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(54) **Title**: TRANSPARENT LAYER FORMING POLYMER

(57) **Abstract**: Embodiments in accordance with the present invention provide polymers for forming layers/films useful in the manufacture of a variety of types of optoelectronic displays. Such embodiments also provide compositions of such polymers for forming such layers/films where the formed layers/films have high transparency over the visible light spectrum.

Transparent Layer Forming Polymer

CROSS-REFERENCED TO RELATED APPLICATION

[0001] This application is entitled to and claims priority to the U.S. Provisional Patent having serial number 61/422763, filed December 14, 2010 and entitled "Transparent Layer Forming Polymer" Such Provisional Patent is incorporated herein by reference in its entirety.

TECHNICAL FIELD

[0002] Embodiments disclosed hereinbelow relate generally to polymers for forming layers/films useful in the manufacture of a variety of types of displays and more specifically norbornene-type polymers and compositions thereof for forming such layers/films having high transparency over the visible light spectrum.

BACKGROUND

[0003] In the manufacture of liquid crystal displays, organic light emitting diode displays and other optoelectronic devices, there is a need for the forming of a number of different transparent organic and inorganic layers. For example, LCDs typically encompass color filter layers, polarizing layers, leveling layers, scratch preventative layers and the like. As the manufacturing processes for such displays continues to evolve, the materials that are used for such layers often must also evolve or change to meet more demanding requirements resulting from the aforementioned evolution. Therefore a need exists for transparent layers which can meet such evolved requirements.

DETAILED DESCRIPTION

[0004] Exemplary embodiments in accordance with the present disclosure will be described with reference to the Examples and Claims provided hereinafter. Various modifications, adaptations or variations of such exemplary embodiments described herein may become apparent to those skilled in the art as such are disclosed. It will be understood that all such modifications, adaptations or variations that rely upon the teachings of the present invention, and through which these teachings have advanced the art, are considered to be within the scope and spirit of the present invention.

[0005] As used herein, the articles "a," "an," and "the" include plural referents unless otherwise expressly and unequivocally limited to one referent.

[0006] Since all numbers, values and/or expressions referring to quantities of ingredients, reaction conditions, etc., used herein and in the claims appended hereto, are subject to the various uncertainties of measurement encountered in obtaining such values, unless otherwise indicated, all are to be understood as modified in all instances by the term "about."

[0007] As used herein, molecular weight values of polymers, such as weight average molecular weights (Mw) and number average molecular weights (Mn), are determined by gel permeation chromatography using polystyrene standards.

[0008] As used herein, and unless otherwise stated, where polymer glass transition temperature (Tg) values are provided, they were determined by differential scanning calorimetry in accordance with American Society for Testing and Materials (ASTM) method number D3418.

[0009] As used herein, and unless otherwise stated, where polymer decomposition temperatures (T_d) are provided, they will be understood to be the temperature, determined by thermogravimetric analysis at a heating rate of 10°C/minute under nitrogen, where a specific weight percent (wt%) of a polymer has determined to have decomposed (lost by vaporization). The terms T_{d1}, T_{d5}, T_{d50} and T_{d95} indicate the temperatures at which 1 wt%, 5 wt%, 50 wt% and 95 wt% of the polymer has decomposed.

[0010] Where a numerical range is disclosed herein such range is continuous, inclusive of both the minimum and maximum values of the range as well as every value between such minimum and maximum values. Still further, where a range refers to integers, every integer between the minimum and maximum values of such range is included. In addition, where multiple ranges are provided to describe a feature or characteristic, such ranges can be combined. That is to say that, unless otherwise indicated, all ranges disclosed herein are to be understood to encompass any and all subranges subsumed therein. For example, a stated range of from "1 to 10" should be considered to include any and all subranges between the minimum value of 1 and the maximum value of 10. Exemplary subranges of the range 1 to 10 include, but are not limited to, 1 to 6.1, 3.5 to 7.8, and 5.5 to 10.

[0011] As used herein, the phrases "transparent polymer", "transparent layer" or "transparent film" will be understood to mean a polymer, layer or film that is essentially transparent to radiation in the range of 400nm to 750nm (the visible light range). That is to say that such a transparent polymer or transparent layer will allow at least 95% transmission of visible light in the aforementioned range to pass therethrough. While transmission over the entire visible spectrum is mentioned herein, the actual measurement of % transmission is performed at 400nm as transmission of light at the low end of the visible spectrum is generally more problematic than higher wavelengths.

[0012] As used herein, "hydrocarbyl" refers to a hydrocarbon a group that contains only carbon and hydrogen, non-limiting examples being alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkynyl, aryl, aralkyl and alkaryl.

[0013] As used herein, the terms "alkyl" and "cycloalkyl" refer, respectively, to acyclic or cyclic saturated hydrocarbyls having an appropriate carbon chain length from C_1 to C_{25}. Non-limiting examples of suitable alkyl groups include, but are not limited to, $-CH_3$, $-(CH_2)_3CH_3$, $-(CH_2)_4CH_3$, $-(CH_2)_5CH_3$, $-(CH_2)_9CH_3$, $-(CH_2)_{23}CH_3$, cyclopentyl, methylcyclopentyl, cyclohexyl and methylcyclohexyl.

[0014] As used herein the terms "alkenyl" and "cycloalkenyl" refer, respectively, to acyclic or cyclic saturated hydrocarbon groups having at least one carbon to carbon double bond and an appropriate carbon chain length of from C_2 to C_{25}. Non-limiting examples include, among others, vinyl groups and groups derived from propylene, butene, cyclopentene, cyclohexane and isopropylprenyl.

[0015] As used herein the term "aryl" refers to aromatic hydrocarbyls that include, without limitation, groups such as phenyl, biphenyl, benzyl and xylyl.

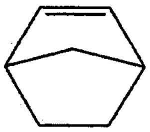
[0016] The terms "alkaryl" or "aralkyl" are used herein interchangeably and refer to an aromatic hydrocarbyl substituted with at least one alkyl, cycloalkyl, alkenyl or cycloalkenyl group, for example, groups derived from toluene, butylbenzene, cyclohexylbenzene and 1,2-dihydro-1,1'-biphenyl.

[0017] As used herein, "halohydrocarbyl" refers to any of the previously described hydrocarbyl groups where at least one hydrogen has been replaced by a halogen and "perhalocarbyl" refers to such a hydrocarbyl group where all hydrogens have been replaced by a halogen, e.g. pentafluorobenzene, respectively.

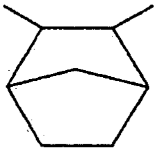
[0018] As used herein the term "heterohydrocarbyl" refers to any of the previously described hydrocarbyl groups where at least one of the carbon atoms is replaced with N, O, S, Si or P. Non-limiting examples include heterocyclic aromatic groups such as pyrrolyl, furanyl, and pyridenyl as well as non-aromatic groups such as epoxies, alcohols, ethers, thioethers and silyl ethers. .

