(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) **International Patent Classification:**
G02B 5/20 (2006.01)   C07D 307/89 (2006.01)
C07D 493/04 (2006.01)   C07D 311/78 (2006.01)

(21) **International Application Number:**
PCT/US2017/046432

(22) **International Filing Date:**
11 August 2017 (11.08.2017)

(25) **Filing Language:** English

(26) **Publication Language:** English

(30) **Priority Data:**
62/374,247   12 August 2016 (12.08.2016)   US
62/476,959   27 March 2017 (27.03.2017)   US

(71) **Applicant: AKRON POLYMER SYSTEMS, INC.** [US/US]; 62 N. Summit Street, Akron, Ohio 44308 (US).

(72) **Inventors: ZHENG, Xiaoliang**; 6006 Nicholson Drive, Hudson, Ohio 44236 (US). **PHILLIPS, Alan**; 151 Sun Chase Court, Johnson City, Tennessee 37615 (US). **WANG, Bin**; 1005 Greenview Place, Kingsport, Tennessee 37660 (US). **WANG, Peiyao**; 766 Carnegie Avenue, Apt. B5, Akron, Ohio 44314 (US). **HU, Lang**; 999A Snowfall Spur, Akron, Ohio 44313 (US). **LI, Wentao**; 932 Cooks Valley Road, Apartment 71, Kingsport, Tennessee 37664 (US). **DENG, Liu**; 2553 Rivermont Circle, Kingsport, Tennessee 37660 (US). **KUO, Thauming**; 1400 Lamar Court, Kingsport, Tennessee 37664 (US). **ZHANG, Dong**; 1380 Walnut Ridge Road, Uniontown, Ohio 44685 (US). **HARRIS, Frank**; 872 Coventry Street, Boca Raton, Florida 33487 (US). **GERMROTH, Ted**; 1974 Cooks Valley Road, Kingsport, Tennessee 37664 (US).

(74) **Agent: SLEPECKY, Adam P.**; Calfee, Halter & Griswold LLP, The Calfee Building, 1405 East Sixth Street, Cleveland, Ohio 44114-1607 (US).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,

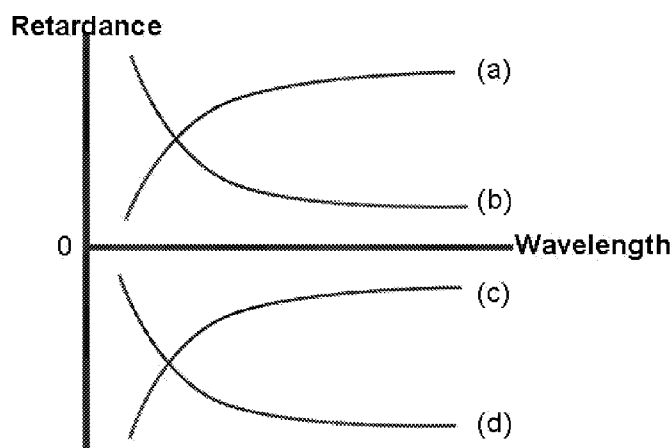(54) **Title:** OPTICAL COMPENSATION FILM HAVING REVERSED WAVELENGTH DISPERSION

FIG. 1

(57) **Abstract:** Disclosed is an optical compensation film made of a solution cast of a polymer blend comprising a nitrated styrenic fluoropolymer and a polyimide. The compensation film is a positive-C plate having reversed wavelength dispersion that is capable of providing an achromatic (or broadband) retardation compensation. The optical film of the invention can be used in an optical device such as liquid crystal display (LCD) or organic light emitting diode (OLED) display.

TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

OPTICAL COMPENSATION FILM HAVING REVERSED WAVELENGTH DISPERSION

CROSS-REFERENCE TO RELATED APPLICATIONS

[001]   This application claims priority to and the benefit of U.S. Provisional Patent Applications No. 62/476,959, filed March 27, 2017, and No. 62/374,247, filed August 12, 2016, the entire content of which is incorporated by reference herein.

FIELD OF THE INVENTION

[002]   This invention pertains to a wide-view optical compensation film having positive out-of-plane retardation. More specifically, this invention relates to a positive-C plate having reversed wavelength dispersion that is capable of providing an achromatic (or broadband) retardation compensation. The optical film of the invention may be used in an optical device such as liquid crystal display (LCD), organic light emitting diode (OLED) display, 3D display, optical switch, or waveguide where a controlled light management is desirable.

BACKGROUND OF THE INVENTION

[003]   It is known in the art of optical compensation that the phase retardation of light varies according to wavelength, causing color shift. This wavelength dependence (or dispersion) characteristic of the compensation film may be taken into account when designing an optical device so that color shift is reduced. Wavelength dispersion curves are defined as "normal (or "proper") or "reversed" with respect to the compensation film having positive or negative retardance (or retardation). A compensation film with positive retardance (positive A- or C-plate) may have a normal curve in which the value of phase retardation is increasingly positive toward shorter wavelengths or a reversed curve in which the value of phase retardation is decreasingly positive toward shorter wavelengths. A compensation film with negative retardance (negative A- or C- plate) may have a normal curve in which the value of phase retardation is increasingly negative toward shorter wavelengths or a reversed curve in which the value of phase retardation is decreasingly negative toward shorter wavelengths. Exemplary shapes of these curves are depicted in FIG. 1.

[004]   Wave plates are customarily named as follows in accordance with their refractive index profiles:

positive C-plate: $n_x=n_y<n_z$; negative C-plate: $n_x=n_y>n_z$

positive A-plate: $n_x>n_y=n_z$; negative A-plate: $n_x<n_y=n_z$

wherein, n_x and n_y represent in-plane refractive indices, and n_z the thickness refractive index.

C-plate and A-plate wave plates are uniaxial birefringent plates. A wave plate can also be biaxial birefringent, where n_x, n_y, and n_z are all not equal; such plates are customarily called biaxial films.

[005]   An A-plate having in-plane retardation (R_e) equal to a quarter of the wavelength ($\lambda/4$) is called quarter wave plate (QWP). Likewise, an A-plate having R_e equal to half of the wavelength ($\lambda/2$) is called half wave plate (HWP). An ideal achromatic QWP would be able to retard an incident polarized light by $\lambda/4$ at every wavelength. In order to achieve this ideal achromatic QWP, the wavelength dispersion of the QWP has to be reversed and must satisfy the following equations:

$$R_e(450)/R_e(550)= 0.818 \text{ and } R_e(650)/R_e(550) = 1.182,$$

wherein $R_e(450)$, $R_e(550)$, and $R_e(650)$ are in-plane retardations at the light wavelengths of 450 nm, 550nm, and 650 nm respectively. An achromatic (or broadband) wave plate is highly desirable since it can direct the light in the same manner at each wavelength to yield the optimal viewing quality. A common wave plate, however, exhibits a normal dispersion curve, which is not suitable for broadband wave plate application.

