L/S) or contact hole (CH) pattern. In an example of a L/S directed self-assembly array, the block copolymer can form self-aligned lamellar regions which can form parallel line-space patterns of different pitches in the trenches between pre-patterned lines, thus enhancing pattern resolution by subdividing the space in the trench between the topographical lines into finer patterns. For example, a diblock copolymer or a triblock copolymer which is capable of microphase separation and comprises a block rich in carbon (such as styrene or containing some other element

like Si, Ge, Ti) which is resistant to plasma etch, and a block which is highly plasma etchable or removable, can provide a high-resolution pattern definition. Examples of highly etchable blocks can comprise monomers which are rich in oxygen, and which do not contain refractory elements and can form blocks which are highly etchable, such as methyl methacrylate. The plasma etching gases used in the etching process of defining the self-assembly pattern typically are those used in processes employed to make integrated circuits (IC). In this manner, very fine patterns can be created in typical IC substrates than were definable by conventional lithographic techniques, thus achieving pattern multiplication. Similarly, features such as contact holes can be made denser by using graphoepitaxy in which a suitable block copolymer arranges itself by directed self-assembly around an array of contact holes or posts defined by conventional lithography, thus forming a denser array of regions of etchable and etch resistant domains which when etched give rise to a denser array of contact holes. Consequently, graphoepitaxy has the potential to offer both pattern rectification and pattern multiplication.

[0005] In chemical epitaxy, or pinning chemical epitaxy, the self-assembly of the block copolymer is formed on a surface whose guiding features are regions of differing chemical affinity, having no, or insignificant topography (a.k.a. non-guiding topography) which predicates the directed self-assembly process. For example, the surface of a substrate could be patterned with conventional lithography (UV, Deep UV, e-beam EUV) to create surfaces of different chemical affinity in a line and space (L/S) pattern in which exposed areas whose surface chemistry had been modified by irradiation alternate with areas which are unexposed and show no chemical change. These areas present no topographical difference but do present a surface chemical difference or pinning to direct self-assembly of block copolymer segments. Specifically, the directed self-assembly of a block copolymer whose block segments contain etch resistant (such as styrene repeat unit) and rapidly etching repeat units (such as methyl methacrylate repeat units) would allow precise placement of etch resistant block segments and highly etchable block segments over the pattern. This technique allows for the precise placement of these block copolymers and the subsequent pattern transfer of the pattern into a substrate after plasma or wet etch processing. Chemical epitaxy has the advantage that it can be fine-tuned by changes in the chemical differences to help improve line-edge roughness and CD control, thus allowing for pattern rectification. Other types of patterns such as repeating contact holes (CH) arrays could also be pattern rectified using chemoepitaxy.

[0006] Neutral layers are layers on a substrate or the surface of a treated substrate which have no affinity for either of the block segment of a block copolymer employed in directed self-assembly. In the graphoepitaxy method of directed self-assembly of block copolymer, neutral layers are useful as they allow the proper placement or orientation of block polymer segments for directed self-assembly which leads to proper placement of etch resistant block polymer segments and highly etchable block polymer segments relative to the substrate. For instance, in surfaces containing line and space features which have been defined by conventional radiation lithography, a neutral layer allows block segments to be oriented so that the block segments are oriented perpendicular to the surface of the substrates, an orientation which is ideal for both pattern rectification and pattern multiplication depending on the length of the block segments in the block copolymer as related to the length between the lines defined by conventional lithography. If a substrate interacts too strongly with one of the block segments it would cause it to lie flat on that surface to maximize the surface of contact between the segment and the substrate; such a surface would perturb the desirable perpendicular alignment which can be used to either achieve pattern rectification or pattern multiplication based on features created through conventional lithography. Modification of selected small areas or pinning of substrate to make them strongly interactive with one block of the block copolymer and leaving the remainder of the surface coated with the neutral layer can be useful for forcing the alignment of the domains of the block copolymer in a desired direction, and this is the basis for the pinned chemoepitaxy or graphoepitaxy employed for pattern multiplication.

[0007] Although self-assembly using polystyrene-b-polymethylmethacrylate (PS-b-PMMA) is widely used as next generation patterning material in lithography, with the nano-phase separation assembly process generating well aligned arrays of domains, this occurs with the formation of considerable amounts of defects, if the film thickness exceeds beyond 50 nm. These defects are significant in contact hole and line/space multiplication processes and need to be reduced significantly to improve device yield in any commercially viable IC-manufacturing employing directed self-assembly. One of the origins of the defects is an insufficient diffusion of block segments that generates defects such as dislocation, bridges, networks and line or cylinder collapse etc. Thus, there is a need for new materials and processes which can affect self-assembly of block copolymer domains having a greatly reduced number of these defects even in films having a thickness beyond 50 nm.

DETAILED DESCRIPTION OF DRAWINGS

[0008] **FIG. 1** SEM pictures taken at 2 and 4 or 50 FOV of the annealed and plasma etched Block copolymer (BCP) formulations which contained the inventive radically polymerized h-PS oligomeric additives 1, 2, 3, 5, 6, or 7 showing good contact hole (CH) self-assembly with no defects.

[0009] **FIG. 2** SEM pictures taken at 2 and 4 FOV of the annealed and plasma etched Block copolymer (BCP) formulations which contained the comparative radically polymerized h-PS oligomeric additives 4 or the anionic polymerized h-PS oligomeric additives 1 or 2 showing poor contact hole (CH) self-assembly with defects.

SUMMARY OF INVENTION

[0010] We have found a number of low T_g oligomeric styrenic additives prepared by standard radical polymerization, which can be used as additives with block copolymers (BCP), forming novel block copolymer compositions, which by adjusting wt. % of the low T_g styrenic additives show improved performance. Surprisingly, low T_g styrenic additives synthesized by controlled synthetic methods, such as anionic polymerization, showed very bad morphology during self-assembly annealing when formulated with BCP. In contrast and surprisingly, low T_g oligomeric styrenic additives prepared by standard radical polymerization, when used as BCP additives, imparted good self-assembled morphology during this self-assembly annealing, when these are adjusted to a specific range of M_w and polydispersity. This interesting phenomenon indicates that BCP formulation kinetics is surprisingly strongly influenced by the mobility capability of oligomer additives of smaller size and chemically random structures by strongly contributing to better kinetics of BCP formulations.

[0011] Specifically, the present invention relates to 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 at least one low T_g oligomeric polystyrenic additive in which each additive individually has a T_g which ranges from 68.0°C to 90.0°C and has an M_w which ranges from 2,500 g/mole to 8,000 g/mole, has a polydispersity from 1.20 to 1.80, and further wherein said styrenic additive is selected from the group consisting of at least one styrenic homopolymer prepared by radical polymerization, at least one styrenic random copolymer prepared by radical polymerization, whose repeat units only consist of styrenic repeat units and where at least two styrenic repeat units are present, a mixture of

at least one said styrenic homopolymer and at least one said styrenic random copolymer; and c) is an organic spin casting solvent.

[0012] Another aspect of this invention is the method of using the above-described compositions in a self-assembly process followed by pattern transfer of the self-assembled pattern into a substrate.

DETAILED DESCRIPTION OF THE INVENTION

[0013] It is to be understood that both the foregoing general description and the following detailed description are illustrative and explanatory, and are not restrictive of the subject matter, as claimed. In this application, the use of the singular includes the plural, the word "a" or "an" means "at least one", and the use of "or" means "and/or," unless specifically stated otherwise. Furthermore, the use of the term "including," as well as other forms such as "includes" and "included," is not limiting. Also, terms such as "element" or "component" encompass both elements and components comprising one unit and elements or components that comprise more than one unit, unless specifically stated otherwise. As used herein, the conjunction "and" is intended to be inclusive and the conjunction "or" is not intended to be exclusive unless otherwise indicated. For example, the phrase "or, alternatively" is intended to be exclusive. As used herein, the term "and/or" refers to any combination of the foregoing elements including using a single element.

[0014] The term C-1 to C-4 alkyl embodies methyl and C-2 to C-4 linear alkyls and C-3 to C-4 branched alkyl moieties, for example as follows: methyl(-CH_3), ethyl (-CH_2-CH_3), n-propyl (-CH_2-CH_2-CH_3), isopropyl (-$CH(CH_3)_2$, n-butyl (-CH_2-CH_2-CH_2-CH_3), tert-butyl (-$C(CH_3)_3$), isobutyl (CH_2-$CH(CH_3)_2$, 2-butyl (-$CH(CH_3)CH_2$-CH_3). Similarly, the term C-1 to C-8 alkyl embodies methyl C-2 to C-8 linear, C-3 to C-8 branched alkyls, C-4 to C-8 cycloalkyls (e.g., cyclopentyl, cyclohexyl etc) or C-5-C-8 alkylenecycloalkyls (e.g. -CH_2-cyclohexyl, CH_2-CH_2-cyclopentyl etc.

[0015] The term C-2 to C-5 alkylene embodies C-2 to C-5 linear alkylene moieties (e.g., ethylene, propylene etc.) and C-3 to C-5 branched alkylene moieties (e.g., -$CH(CH_3)$-, -$CH(CH_3)$-CH_2-, etc.).

[0016] Di-block and triblock copolymers of styrenic and acrylic moieties useful as components in the inventive compositions described herein may be made by a variety of methods, such as anionic polymerization, atom transfer radical polymerization (ATRP), Reversible addition-fragmentation chain transfer (RAFT) polymerization, living radical polymerization and the like (Macromolecules 2019, 52, 2987−2994; Macromol. Rapid Commun. 2018, 39, 1800479; A. Deiter Shluter et al Synthesis of Polymers, 2014, Volume 1, p315; Encyclopedia of Polymer Science and Technology, 2014, Vol 7, p 625.)

[0017] The random copolymer poly(styrene-co-methyl methacrylate) is abbreviated as "P(S-co-MMA)," and the oligomeric version of this materials is abbreviated oligo(S-co-MMA). Similarly, the block copolymer poly(styrene-block-methyl methacrylate) is abbreviated as P(S-b-MMA)

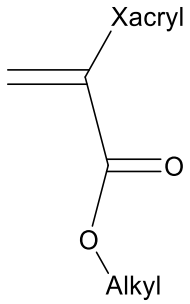
[0018] The term "g/mole," is an abbreviation of grams per mole.

[0019] The term "CH," is an abbreviation for contact hole lithographic features, the term "L/S," is an abbreviation for line and space lithographic features.

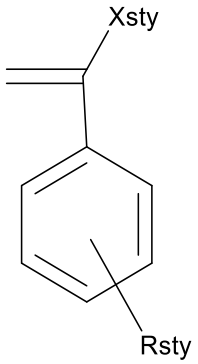
[0020] In the following descriptions the term "Synth." is an abbreviation for synthesis; the term "Comp". is an abbreviation for comparative; and the term "Ex." is an abbreviation for Example.

[0021] The term oligomer, oligo and oligomeric polymer as used herein, denote low T_g additives and denote a low molecular weight polymer whose molecular weight range is specific to the additive type as indicated herein.