[0019] Additionally, it will be understood that the term "hydrocarbyl" is a generic term inclusive of the more specific terms halohydrocarbyl, perhalohydrocarbyl and heterohydrocarbyl. Further, it will be understood that any of such moieties can be further substituted and where appropriate, in terms of the number of carbon atoms, linear, branched or cyclic. Non-limiting examples of suitable substituent groups include, among others, hydroxyl groups, epoxy groups, benzyl groups, carboxylic acid and carboxylic acid ester groups, amides and imides. Still further, it will be understood that the term "hydrocarbylene" refers to a divalent radical formed by removing a hydrogen atom from any of the aforementioned hydrocarbyls.

[0020] The term "norbornene-type" is used herein to mean a monomer in accordance with Structure 1 shown below, or a polymeric material that was formed from at least one such norbornene-type monomer and therefore has at least one repeat unit in accordance with Structure 2, also shown below:



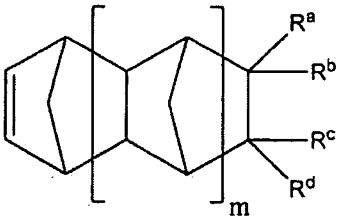
1



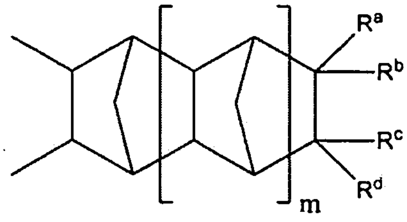
2

[0021] It will be understood that where various compounds are described as monomers and/or polymerizable monomers, that such compounds are structurally analogous to Structure 1, above. That is to say, such compounds have a polymerizable double bond as shown in 1 above. It will also be understood, that when such monomers are polymerized, they are incorporated into a polymer structure as "repeat units" or "repeating units" that are structurally analogous to Structure 2, above. That is to say that, the polymerization occurs across the double bond of Structure 1 as shown in Structure 2 and the resulting polymer is generally referred to as a vinyl addition polymer.

[0022] Further, the term norbornene-type monomer is used herein to mean, in addition to norbornene itself, any substituted norbornene(s), or substituted and unsubstituted higher cyclic derivatives thereof. Formulae A1 and A2, shown below, are representative of such norbornene-type monomers and the norbornene-type repeating units derived from such monomers, respectively:



A1



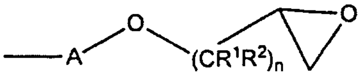
A2

[0023] where m is 0, 1 or 2 and each occurrence of R^a, R^b, R^c and R^d independently represents hydrogen, a hydrocarbyl or another substituent. It should be noted that in deriving a repeating unit represented by Formula A2 from a monomer represented by Formula A1, the substitution and nature of any of R^a, R^b, R^c and R^d is unmodified; thus it can be said that repeating units of polymer embodiments of the present disclosure are unmodified repeating units.

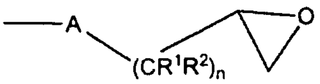
[0024] Embodiments in accordance with the present disclosure are directed to norbornene-type polymers, compositions that encompass such polymers and methods that utilize such polymer compositions to form a transparent polymer layer or film having a pencil hardness of 4H or higher, that retains at least 95% of its initial transparency at 400nm after exposure in air to a temperature of 280°C for 30 min; that exhibits a high degree of thermal stability in that the percent weight loss of such film does not exceed 1% during exposure, in air, to a temperature of 280°C for 30min and that exhibits no more than a 2% change in film thickness (for a 3 um film) after soaking in N-Methyl-2-pyrrolidone (NMP) at 40°C for 10min.

[0025] It has been found that the aforementioned norbornene-type polymers encompass at least two distinct types of monomers that are in accordance with Formula A1. That is to say, a first type of norbornene-type monomer encompassing a crosslinkable hydrocarbyl pendent group and a second type of norbornene-type monomer encompassing a hydrocarbyl group selected to provide, among other things, the desired high transparency over the visible light spectrum to the resulting polymer.

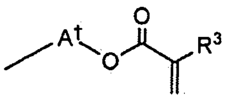
[0026] For said first type of monomer, at least one of R^a, R^b, R^c, and R^d is a hydrocarbyl group in accordance with one of Formulae B, C or D:



(B);



(C); or

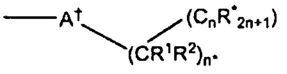


(D)

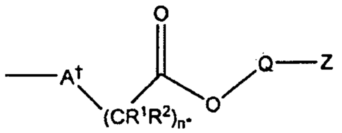
[0027] where in each of Formulae B and C, n is an integer from 1 to 4; A, if present, is a hydrocarbyl linking group selected from methylene, or a C_2 to C_6 alkylene and R^1 and R^2 are each independently selected from hydrogen, fluorine, methyl, perfluromethyl, ethyl or perfluoroethyl. Non-limiting examples of suitable hydrocarbyl linking groups A, include methylene, ethylene, propylene, isopropylene, butylene, isobutylene and hexylene. Non-limiting examples of useful glycidyl alkyl ether pendent groups in accordance with Formula B include, but are not limited, to glycidyl methyl ether, glycidyl ethyl ether, glycidyl propyl ether, glycidyl isopropyl ether, glycidyl butyl ether, glycidyl isobutyl ether, glycidyl hexyl ether. Non-limiting examples of useful alkyl epoxy pendent groups in accordance with Formula C include, but are not limited, butyl epoxy, pentyl epoxy, hexyl epoxy and octyl epoxy.

[0028] For Formula D, $A^\dagger$, if present, is a linking group selected from methylene, or a C_2 to C_6 alkylene or ether, R^3 represents hydrogen, methyl, a C_2-C_4 hydrocarbyl, a nitrile (CN), a C_1-C_3 perfluorohydrocarbyl or a halogen (F, Cl, Br). Representative perfluorohydrocarbyls include but are not limited to perfluoromethyl and perfluoroethyl.

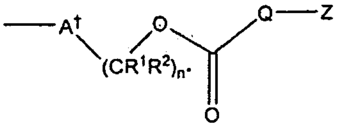
[0029] For said second type of monomer, at least one of R^a, R^b, R^c, and R^d is hydrocarbyl group in accordance with one of Formulae E, F, G, or H:



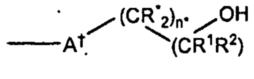
E



F



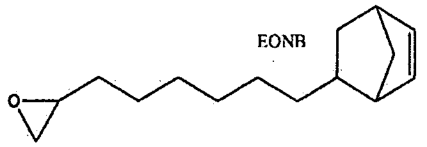
G



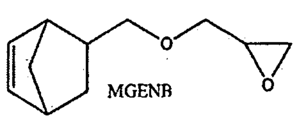
H

[0030] where $A^{\dagger}$, if present, is as defined above; n is an integer from 1 to 6, n* is an integer from 0 to 3, each R* independently represents hydrogen or fluorine, R^1 and R^2 are each independently selected from hydrogen, fluorine, methyl, perfluromethyl, ethyl or perfluoroethyl. Non-limiting examples of suitable pendent groups in accordance with Formula E include, but are not limited to, C_3 to C_{10} alkyl and perfluroalkyl hydrocarbyl groups such as $-A^{\dagger}-C_4F_9$ or $-A^{\dagger}-C_6F_{13}$. Non-limiting examples of suitable pendent groups in accordance with Formulae F and G include, but are not limited to, C_1 to C_6 acetates and carboxylates, respectively, where Q, if present, is selected from a C_2 to C_9 alkylene and Z is selected from one of $(C_nR^{*}_{2n+1})$ or $(CR^{*}_2)_n(CR^1R^2)_nOH$. Exemplary acetates and carboxylates include, among others, $-A^{\dagger}-CH_2-C(O)OC_2H_5$, $-A^{\dagger}-C(CF_3)_2-C(O)OC_4H_9$, $-A^{\dagger}-CH_2-OC(O)CH_3$ or $-A^{\dagger}-C(CF_3)_2-OC(O)C_4H_9$. Non-limiting examples of suitable pendent groups in accordance with Formula H include, but are not limited to, C_3 to C_{10} alcohols, acetals and ether-alcohols such as $-CH_2-O-CH_2-C(CF_3)_2-OH$ (where n* is 0, $A^{\dagger}$ is $-CH_2-O-CH_2-$ and each of R^1 and R^2 is perfluoromethyl) or $-CH_2-C(CF_3)_2-OH$ (where n* is 0, $A^{\dagger}$ is $-CH_2-$ and each of R^1 and R^2 is perfluoromethyl).

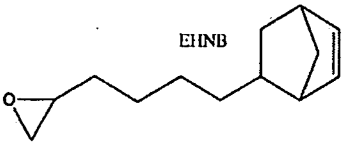
[0031] Exemplary first type monomer embodiments in accordance with the present disclosure include, but are not limited to:



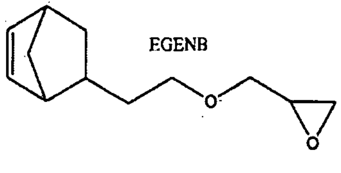
EONB



MGENB

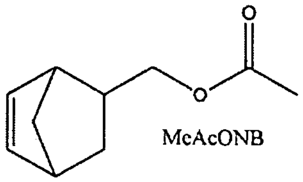


EHNB

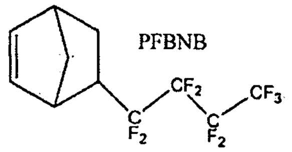


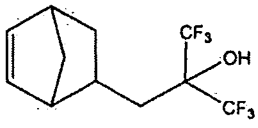
EGENB

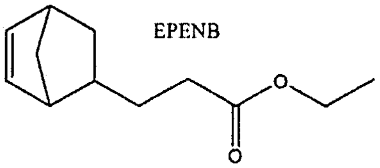
[0032] Exemplary second type monomer embodiments in accordance with the present disclosure include, but are not limited to:

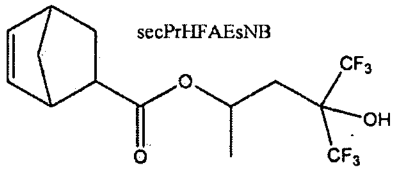

McAcONB


MMHFPNB


PFBNB


HFANB


EPENB


secPrHFAEsNB

[0033] For ease of understanding, the chemical names and related acronyms for each of the four exemplary first type monomer embodiments and each of the six exemplary second type monomers are provided below. 2-(6-(bicyclo[2.2.1]hept-5-en-2-yl)hexyl)oxirane (EONB), 2-((2-(bicyclo[2.2.1]hept-5-en-2-yl)methoxy)methyl)oxirane (MGENB), 2-(6-(bicyclo[2.2.1]hept-5-en-2-yl)butyl)oxirane (EHNB), 2-((2-(bicyclo[2.2.1]hept-5-en-2-yl)ethoxy)methyl)oxirane (EGENB), bicyclo[2.2.1]hept-5-en-2-ylmethyl acetate (MeAcONB), 2-((2-(bicyclo[2.2.1]hept-5-en-2-yl)methoxy)-1,1,1,3,3,3-hexafluoro-2-methylpropan-2-ol (MMHFPNB), 5-(perfluorobutyl)bicyclo[2.2.1]hept-2-ene (PFBNB), 2-(bicyclo[2.2.1]hept-5-en-2-ylmethyl)-1,1,1,3,3,3-hexafluoropropan-2-ol (HFANB), ethyl 3-(bicyclo[2.2.1]hept-5-en-2-yl)propanoate (EPENB) and 5,5,5-trifluoro-4-hydroxy-4-(trifluoromethyl)pentan-2-yl bicyclo[2.2.1]hept-5-ene-2-carboxylate (secPrHFAEsNB).

[0034] As previously mentioned, embodiments in accordance with the present disclosure are directed to norbornene-type layer forming polymers, compositions that encompass such polymers and methods that utilize such polymer compositions to form a transparent polymer layer. It will therefore be understood that such norbornene-type layer forming polymer embodiments are formed via 2, 3 enchainment of at least one of said first type of monomer and at least one of said second type of monomer as are exemplified by Examples 1 through 6, presented below as non-limiting representations of some polymer embodiments in accordance with the present disclosure.

[0035] Further, it will be understood, that the layer forming compositions in accordance with the present disclosure encompass one of more layer forming polymer embodiments, a casting solvent and one or more additives. Such layer forming composition embodiments are exemplified by Examples 7 through 12, presented below as non-limiting representations of some polymer composition embodiments in accordance with the present disclosure.

[0036] With regard to the aforementioned casting solvents of such polymer composition embodiments, such casting solvents include, but are not limited, to *N*-methylpyrrolidone (NMP), Gamma-Butyrolactone (GBL), *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), methyl lactate, ethyl lactate, butyl lactate, methyl ethyl ketone (MEK), methyl amyl ketone (MAK), cyclohexanone and mixtures thereof.

[0037] With regard to the aforementioned additives of such polymer composition embodiments, such additives include, but are not limited to, thermal acid generators (TAGs), antioxidants and synergists where exemplary TAGs include, among others, SI-45L, SI-60L, SI-80L, SI-100L, SI-110L, SI-150L, SI-145L, 150 and 160 manufactured by SANSHIN CHEMICAL INDUSTRY CO., LTD.; and ADEKAOPTON CP-77 and CP-66 manufactured by ADEKA CORPORATION, where SI-150L is (dimethyl-p-acetoxysulfoniumhexafluoro antimonate), SI-100L is (dibenzylmethyl-p-hydroxyphenylsulfoniumhexafluoro antimonate), SI-60L is (1-naphtylmethylmethyl-p-hydroxyphenylsulfonium hexafluoroantimonate.