[006]   Similar to positive A-plates, positive C-plates having reversed wavelength dispersion curves are also desirable for broadband applications. Such C-plates can satisfy the following equations:

$$R_{th}(450)/R_{th}(550)= 0.818 \text{ and } R_{th}(650)/R_{th}(550) = 1.182,$$

wherein $R_{th}(450)$, $R_{th}(550)$, and $R_{th}(650)$ are out-of-plane retardations at the light wavelengths of 450 nm, 550 nm, and 650 nm respectively. There exists a need for a positive C-plate having reversed wavelength dispersion characteristics with respect to out-of-plane retardation.
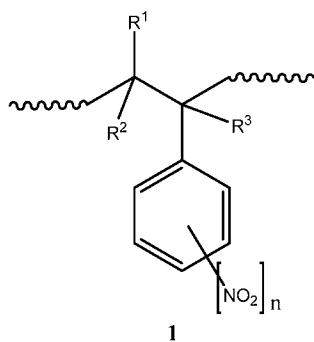
[007]   A-plates are commonly used in liquid crystal displays (LCDs) as compensation films to improve the viewing angles. They can also be used in an OLED (organic light emitting diode) display device. For example, a QWP can be being used with a linear polarizer to provide a circular polarizer in an OLED device to reduce the ambient light reflected by OLED for improved viewing quality. These applications typically utilize the in-plane retardation provided by the A-plate for in-plane phase-shift compensation. For example, A-plate combining with C-plate is particularly useful in reducing light leakage of the crossed polarizers at oblique viewing angles. The A-plate, however, also exhibits a negative out-of-plane retardation R_{th}, which is defined by the equation $R_{th} = [n_z-(n_x+n_y)/2] \times d$ with a value of $|R_e/2|$ arising from its orientation. This characteristic can be beneficial when a negative R_{th} is desirable in an optical device. For example, in a vertically aligned (VA) mode LCD, the liquid crystal molecules in the LC cell are aligned in a homeotropic manner, which results in positive retardation. An A-plate, thus, can provide an out-of-plane compensation in addition to in-plane compensation in VA-LCD. In other devices, such as in-plane switch (IPS) mode LCD and OLED display, however, the R_{th} exhibited in the A-plate is not desirable since it can cause phase shift in off-axis light and lead to light leakage. Thus, there exists an additional need in the art to provide a positive in-plane retarder having reduced out-of-plane retardation for improved viewing angle and contrast ratio of the display. The reduction of the out-of-plane retardation can be achieved by using a positive-C plate in combination with the A-plate. Further, it is most desirable that the positive-C plate has a reversed wavelength dispersion characteristic in order to achieve the achromatic compensation.

SUMMARY OF THE INVENTION

[008]   Embodiments disclosed herein are directed to an optical compensation film, which is made by solution casting of a polymer blend comprising:

>   (a) a nitrated styrenic fluoropolymer and

>   (b) a polyimide,

wherein said optical compensation film has positive out-of-plane retardations that satisfy the relations of $0.7 < R(450)/R(550) < 1$ and $1 < R(650)/R(550) < 1.25$, wherein R(450), R(550), and R(650) are out-of-plane retardations at the light wavelengths of 450 nm, 550 nm, and 650 nm respectively, and wherein the nitrated styrenic fluoropolymer has a styrenic moiety of:
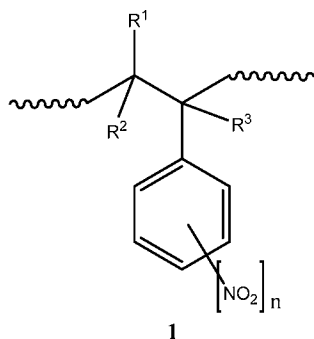
1

wherein R^1, R^2, and R^3 are each independently hydrogen atoms, alkyl groups, substituted alkyl groups, or halogens, wherein at least one of R^1, R^2, and R^3 is a fluorine atom, and wherein n is an integer from 1 to 5 representing the number of the nitro group(s) on the styrenic ring.

[009] In another embodiment, the nitrated styrenic fluoropolymer (a) is present from about 60% to about 90% or from about 70% to about 80%, and the polyimide (b) is from about 10% to about 40% or from about 20% to about 30%, based on the total weight of (a) and (b).
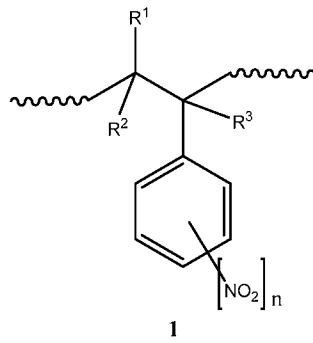
[010] In a further embodiment, this invention provides a multilayer optical film comprising the optical compensation film of the present invention and an A-plate having a refractive index profile of $n_x > n_y = n_z$, wherein n_x and n_y represent in-plane refractive indices, and n_z the thickness refractive index.

[011] In certain other embodiments, a polymer resin is provided. The resin has a moiety of:

1

wherein R^1, R^2, and R^3 are each independently hydrogen atoms, alkyl groups, substituted alkyl groups, or halogens, wherein at least one of R^1, R^2, and R^3 is a fluorine atom, and wherein n is an integer from 1 to 5 representing the number of the nitro group(s) on the styrenic ring. In certain embodiments, the polymer resin comprises a mixture or copolymer of a styrenic fluoropolymer (above) and a polyimide.

[012] In other embodiments of the present invention, a polymer solution is provided. The polymer solution comprises a solvent and a polymer having a styrenic moiety of:

4

1

wherein R¹, R², and R³ are each independently hydrogen atoms, alkyl groups, substituted alkyl groups, or halogens, wherein at least one of R¹, R², and R³ is a fluorine atom, and wherein n is an integer from 1 to 5 representing the number of the nitro group(s) on the styrenic ring. In certain embodiments, the polymer in the polymer solution comprises a mixture or copolymer of a styrenic fluoropolymer (above) and a polyimide.

BRIEF DESCRIPTION OF THE DRAWINGS

[013]   FIG. 1 is a graph depicting the shapes of exemplary wavelength dispersion curves for: (a) a reversed curve for positive retardation, (b) a normal curve for positive retardation, (c) a normal curve for negative retardation and (d) a reversed curve for negative retardation.
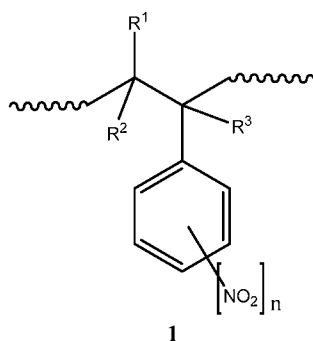
DETAIL DESCRIPTION OF THE INVENTION

[014]   Retardation (R) of a wave plate is defined by the equation $R = \Delta n \times d$, wherein Δn is the birefringence and d is the thickness of the wave plate. Birefringence is classified into in-plane birefringence $\Delta n_{in} = n_x - n_y$ and out-of-plane birefringence $\Delta n_{th} = n_z - (n_x + n_y)/2$. In-plane retardation is represented by the equation $R_e = (n_x - n_y) \times d$ and out-of-plane retardation by $R_{th} = [n_z - (n_x + n_y)/2] \times d$.

[015]   Birefringence (Δn) of a wave plate may be measured by determining the birefringence of a wave plate over a wavelength range of about 400 nm to about 800 nm at different increments. Alternatively, birefringence may be measured at a specific light wavelength. Throughout this description, when a birefringence or retardation relation is given without specifying a wavelength, it is meant to be true throughout the wavelength range of about 400 nm to about 800 nm.