[0022] The term acrylic as used herein encompasses repeat unit derived from acrylate derivatives, for example ones derived from acrylate derivatives having the following structure, wherein the Alkyl moiety may be a C-1 to C-8 alkyl, and Xacryl is either H or a C-1 to C-4 alkyl:



[0023] The term styrenic as used herein encompasses repeat units derived from styrene derivatives, for example one derived from styrene derivatives having the following structure wherein Xsty moiety is H or a C-1 to C-4 alkyl and the Rsty moiety is H or a C-1 to C-8 moiety:



Composition

[0024] One aspect of this invention is 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 at least one low T_g oligomeric polystyrenic additive in which each additive individually has a T_g which ranges from 68.0°C to 90.0°C and has an M_w which ranges from 2,500 g/mole to 8,000 g/mole, has a polydispersity from 1.20 to 1.80, and further wherein said styrenic additive is selected from the group consisting of

at least one styrenic homopolymer prepared by radical polymerization,

at least one styrenic random copolymer prepared by radical polymerization, whose repeat units only consist of styrenic repeat units and where at least two styrenic repeat units are present, and a mixture of at least one said styrenic homopolymer and at least one said styrenic random copolymer.

c) is an organic spin casting solvent.

[0025] In one aspect of the above-described inventive composition it consists essentially of components a) b) and c). In one aspect of this embodiment the term "consist essentially of" entails that other components may be present that do not affect the performance of the material and are present only in a concentration totaling 10 wt. % of the composition. In another aspect of this embodiment, these other components are present only in a concentration totaling 5 wt. % of the composition. In a further aspect of this embodiment these other components are present only in a concentration totaling 1 wt. %. In still another aspect of this embodiment these other components are present in a concentration totaling 0.5 wt. %.

In another aspect of the above-described inventive composition it consists of components a), b) and c).

1) Component b) low T_g oligomeric polystyrenic additive

[0026] In another aspect of the above-described inventive composition it is one where each component b) additive individually has a T_g which ranges from 68.0°C to 90.0°C. In another aspect of this embodiment, it ranges from 68.5°C to 90.0°C. In another aspect of this embodiment, it ranges from 68.6°C to 90.0°C. In another aspect of this embodiment, it ranges from 68.7°C to 90.0°C. In another aspect of this embodiment, it ranges from 68.7°C to 90.0°C. In another aspect of this embodiment, it ranges from 68.8°C to 90.0°C. In another aspect of this embodiment, it

ranges from 68.8°C to 90.0°C. In another aspect of this embodiment, it ranges from 68.9°C to 90.0°C. In another aspect of this embodiment, it ranges from 69.0°C to 90.0°C. In another aspect of this embodiment, it ranges from 69.1°C to 90.0°C. In another aspect of this embodiment, it ranges from 69.2°C to 90.0°C. In another aspect of this embodiment, it ranges from 69.3°C to 90.0°C. In another aspect of this embodiment, it ranges from 69.3°C to 89.9°C. In another aspect of this embodiment, it ranges from 69.3°C to 89.8°C. In another aspect of this embodiment, it ranges from 69.0°C to 89.7°C. In another aspect of this embodiment, it ranges from 69.3°C to 89.7°C.

[0027] In another aspect of this embodiment, it ranges from 68.0°C to 90.0°C. In another aspect of this embodiment, it ranges from 68.0°C to 89.0°C. In another aspect of this embodiment, it ranges from 68.0°C to 88.0°C. In another aspect of this embodiment, it ranges from 68.0°C to 87.0°C. In another aspect of this embodiment, it ranges from 68.0°C to 86.0°C. In another aspect of this embodiment, it ranges from 68.0°C to 85.0°C. In another aspect of this embodiment, it ranges from 68.0°C to 84.9°C. In another aspect of this embodiment, it ranges from 68.0°C to 84.8°C. In another aspect of this embodiment, it ranges from 68.0°C to 84.7°C. In another aspect of this embodiment, it ranges from 68.0°C to 84.6°C. In another aspect of this embodiment, it ranges from 68.0°C to 84.5°C. In another aspect of this embodiment, it ranges from 68.0°C to 84.4°C. In another aspect of this embodiment, it ranges from 68.1°C to 84.4°C. In another aspect of this embodiment, it ranges from 68.2°C to 84.4°C. In another aspect of this embodiment, it ranges from 68.3°C to 84.4°C. In another aspect of this embodiment, it ranges from 68.3°C to 84.4°C. In another aspect of this embodiment, it ranges from 68.4°C to 84.4°C. In another aspect of this embodiment, it ranges from 68.5°C to 84.4°C. In another aspect of this embodiment, it ranges from 68.6°C to 84.4°C. In another aspect of this embodiment, it ranges from 68.7°C to 84.4°C. In another aspect of this embodiment, it ranges from 68.8°C to 84.4°C. In another aspect of this embodiment, it ranges from 68.9°C to 84.4°C. In another aspect of this embodiment, it ranges from 69.0°C to 84.4°C. In another aspect of this embodiment, it ranges from 69.1°C to 84.4°C. In another aspect of this embodiment, it ranges from 69.2°C to 84.4°C. In another aspect of this embodiment, it ranges from 69.3°C to 84.4°C.

[0028] In another aspect of the above-described inventive composition it is one where each component b) additive individually has a polydispersity which ranges from 1.30 to 1.80. In another aspect of this embodiment, it ranges from 1.35 to 1.80. In another aspect of this embodiment, it

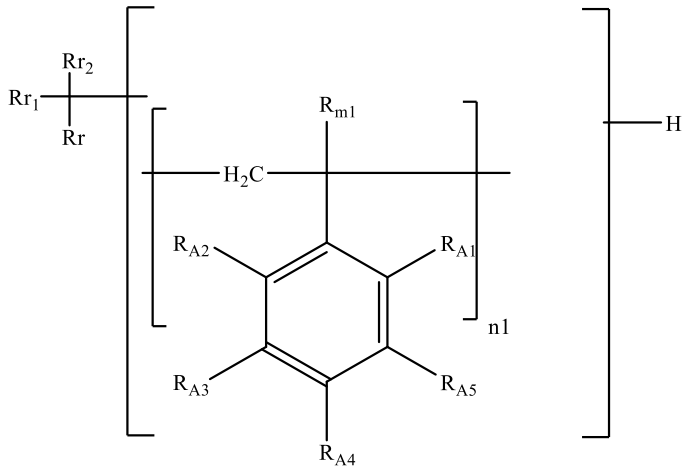
ranges from 1.36 to 1.80. In another aspect of this embodiment, it ranges from 1.37 to 1.80. In another aspect of this embodiment, it ranges from 1.38 to 1.80. In another aspect of this embodiment, it ranges from 1.39 to 1.80. In another aspect of this embodiment, it ranges from 1.40 to 1.80. In another aspect of this embodiment, it ranges from 1.40 to 1.75. In another aspect of this embodiment, it ranges from 1.40 to 1.74. In another aspect of this embodiment, it ranges from 1.40 to 1.73. In another aspect of this embodiment, it ranges from 1.40 to 1.72. In another aspect of this embodiment, it ranges from 1.40 to 1.71. In another aspect of this embodiment, it ranges from 1.40 to 1.71. In another aspect of this embodiment, it ranges from 1.40 to 1.70. In another aspect of this embodiment, it ranges from 1.40 to 1.69.

[0029] In another aspect of the above-described inventive composition it is one where each said at least one low T_g oligomeric polystyrenic additive of said component b) individually has an M_w which ranges from 2,700 g/mole to 8,000 g/mole. In another aspect of this embodiment, it ranges from 2,800 g/mole to 8,000 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 7,900 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 7,800 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 7,700 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 7,600 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 7,500 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 7,400 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 7,300 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 7,200 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 7,100 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 7,000 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 6,900 g/mole. In another aspect of this embodiment, it ranges from 2,900 g/mole to 6,800 g/mole.

[0030] In another aspect of the composition, said component b) additive, is either at least one said styrenic homopolymer or said styrenic random copolymer which are prepared by radical polymerization. In one aspect of this embodiment, it consists of one said styrenic homopolymer prepared by radical polymerization.

[0031] In another aspect of the composition described herein, said component b) additive is at least one said styrenic homopolymer, and further has structure (A), whose repeat units consist of ones having structure (I). In structure (I), n1 is the number of repeating units and designates that this is a repeat unit, R_{A1}, R_{A2}, R_{A3}, R_{A4}, R_{A5}, are individually selected from selected from H or a C-1 to C-

8 alkyl, R_{m1}, is H or methyl, and said styrenic homopolymer has two end groups, as shown in structure, (A) one of which is H and the other is a methyl moiety substituted with Rr, Rr_1 and Rr_2, wherein Rr_1, is a C-1 to C-8 alkyl, Rr_2 is selected from a C-1 to C-8 alkyl, 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. In another aspect of this embodiment, R_{A1}, R_{A2}, R_{A3}, R_{A4}, R_{A5}, are individually selected from selected from H or a C-1 to C-4 alkyl. In another aspect of this embodiment, R_{A1}, R_{A2}, R_{A3}, R_{A4}, R_{A5}, are H. In another aspect of this embodiment Rm_1 is H. In another aspect of this embodiment, R_{A1}, R_{A2}, R_{A3}, R_{A4}, R_{A5}, are H and R_{m1} are H. In another aspect of this embodiment Rr is a cyano moiety (-CN). In another aspect of this embodiment, said component b) additive consists of one said styrenic homopolymer of structure (A). In another aspect of this embodiment, said component b) additive, is at least two different styrenic homopolymers of structure (A).

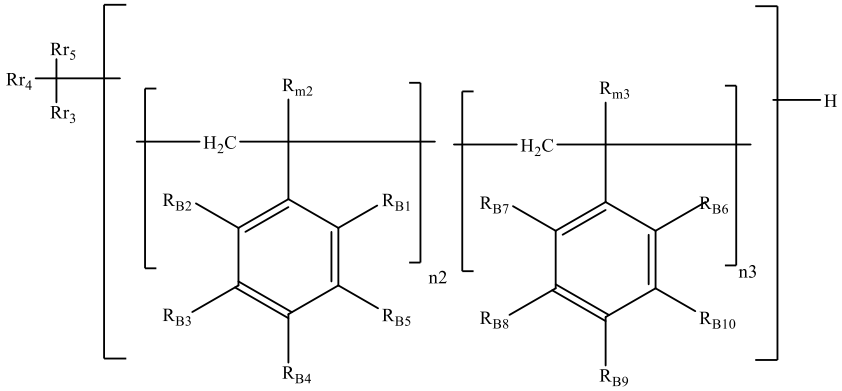


(I) (A)

[0032] In another aspect of the composition, said component b) additive, is either at least two said styrenic homopolymer or at least two said styrenic random copolymers which are both prepared by radical polymerization. In one aspect of this embodiment, it is two said styrenic homopolymers prepared by radical polymerization.