[0038] With regard to antioxidants/synergists, the trade names of exemplary materials include, among others, ADEKA STAB AO-20, ADEKA STAB AO-30, ADEKA STAB AO-40, ADEKA STAB AO-50, ADEKA STAB AO-60, ADEKA STAB AO-80, ADEKA STAB AO-330, Sumilizer GM, Sumilizer GS, Sumilizer GA-80, Sumilizer MDP-S, Sumilizer BBM-S, Sumilizer WX-R, IRGANOX 1010, IRGANOX 1035, IRGANOX 1076, IRGANOX 1098, IRGANOX 1135,

IRGANOX 1330, IRGANOX 1726, IGRANOX 1425, IRGANOX 1520, IRGANOX 245, IRGANOX 259, IRGANOX 3114, IRGANOX 565, ADEKA STAB PEP-4C, ADEKA STAB PEP-8, ADEKA STAB PEP-8W, ADEKA STAB PEP-36, ADEKA STAB HP-10, ADEKA STAB 2112, ADEKA STAB 1178, ADEKA STAB 1500, ADEKA STAB C, ADEKA STAB 135A, ADEKA STAB 3010, IRGAFOS 12, IRGAFOS 38, Sumilizer TPL-R, Sumilizer TPM, Sumilizer TDS, Sumilizer TP-D, Sumilizer MB, ADEKA STAB AO-412S, ADEKA STAB AO-503, IRGANOX PS 800FD or IRGANOX PS 802FD, where the ADEKA materials listed above are products of Adeka Corporation, Tokyo, Japan; the Sumilizer materials listed above are products of Sumitomo Chemical Co., Ltd., Tokyo, Japan; and the IRGANOX or IRGAFOS materials listed above are products of Ciba Specialty Chemicals Corp. The chemical structures of the above materials, as well as alternate trade names and suppliers can be found in Appendix 'A', attached hereto.

[0039] Still further, it will be understood that Examples 1 through 12 are non-limiting examples. That is to say that such are provided only to demonstrate that some embodiments in accordance with the present invention have been actually reduced to practice. In view of the disclosure of norbornene-type monomers provided hereinabove, one of ordinary skill will know that the aforementioned examples are not the only possible polymer and/or composition embodiments that can be in accordance with this disclosure.

[0040] With regard to methods the utilize polymer compositions embodiments in accordance with the present disclosure, such method embodiments encompass the forming of a desired/appropriate polymer composition and applying or casting such composition over/onto a substrate. Such casting encompasses any appropriate method for applying a polymer composition onto a substrate, for example by a spin coating, a spray coating or a doctor blade method. Further, with regard to film forming embodiments in accordance with the present disclosure, such embodiments encompass a post application bake (PAB) and a curing bake, where the latter is performed at a temperature sufficient to activate the thermal acid generator (TAG) that is present in the polymer composition where such TAG activation initiates crosslinking of the polymer which serves to, among other things, harden the layer/film.

[0041] Further to the use of the layer/film embodiments in accordance with the present disclosure, reference is made to US Patent No. 7,361,931 which describes that conventional known flat panel displays, including active matrix liquid crystal displays, have a configuration where a thin film transistor (TFT) for switching is provided to each of a number of display pixels. The '931 patent further describes that a masking means (a light shielding means) must be provided to prevent light from entering the TFTs and therefore such masking means results in the substrate having irregularity thereon. One skilled in the art should realize that eliminating or reducing such irregularity is desirable and that embodiments in accordance with the present disclosure can provide such a desirable result. Further, as demonstrated herein, such polymer layer or film embodiments exhibit characteristics of high transparency across the visible light spectrum, excellent thermal stability, resistance to NMP, a solvent common to the manufacture of such displays, and hardness sufficient to avoid or minimize handling induced film or layer defects.

Example 1: Polymer synthesis of MeOAcNB/MGENB (80:20)

[0042] MeOAcNB (bicyclo[2.2.1]hept-5-en-2-ylmethyl acetate, 7.87 g, 47.4 mmol) and MGENB (2.13 g, 11.8 mmol) was dissolved in toluene (15.17 g) and MEK (1.17 g) and charged to a reaction vessel. The solution was sparged with nitrogen for 30 min to remove oxygen and then heated to 60 °C. Once at temperature, (η^6-toluene)Ni(C_6F_5)$_2$ (0.164 g, 0.34 mmol) in 7.00 g of toluene (prepared in a glove box) was added via syringe to the reaction vessel. The mixture was allowed to stir at 60 °C for 4.0 hr, after which the solution was cooled to room temperature. The reaction mixture diluted 50g of toluene was then treated with an acetic acid (2.65 g, 44.0 mmol) and 30% conc. of H_2O_2aq (5.02g 44.0 mmol) to remove Ni residues and then washed with water. The solvents were removed by rotovaporation to give a light yellow solid. The yellow solid was redissolved in THF (50 wt%) and was added to hexane (20 fold excess) to give a light yellow powder that was filtered and dried by the vacuum at 40 °C for 16 hr. Approximately, 8.6 g (86 %) of the MeOAcNB/MGENB polymer was isolated. The molar ratio of MeOAcNB and MGENB was determined to be 80 to 20 by ^{13}C NMR.

Example 2: Polymer synthesis of HFANB/C_4F_9NB/MGENB (60:20:20)

[0043] HFANB (3.13 g, 11.4 mmol), C_4F_9NB (1.19 g, 3.8 mmol) and MGENB (0.68 g, 3.8 mmol) was dissolved in toluene (8.85 g) and MEK (0.75 g) and charged to a reaction vessel. The solution was sparged with nitrogen for 30 min to remove oxygen and then heated to 60 °C. Once at temperature, (η^6-toluene)Ni(C_6F_5)$_2$ (0.184 g, 0.38 mmol) in 5.40 g of toluene (prepared in a glove box) was added via syringe to the reaction vessel. The mixture was allowed to stir at 60 °C for 14.0 hr, after which the solution was cooled to room temperature. The reaction mixture diluted toluene (20 g) and THF (10 g) was then treated with an acetic acid (3.60 g, 60.0 mmol) and 30% H_2O_2aq (6.81 g 60.0 mmol) to remove Ni residues and then washed with water. The solvents were removed by rotovaporation to give a light yellow solid. The yellow solid was redissolved in THF (50 wt%) and was added to hexane (20 fold excess) to give a light yellow powder that was filtered and dried by the vacuum at 40 °C for 16 hr. Approximately, 3.48 g (70 %) of the HFANB/C_4F_9NB/MGENB polymer was isolated.

Example 3: Polymer synthesis of HFANB/C_4F_9NB/MGENB (40:40:20)

[0044] HFANB (2.08 g, 7.6 mmol), C_4F_9NB (2.38 g, 7.6 mmol) and MGENB (0.68 g, 3.8 mmol) was dissolved in toluene (8.85 g) and MEK (0.75 g) and charged to a reaction vessel. The solution was sparged with nitrogen for 30 min to remove oxygen and then heated to 60 °C. Once at temperature, (η^6-toluene)Ni(C_6F_5)$_2$ (0.184 g, 0.38 mmol) in 5.40 g of toluene (prepared in a glove box) was added via syringe to the reaction vessel. The mixture was allowed to stir at 60 °C for 14.0 hr, after which the solution was cooled to room temperature. The reaction mixture diluted toluene (20 g) and THF (10 g) was then treated with an acetic acid (3.60 g, 60.0 mmol) and 30% H_2O_2aq (6.81 g 60.0 mmol) to remove Ni residues and then washed with water. The solvents were removed by rotovaporation to give a light yellow solid. The yellow solid was redissolved in THF (50 wt%) and was added to hexane (20 fold excess) to give a light yellow powder that was filtered and dried by the vacuum at 40 °C for 16 hr. Approximately, 3.60 g (70 %) of the polymer was isolated.