[016] In one embodiment of the present invention, there is provided an optical compensation film, which is made by solution casting of a polymer blend comprising:

(a) a nitrated styrenic fluoropolymer and

(b) a polyimide,

wherein said optical compensation film has positive out-of-plane retardations that satisfy the relations of $0.7 < R(450)/R(550) < 1$ and $1 < R(650)/R(550) < 1.25$, wherein R(450), R(550), and R(650)are out-of-plane retardations at the light wavelengths of 450 nm, 550 nm, and 650 nm respectively and wherein the nitrated styrenic fluoropolymer has a styrenic moiety of:

1

wherein R^1, R^2, and $R^3$are each independently hydrogen atoms, alkyl groups, substituted alkyl groups, or halogens, wherein at least one of R^1, R^2, and R^3 is a fluorine atom, and wherein n is an integer from 1 to 5 representing the number of the nitro group(s) on the styrenic ring.

[017] In another embodiment, the nitrated styrenic fluoropolymer (a) is from about 60% to about 90% or from about 70% to about 80%, and the polyimide (b) is from about 10% to about 40% or from about 20% to about 30%, based on the total weight of (a) and (b).

[018] The optical compensation film in accordance with the present invention has a positive out-of-plane retardation (R_{th}) and a reversed out-of-plane wavelength dispersion characteristic, by which the value of phase retardation is decreasingly positive toward shorter wavelengths. This dispersion characteristic is expressed by the ratios of the retardations as measured at the wavelengths of 450 nm, 550 nm, and 650 nm, which satisfy the relations of $R(450)/R(550) < 1$ and $R(650)/R(550) > 1$. The ratio of R(450)/R(550) can be 0.71 to 0.99, 0.72 to 0.98, 0.74 to 0.97, 0.76 to 0.96, 0.78 to 0.95, 0.8 to 0.9, or 0.81 to 0.85. The ratio of R(650)/R(550) can be 1.01 to 1.24, 1.02 to 1.23, 1.03 to 1.22, 1.04 to 1.21, 1.05 to 1.2, or 1.1 to 1.19. In one

embodiment, the positive out-of-plane retardations satisfy the relations of $0.8 < R(450)/R(550) < 0.9$ and $1.01 < R(650)/R(550) < 1.2$.

[019] In embodiments disclosed herein, the out-of-plane retardation (R_{th}) of the optical compensation film is from about 50 nm to about 200 nm at the wavelength (λ) 550 nm; most preferably from about 100 nm to about 150 nm. Preferably, the film thickness is from about 5 to about 30 micron (μm); most preferably from about 5 micron to about 20 micron.

[020] In certain embodiments, the nitrated styrenic fluoropolymer (a) suitable for this invention comprises the styrenic moiety in the polymer main chain shown below:
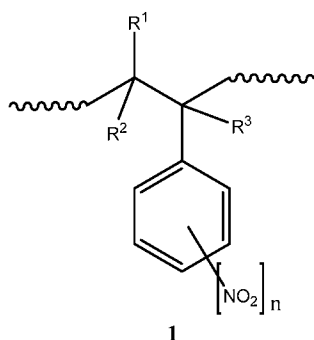
1

wherein R^1, R^2, and R^3 are each independently hydrogen atoms, alkyl groups, substituted alkyl groups, or halogens, wherein at least one of R^1, R^2, and R^3 is a fluorine atom, and wherein n is an integer from 1 to 5 representing the number of the nitro group(s) on the styrenic ring.

[021] In the nitrated styrenic fluoropolymer (a), each styrenic moiety may or may not be substituted (but at least one is substituted); the average number of the nitro group(s) on a styrenic moiety in the styrenic fluoropolymer can range from about 0.2 to about 1, which is referred to herein as the degree of substitution (DS) of the nitro groups in the polymer. Desirably, the DS of the nitro group ranges from about 0.5 to about 0.9, from 0.6 to 0.8, or from 0.65 to 0.75.

[022] The nitrated styrenic fluoropolymer (a) may be prepared by nitration of a styrenic fluoropolymer, which may be a homopolymer or a copolymer. Examples of the homopolymer include, but are not limited to, poly(α,β,β-trifluorostyrene), poly(α,β-difluorostyrene), poly(β,β-difluorostyrene), poly(α-fluorostyrene), or poly(β-fluorostyrene). In one embodiment the styrenic fluoropolymer is poly(α,β,β-trifluorostyrene). The copolymer may be prepared by copolymerization of one or more of the fluorine-containing monomers with one or more ethylenically unsaturated monomers. Examples of such fluorine-containing monomers include,

but are not limited to, α,β,β-trifluorostyrene, α,β-difluorostyrene, β,β-difluorostyrene, α-fluorostyrene, β-fluorostyrene, and combinations thereof.

[023] In one embodiment, the styrenic fluoropolymer is a copolymer of α,β,β-trifluorostyrene with one or more ethylenically unsaturated monomers selected from the group comprising styrene, methyl acrylate, methyl methacrylate, butyl acrylate, butyl methacrylate, 2-ethylhexyl acrylate, acrylic acid, methacrylic acid, α-methyl styrene, 4-methylstyrene, vinyl biphenyl, acrylonitrile, isoprene, and combinations thereof.

[024] In certain embodiments disclosed herein, the polyimide (b) contains rigid rod-like groups that are capable of forming in-plane orientation when solution cast onto a substrate. The polymer film thus prepared exhibits negative out-of-plane birefringence and is commonly known as a negative C-plate for optical retardation compensation. Unlike un-substituted styrenic fluoropolymer, such as poly(α,β,β-trifluorostyrene), the nitrated styrenic fluoropolymer is miscible with polyimide in a solvent and the mixture can be made into a clear film of optical quality. Blending of the nitrated styrenic fluoropolymer with polyimide enables the wavelength dispersion curve of the styrenic fluoropolymer film to change from normal to reverse, which is highly desirable for achromatic broadband applications.

[025] In embodiments disclosed herein, polyimides are prepared by reacting an aromatic dianhydride with an aromatic diamine. The aromatic dianhydride can be based on benzene (Formulae 2-5, below) or naphthalene (Formulae 6-7, below); the aromatic diamine can also be based on either benzene (Formulae 8 and 9, below) or naphthalene (Formulae 10 and 11, below). Polyimides suitable for this invention have been disclosed in US Patent Nos. 5344916, 5480964, 5580950, and 7820253, the contents of which are incorporated by reference herein in their entirety. Desirably, the polyimides are prepared by reacting one or more of the dianhydrides, such as pyromellitic dianhydride (PMDA) (2), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) (3), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (4), 4,4'-(ethyne-1,2-diyl) diphthalic anhydride (EDDPA) (5), 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNDA) (6), and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) (7), with one or more of the diamines, such as 2,4-diaminomesitylene (DAM) (8), 2,2'-bis(trifluoromethyl)benzidine (PFMB) (9), 1,5-naphthalenediamine (DAN) (10), [1,1'-binaphthalene]-5,5'-diamine (DABN) (11), 3,5-diethyl-toluene-2,6-diamine (2,6-DETDA) (12), 3,5-diethyl-toluene-2,4-diamine (2,4-DETDA) (13), and 4,4'-(9-fluorenylidene)dianiline) (FRDA) (14). The most desirable