[0033] In another aspect of the composition, said component b) additive is at least one said styrenic random copolymer which has structure (B), wherein its repeat units consist of two different repeat units of structure (II) and (III), where, respectively, n2 and n3 are the number of these repeating units and designate that these are repeating units, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5}, R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} are independently selected from H or a C-1 to C-8 alkyl, R_{m2}, R_{m3} are independently selected from H or methyl; and said styrenic random copolymer has two end groups as shown in structure

(B) one of which is H and the other is a methyl moiety substituted with Rr_3, Rr_4 and Rr_5, wherein Rr_4, is a C-1 to C-8 alkyl, Rr_5 is selected from a C-1 to C-8 alkyl, Rr_3 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. In another aspect of this embodiment, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5}, R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} are independently selected from H or a C-1 to C-4 alkyl. In another aspect of this embodiment, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5}, and at least one of R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} is a C-1 to C-4 alkyl, in one aspect of this embodiment it is a methyl. In another aspect of this embodiment, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5} are all H, and at least one of R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} is a C-1 to C-4 alkyl; in one aspect of this embodiment, it is a methyl. In another aspect of this embodiment, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5}, R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} are all H. In another aspect of these embodiment R_{m2} and R_{m3} are both H. In another aspect of this embodiment Rr_3 is a cyano moiety (-CN). In another aspect of this embodiment said component b) additive, consists of one said styrenic random copolymer of structure (B). In another aspect of this embodiment said component b) consists of at least two different said random styrenic copolymers of structure (B).



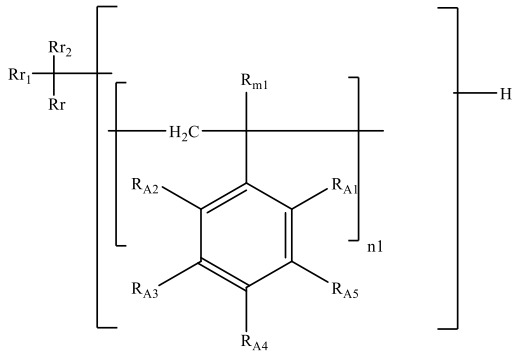
(II) (III) (B)

[0034] In another aspect of the composition, said component b) additive, is a mixture of at least one said styrenic homopolymer and a least one said styrenic random copolymer prepared by radical polymerization. In another aspect of this embodiment, it consists of one said styrenic homopolymer and one said random copolymer prepared by radical polymerization.

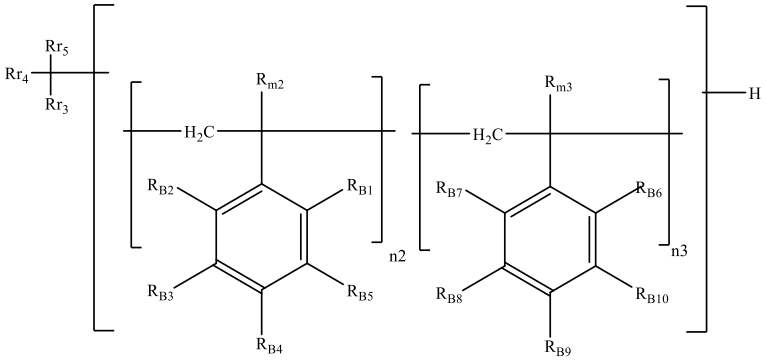
[0035] In another aspect of the composition, said component b) additive is a mixture of at least one said styrenic homopolymer of structure (A) and at least one said styrenic random copolymer of structure (B). In this aspect said styrenic homopolymer has structure (A), which has repeat units of structure (I), and two end group as shown is structure (A). In the repeat units of structure (I), n1 is

the number of repeating units and designates that this is a repeat unit, R_{A1}, R_{A2}, R_{A3}, R_{A4},, R_{A5}, are individually selected from H or a C-1 to C-8 alkyl, R_{m1}, is H or methyl. Further, as shown in structure (A) one of the end groups is H and the other one is a methyl moiety substituted with Rr, Rr_1 and Rr_2, wherein Rr_1, is a C-1 to C-8 alkyl, Rr_2 is selected from 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. In another aspect of this embodiment R_{A1}, R_{A2}, R_{A3}, R_{A4}, R_{A5}, are individually selected from H or a C-1 to C-4 alkyl. In another aspect of this embodiment, R_{A1}, R_{A2}, R_{A3}, R_{A4}, and R_{A5}, are all H. In another aspect of this embodiment Rm_1 is H. In another aspect of this embodiment, R_{A1}, R_{A2}, R_{A3}, R_{A4}, R_{A5}, are H and R_{m1} is H. In another aspect of this embodiment Rr is a cyano moiety (-CN).

Further, in this embodiment of the invention wherein said component b) additive is a mixture of at least one said styrenic homopolymer of structure (A) and at least one said styrenic random copolymer of structure (B), in said styrenic random copolymer of structure (B) the repeat units consist of two repeat units of structure (II) and (III) and said styrenic random copolymer has two end groups, where, in structures (II) and (III) respectively, n2 and n3 are the number of these repeating units and designate that these are repeating units, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5}, R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} are independently selected from H or a C-1 to C-8 alkyl, R_{m2}, R_{m3} are independently selected from H or methyl. The two end groups are shown in structure (B), one of these is H and the other one is a methyl moiety substituted with Rr_3, Rr_4 and Rr_5, wherein Rr_4, is a C-1 to C-8 alkyl, Rr_5 is selected from a C-1 to C-8 alkyl, Rr_3 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. In another aspect of this embodiment, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5}, R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} are independently selected from H or a C-1 to C-4 alkyl. In another aspect of this embodiment, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5} are all H, and at least one of R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} is a C-1 to C-4 alkyl; in one aspect of this embodiment, it is a methyl. In another aspect of this embodiment, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5}, R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} are all H. In another aspect of these embodiments R_{m2} and R_{m3} are both H. In another aspect of this embodiment Rr_3 is a cyano moiety (-CN).



(I) (A)



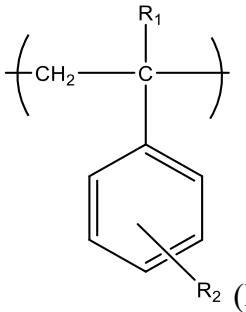
(II) (III) (B)

2) Component a) block copolymer component

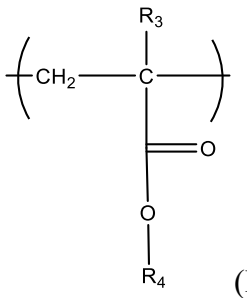
[0036] In another aspect of the composition, said component a) is selected from either a single triblock copolymer and blends of at least two different triblock copolymers, or a single diblock copolymer and blends of at least two different diblock copolymers.

[0037] In another aspect of the composition, said component a) is an ABA triblock copolymer component selected from the group consisting of ABA triblock copolymer a-1t), a ABA triblock copolymer a-2t) and a blend of two ABA triblock, having different composition, copolymer 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 styrenic repeat units of structure (I') from 40 mole % to 80 mole % and for the acrylic 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')

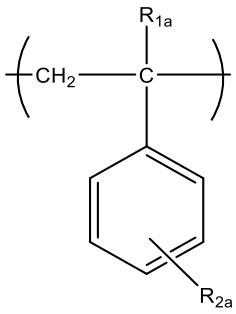


(II')

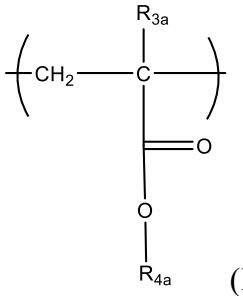
Further, in this aspect, ABA triblock copolymer a-2t) is an ABA triblock copolymer, comprising a middle B) block segment of repeat units having styrenic structure (Ia), and two end block A) segments of equal length having acrylic structure (IIa), wherein R_{1a} and R_{3a} are independently selected from 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.

Further, still in this aspect, the mole % values, based on the total moles of repeat units of structures (Ia) and (IIa), are for the styrenic repeat units of structure (Ia) from 40 mole % to 80 mole % and for the acrylic 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). Finally in this aspect said triblock copolymer a-2t) has a polydispersity from 1.0 to 1.1, and also has an M_n from 70,000 g/mole to 350,000 g/mol.



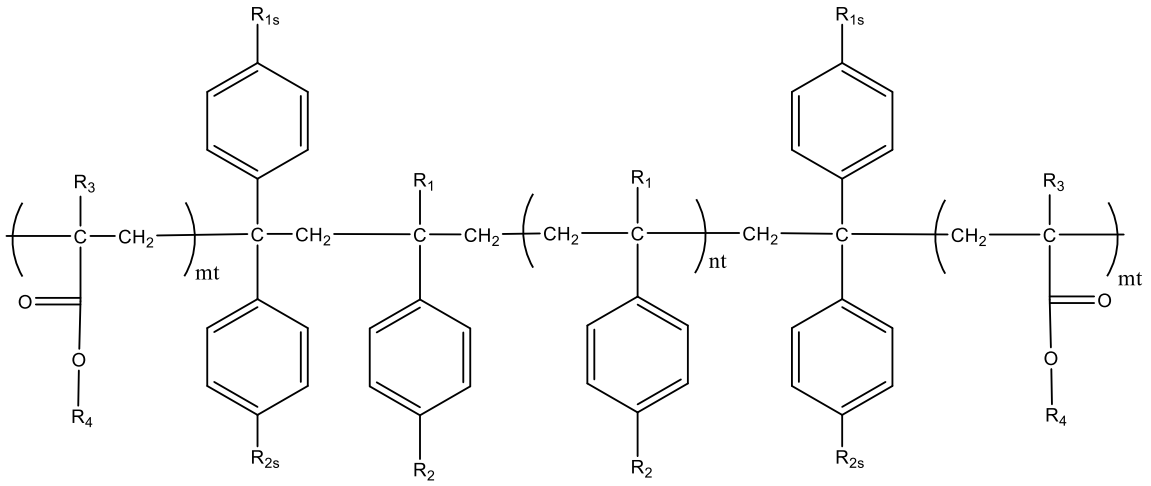
(Ia)



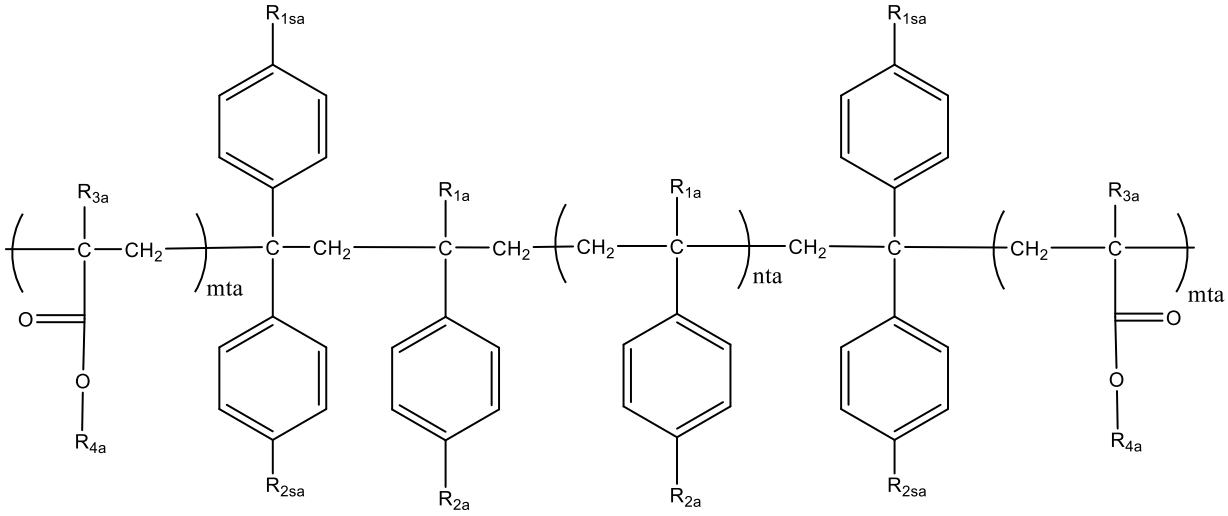
(IIa).