Example 4: Polymer synthesis of HFANB/MGENB (80:20)

[0045] HFANB (4.30 g, 15.7 mmol) and MGENB (0.70 g, 3.9 mmol) was dissolved in toluene (9.25 g) and MEK (0.75 g) and charged to a reaction vessel. The solution was sparged with nitrogen for 30 min to remove oxygen and then heated to 60 °C. Once at temperature, (η^6-toluene)Ni(C_6F_5)$_2$ 0.190 g, 0.39 mmol) in 5.00 g of toluene (prepared in a glove box) was added via syringe to the reaction vessel. The mixture was allowed to stir at 60 °C for 7.0 hr, after which the solution was cooled to room temperature. The reaction mixture THF (20 g) was then treated with an acetic acid (3.72 g, 62.0 mmol) and 30% H_2O_2aq (7.03 g 60.0 mmol) to remove Ni residues and then washed with water. The solvents were removed by rotovaporation to give a light yellow solid. The yellow solid was redissolved in THF (50 wt%) and was added to hexane (20 fold excess) to give a light yellow powder that was filtered and dried by the vacuum at 40 °C for 16 hr. Approximately, 3.25 g (65 %) of the HFANB/MGENB polymer was isolated.

Example 5: Polymer synthesis of MeOAcNB/EONB (80:20)

[0046] MeOAcNB (7.51 g, 45.2 mmol) and EONB (2.49 g, 11.3 mmol) was dissolved in toluene (16.00 g) and MEK (2.33 g) and charged to a reaction vessel. The solution was sparged with nitrogen for 30 min to remove oxygen and then heated to 60 °C. Once at temperature, (η^6-toluene)Ni(C_6F_5)$_2$ 0.156 g, 0.32 mmol) in 5.00 g of toluene (prepared in a glove box) was added via syringe to the reaction vessel. The mixture was allowed to stir at 60 °C for 4.0 hr, after which the solution was cooled to room temperature. The reaction mixture diluted in toluene (30 g) and THF (20 g) was then treated with an acetic acid (3.06 g, 51.0 mmol) and 30% H_2O_2aq (5.77 g 51.0 mmol) to remove Ni residues and then washed with water. The solvents were removed by rotovaporation to give a light yellow solid. The yellow solid was redissolved in THF (50 wt%) and was added to hexane (20 fold excess) to give a light yellow powder that was filtered and dried by the vacuum at 40 °C for 16 hr. Approximately, 9.06 g (91 %) of the MeOAcNB/EONB polymer was isolated.

Example 6: Polymer synthesis of EPENB/MGENB (80:20)

[0047] EPENB (4.66 g, 24.0 mmol) and MGENB (1.32 g, 6.0 mmol) was dissolved in toluene (12.00 g) and MEK (0.9 g) and charged to a reaction vessel. The solution was sparged with nitrogen for 30 min to remove oxygen and then heated to 60 °C. Once at temperature, (η^6-toluene)Ni(C_6F_5)$_2$ (0..073 g, 0.15 mmol) in 5.00 g of toluene (prepared in a glove box) was added via syringe to the reaction vessel. The mixture was allowed to stir at 60 °C for 5.0 hr, after which the solution was cooled to room temperature. The reaction mixture diluted in toluene (10 g) and THF (6 g) was then treated with an acetic acid (1.4 g, 23.3 mmol) and 30% H_2O_2aq (2.7 g 23.8 mmol) to remove Ni residues and then washed with water. The solvents were removed by rotovaporation to give a light yellow solid. The yellow solid was redissolved in THF (50 wt%) and was added to hexanes (20 fold excess) to give a white powder that was filtered and dried by the vacuum at 40 °C for 16 hr. Approximately, 4.1 g (70%) of the EPENB/MGENB polymer was isolated (GPC Mw = 78,400 Mn = 44,000).

[0048] The yield, Mw and Mn for each of the polymerization examples provided above are summarized in Table 1, below. Mn and Mw are determined by a standard GPC technique using a polystyrene standard.

Table 1

Polymer Examples						
	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex. 6
Polymerization Yield (%)	86	70	70	65	91	70
Mw	45700	26400	18500	28300	41800	78400
Mn	30700	14800	13000	16400	23700	44000

[0049] In the composition examples that follow, Examples 7-12, three specific antioxidant/synergist materials are used. The manufacturer of each material as well as the material's chemical name is provided the first time each is used in the examples below, thereafter only the manufacturer's trade designation was provided.

[0050] While each polymer composition, of Examples 7-12, encompasses the same three antioxidant/synergist components it should be understood that as such examples are non-limiting, the use of these specific components is illustrative only and should be understood only to indicated that for the type of thermal and optical stability exhibited by film embodiments of the present disclosure, the use of more than one type of antioxidant/synergist is advantageous, where such types of antioxidants/synergists encompass phenolics, phosphites, thioethers and mixtures thereof.

[0051] Notwithstanding, the selection of such specific antioxidant/synergist components was made on the basis of the results shown in the experimental matrix of Table 2. For each composition 1-22, the base polymer was a MeOAcNB homopolymer cast onto a glass wafer to form a 3 µm film as measured after a post application bake (PAB) at 110°C for 100sec. A measurement of the % transparency of the twenty-two 3um films, nineteen sample compositions (with the additives indicated) and three control compositions (with no additives) was made at 400nm after each film was heated for 30 minutes at 280°C and a selection of the specific three additive package was made

Table 2

	Additive - A		Additive - B		C		400nm, 3um FT
Exp No.	type	phr	type	phr	type	phr	Transparency (%)
1	-	-	-	-	-	-	18.4
2	AO-30	1	PEP-36	1	-	-	41.4
3	AO-40	1	HP-10	1	-	-	23.1
4	AO-60	1	PEP-36	1	-	-	50.1
5	AO-80	1	HP-10	1	-	-	38.4
6	AO-30	1	HP-10	1	-	-	34.5
7	AO-40	1	PEP-36	1	-	-	19.6
8	AO-60	1	HP-10	1	-	-	67.9
9	AO-80	1	PEP-36	1	-	-	63.8
10	-	-	-	-	-	-	6.5
11	AO-60	3	PEP-36	3	-	-	65.5
12	AO-80	3	PEP-36	3	-	-	25
13	AO-20	3	PEP-36	3	-	-	12.2
14	AO-330	3	PEP-36	3	-	-	26.7
15	AO-60	3	HP-10	3	-	-	59.2
16	AO-80	3	HP-10	3	-	-	39
17	AO-20	3	HP-10	3	-	-	16.6
18	AO-330	3	HP-10	3	-	-	25.4
19	-	-	-	-	-	-	10.2
20	AO-60	3	PEP-36	3	-	-	63.5
21	AO-60	3	PEP-36	3	AO-412S	1	79.9
22	AO-60	3	PEP-36	3	AO-412S	3	96

[0052] It is of course understood by one skilled in the art that the specific additive package used in each of Examples 7-12, below is provided for illustrative purposes only. That is to say that the selection of such a successful package based on a small experimental design, illustrates that another antioxidant/synergist additive package can be readily determined without the need for undue experimentation. Any such alternate packages being the result of the teachings provided herein, it will be understood that they are with the scope of the embodiments of the present disclosure.