dianhydrides are 6FDA (4), EDDPA (5), and BNDA (6), and the most desirable diamines are DAM (8), 2,6-DETDA (12), 2,4-DETDA (13), and FRDA (14). In one embodiment, the aromatic dianhydride is one or more selected from the group consisting of 6FDA (4), EDDPA (5), BNDA (6), and combinations thereof, and the aromatic diamine is one or more selected from the group consisting of DAM (8), 2,6-DETDA (12), 2,4-DETDA (13), FRDA (14), and combinations thereof. Various chemical compositions of dianhydrides and aromatic diamines are shown below:
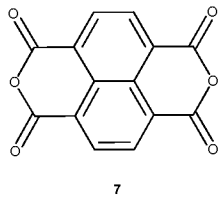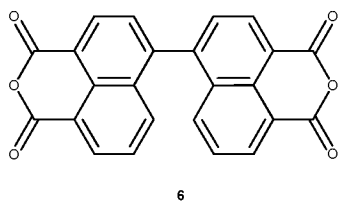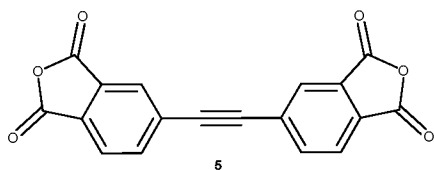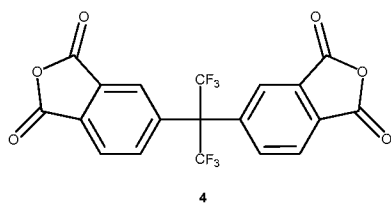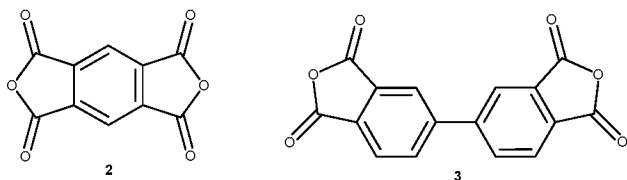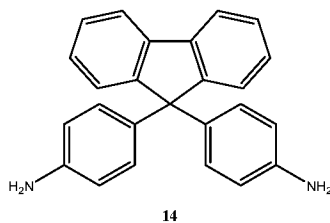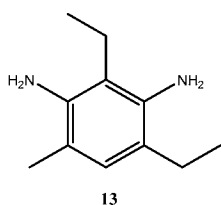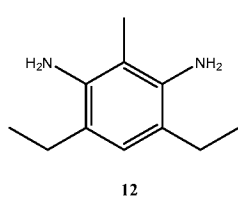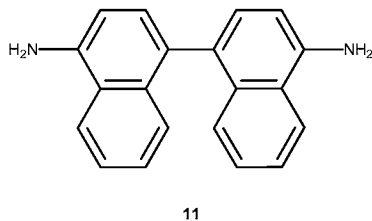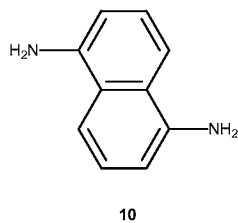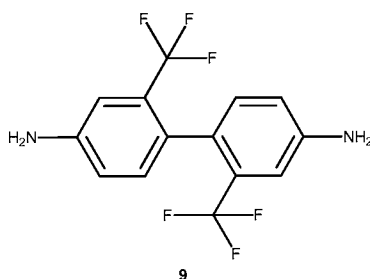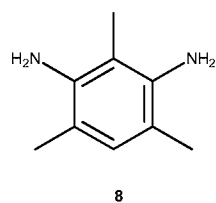
[026] Other dianhydrides or diamines suitable for forming the polyimides used herein include those of Formulae **15** (5,5'-[1,4-phenylenebis(1,3,4-oxadiazole-5,2-diyl)]bis-1,3-isobenzofurandione), **16** (5,5'-(1,3,4-oxadiazole-2,5-diyl)bis-1,3-isobenzofurandione), **17** (4,4'-(1,4-phenylene)-bis(1,3,4-oxadiazole-2,5-diyl)di(o-toluidine)), **18** (4,4'-methylenebis(2,6-diethyl-aniline)), **19** (4,4'-(hexafluoroisopropylidene)dianiline), and **20** (4,4'-(hexafluoroisopropylidene)-bis(p-phenyleneoxy)dianiline). These additional dianhydrides and diamines are shown below:
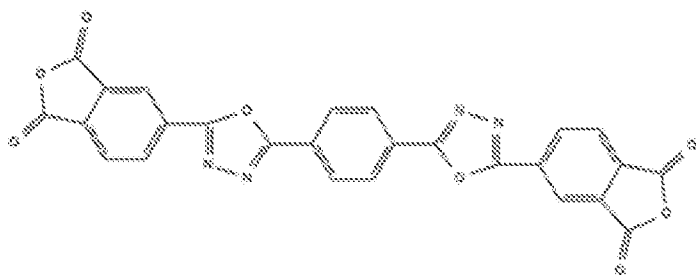
15
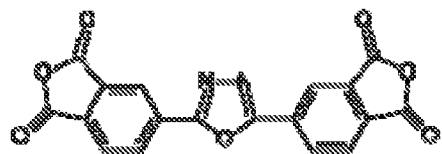
16
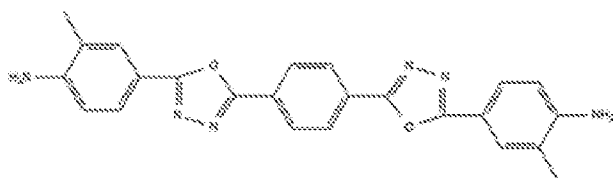
17

18

19

20

[027] In further embodiments, the nitrated styrenic fluoropolymer (a) has an average degree of substitution (DS) ranging from about 0.6 to about 0.8 for the nitro group(s) on the styrenic ring and the polyimide (b) is the reaction product of components comprising:

    i.   4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) in an amount from about 40 to about 60 molar percent, based on the total moles of (i) and (ii),

    ii.   4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNDA) in an amount from about 40 to about 60 molar percent, based on the total moles of (i) and (ii),

   iii.   2,4-diaminomesitylene (DAM) in an amount from about 60 to about 80 molar percent, based on the total moles of (iii) and (iv), and

   iv.   4,4'-(9-fluorenylidene)dianiline) (FRDA) in an amount from about 20 to about 40 molar percent, based on the total moles of (iii) and (iv).

[028] In another embodiment, the nitrated styrenic fluoropolymer (a) has an average degree of substitution (DS) ranging from about 0.6 to about 0.8 for the nitro group(s) on the styrenic ring and the polyimide (b) is the reaction product of components comprising:

    i.   4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) in an amount from about 40 to about 60 molar percent, based on the total moles of (i) and (ii),

    ii.   4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNDA) in an amount from about 40 to about 60 molar percent, based on the total moles of (i) and (ii), and
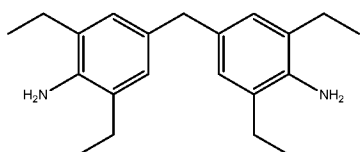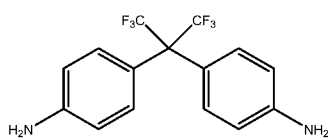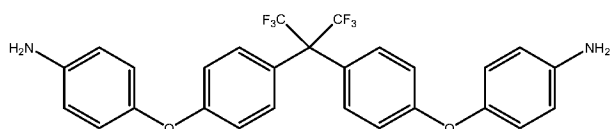
   iii.   2,4-diaminomesitylene (DAM).

[029] In yet another embodiment, the nitrated styrenic fluoropolymer (a) has an average degree of substitution (DS) ranging from about 0.6 to about 0.8 for the nitro group(s) on the styrenic ring and the polyimide (b) is the reaction product of components comprising:

    i.   4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) in an amount from about 20 to about 40 molar percent, based on the total moles of (i) and (ii),

    ii.   4,4'-(ethyne-1,2-diyl) diphthalic anhydride (EDDPA) in an amount from about 60 to about 80 molar percent, based on the total moles of (i) and (ii), and

   iii.   a mixture of 3,5-diethyl-toluene-2,6-diamine (2,6-DETDA) and 3,5-diethyl-toluene-2,4-diamine (2,4-DETDA).