[0038] In another aspect of the composition, where 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), more specifically, R_1, R_{1a}, R_2 and R_{2a} are H and R_3, R_{3a}, R_4, and R_{4a} are methyl. In another aspect of the composition, wherein said component a) is a triblock copolymer as described

above, in one embodiment this component a) is 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, and 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. Further in this embodiment the mole % values, based on the total moles of both styrenic and acrylic repeat in structure (ABA-1), are for the styrenic repeat units 40 mole % to 80 mole % and for the acrylic 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 of structure (ABA-1) has a polydispersity from 1.0 to 1.1 and has an M_n from 70,000 g/mole to 350,000 g/mole and said triblock copolymer of Structure (ABA-2) has a polydispersity from 1.0 to 1.1, and also has an M_n from 70,000 g/mole to 350,000 g/mol. In another aspect of this embodiment R_1, R_{1a}, R_2, R_{2a}, R_{1s}, R_{1sa}, R_{2s}, R_{2sa} are H and R_3, R_{3a}, R_4, and R_{4a} are methyl. In one aspect of this embodiment component a) consists only of said ABA triblock copolymer of structure (ABA-1), in another aspect of this embodiment component a) consist only of said ABA triblock copolymer of structure (ABA-2), and in another aspect of this embodiment said component a) consists of a mixture of said triblock copolymer of structures (ABA-1) and (ABA-2). In another aspect of this embodiment of the blend of a-1t) and a-2t) it is one whose total mole % of styrenic repeat units of structure (I') and (Ia) is from 60 mole % to 75 mole % and where the total mole % of the acrylic repeat units of structures (II') and (IIa) is from 25 mole % to 40 mole % and component.



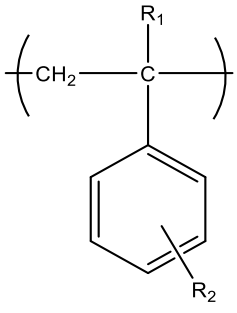
(ABA-1)



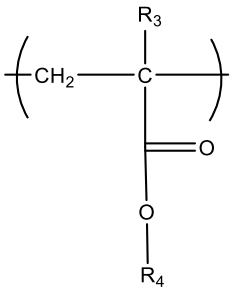
(ABA-2).

[0039] In another aspect of the composition, said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2).

[0040] In this aspect, 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. Further in this aspect, 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 %. Further still in this aspect, 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'). Further in this aspect, said diblock copolymer a-1) has a polydispersity from 1.0 to 1.1 and has an M_n from 50,000 g/mole to 150,000 g/mole.

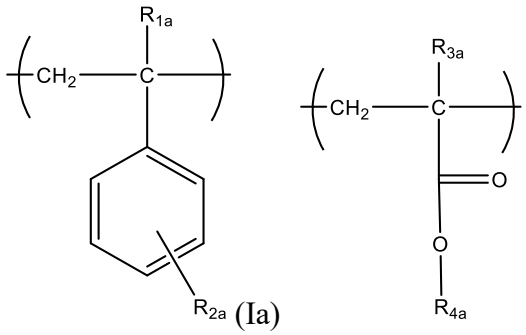


(I')



(II')

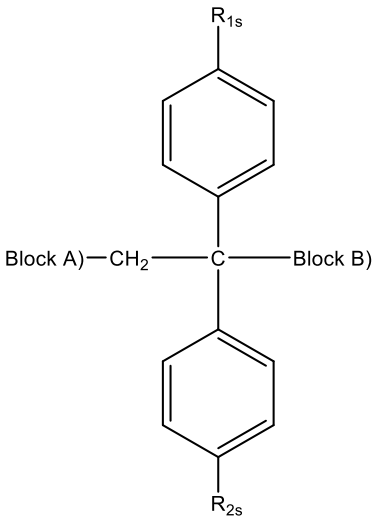
[0041] Further, in another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), a-2) is a di-block copolymer of a block A-a), with repeat units having styrenic 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, R_{4a} is a C-1 to C-8 alkyl. Further in this aspect, 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 %. Further still in this aspect 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). Further still, in this aspect, said diblock copolymer a-2) has a polydispersity from 1.0 to 1.1, and also has an M_n from 30,000 g/mole to 90,000 g/mole.



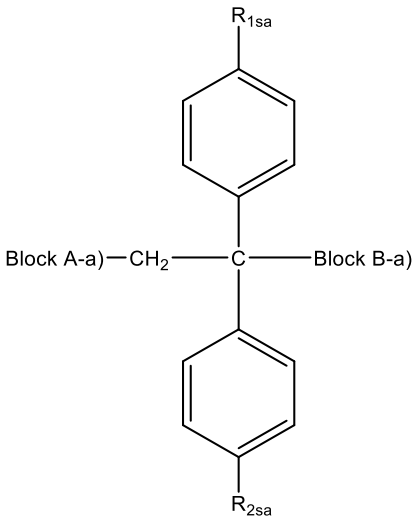
(Ia) (IIa)

[0042] Further, in another aspect of the composition, wherein said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), a-2), R_1, R_{1a}, R_2 and R_{2a} are H and R_3, R_{3a}, R_4, and R_{4a} are methyl.

[0043] In another aspect of the embodiments, where component a) are diblock copolymers a-1) and a-2), these 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. In one aspect of this embodiment R_{1s}, R_{2s}, R_{1sa}, and R_{2sa} are hydrogen.



(I-S)



(I-S-a).

[0044] In another aspect of the composition, said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1) and a blend of a-1) and a-2). In this embodiment the diblock copolymer component a-1) and/or the diblock copolymer component a-2) independently have polydispersities ranging from 1.00 to 1.03. In another aspect of this embodiment the diblock copolymer component a-1) has an M_n from 93,000 g/mole to 105,300 g/mole.

[0045] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1)and a blend of a-1) and a-2), for the diblock copolymer component a-1), 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 %.

[0046] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1) and a blend of a-1) and a-2), for the diblock copolymer component a-1), 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 %.

[0047] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1) and a blend of a-1) and a-2), for the diblock copolymer component a-1), the mole % values, for the repeat units of structure (I') are from 40 mole % to 80 mole % and for the repeat units of structure (II') from 20 mole % to 60 mole %.

[0048] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1) and a blend of a-1) and a-2), for the diblock copolymer component a-1), 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 %.

[0049] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-2) and a blend of a-1) and a-2), the diblock copolymer component a-2), these two different diblock copolymers independently have polydispersities ranging from 1.00 to 1.03.

[0050] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-2) and a blend of a-1) and a-2), the diblock copolymer component a-2) has an M_n from 40,800 g/mole to 61,200 g/mole.

[0051] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), 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 % for either a single block copolymer a-1) or a-2) or in a blend of a-1) and a-2).

[0052] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), 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).

[0053] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), component a) is a blend of a-1) and a-2).

[0054] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), said component a) is either a-1) or a-2).

[0055] In another aspect of the composition, component a) is from 0.5 wt. % to 2.0 wt. % of the total composition.

[0056] In another aspect of the composition, where said component a) is a diblock copolymer component selected from the group consisting of a diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), said component a) is from 0.5 wt. % to 2.0 wt. % of the total composition.

[0057] In another aspect of the composition, wherein component 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), the total mole % of styrenic repeat units of structures (I') and (Ia) is from 40 mole % to 60 mole % and whose total mole % of acrylic repeat units of structure (II) and (IIa) is from 40 mole % to 60 mole %.

[0058] In another aspect of the composition, wherein component 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) the total mole % of styrenic repeat units of structure (I') and (Ia) is from 65 mole % to 70 mole % and further wherein the total mole % of the acrylic repeat units of structures (II') and (IIa) is from 30 mole % to 35 mole %.

[0059] In another aspect of the composition, where said component a) is selected from the group consisting of triblock copolymer component 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 25 mole % to 40 mole %.

[0060] In another aspect of the composition, where said component a) is selected from the group consisting of triblock copolymer component 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 40 mole % to 60 mole % and further wherein the total mole % of the acrylic repeat units of structures (II') and (IIa) is from 40 mole % to 60 mole % and component b) additive, said low T_g oligomeric polystyrenic additive is said at least one styrenic homopolymer prepared by radical polymerization.

[0061] In any of the above-described embodiments, component b) is from 0.05 wt. % to 2.0 wt. % of the total composition including solvent. In another aspect of this embodiment the component b) additive, this component may be from 0.05 wt. % to 0.5 wt. % of the total weight of the composition including the spin casting organic solvent. In another aspect of this embodiment, it is from 0.08

wt. % to 0.4 wt. %. In another aspect of this embodiment, it is from 0.1 wt. % to 0.4 wt. %. In another aspect of this embodiment, it is from 0.15 wt. % to 0.4 wt. %. In yet another aspect of this embodiment it is from 0.2 wt. % to 0.3 wt. %.

3) Component c) Spin casting organic solvent

[0062] For component c), the spin casting organic solvent, suitable solvents for dissolving the above-described inventive compositions include a glycol ether derivative such as ethyl cellosolve, methyl cellosolve, propylene glycol monomethyl ether (PGME), diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, dipropylene glycol dimethyl ether, propylene glycol n-propyl ether, or diethylene glycol dimethyl ether; a glycol ether ester derivative such as ethyl cellosolve acetate, methyl cellosolve acetate, or propylene glycol monomethyl ether acetate (PGMEA); carboxylates such as ethyl acetate, n-butyl acetate and amyl acetate; carboxylates of di-basic acids such as diethyloxylate and diethylmalonate; dicarboxylates of glycols such as ethylene glycol diacetate and propylene glycol diacetate; and hydroxy carboxylates such as methyl lactate, ethyl lactate (EL), ethyl glycolate, and ethyl-3-hydroxy propionate; a ketone ester such as methyl pyruvate or ethyl pyruvate; an alkoxycarboxylic acid ester such as methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, ethyl 2-hydroxy-2-methylpropionate, or methylethoxypropionate; a ketone derivative such as methyl ethyl ketone, acetyl acetone, cyclopentanone, cyclohexanone or 2-heptanone; a ketone ether derivative such as diacetone alcohol methyl ether; a ketone alcohol derivative such as acetol or diacetone alcohol; a ketal or acetal like 1,3 dioxalane and diethoxypropane; lactones such as butyrolactone; an amide derivative such as dimethylacetamide or dimethylformamide, anisole, and mixtures thereof.