Examples 7-12: Preparation of thermally curable composition

[0053] For each of Examples 7 through 12, 2.0g of the polymer obtained from Examples 1 through 6, respectively, was used to prepare a 17 weight percent (wt%) polymer solution in PGMEA. The formulation additives listed below, each in the amount indicated, were then added to and dissolved in the polymer solution, however, for Example 12, after which and the solution was filtered through a 1 micron syringe filter.

[0054] For each example, SI-150L was added as 0.08g of a 50 wt % GBL solution, where SI-150L is the trade name of Sanshin Chemical Industry CO., LTD. for (dimethyl-p-acetoxysulfoniumhexafluoro antimonate). For each of the antioxidant/synergist additives, the amount, in grams, added for each additive is indicated in Table 3, below. The additives used were ADK STAB AO-60, the trade name of ADEKA CORPORATION for (pentaerythritol tetrakis{3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate}); ADK STAB PEP-36 the trade name of ADEKA CORPORATION for (3,9-Bis(2,6-di-tert-butyl-4-methyl phenoxy)-2,4,8,10-tetraoxa-3,9-diphosphaspiro(5.5)undecane; and ADEKA SATB AO-412S the trade name of ADEKA CORPORATION for (2,2-bis[[3-(dodecylthio)-1-oxopropoxy]methyl]propane-1,3-diylbis[3-(dodecylthio)propionate]).

Table 3

Additive	Ex. 7	Ex. 8	Ex.9	Ex. 10	Ex. 11	Ex. 12
AO-60	0.1	0.06	0.06	0.06	0.1	0.06
PEP-36	0.03	0.06	0.06	0.06	0.03	0.03
AO-412S	0.1	0.06	0.06	0.06	0.1	0.06

Evaluation procedure for the cured material

[0055] Each of the thermally curable compositions exemplified above were evaluated with regard to Transparency, Thermal Stability, Pencil Hardness and NMP tolerance. The general procedure for each evaluation test is provided below with the evaluation test results provided in Table 4.

Transparency

[0056] Each formulated solution was spun-cast onto a glass wafer to form a 3um film. After casting, the film received a post application bake (PAB) at 110°C for 100sec. Transparency at 400nm was measured before and after thermal treatment in air at 280°C for 30min.

Thermal stability

[0057] Each formulated solution was spun-cast onto a 4 inch silicon wafer to form a 3 µm film. After casting, the film received a post application bake (PAB) at 110°C for 100sec and a subsequent cure bake, performed in air for 30 min at 250°C. A portion of the cured film was scratched off the silicon wafer and a TG/DTA analysis performed thereon. The measurement condition was 10°C per minute temperature ramp under N_2 flow and the result is provided as the temperature where 1% weight loss was observed..

Pencil Hardness

[0058] Each formulated solution was spun-cast onto a 4 inch silicon wafer to form a 3 µm film. After casting, the film received a post application bake (PAB) at 110°C for 100sec and a subsequent cure bake, performed in air for 30 min at 250°C. After the cure bake, a pencil hardness test was performed using the procedure of ASTM D3363 except for the absence of specific temperature and humidity control, ambient (at the time of testing) temperature and humidity control was employed.

NMP (*N*-methylpyrrolidone) tolerance

[0059] Each formulated solution was spun-cast onto a 4 inch silicon wafer to form a 3 µm film. After casting, the film received a post application bake (PAB) at 110°C for 100sec and a subsequent cure bake, performed in air for 30 min at 250°C. After the cure bake the film thickness was measured, the film soaked in NMP at 40°C for

10min and the film thickness remeasured. The difference in film thick was recorded as percent film thickness loss.

TABLE 4

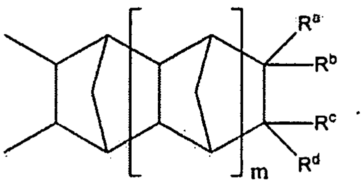
Evaluation Examples						
Test	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex 11	Ex. 12
Transparency before Heating (%)	100	100	100	100	100	100
Transparency (after 280°C for 30min) (%)	98	100	100	100	100	97
1% weight loss temperature (°C)	297	290	295	290	308	313
Pencil hardness	4H	4H	4H	4H	6H	4H
NMP tolerance* (%)	<1.0	<1.0	<1.0	12	<1.0	<1.0

*: calculated with after/before film thickness

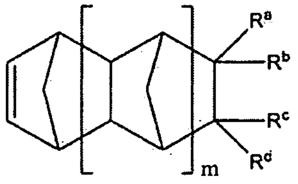
[0060] By now it should be realized that the polymer, polymer composition and polymer layer embodiments that have been described are useful for forming layers capable of meeting the requirements for transparent layers employed in the manufacture of liquid crystal displays, organic light emitting diode displays and other optoelectronic devices.

CLAIMS:

1. A layer forming polymer comprising a first type of norbornene-type repeating unit and a second type of norbornene-type repeating unit each represented by Formula A, such types of repeating units derived from norbornene-type monomers represented by Formula A1:



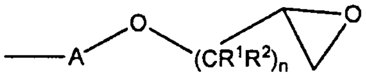
A



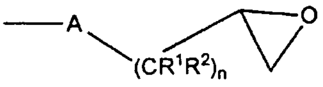
A1

where m is 0, 1 or 2, at least one of R^a, R^b, R^c and R^d for the said first type of repeating unit is a crosslinkable hydrocarbyl pendent group and at least one of R^a, R^b, R^c and R^d for the said second type of repeating unit is distinct from said first type of repeating unit and is a hydrocarbyl pendent group having high transparency in the visible light spectrum.

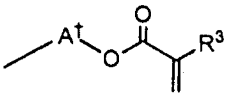
2. The layer forming polymer of Claim 1 where for said first type of repeating unit, one of R^a, R^b, R^c and R^d is a crosslinkable hydrocarbyl pendent group represented by one of Formulae B, C or D:



(B);



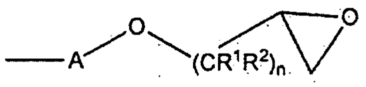
(C); or



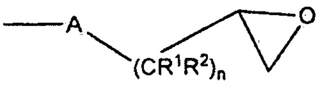
(D)

where for Formulae B and C, n is an integer from 1 to 4, A is an optional linking group selected from methylene, a C_2 to C_6 alkylene and R^1 and R^2 are each independently selected from H, methyl or ethyl; and for Formula D, $A^{\dagger}$ is an optional linking group selected from methylene, a C_2 to C_6 alkylene or a C_2 to C_6 ether and R^3 represents hydrogen, a C_1-C_4 hydrocarbyl, a nitrile (CN), a C_1-C_3 perfluorohydrocarbyl or F, Cl or Br.