[030] In certain embodiments disclosed herein, the optical compensation film is prepared by casting from a solution blend comprising one or more of nitrated styrenic fluoropolymers and one or more of polyimides. The solution blend may be prepared by mixing the fluoropolymer solution and the polyimide solution, or it may be prepared by dissolving a mixture of powdery fluoropolymer and polyimide in a solvent. Suitable solvents include methyl ethyl ketone, cyclopentanone, toluene, methyl isobutyl ketone, methylene chloride, chloroform, 1,2-

dichloroethane, methyl amyl ketone, methyl isopropyl ketone, methyl isoamyl ketone, ethyl acetate,n-butyl acetate, propylene glycol methyl ether acetate, and a mixture thereof. In another embodiment, the solution blend further comprises one or more additives that are capable of increasing the positive out-of-plane retardations of the optical compensation film of the invention and/or improving the desirable relations of $0.7 < R(450)/R(550) < 1$ and $1 < R(650)/R(550) < 1.25$, such as by facilitating the tuning or ease of control of the relations $R(450)/R(550)$ and $R(650)/R(550)$, both individually and relative to one another, with respect to the polymer blend and related films. Examples of the additives include, but are not limited to, IR absorbers, UV absorbers, and diimide compounds, which are prepared either by reacting a dianhydride with a monoamine or by reacting a diamine with a monoanhydride.

[031] In one embodiment, the optical compensation film of the invention is prepared by being solution cast on a substrate. The casting of a polymer solution onto a substrate may be carried out by a method known in the art such as, for example, spin coating, spray coating, roll coating, curtain coating, or dip coating. Substrates are known in the art, which include triacetylcellulose (TAC), cyclic olefin polymer (COP), polyester, polyvinyl alcohol, cellulose ester, cellulose acetate propionate (CAP), polycarbonate, polyacrylate, polyolefin, polyurethane, polystyrene, glass, other materials commonly used in LCD devices, and still other materials commonly used in OLED display devices.

[032] Preferably, the nitrated styrenic fluoropolymer component, when cast into film, has an out-of-plane birefringence (Δn_{th}) satisfying the equation of $\Delta n_{th} > 0.02$ or >0.025 or >0.03, or >0.035. Higher birefringence materials have an advantage in that they can provide sufficient positive out-of-plane retardations (R_{th}) as thin films to reduce or eliminate the negative R_{th} exhibited in polyimide films.

[033] When combined with an A-plate, the optical compensation film of this invention can eliminate the undesirable negative out-of-plane retardation present in the A-plate. Further, due to its reversed dispersion characteristics, the optical film of the invention can provide an achromatic compensation for optimal improvement of the viewing quality.

[034] Further embodiments comprise the optical compensation film described in embodiments herein and an A-plate having a refractive index profile of $n_x > n_y = n_z$, wherein n_x and n_y represent in-plane refractive indices, and n_z the thickness refractive index. In one embodiment, said A-plate is a quarter wave plate (QWP). In one embodiment, a QWP in combination with a linear

polarizer functions as a circular polarizer. Such a circular polarizer can be used in an OLED display device to reduce the ambient light and thus improve the viewing quality.

[035] The multilayer film of the present invention may be obtained by lamination,by solution casting, or by any other suitable means of creating a polymer film. In one embodiment, the solution of the polymer blend of the nitrated styrenic fluoropolymer (a) and the polyimide (b) is cast onto an A-plate to obtain a multilayer film.

[036] Similarly, embodiments disclosed herein comprising films of the polymer blend of the nitrated styrenic fluoropolymer (a) and the polyimide (b) can also be combined with a B-plate having a refractive index profile of $n_x > n_y \neq n_z$. In one aspect, said B-plate is a biaxial quarter wave plate (QWP). In another embodiment, a biaxial QWP in combination with a linear polarizer functions as a circular polarizer. Such a circular polarizer can be used in an OLED display device to reduce the ambient light and thus improve the viewing quality.

[037] The optical compensation film of the present invention may be used in a liquid crystal display device including an in-plane switching liquid crystal display device, in an OLED display device, in a 3D display device, in a circular polarizer, or in 3D glasses. Said display devices may be used for television, computer, mobile phone, camera, and other applications.

[038] In additional embodiments of the present invention, a polymer resin is provided. The polymer resin has a moiety of:

1
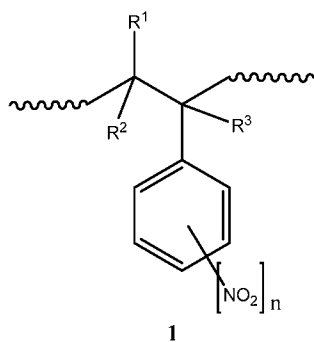
[039] wherein R^1, R^2, and R^3 are each independently hydrogen atoms, alkyl groups, substituted alkyl groups, or halogens, wherein at least one of R^1, R^2, and R^3 is a fluorine atom, and wherein n is an integer from 1 to 5 representing the number of the nitro group(s) on the styrenic ring.

[040] In certain embodiments, the polymer resin comprises a mixture or copolymer of a styrenic fluoropolymer (above) and a polyimide.

[041] In certain embodiments of the polymer resin, the DS for the nitro group is greater than 0.25. In certain embodiments the DS for the nitro group is greater than 0.4. In certain embodiments of the polymer resin, the DS for the nitro group is greater than 0.6. In certain embodiments of the polymer resin, the DS for the nitro group is greater than 0.8.

[042] In one embodiment of the present invention, a polymer solution is provided. The polymer solution comprises a solvent and a polymer having a styrenic moiety of:

1
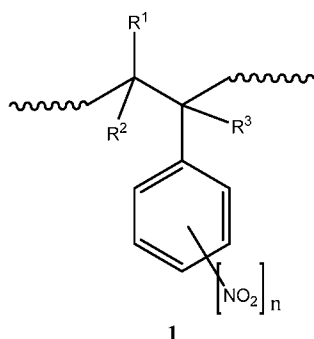
[043] wherein R^1, R^2, and R^3 are each independently hydrogen atoms, alkyl groups, substituted alkyl groups, or halogens, wherein at least one of R^1, R^2, and R^3 is a fluorine atom, and wherein n is an integer from 1 to 5 representing the number of the nitro group(s) on the styrenic ring.

[044] In certain embodiments, the polymer in the polymer solution comprises a mixture or copolymer of a styrenic fluoropolymer (above) and a polyimide.

[045] In certain embodiments of the polymer solution, the solvent is selected from the group consisting of: toluene, methyl isobutyl ketone, cyclopentanone, methylene chloride, 1,2-dichloroethane, methyl amyl ketone, methyl ethyl ketone, methyl isoamyl ketone, and mixtures thereof. In certain embodiments of the polymer solution, the solvent is selected from the group consisting of: methyl ethyl ketone, methylene chloride, cyclopentanone, and mixtures thereof.

[046] In certain embodiments of the polymer solution, the DS for the nitro group is greater than 0.25. In certain embodiments of the polymer solution, the DS for the nitro group is greater than 0.4. In certain embodiments of the polymer solution, the DS for the nitro group is greater than 0.6. In certain embodiments of the polymer solution, the DS for the nitro group is greater than 0.8.