[0063] Additionally, the above described inventive composition may further comprise additives selected from the group consisting of: surfactants, inorganic-containing polymers; additives including small molecules, inorganic-containing molecules, surfactants, photoacid generators, thermal acid generators, quenchers, hardeners, cross-linkers, chain extenders, and the like; and combinations comprising at least one of the foregoing, wherein one or more of the additional components and/or additives co-assemble with the block copolymer to form the block copolymer assembly.

Processes

[0064] Another aspect of this invention is a process comprising steps:

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

ii) coating the composition of any one of the inventive compositions described herein 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 280°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.

[0065] Another aspect of this invention is 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, where component 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), whose total mole % of styrenic repeat units of structures (I') and (Ia) is from 40 mole % to 60 mole % and whose total mole % of acrylic repeat units of structure (II') and (IIa) is from 40 mole % to 60 mole %, 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 280°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.

[0066] Another aspect of this invention is 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, where component 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), 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 %, 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 280°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.

[0067] Another aspect of this invention is a process for forming a line and space array comprising steps:

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

iic) coating the composition, wherein component a) is selected from the group consisting of triblock copolymer component 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 25 mole % to 40 mole %, onto said neutral layer, to form a film,

iiic) baking said film, in an inert gas atmosphere, at a temperature selected from 240°C to 280°C, to form a self-assembled film, and

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

[0068] Another aspect of this invention is a process for forming a contact hole array comprising steps:

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

iid) coating the composition, wherein component a) is selected from the group consisting of triblock copolymer component 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 25 mole % to 40 mole %, onto said neutral layer, to form a film,

iiid) baking said film, in an inert gas atmosphere, at a temperature selected from 240°C to 280°C, to form a self-assembled film, and

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

EXAMPLES

Chemicals and Characterization

[0069] All chemicals unless otherwise indicated were purchased from Sigma Aldrich (3050 Spruce St., St. Louis, MO 63103). Chemicals used in anionic polymerization were purified as described in the literature (e.g., "Techniques in High-Vacuum Anionic Polymerization" by David Uhrig and Jimmy Mays and *Journal of Polymer Science: Part A: Polymer Chemistry*, Vol. 43, 6179–6222 (2005))

[0070] All synthetic experiments were carried out under N_2 atmosphere. Lithographic experiments were carried out as described in the text.

[0071] Lithographic Experiments were done using a TEL Clean ACT8 track. SEM pictures were taken with an applied Materials NanoSEM_3D Scanning electron microscope picture are shown at either 2 FOV magnification or 4 FOV magnification (Field of view (FOV) = 5 μm).

[0072] Etching experiments were done using standard isotropic oxygen etching conditions for self-assembled films block copolymer of methyl methacrylate and styrene.

[0073] Unless otherwise indicated Molecular weight measurements (a.k.a. M_w M_n polydispersity) were done by Gel permeation chromatography (PSS Inc. Germany) equipped with 100Å, 500 Å, 10^3 Å, 10^5 Å and 10^6 Å μ-ultrastyragel columns using THF solvent as an eluent. Polystyrene polymer standards were used for calibration. In these measurements the term "K," is synonymous with 1000 g/mole or 1000 Daltons.

[0074] DSC measurement of glass transition temperature were done using a TA instrument DSC Q1000 under nitrogen with a heating rate of 10°C/min. The glass transition temperature (T_g) was measured in first heating scan from 0 to 120°C. The midpoint of endothermic transition was considered.

[0075] TGA analysis reported herein were done using a TA instrument TGA 550 under nitrogen with a heat rate of 10°C/min. The temperatures at which weight losses at 1% and 5% were recorded.

[0076] ^1H NMR spectra were recorded using Bruker Advanced III 400 MHz spectrometer in CD_2Cl_2.

Synthesis of Neutral layers and Block Copolymers

Synthesis Example 1: Synthesis of P(S-co-VBCB-co-MMA)-Bz-OH Neutral Layer Material

[0077] The synthesis of the Azo initiator was described in US9574104B1 and was used in this polymerization. In a 2L 4-neck round bottomed flask equipped with a stir bar, a reflux condenser, a temperature controller and a nitrogen sparging tube, styrene (143.8 g, 1.38 mole), methyl methacrylate (184.9 g, 1.84 mole), 4-vinylbenzocyclobutene (180.0 g, 1.38 mole), and 2-butanone (620 g) were added. The reaction mixture was stirred while nitrogen was sparged in for 20 min. The mixture was heated in a heating mantle with the temperature controller set to 80°C. At 80°C, a solution of Azo-initiator (3.05 g, 5.07 mmol) in 2-butanone (12.2 g) was added over 1 minute. The mixture was heated at 80°C for 20 hours. An additional solution of Azo-initiator (1.22 g) in 2-butanone (4.88 g) was added over 1 minute. The heating of the mixture was continued at 80°C for 24 hours. The mixture was cooled, diluted with 2-butanone (900 g), then slowly precipitated in IPA (15 L). The precipitate was collected by vacuum filtration and oven dried. The residue was re-dissolved in THF (15% solids) and precipitated in MeOH (15 L). The precipitate was collected by vacuum filtration and oven dried. The solid was redissolved in 2-butanone (1900 g), filtered through a 0.2µm nylon filter and slowly precipitated into IPA (15 L). The precipitate was collected by vacuum filtration and oven dried. The polymer is an off-white solid, 290 g (57.0 %). GPC: 38,842 g/mol M_n, 90,053 g/mol M_w, 2.30 PDI.

Synthesis Example 2: Synthesis of P(S-b-MMA) (78K-b-39K)

[0078] Styrene and methyl methacrylate monomers were distilled in the presence of dehydrating agents into calibrated ampules and stored under N_2. Liquids were transferred into the reactor either via ampule or using stainless steel cannula under N_2. Into a dry 1 L round bottom reactor equipped with side arms for connecting ampules, magnetic stir bar, nitrogen/vacuum three-way septum adapter, was added 700 mL dry tetrahydrofuran. The temperature of the reactor was reduced to -78°C using dry ice-acetone bath. Then, after titrating the impurities, 0.2 mL (1.4 M solution) of *sec*-butyllithium was added into the reactor. Then 20 g (0.192 moles) of styrene was added from its ampule into the reactor under fast stirring. The reaction solution turned into yellow-orange and the reaction was stirred over 30 minutes. Subsequently, 0.06 g (0.0003 moles) of 1,1'-diphenylethylene (DPE) in 2.5 mL of dry toluene was added via ampule into the reactor. The orange color of the reaction mixture turned into dark brick-red indicating conversion of styryllithium active centers to delocalized DPE adduct carbanion. After 2 min of stirring, a small

amount (2 mL) of the reaction mixture was withdrawn for PS block molecular weight analysis. Then methyl methacrylate (9.98 g, 0.0998 moles) was added via ampule. The reaction was terminated after 30 min with 1 mL of degassed methanol. The block copolymer was recovered by precipitation in excess isopropanol (5 times of the polymer solution) containing 10 % water, filtered, and dried at 55°C for 12 h under vacuum giving 28 g of P(S-b-MMA) (94 % yield) consisting of 66 mol. % of polystyrene block and 34 mol. % of polymethylmethacrylate block.

Gel permeation chromatography equipped with 100Å, 500 Å, 10^3 Å, 10^5 Å and 10^6 Å μ-ultrastyragel columns showed that the 1st P(SDPE) block had M_n (GPC) = 64,622 g/mol and M_w/M_n = 1.02 with respect to PS calibration standards. The diblock copolymer molecular weight obtained from GPC is $M_{n,PS\text{-}b\text{-}PMMA}$ = 107,150 g/mol and M_w/M_n = 1.01.

Synthesis Example 3: Synthesis of P(S-b-MMA) (34K-b-17K)

[0079] PS-PMMA (34-17K) was synthesized using the same procedure described in example 2. To achieve the target M_n of PS block and PMMA block, 0.42 mL of 1.4 M solution of *sec*-butyllithium was added while keeping the quantity of styrene and MMA same as in example 2. Gel permeation chromatography equipped with 100Å, 500 Å, 10^3 Å, 10^5 Å and 10^6 Å μ-ultrastyragel columns showed that the 1st P(SDPE) block had M_n (GPC) = 34,872 g/mol and M_w/M_n = 1.03 with respect to PS calibration standards. The diblock copolymer molecular weight obtained from GPC is $M_{n,PS\text{-}b\text{-}PMMA}$ = 49,240 g/mol and M_w/M_n = 1.02. ^{1}H NMR showed 66.1 mol. % of polystyrene block and 33.9 mol. % of polymethylmethacrylate block.

Synthesis Example 4 Synthesis of P(S-b-MMA) (45k-b-51k)

[0080] P(S-b-MMA) (45K-b-51K) was synthesized using the same procedure as described in example 2. To achieve target M_n and compositions of PS and PMMA block, the amount of initiator and monomer quantities were changed. Briefly, 20 g (0.192 moles) of styrene was polymerized with 0.32 mL (1.4M solution) of *sec*-butyllithium. Then 0.095 g (0.0005 moles) of 1,1'-diphenylethylene (DPE) in 2.5 ml of dry toluene was added via ampule into the reactor. The orange color of the reaction mixture turned into dark brick-red indicating conversion of styryllithium active centers to delocalized DPE adduct carbanion. After 2 min of stirring, a small amount (2 mL) of the reaction mixture was withdrawn for PS block molecular weight analysis. Then methyl methacrylate (22.85 g, 0.23 moles) was added via ampule. The reaction was terminated after 30 min with 1 mL of degassed methanol. The block copolymer was recovered by precipitation in excess isopropanol (5 times of the polymer solution) containing 10 % water, filtered, and dried at 55°C for 12 h under

vacuum giving 40 g of P(S-b-MMA) (94 % yield) consisting of 46.9 mol. % of polystyrene block and 53.1 mol. % of polymethylmethacrylate block.

Gel permeation chromatography equipped with 100Å, 500 Å, 10^3 Å, 10^5 Å and 10^6 Å μ-ultrastyragel columns showed that the 1st P(SDPE) block had M_n (GPC) = 45,048 g/mol and M_w/M_n = 1.04 with respect to PS calibration standards. The diblock copolymer molecular weight obtained from GPC is $M_{n,PS\text{-}b\text{-}PMMA}$ = 88,348 g/mol and M_w/M_n = 1.02.