3. The layer forming polymer of Claim 2 where the crosslinkable pendent group is represented by Formula B or Formula C:

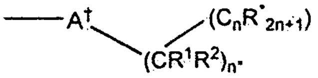


(B);

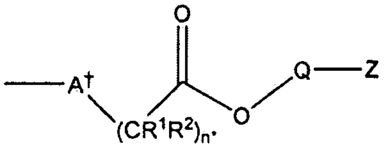


(C).

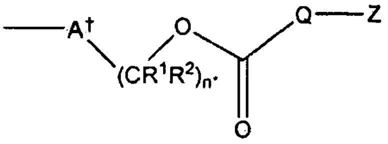
4. The layer forming polymer of Claim 1 where for said second type of repeating unit, one of R^a, R^b, R^c and R^d is a hydrocarbyl pendent group represented by one of Formulae E, F, G or H and the others of R^a, R^b, R^c and R^d are hydrogen:



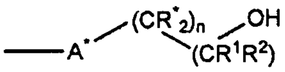
E



F



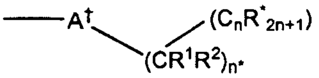
G



H

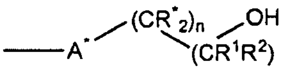
where $A^{\dagger}$, if present, is a linking group selected from methylene, a C_2 to C_6 alkylene or a C_2 to C_6 ether, each R* independently represents a hydrogen or a fluorine, R^1 and R^2 are each independently selected from hydrogen, fluorine, methyl, perfluromethyl, ethyl or perfluoroethyl, n is an integer from 1 to 6 and n* is an integer from 0 to 3, Z is selected from one of $(C_nR^*_{2n+1})$, $(CR^1R^2)_n$, $(CR^*_2)_n(CR^1R^2)_nOH$ and Q, if present, is selected from a C_2 to C_9 alkylene.

5. The layer forming polymer of Claim 4 where the hydrocarbyl pendent group is represented by Formula E, where each of R*, R^1 and R^2 are fluorine:



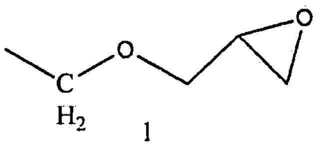
E .

6. The layer forming polymer of Claim 4 where the hydrocarbyl pendent group is represented by Formula H, where n is 1, 2 or 3, R^1 and R^2 are each $-CF_3$ and each R* is hydrogen.

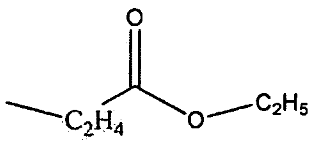


H .

7. The layer forming polymer of Claim 1 where the crosslinkable pendent group is represented by Formula 1 and the pendent group having high transparency is represented by Formula 2:

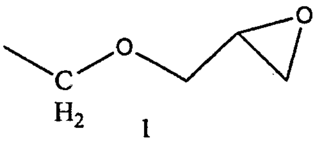


1



2 .

8. The layer forming polymer of Claim 1 where the crosslinkable pendent group is represented by Formula 1 and the pendent group having high transparency is represented by Formula 3:



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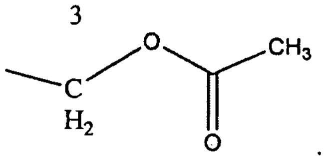
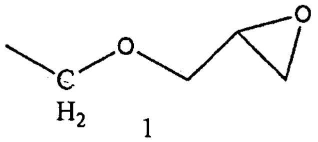


9. The layer forming polymer of Claim 1 where the crosslinkable pendent group is represented by Formula 1 and the pendent group having high transparency is represented by Formula 4:



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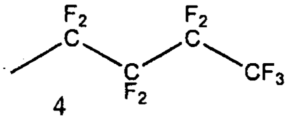

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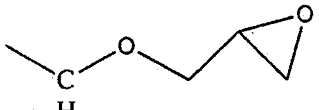
10. The layer forming polymer of Claim 1 where the crosslinkable pendent group is represented by Formula 1 and the pendent group having high transparency is represented by Formula 5:



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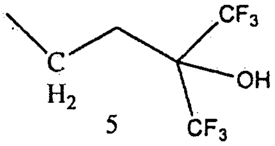
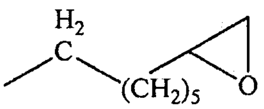


5

.

11. The layer forming polymer of any of Claims 7, 8, 9 or 10 where the crosslinkable pendent group is represented by Formula 6 or Formula 7:



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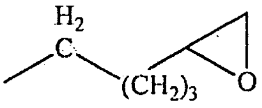

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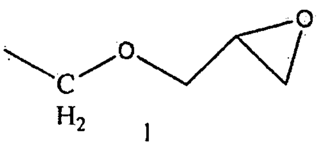
12. The layer forming polymer of Claim 1 comprising a first type of repeating unit having a crosslinkable pendent group selected from the groups represented by Formulae 1, 6 or 7:



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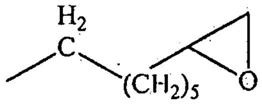
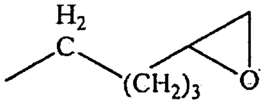


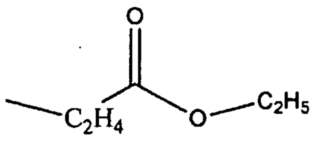
6



7

,

a second type of repeating unit selected from the pendent groups represented by Formula 2, 3, 4 or 5:



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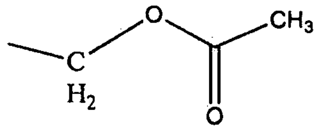

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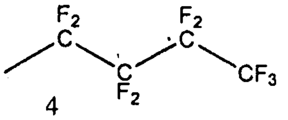
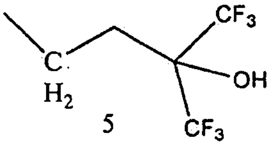


4



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and further comprising a third type of repeating unit, distinct from said second type of repeating unit, also selected from the pendent groups represented by Formula 2, 3, 4 or 5.

13. The layer forming composition of any of Claims 1-12 further comprising a casting solvent.

14. The layer forming composition of Claim 13 where said casting solvent is selected from one or more of *N*-methylpyrrolidone (NMP), Gamma-Butyrolactone (GBL), *N,N*-dimethylacetamide (DMA), dimethyl sulfoxide (DMSO), diethylene glycol dimethyl ether, diethylene glycol dibutyl ether, propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), methyl lactate, ethyl lactate, butyl lactate, methyl ethyl ketone or cyclohexanone.

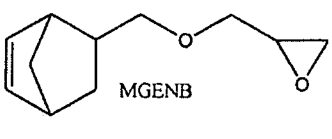
15. The layer forming composition of Claim 13 further comprising a thermal acid generator (TAG) and an antioxidant/synergist additive.

16. The layer forming composition of Claim 11 where the TAG is selected from SI-150L (dimethyl-p-acetoxysulfoniumhexafluoro antimonate), SI-100L (dibenzylmethyl-p-hydroxyphenylsulfoniumhexafluoro antimonate) or SI-60L (1-naphtylmethylmethyl-p-hydroxyphenylsulfoniumhexafluoroantimonate.