[047]   When any of the resins described herein is combined with a solvent described herein to form a solution and then solution-cast as a film, the film formed from the resin exhibits the properties in accordance with the other embodiments disclosed herein.

EXAMPLES

[048]   The following examples describe and demonstrate exemplary embodiments of the polymers, polymer solutions, polymer films, and methods described herein. The exemplary embodiments are provided solely for the purpose of illustration and are not to be construed as limitations of the present disclosure, as many variations thereof are possible without departing from the spirit and scope of the present disclosure.

Example 1: Synthesis of Nitrated Poly(α,β,β-trifluorostyrene)(N-PTFS 1) Having DS= 0.68

[049]   Materials: Poly(α,β,β-trifluorostyrene)(PTFS) was an internal product with an intrinsic viscosity (IV) of 1.10dL/g, used as received. Dichloromethane (DCM) was from Acros, purified by passing through SiO_2. HNO_3 was from Acros (68%-70%), used as received. H2SO4 was from Sigma Aldrich (95.0%-98.0%), used as received.

[050]   To a one-liter three-neck round-bottom flask equipped with nitrogen inlet/outlet and a mechanical stirrer was charged a solution of PTFS (IV, 1.10 dL/g) in dichloromethane (DCM) (200 g, 5 weight %). Separately, a mixed acid solution was prepared by adding concentrated sulfuric acid (31.18 g) to nitric acid (11.75 g). The flask was placed in a water bath at room temperature. To the stirred PTFS solution in the flask was added the mixed acid over a period of 10 minutes. The reaction mixture was allowed to react at room temperature for 23 hours and was subsequently quenched by adding deionized water/ice (500 ml). The water phase at the top was then decanted and the organic phase washed repeatedly with deionized water to remove the acids. The resulting organic layer was precipitated into methanol (about one liter) and ground in a high speed blender to yield a powder suspension. The powder was then filtered and washed repeatedly with water and methanol. The resulting product was dried at 80°C under reduced pressure overnight. Intrinsic viscosity (IV) of the polymer was 1.20 dL/g, measured by a Cannon® auto capillary viscometer using N-methyl-2-pyrrolidone (NMP) as the solvent at 30°C. The degree of substitution (DS) of the nitro group in the product was determined to be 0.68 by elemental analysis (EA).

Example 2: Synthesis of Nitrated Poly(α,β,β-trifluorostyrene)(N-PTFS 2) Having DS= 0.86

[051]   To a one-liter three-neck round-bottom flask equipped with nitrogen inlet/outlet and a mechanical stirrer was charged a solution of PTFS (IV, 1.10 dL/g) in dichloromethane (DCM) (322 g, 5 weight %). Separately, a mixed acid solution was prepared by adding concentrated sulfuric acid (70.60 g) to nitric acid (27.81 g). The flask was placed in a water bath at room temperature. To the stirred PTFS solution in the flask was added the mixed acid over a period of 10 minutes. The reaction mixture was allowed to react at room temperature for 21 hours and subsequently quenched by adding deionized water/ice (800 ml). The water phase at the top was then decanted and the organic phase washed repeatedly with deionized water to remove the acids. The resulting organic layer was precipitated into methanol (about 1.5 liters) and ground in a high speed blender to yield a powder suspension. The powder was then filtered and washed repeatedly with water and methanol. The resulting product was dried at 80°C under reduced pressure overnight. Intrinsic viscosity (IV) of the polymer was 1.20 dL/g, measured by a Cannon® auto capillary viscometer using N-methyl-2-pyrrolidone (NMP) as the solvent at 30°C. The degree of substitution (DS) of the nitro group in the product was determined to be 0.86 by elemental analysis (EA).

Example 3: Synthesis of Polyimide 1 (6FDA/BNDA/DAM, 50/50/100)

[052]   DAM-BNDA-DAM diamine was prepared by reacting 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNDA) with an excess of 2,4-diaminomesitylene (DAM) (molar ratio DAM/BNDA >2.5) in m-cresol at 180°C for 18 hours. The reaction solution was precipitated into an excess of methanol to yield a powder product. The product was then filtered and washed repeatedly with methanol. The resulting product was dried at 80°C under reduced pressure overnight and ready for the next step polymerization.

[053]   To a 100ml three-neck round-bottom flask equipped with nitrogen inlet/outlet and a mechanical stirrer were charged N,N-dimethylacetamide (DMAc) (22ml), DAM-BNDA-DAM (3.2945 g, 5.00 mmol) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (2.1790 g, 4.91 mmol). The reaction mixture was allowed to react at room temperature for 18 hours,

followed by the addition of pyridine (1.0 ml) and acetic anhydride (2.5 ml). The reaction was allowed to continue at 120 °C for two hours. After cooling down, the resulting solution was precipitated into methanol (about 100ml) to yield a fibrous product. The product was then filtered and washed repeatedly with methanol. The resulting product was dried at 80°C under reduced pressure overnight. Intrinsic viscosity (IV) of the polymer was 1.07 dL/g, measured by a Cannon® auto capillary viscometer using N-methyl-2-pyrrolidone (NMP) as the solvent at 30°C.

Example 4: Preparation of Polymer Films Cast from Blends of N-PTFS and Polyimide 1 (6FDA/BNDA/DAM, 50/50/100)

[054] Polymer films were prepared by using N-PTFS 1 and N-PTFS 2 respectively and polyimide 1(6FDA/BNDA/DAM, 50/50/100) at various ratios. A 10 wt.% solution of N-PTFS was prepared by dissolving N-PTFS solid in cyclopentanone. Separately, a 10 wt.% solution of polyimide 1 was prepared in cyclopentanone. The polymer blend solutions were then prepared by mixing the two solutions at various ratios by weight as listed in Table 1, below. The prepared homogenous and clear blend solutions were applied to flat glass substrates using the blade casting method. The coating films were allowed to dry in air overnight and subsequently placed in a vacuum oven at 80°C-150°C for 2 hours. After drying, the films were peeled off. The films were clear.

Example 5: Properties of Polymer Films Cast from Blends of N-PTFS and Polyimide 1 (6FDA/BNDA/DAM, 50/50/100)

[055] Birefringence and thickness of the free standing films were measured by the Metricon Model 2010/M Prism Coupler using single film mode at a wavelength of 633nm. The retardation and the dispersion were determined by the J. A. Woollam M-2000 or RC2 Ellipsometry. The birefringence at 633nm, the thickness, and the dispersion factors $R(450)/R(550)$ and $R(650)/R(550)$ are listed in Table 1.