Synthesis of Inventive and Comparative h-PS Oligomeric Additives

Synthesis Example 5: Synthesis of h-PS Additive 1

[0081] Styrene (59.1 g, 568 mmol), 1-dodecanethiol (4.15 g, 20.5 mmol), AIBN (3.37 g, 20.5 mmol) and 2-butanone (62.5 g) were added into a flask and sparged with nitrogen for 30 minutes. The mixture was heated in an 80°C oil bath for 16 hours. The mixture was cooled to room temperature, diluted with acetone and precipitated in methanol. The polymer was collected, re-dissolved in ethyl acetate as a 15% solids solution, washed thrice with DI water and precipitated in isopropanol. The polymer was collected and dried in a vacuum overnight at 50°C. 36.7 g (60 %) white powder, GPC: 3,436 g/mol Mn, 5,455 g/mole M_w, 1.59 PDI

Synthesis Example 6: Synthesis of h-PS Additive 2

[0082] Styrene (381.3 g, 3.66 mol), 1-dodecanethiol (23.03 g, 114 mmol), AIBN (18.7 g, 114 mmol) and 2-butanone (400 g) were added into a flask and sparged with nitrogen for 30 minutes. The mixture was heated in an 80°C oil bath for 16 hours. The mixture was cooled to room temperature, diluted with acetone and precipitated in methanol. The polymer was collected, re-dissolved in ethyl acetate as a 15% solids solution, washed thrice with DI water and precipitated in isopropanol. The polymer was collected and dried in a vacuum overnight at 50°C. 263 g (67 %) white powder, GPC: 4,267 g/mol M_n, 6,814 g/mole M_w, 1.60 PDI

Synthesis Example 7: Synthesis of h-PS Additive 3

[0083] Styrene (47.9 g, 459 mmol), 1-dodecanethiol (2.65 g, 13 mmol), AIBN (2.15 g, 13 mmol) and 2-butanone (50 g) were added into a flask and sparged with nitrogen for 30 minutes. The mixture was heated in an 80°C oil bath for 16 hours. The mixture was cooled to room temperature, diluted with acetone and precipitated in methanol. The polymer was collected, re-dissolved in ethyl acetate as a 15% solids solution, washed thrice with DI water and precipitated in isopropanol. The polymer was collected and dried in a vacuum overnight at 50°C. 33.9 g (69 %) white powder, GPC: 4,729 g/mol M_n, 7,698g/mole M_w, 1.63 PDI

Synthesis Example 8: Synthesis of h-PS Comparative Additive 4

[0084] Styrene (59.8 g, 574 mmol), 1-dodecanethiol (3.32 g, 16 mmol), AIBN (2.69 g, 16 mmol) and 2-butanone (62.5 g) were added into a flask and sparged with nitrogen for 30 minutes. The mixture was heated in an 80°C oil bath for 16 hours. The mixture was cooled to room temperature, diluted with acetone and precipitated in methanol. The polymer was collected by filtration, re-dissolved in ethyl acetate as a 15% solids solution, washed thrice with DI water and precipitated in isopropanol. The polymer was collected by filtration and dried in a vacuum overnight at 50°C. 44 g (72 %) white powder, GPC: 9,301 g/mol M_n, 15,538 g/mole M_w, 1.67 PDI

Synthesis Example 9: Synthesis of h-PS Additive 5

Styrene (53.2 g, 511 mmol), 1-dodecanethiol (11.48 g, 6 mmol), AIBN (9.32 g, 29 mmol) and 2-butanone (62.5 g) were added into a flask and sparged with nitrogen for 30 minutes. The mixture was heated in an 80°C oil bath for 16 hours. The mixture was cooled to room temperature, diluted with acetone and precipitated in methanol. The polymer was collected, re-dissolved in ethyl acetate as a 15% solids solution, washed thrice with DI water and precipitated in isopropanol. The polymer was collected and dried in a vacuum overnight at 50°C. 16.2 g (28 %) white powder, GPC: 1,952 g/mol M_n, 2,898 g/mole M_w, 1.48 PDI

Synthesis Example 10: Synthesis of h-PS Additive 6

Styrene (55.4 g, 532 mmol), 1-dodecanethiol (8.73 g, 43 mmol), AIBN (7.08 g, 43 mmol) and 2-butanone (62.5 g) were added into a flask and sparged with nitrogen for 30 minutes. The mixture was heated in an 80°C oil bath for 16 hours. The mixture was cooled to room temperature, diluted with acetone and precipitated in methanol. The polymer was collected by filtration, re-dissolved in ethyl acetate as a 15% solids solution, washed thrice with DI water and precipitated in isopropanol. The polymer was collected by filtration and dried in a vacuum overnight at 50°C. 26.7 g (45 %) white powder, GPC: 2,425 g/mol M_n, 3,386 g/mole M_w, 1.40 PDI

Synthesis Example 11: Synthesis of h-PS Additive 7

[0085] Styrene (57.7 g, 554 mmol), 1-dodecanethiol (5.90 g, 29 mmol), AIBN (4.79 g, 29 mmol) and 2-butanone (62.5 g) were added into a flask and sparged with nitrogen for 30 minutes. The mixture was heated in an 80°C oil bath for 16 hours. The mixture was cooled to room temperature, diluted with acetone and precipitated in methanol. The polymer was collected by filtration, re-dissolved in ethyl acetate as a 15% solids solution, washed thrice with DI water and precipitated in

isopropanol. The polymer was collected by filtration and dried in a vacuum overnight at 50°C. 39.1 g (65 %) white powder, GPC: 2,323 g/mol M_n, 3,934 g/mole M_w, 1.69 PDI.

Synthesis Example 12: Synthesis of h-PS Comparative Additive 1

[0086] Styrene (27.3 g, 262 mmol) and cyclohexane (181 g) were added into a Schlenk flask and degassed thrice using freeze-thaw technique. The mixture was titrated with sec-BuLi until a yellow color persists. Sec-BuLi (2.79 mL, 1.4M in cyclohexane, 4 mmol) was added to initiate the polymerization and the mixture stirred at room temperature for 2 hours. The mixture was diluted with acetone and precipitated in methanol. The polymer was collected by filtration, re-dissolved in ethyl acetate as a 15% solids solution, washed thrice with DI water and precipitated in isopropanol. The polymer was collected and dried in a vacuum overnight at 50°C. 19 g (70 %) white powder, GPC: 5475 g/mol M_n, 5937 g/mole M_w, 1.08 PDI

Synthesis Example 13: Synthesis of h-PS Comparative Additive 2

[0087] Styrene (31.2 g, 300 mmol) and cyclohexane (207 g) were added into a Schlenk flask and degassed thrice using freeze-thaw technique. The mixture was titrated with sec-BuLi until a yellow color persists. Sec-BuLi (2.79 mL, 1.4M in cyclohexane, 4 mmol) was added to initiate the polymerization and the mixture stirred at room temperature for 2 hours. The mixture was diluted with acetone and precipitated in methanol. The polymer was collected by filtration, re-dissolved in ethyl acetate as a 15% solids solution, washed thrice with DI water and precipitated in isopropanol. The polymer was collected by filtration, and dried in a vacuum overnight at 50°C. 24 g (76 %) white powder, GPC: 6700 g/mol M_n, 7300 g/mole M_w, 1.09 PDI

[0088] Described as follows are experiments which were done on annealable block copolymer formulations which by adjusting the wt. % amount of specific oligomeric styrenic additives to affect observed morphologies and LCDU and Twist dependencies (which describe the quality of contact holes and multiplicity of the contact holes for perfect alignment over a pre-pattern) which were observed. It was surprisingly found that higher wt. % content of oligomeric polystyrene additives imparted improved performance but only with certain types of these oligomers. Specifically in investigating homo oligomeric polystyrene which was 100 mole % homopolymerized styrene (h-PS), it was unexpectedly found that such material prepared by controlled synthetic method, such as anionic polymerization showed very bad morphologies to block copolymer in which these were used during DSA processing; whereas h-PS oligomeric additive prepared by radical polymerization withing the claimed M_w range showed good morphology during the same DSA processing of block

copolymers and further there was strong correlation with the molecular weight of these additives and their effectiveness in imparting good morphology to block copolymer formulation during self-assembly annealing. Indeed, surprisingly, h-PS which was outside the claimed M_w range also showed bad morphologies when blended with block copolymers during self-assembly. Although not bound by theory, it is believed that this phenomenon indicated that in BCP formulations the kinetics of annealing during self-assembly was unexpectedly strongly influenced by some complex mobility factors imparted by oligomer additives which have both smaller sized and are also possess chemically random oligomeric structures which contributed to better kinetics of these BCP formulation.

Synthesis and properties of h-PS oligomers

[0089] Synthetic Examples 5 to 13 show how the inventive and comparative h-PS oligomeric materials were synthesized, and Table 1 and Table 2 summarize the properties of these materials and also give a summary of the performance of these when used as additives for a block copolymer during annealing on a neutral layer coated substrate.

[0090] The inventive h-PS oligomers of Tables 1 and the comparative formulations of Table 2 were prepared which contained 20 wt. % of total solids of these h-PS oligomers which contained 80 wt. % of total solids of the block copolymer (BCP) **Synthesis Example 2: Synthesis of P(S-b-MMA) (78K-b-39K)** diluted to 1.2 wt. % solids in the spin casting solvent PGMEA. The solutions were filtered using 0.2 micron PTFE filters.

[0091] All additives shown in the following processing results and Tables 1 and 2 were blended with the block copolymer at a 20 wt.% where the block copolymer makes up 80 wt. % of the total of the additive and the block polymer. Specifically, this was done employing 0.8 grams of PS-b-PMMA, 0.2 grams of the additive to be tested and 82.3 grams of PGMEA.

Processing conditions

[0092] Example 1: Synthesis of P(S-co-VBCB-co-MMA)-Bz-OH Neutral Layer Material was spin coated on a Si wafer from a 1.2 wt. % solution in PGMEA and baked at 250 °C for 2 min to form a 7 nm thick crosslinked neutral layer. Then formulations containing h-PS oligomeric additives 1 to 3 and 5 to 7 and comparative additives 1, 2 and 4 were individually spin coated on this crosslinked neutral layer to form 47 nm thick coatings of the block copolymer formulation containing h-PS oligomeric additives 1 to 3 and 5 to 7 and comparative additives 1, 2 and 4. These coatings were

baked at 110ºC, for 1 min, and then annealed at 260°C for 15 min under N_2. This annealed coating was then etched using a O_2 plasma etch to give the contact holes.

[0093] Table 1 shows a summary of the properties of different types of inventive h-PS oligomers prepared by radical polymerization which were investigated and their annealing performance. As shown in Table 1 and FIG. 1, when blended with a block copolymer these materials showed good performance with no collapse of the self-assemble cylindrical morphology of the block copolymer during the quick annealing process enabled by the inventive h-PS oligomers when a composition is coated and annealed on a neutral layer.

[0094] Table 2 shows a summary of the properties of different types of comparative h-PS oligomers prepared by either radical or anionic polymerization which were investigative. These materials showed poor performance with collapse of the self-assembled cylindrical morphology during the quick annealing process when coated and annealed on a neutral layer coated substrate.