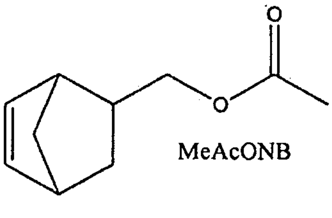
17. The layer forming composition of Claim 12 where said antioxidant/synergist additive is selected from one or more of ADEKA STAB AO-20, ADEKA STAB AO-30, ADEKA STAB AO-40, ADEKA STAB AO-50, ADEKA STAB AO-60, ADEKA STAB AO-80, ADEKA STAB AO-330, Sumilizer GM, Sumilizer GS, Sumilizer GA-80, Sumilizer MDP-S, Sumilizer BBM-S, Sumilizer WX-R, IRGANOX 1010, IRGANOX 1035, IRGANOX 1076, IRGANOX 1098, IRGANOX 1135, IRGANOX 1330, IRGANOX 1726, IGRANOX 1425, IRGANOX 1520, IRGANOX 245, IRGANOX 259, IRGANOX 3114, IRGANOX 565, ADEKA STAB PEP-4C, ADEKA STAB PEP-8, ADEKA STAB PEP-8W, ADEKA STAB PEP-36, ADEKA STAB HP-10, ADEKA STAB 2112, ADEKA STAB 1178, ADEKA STAB 1500, ADEKA STAB C, ADEKA STAB 135A, ADEKA STAB 3010, IRGAFOS 12, IRGAFOS 38 Sumilizer TPL-R, Sumilizer TPM, Sumilizer TDS, Sumilizer TP-D, Sumilizer MB, ADEKA STAB AO-412S, ADEKA STAB AO-503, IRGANOX PS 800FD or IRGANOX PS 802FD

18. A layer forming composition comprising a norbornene-type polymer, a thermal acid generator, cyclicneopentane tetraylbis(2,6-di-t-butyl-4-methylphenyl phosphite), tetrakis[methylene 3-(3',5'-di-t-butyl-4-hydroxyphenyl) propionate]methane and pentaerythrityltetra(betalaurylthiopropionate).

19. The layer forming composition of Claim 18, where said norbornene-type polymer comprises repeating units derived from:


MGENB

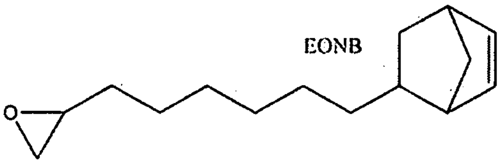
and


MeAcONB

, and where said thermal acid generator is selected from SI-150L (dimethyl-p-acetoxysulfoniumhexafluoro antimonate), SI-100L (dibenzylmethyl-p-hydroxyphenylsulfoniumhexafluoro antimonate) or SI-60L (1-naphtylmethylmethyl-p-hydroxyphenylsulfoniumhexafluoroantimonate.

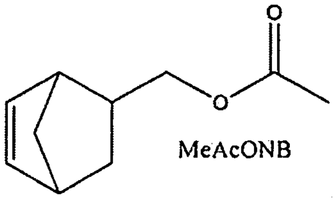
20. The layer forming composition of Claim 19, where said thermal acid generator is SI-150L and where such layer forming composition further comprises ADEKA STAB AO-60, ADEKA STAB AO-412S and ADEKA STAB PEP-36.

21. The layer forming composition of Claim 18, where said norbornene-type polymer comprises repeating units derived from:



EONB

and



MeAcONB

, and where said thermal acid generator is selected from SI-150L (dimethyl-p-acetoxysulfoniumhexafluoro antimonate), SI-100L (dibenzylmethyl-p-hydroxyphenylsulfoniumhexafluoro antimonate) or SI-60L (1-naphtylmethylmethyl-p-hydroxyphenylsulfoniumhexafluoroantimonate.

22. The layer forming composition of Claim 21, where said thermal acid generator is SI-150L and where such layer forming composition further comprises ADEKA STAB AO-60, ADEKA STAB AO-412S and ADEKA STAB PEP-36.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2011/064569

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F232/08 G03F7/038
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F G03F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/062378 A1 (CHOKI KOJI [JP] ET AL) 11 March 2010 (2010-03-11) paragraph [0031] paragraph [0071] - paragraph [0073] examples -----	1-5, 12-15,17
X	EP 1 771 491 A1 (PROMERUS LLC [US] PROMERUS LLC [US]; SUMITOMO BAKELITE CO [JP]) 11 April 2007 (2007-04-11) paragraph [0029] paragraph [0037] - paragraph [0040] paragraph [0058] - paragraph [0060] paragraph [0074] example 1 Formulation and Process examples -----	1-5, 12-15,17

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 9 February 2012	Date of mailing of the international search report 23/05/2012
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Thomas, Dominik

2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2011/064569

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

9(completely); 1-5, 12-15, 17(partially)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 9(completely); 1-5, 12-15, 17(partially)

   A layer forming polymer comprising a first type of norbomene-type repeating unit and a second type of norbornene-type repeating unit each represented by Formula B of claim 2 and Formula E of claim 4;

   ---

2. claims: 7, 19, 20(completely); 1-4, 12-15, 17(partially)

   A layer forming polymer comprising a first type of norbomene-type repeating unit and a second type of norbornene-type repeating unit each represented by Formula B of claim 2 and Formula F of claim 4;

   ---

3. claims: 8(completely); 1-4, 12-15, 17(partially)

   A layer forming polymer comprising a first type of norbomene-type repeating unit and a second type of norbornene-type repeating unit each represented by Formula B of claim 2and Formula G of claim 4;

   ---

4. claims: 10(completely); 1-4, 6, 12-15, 17(partially)

   A layer forming polymer comprising a first type of norbomene-type repeating unit and a second type of norbornene-type repeating unit each represented by Formula B of claim 2 and Formula H of claim 4;

   ---

5. claims: 11, 16, 21, 22(completely); 1-6, 12-15, 17(partially)

   A layer forming polymer comprising a first type of norbomene-type repeating unit and a second type of norbornene-type repeating unit each represented by Formula C of claim 2 and Formulas E-H of claim 4;

   ---

6. claims: 1-6, 13-15(all partially)

   A layer forming polymer comprising a first type of norbomene-type repeating unit and a second type of norbornene-type repeating unit each represented by Formula D of claim 2 and Formula E-H of claim 4;

   ---

7. claim: 18

   A layer forming composition comprising a norbornene-type polymer, a thermal acid generator, cyclicneopentane

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

tetraylbis(2,6-di-t-butyl-4-methylphenyl phosphite),
tetrakis[methylene 3-(3',5'-di-t-butyl-4-hydroxyphenyl)
propionate]methane and
pentaerythrityltetra(betalaurylthiopropionate).

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2011/064569

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2010062378 A1	11-03-2010	EP 1695128 A2	30-08-2006
		JP 2007512577 A	17-05-2007
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		KR 20060124627 A	05-12-2006
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		WO 2005052641 A2	09-06-2005
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		US 2006020068 A1	26-01-2006
		WO 2006016925 A1	16-02-2006