Table 1. N-PTFS/Polyimide 1 Blend Films

ID	N-PTFS	Polyimide (PI)	N-PTFS/PI weight ratio	Δn^{633nm}	Thickness µm	R(450)/ R(550)	R(650)/ R(550)
Film 1			80.3/19.7	0.0137	15	0.939	1.002
Film 2			77.6/22.4	0.0122	17	0.890	1.014
Film 3	DS=0.68		75.6/24.4	0.0101	15	0.858	1.027
Film 4			73.6/26.4	0.0088	14	0.801	1.040
Film 5			71.6/28.4	0.0076	16	0.738	1.060
Film 6		Polyimide 1 6FDA/BNDA/DAM (50/50/100)	69.2/30.8	0.0060	15	0.592	1.108
Film 7			80.0/20.0	0.0169	14	0.959	0.994
Film 8			77.9/22.1	0.0149	14	0.932	1.001
Film 9	DS=0.86		75.3/24.7	0.0127	15	0.874	1.019
Film 10			74.0/26.0	0.0115	15	0.843	1.024
Film 11			70.9/29.1	0.0095	15	0.753	1.050
Film 12			68.5/31.5	0.0078	15	0.666	1.075

Example 6: Synthesis of Polyimide 2 (6FDA/EDDPA/DAM, 50/50/100)

[056] To a 100ml three-neck round-bottom flask equipped with nitrogen inlet/outlet and a mechanical stirrer were charged DMAc (24ml), DAM (1.5037 g, 10.01 mmol), 4,4'-(ethyne-1,2-diyl) diphthalic anhydride (EDDPA) (1.5926 g, 5.00 mmol), and 6FDA (2.2285 g, 5.02 mmol). The reaction mixture was allowed to react at room temperature for 18 hours, followed by the addition of pyridine (2.0 ml) and acetic anhydride (5.0 ml). The reaction was allowed to continue at 120 °C for two hours. After cooling down, the resulting solution was precipitated into methanol (about 100 ml) to yield a fibrous product. The product was then filtered and washed repeatedly with methanol. The resulting product was dried at 80°C under reduced pressure overnight. Intrinsic viscosity (IV) of the polymer was 1.35 dL/g, measured by a Cannon® auto capillary viscometer using N-methyl-2-pyrrolidone (NMP) as the solvent at 30°C.

Example 7: Preparation of Polymer Films Cast from Blends of N-PTFS and Polyimide 2 (6FDA/EDDPA/DAM)

[057] Polymer films were prepared by using N-PTFS 1 and N-PTFS 2 respectively and polyimide 2 (6FDA/EDDPA/DAM, 50/50/100) at various ratios. A 10 wt.% solution of N-PTFS was prepared by dissolving N-PTFS solid in cyclopentanone. Separately a 10 wt.% solution of polyimide 2 was prepared in cyclopentanone. The polymer blend solutions were then prepared by mixing the two solutions at various ratios as listed in table 2. The prepared homogenous and clear blend solutions were applied to flat glass substrates using the blade casting method. The coating films were allowed to dry in air overnight and subsequently placed in a vacuum oven at 80°C-150°C for 2 hours. After drying, the films were peeled off. The films were clear.

Example 8: Properties of Polymer Films Cast from Blends of N-PTFS and Polyimide 2 (6FDA/EDDPA/DAM, 50/50/100)

[058] Birefringence and thickness of the free standing films were measured by the Metricon Model 2010/M Prism Coupler using single film mode at a wavelength of 633nm. The retardation and the dispersion were determined by the J. A. Woollam M-2000 or RC Ellipsometry. The birefringence at 633nm, the thickness, the dispersion factors R(450)/R(550) and R(650)/R(550) are listed in Table 2.

Table 2. N-PTFS/Polyimide 2 Blend Films

ID	N-PTFS	Polyimide (PI)	N-PTFS/PI weight ratio	Δn^{633nm}	Thickness μm	R(450)/ R(550)	R(650)/ R(550)
Film 13			84.1/15.9	0.0185	9.3	1.013	0.988
Film 14			79.8/20.2	0.0160	9.2	0.958	1.001
Film 15			78.2/21.9	0.0131	9.1	0.955	1.004
Film 16	DS=0.68		76.0/24.0	0.0114	9.2	0.919	1.013
Film 17			74.3/25.7	0.0099	9.2	0.895	1.017
Film 18			72.2/27.8	0.0077	9.3	0.828	1.032
Film 19		Polyimide 2 6FDA/EDDPA/DAM (50/50/100)	69.9/30.1	0.0063	9.5	0.722	1.076
Film 20			68.2/31.8	0.0047	9.8	0.616	1.101
Film 21			83.8/16.2	0.0192	9.1	1.021	0.979
Film 22			80.0/20.0	0.0162	9.1	1.001	0.988
Film 23			78.2/21.8	0.0147	9.2	0.973	1.000
Film 24	DS=0.86		75.9/24.1	0.0127	9.1	0.945	1.007
Film 25			73.7/26.3	0.0108	7.7	0.913	1.010
Film 26			72.2/27.8	0.0094	10.2	0.874	1.030
Film 27			70.0/30.0	0.0076	10.1	0.803	1.039
Film 28			67.8/32.2	0.0057	9.7	0.708	1.069

Example 9: Synthesis of Nitrated Poly(α,β,β-trifluorostyrene) (N-PTFS 3) Having DS= 0.72

[059] Poly(α,β,β-trifluorostyrene) (PTFS; IV, 1.10 dL/g) (1.2 kg) was mixed with 1,2-dichloroethane (13.8 kg) in a 19 L reactor under nitrogen. The mixture was heated to 50 °C with agitation. Once all solids dissolved, the mixture was further heated to 55 °C, upon which a pre-made mixture of sulfuric acid (98%, 2.89 kg) and nitric acid (69%, 1.12 kg) was added in 2.5 hours. The mixture was then heated to 60 °C and held for 4 hours. Propionic acid (13.3 kg) was added to precipitate the product while the mixture was being cooled to room temperature. The resulting suspension was filtered, and the crude powder product was washed first with propionic acid twice and then with methanol repeatedly. The resulting product was dried at 60 °C under reduced pressure to give 1.3 kg powder product. The degree of substitution (DS) of the nitro group in the product was determined to be 0.72 by elemental analysis (EA).

Example 10: Synthesis of Polyimide 3 (6FDA/BNDA/DAM/FRDA, 50/50/70/30)

[060] DAM-BNDA-DAM diamine was prepared by reacting 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNDA) with an excess of 2,4-diaminomesitylene (DAM) (molar ratio DAM/BNDA >2.5) in m-cresol at 180°C for 18 hours. The reaction solution was precipitated into an excess of methanol to yield a powder product. The product was then filtered and washed repeatedly with methanol. The resulting product was dried at 80°C under reduced pressure overnight and ready for the next step polymerization.

[061] FRDA-BNDA-FRDA diamine was prepared by reacting 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNDA) with an excess of 4,4'-(9-fluorenylidene)dianiline (FRDA) (molar ratio FRDA/BNDA >2.5) in m-cresol at 180°C for 18 hours. The reaction solution was precipitated into an excess of methanol to yield a powder product. The product was then filtered and washed repeatedly with methanol. The resulting product was dried at 80°C under reduced pressure overnight and ready for the next step polymerization.

[062] To a 100ml three-neck round-bottom flask equipped with nitrogen inlet/outlet and a mechanical stirrer were charged N,N-dimethylacetamide (DMAc) (20ml), DAM-BNDA-DAM (1.845 g, 2.80 mmol), FRDA-BNDA-FRDA (1.266 g, 1.20 mmol) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (1.777 g, 4.00 mmol). The reaction mixture was allowed to react at room temperature for 18 hours, followed by the addition of pyridine (1.0 ml) and acetic anhydride (2.5 ml). The reaction was allowed to continue at 120 °C for two hours. After cooling down, the resulting solution was precipitated into methanol (about 100ml) to yield a fibrous product. The product was then filtered and washed repeatedly with methanol. The resulting product was dried at 80°C under reduced pressure overnight. Intrinsic viscosity (IV) of the polymer was 0.49dL/g, measured by a Cannon® auto capillary viscometer using N-methyl-2-pyrrolidone (NMP) as the solvent at 30°C.