[0095] Table 1 Additive characterization and thermal property

h-PS Inventive Additives	Polymerization method	M_w	M_n	PDI	TGA, °C 1 wt. % loss	TGA, °C 5 wt. % loss	DSC (Tg, °C)	Annealing Performance with BCP
Additive 1	Radical by AIBN initiator EX. 5	5.5k	3.4k	1.59	281.8	314.2	84.4	Good self-assembly no collapse
Additive 2	Radical by AIBN initiator EX 6	6.8k	3.8k	1.76	283.7	318.4	82.3	Good self-assembly no collapse
Additive 3	Radical by AIBN initiator EX 7	7.7k	4.7k	1.63	280.1	312.0	89.7	No Data
Additive 5	Radical by AIBN initiator EX. 9	2.9k	2.0k	1.48	248.7	279.5	79.6	Good self-assembly no collapse
Additive 6	Radical by	3.4k	2.4k	1.40	255.9	289.5	78.5	Good self-

	AIBN initiator EX. 10							assembly no collapse
Additive 7	Radical by AIBN initiator EX. 11	3.9k	2.3k	1.69	275.5	311.3	69.3	Good self-assembly no collapse

[0096] Table 2. Additive characterization and thermal property of comparative examples

h-PS Comparative Additives	Polymerization method	M_w	M_n	PDI	TGA °C 1 wt.% loss	TGA, °C 5 wt. % loss	DSC Tg, °C	Annealing Performance with BCP (Neutrality Evaluation Collapse)
Comparative Additive 4	Radical by AIBN initiator EX 8	15.5k	9.3k	1.67	271.4	315.3	99.0	Poor Self Assembly Collapsed Cylinders Morphology
Comparative Additive 1	Anionic polymerization EX 12	5.9k	5.5k	1.10	346.8	374.2	94.0	Poor Self Assembly Collapsed Cylinders Morphology
Comparative Additive 2	Anionic polymerization EX 13	7.3k	6.7k	1.09	357.8	380.9	95.5	Poor Self Assembly Collapsed Cylinders Morphology

[0097] FIG. 1 shows SEM pictures with a field of view (FOV) of either 2, 4 or 50 for each of the BCP formulations containing the inventive h-PS oligomers prepared by radical polymerization

(Table 1) after these formulations were coated and annealed on a neutral layer coated substrate and plasma etched with an O_2 plasma, where these formulations gave good self-assembly of contact holes which showed defect-free perpendicular contact holes morphology.

[0098] FIG. 2 shows SEM pictures with a field of view (FOV) of either 2, or 4 for each of the BCP formulations containing the comparative h-PS oligomers prepared by either radical polymerization or anionic polymerization (Table 2) after these formulations were coated and annealed on a neutral layer coated substrate and plasma etched with an O_2 plasma, which shows that surprisingly, when these comparative oligomers which deviated either in the claimed M_w range for radically polymerized h-PS (Comparative additive 4) or deviated from the claimed range of polydispersity (Comparative additive 1 and 2), poor self-assembly of contact holes occurred with defects, which were observed as dark spots that are indicative of defects caused by the collapsed perpendicular cylindrical morphology as a result of reduced kinetics for self-assembly. Table 1 shows the thermogravimetric temperatures of the anionic polymerized Comparative Additives 1 and 2 are much higher than their respective radically polymerized Additives 1 and 3, respectively. BCP formulations with Additives 2 and 3, having similar M_w, are both expected to show defect-free perpendicular contact holes morphology as was the case for the formulation with Additive 2 (Table 1).

[0099] Although the disclosed and claimed subject matter has been described and illustrated with a certain degree of particularity, it is understood that the disclosure has been made only by way of example, and that numerous changes in the conditions and order of steps can be resorted to by those skilled in the art without departing from the spirit and scope of the disclosed and claimed subject matter.

CLAIMS

1. A composition comprising components a), b) and c), preferably consisting of the components a), b) and c), wherein

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

b) is at least one low T_g oligomeric polystyrenic additive in which each additive individually has a T_g which ranges from 68.0°C to 90.0°C and has an M_w which ranges from 2,500 g/mole to 8,000 g/mole, has a polydispersity from 1.20 to 1.80, and further wherein said styrenic additive is selected from the group consisting of

at least one styrenic homopolymer prepared by radical polymerization,

at least one styrenic random copolymer prepared by radical polymerization, whose repeat units only consist of styrenic repeat units and where at least two styrenic repeat units are present,

a mixture of at least one said styrenic homopolymer and at least one said styrenic random copolymer,

c) is an organic spin casting solvent.

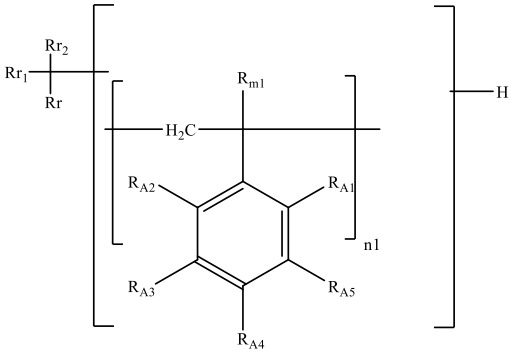
2. The composition of claim 1, wherein in said component b) each additive individually has a T_g which ranges from 69.0°C to 89.7°C, and/or

wherein each additive individually has a polydispersity which is from 1.30 to 1.80, and/or in which each additive individually has an M_w which ranges from 2,900 g/mole to 7,700 g/mole.

3. The composition of claim 1 or 2, wherein said component b) is either at least one said styrenic homopolymer or at least one said styrenic random copolymer or is a mixture of at least one said styrenic homopolymer and at least one said styrenic random copolymer.

4. The composition of any one of claims 1 to 3, wherein said component b) is at least one said styrenic homopolymer, and further it has structure (A), whose repeat units consist of ones having structure (I), where n1 is the number of repeating units and designates that this is a repeat unit, R_{A1}, R_{A2}, R_{A3}, R_{A4}, R_{A5}, are individually selected from H or a C-1 to C-8 alkyl, R_{m1} is H or methyl, and said styrenic homopolymer has two end groups as shown in structure (A) one of which is H and the other is a methyl moiety substituted with Rr, Rr_1 and Rr_2, wherein Rr_1 is a C-1 to C-8 alkyl, Rr_2 is

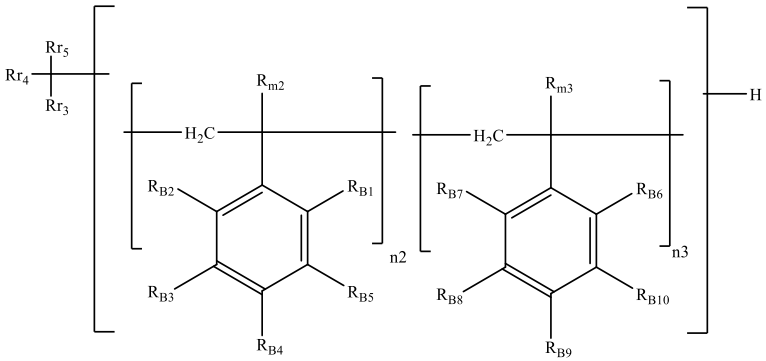
selected from a C-1 to C-8 alkyl, Rr is a cyano moiety (-CN) or a carbonylalkyl moiety (-C(=O)-Ri), wherein Ri is a C-1 to C-8 alkyl or an aryl moiety;



(I) (A);

or wherein said component b) is at least one said styrenic random copolymer which has structure (B), wherein its repeat units consist of two different repeat units of structure (II') and (III), where, respectively, n2 and n3 are the number of these repeating units and designates that these are repeating units, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5}, R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} are independently selected from H or a C-1 to C-8 alkyl, R_{m2}, R_{m3} are independently selected from H or methyl, and

said styrenic random copolymer has two end groups, as shown in structure (B), one of which is H and the other is a methyl moiety substituted with Rr_3, Rr_4 and Rr_5, wherein Rr_4, is a C-1 to C-8 alkyl, Rr_5 is selected from a C-1 to C-8 alkyl, Rr_3 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;



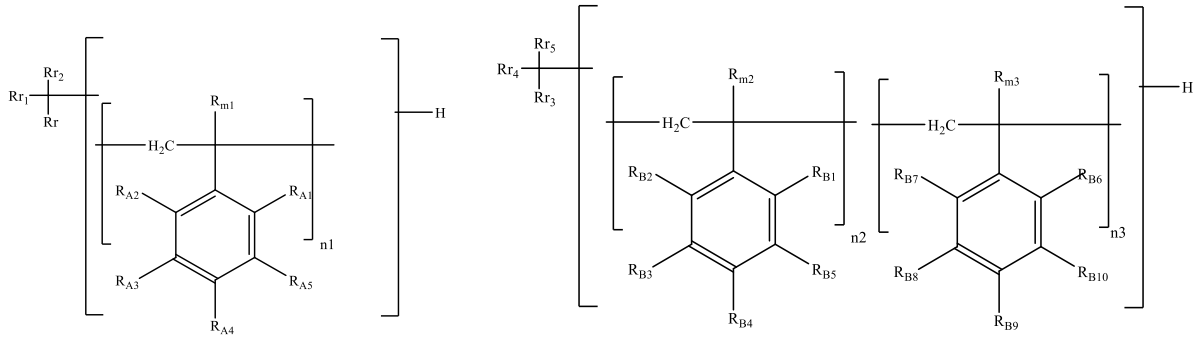
(II) (III) (B);

or wherein said component b) is a mixture of at least one said styrenic homopolymer and at least one said styrenic random copolymer, wherein,

said styrenic homopolymer has structure (A), whose repeat units consist of ones having structure (I), where n1 is the number of repeating units and designates that this is a repeat unit, R_{A1}, R_{A2}, R_{A3},

R_{A4}, R_{A5}, are individually selected from H or a C-1 to C-8 alkyl, R_{m1}, is H or methyl, and said styrenic homopolymer has two end groups as shown in structure (A) one of which is H and the other is a methyl moiety substituted with Rr, Rr_1 and Rr_2, wherein Rr_1, is a C-1 to C-8 alkyl, Rr_2 is selected from a C-1 to C-8 alkyl, 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

further, said styrenic random copolymer has structure (B), wherein its repeat units consist of two repeat units of structure (II') and (III), where, respectively, n2 and n3 are the number of these repeating units designates that these are repeating units, R_{B1}, R_{B2}, R_{B3}, R_{B4}, R_{B5}, R_{B6}, R_{B7}, R_{B8}, R_{B9}, and R_{B10} are independently selected from H or a C-1 to C-8 alkyl, R_{m2}, R_{m3} are independently selected from H or methyl, and said styrenic random copolymer has two end groups as shown in structure (B), one of which is H and the other is a methyl moiety substituted with Rr_2, Rr_3 and Rr_4, wherein Rr_4, is a C-1 to C-8 alkyl, Rr_5 is selected from a C-1 to C-8 alkyl, Rr_3 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;



(I) (A) (II) (III) (B).

5. The composition of any one of claims 1 to 4, 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.

6. The composition of any one of claims 1 to 5, wherein said component a) is an ABA triblock copolymer component selected from the group consisting of ABA triblock copolymer a-1t), a ABA triblock copolymer a-2t) and a blend of two different of ABA triblock copolymer a-1t) and an 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

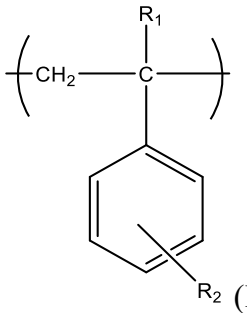
having structure (II'), wherein R_1 and R_3 are independently selected from H and C-1 to C-4 alkyl, R_2 is H or a C-1 to C-8 alkyl, R_4 is a C-1 to C-8 alkyl, and preferably R_1 and R_2 are H, and R_3 and R_4 are methyl,

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

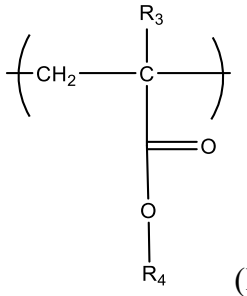
wherein the individual values of the mole % for the repeat units of structures (I') and (II') are selected from their respective ranges to add up to 100 mole % of the total moles of repeat units of structures (I') and (II'), and

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')



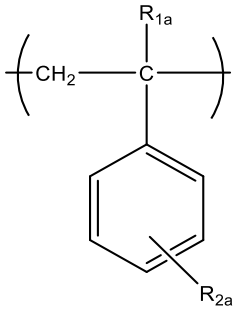
(II');

a-2t) is an ABA triblock copolymer, comprising a middle B) block segment of repeat units having styrenic structure (Ia), and two end block A) 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, and preferably R_{1a} and R_{2a} are H, and R_{3a} and R_{4a} are methyl,

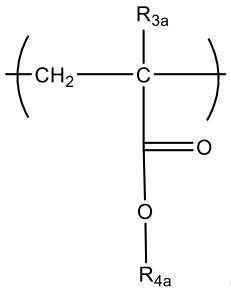
the mole % values, based on the total moles of repeat units of structures (Ia) and (IIa), are for the styrenic repeat units of structure (Ia) from 40 mole % to 80 mole % and for the acrylic repeat units of structure (IIa) from 20 mole % to 60 mole %, and wherein the individual values of the mole % for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

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

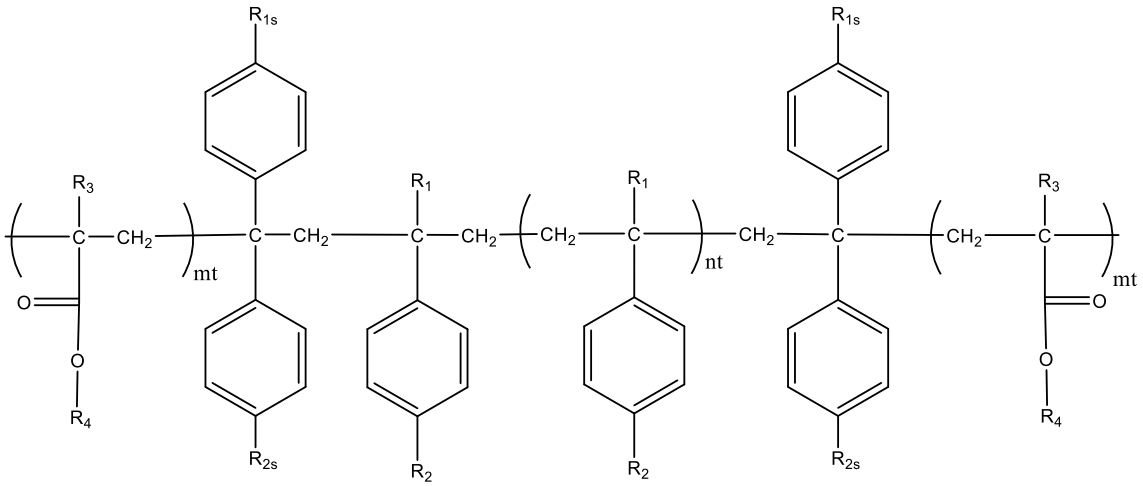


(Ia)

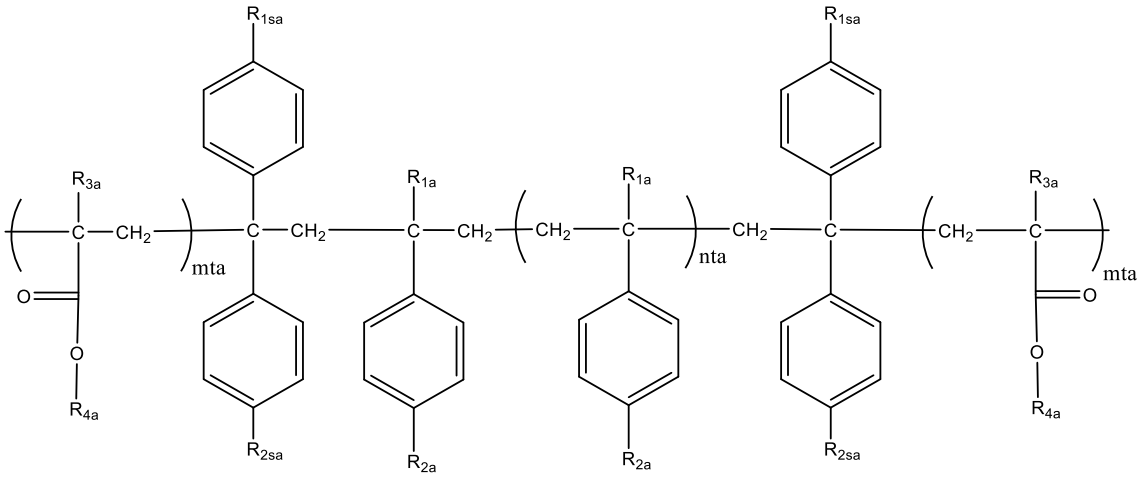


(IIa).

or 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, and R_1, R_{1a}, R_2, R_{2a}, R_3, R_{3a}, R_4 and R_{4a} are defined as in claim 6, and preferably R_1, R_{1a}, R_2, R_{2a} and R_{1s}, R_{1sa} R_{2s} and R_{2sa} are H, and R_3, R_{3a}, R_4, and R_{4a} are methyl,



(ABA-1)



(ABA-2).

7. The composition of any one of claims 1 to 5, wherein

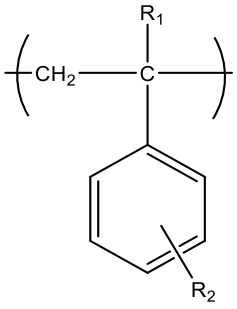
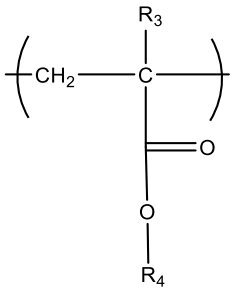
a) is a diblock copolymer component selected from the group consisting of diblock copolymer a-1), diblock copolymer a-2) and a blend of a-1) and a-2), wherein

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 preferably R_1 and R_2 are H, and R_3 and R_4 are methyl, and

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

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, preferably from 1.00 to 1.03, and has an M_n from 50,000 g/mole to 150,000 g/mole, preferably from 93,000 g/mole to 105,300 g/mole,

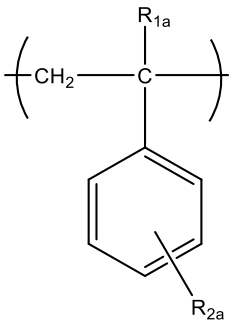
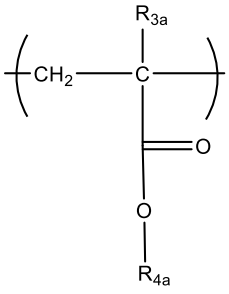

(I’)

(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, R_{4a} is a C-1 to C-8 alkyl, and preferably R1a and R2a are H, and R3a and R4a are methyl, and,

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

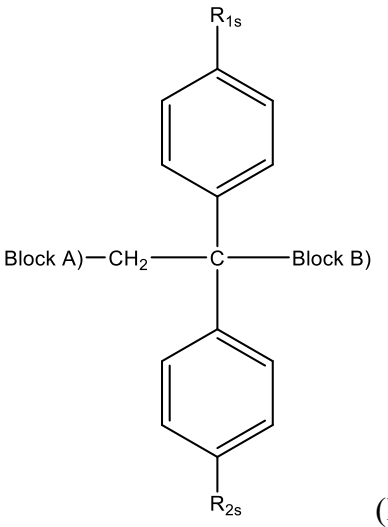
wherein the individual values of the mole % for the repeat units of structures (Ia) and (IIa) are selected from their respective ranges to add up to 100 mole % of the total moles of repeat units of structures (Ia) and (IIa), and

said diblock copolymer a-2) has a polydispersity from 1.0 to 1.1, preferably from 1.00 to 1.03, has an M_n from 30,000 g/mole to 90,000 g/mole, preferably from 40,800 g/mole to 61,200 g/mole,

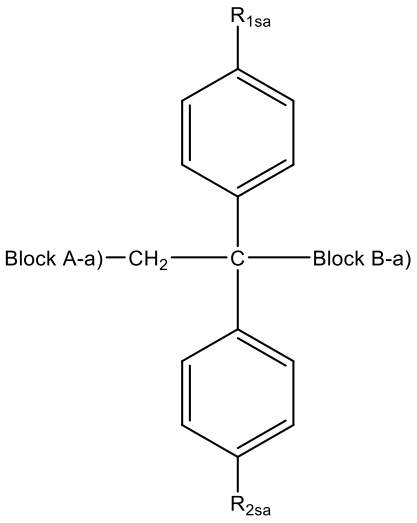

(Ia)

(IIa).

8. The composition of claim 7, 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, and preferably R_{1s}, R_{2s}, R_{1sa}, and R_{2sa} are hydrogen, and preferably component a-1) has a polydispersity from 1.00 to 1.03, and preferably component a-1) has an M_n from 93,000 g/mole to 105,300 g/mole, and preferably component a-2) has a polydispersity from 1.00 to 1.03, and preferably component a-2) has an M_n from 40,800 g/mole to 61,200 g/mole,



(I-S)



(I-S-a).

9. The composition of claims 7 or 8, wherein for component a) the total mole % value 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 % 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 % value 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),
or wherein for component a) the total mole % for the repeat units of structures (I') and (Ia) is from 40 mole % to 80 mole %, preferably from 60 mole % to 75 mole %, and the total mole % for the repeat units of structure (II') and (IIa) is from 20 mole % to 60 mole %, preferably 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 7 to 9, wherein component a) is either a-1) or a-2) or wherein component a) is a blend of a-1) and a-2).

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

12. The composition of claim 6, wherein component a) is selected from the group consisting of triblock copolymer component 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 40 mole % to 80 mole % and whose total mole % of acrylic repeat units of structure (II') and (IIa) is from 20 mole % to 60 mole %, and preferably the total mole % of styrenic repeat units of structure (I') and (Ia) is from 60 mole % to 75 mole % and the total mole % of the acrylic repeat units of structures (II') and (IIa) is from 25 mole % to 40 mole % and component b), said low T_g oligomeric polystyrenic additive is said at least one styrenic homopolymer prepared by radical polymerization.

13. 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 12 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 280°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.

14. The process of claim 13, wherein the process is a process for forming a line and space array and the composition in step ii) is a composition of any one of claims 7, 8, 10 or 11,
wherein component 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), whose total mole % of styrenic repeat units of structures (I') and (Ia) is from 40 mole % to 80 mole % and whose total mole % of acrylic repeat units of structure (II') and (IIa) is from 20 mole % to 60 mole %,
or wherein the process is a process for forming a contact hole array and the composition in step ii) is a composition of claim 7, 8, 10 or 11, wherein component 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), 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 %,
or wherein the process is a process for forming a line and space array and the composition in step ii) is a composition of claim 12.

15. The use of the composition of any one of claims 1 to 12 in a self-assembly process followed by pattern transfer of the self-assembled pattern into a substrate.