Example 11: Preparation of Polymer Films Cast from Blends of N-PTFS and Polyimide 3 (6FDA/BNDA/DAM/FRDA, 50/50/70/30)

[063] Polymer films were prepared by using N-PTFS 3 (DS=0.72) and polyimide 3 (6FDA/BNDA/DAM/FRDA, 50/50/70/30) at various ratios. A 10 wt.% solution of N-PTFS was prepared by dissolving N-PTFS solid in cyclopentanone. Separately, a 10 wt.% solution of polyimide 3 was prepared in cyclopentanone. The polymer blend solutions were then prepared by mixing the two solutions at various ratios as listed in Table 3. The prepared homogenous and clear blend solutions were applied to flat glass substrates using the blade casting method. The coating films were allowed to dry in air overnight and subsequently placed in a vacuum oven at 80°C-150°C for 2 hours. After drying, the films were peeled off. The films were clear.

Example 12: Properties of Polymer Films Cast from Blends of N-PTFS and Polyimide 3 (6FDA/BNDA/DAM/FRDA, 50/50/70/30)

[064] Birefringence and thickness of the free standing films were measured by the Metricon Model 2010/M Prism Coupler using single film mode at a wavelength of 633nm. The retardation and the dispersion were determined by the J. A. Woollam RC2 Ellipsometry. The birefringence at 633nm, the thickness, and the dispersion factors R(450)/R(550) and R(650)/R(550) are listed in Table 3.

Table 3. N-PTFS/Polyimide 3 Blend Films

ID	N-PTFS	Polyimide (PI)	N-PTFS/PI weight ratio	Δn^{633nm}	Thickness µm	R(450)/ R(550)	R(650)/ R(550)
Film 29			83.9/16.1	0.0196	9.0	1.01	0.98
Film 30			81.9/18.1	0.0179	8.8	0.99	0.98
Film 31			79.6/20.4	0.0161	9.6	0.96	0.99
Film 32			77.8/22.2	0.0150	9.2	0.95	1.00
Film 33		Polyimide 3	75.9/24.1	0.0138	9.1	0.91	1.00
Film 34	DS=0.72	6FDA/BNDA/DAM/FRDA	73.9/26.1	0.0124	9.1	0.88	1.02
Film 35		(50/50/70/30)	72.0/28.0	0.0112	9.5	0.84	1.02
Film 36			70.0/30.0	0.0095	9.0	0.77	1.04
Film 37			67.9/32.1	0.0081	9.7	0.70	1.05
Film 38			66.0/34.0	0.0069	9.8	0.57	1.09
Film 39			0/100	-0.0297	11.6	1.34	0.90

Example 13: Synthesis of Polyimide 4 (6FDA/EDDPA/DETDA, 30/70/100)

[065]   To a 5000ml three-neck round-bottom flask equipped with nitrogen inlet/outlet and a mechanical stirrer were charged N,N-dimethylacetamide (DMAc) (1524g), DETDA (169.1 g, 950 mmol), EDDPA (211.3 g, 665 mmol) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (126.4 g, 285 mmol). The reaction mixture was allowed to react at room temperature for 18 hours, followed by the addition of pyridine and acetic anhydride. The reaction was allowed to continue at 120 °C for two hours. After cooling down, the resulting solution was blended with methanol (5 times volume) to yield a polymer product. The product was then filtered and washed repeatedly with methanol. The resulting product was dried at 80°C under reduced pressure overnight. Intrinsic viscosity (IV) of the polymer was 0.88 dL/g, measured by a Cannon® auto capillary viscometer using N-methyl-2-pyrrolidone (NMP) as the solvent at 30°C.

Example 14: Preparation of Polymer Films Cast from Blends of N-PTFS and Polyimide 4 (6FDA/EDDPA/DETDA, 30/70/100)

[066]   Polymer films were prepared by using N-PTFS 3 (DS=0.72) and polyimide 4 (6FDA/EDDPA/DETDA, 30/70/100) at various ratios. A 10 wt.% solution of N-PTFS was prepared by dissolving N-PTFS solid in cyclopentanone. Separately, a 10 wt.% solution of polyimide 4 was prepared in cyclopentanone. The polymer blend solutions were then prepared by mixing the two solutions at various ratios as listed in Table 4. The prepared homogenous and clear blend solutions were applied to flat glass substrates using the blade casting method. The coating films were allowed to dry in air overnight and subsequently placed in a vacuum oven at 80°C-150°C for 2 hours. After drying, the films were peeled off. The films were clear.

Example 15: Properties of Polymer Films Cast from Blends of N-PTFS and Polyimide 4 (6FDA/EDDPA/DETDA, 30/70/100)

[067]   Birefringence and thickness of the free standing films were measured by the Metricon Model 2010/M Prism Coupler using single film mode at a wavelength of 633nm. The retardation and the dispersion were determined by the J. A. Woollam RC2 Ellipsometry. The birefringence

at 633nm, the thickness, and the dispersion factors R(450)/R(550) and R(650)/R(550) are listed in Table 4.

Table 4. N-PTFS/Polyimide 4 Blend Films

ID	N-PTFS	Polyimide (PI)	N-PTFS/PI weight ratio	Δn^{633nm}	Thickness µm	R(450)/ R(550)	R(650)/ R(450)
Film 40			86.4/13.6	0.0182	8.5	1.01	0.96
Film 41		Polyimide 4	80.4/19.6	0.0124	9.1	0.94	0.98
Film 42	DS=0.72	6FDA/EDDPA/DETDA	77.9/22.1	0.0101	8.8	0.88	1.00
Film 43		30/70/100	75.9/24.1	0.0084	8.9	0.83	1.04
Film 44			0/100	-0.0437	11.1	1.24	0.90

Claims

1. An optical compensation film, which is made by solution casting of a polymer blend comprising

    (a) a nitrated styrenic fluoropolymer and

    (b) a polyimide,

    wherein said optical compensation film has positive out-of-plane retardations that satisfy the relations of $0.7 < R(450)/R(550) < 1$ and $1 < R(650)/R(550) < 1.25$, wherein $R(450)$, $R(550)$, and $R(650)$ are out-of-plane retardations at the light wavelengths of 450 nm, 550 nm, and 650 nm respectively and wherein the nitrated styrenic fluoropolymer has a styrenic moiety of:

1

    wherein R^1, R^2, and R^3 are each independently hydrogen atoms, alkyl groups, substituted alkyl groups, or halogens, wherein at least one of R^1, R^2, and R^3 is a fluorine atom, and wherein n is an integer from 1 to 5 representing the number of the nitro group(s) on the styrenic ring.

2. The optical compensation film of claim 1, wherein the positive out-of-plane retardations satisfy the relations of $0.8 < R(450)/R(550) < 0.9$ and $1.01 < R(650)/R(550) < 1.2$.

3. The optical compensation film of claim 1, wherein the nitrated styrenic fluoropolymer (a) is from about 60% to about 90% and the polyimide (b) is from about 10% to about 40%, based on the total weight of (a) and (b).

4. The optical compensation film of claim 1, wherein the nitrated styrenic fluoropolymer has an average degree of substitution ranging from about 0.5 to about 0.9 for the nitro group(s) on the styrenic ring.

5. The optical compensation film of claim 1, wherein the nitrated styrenic fluoropolymer is poly(α,β,β-trifluorostyrene).

6. The optical compensation film of claim 1, wherein the polyimide is a reaction product ofcomponents comprising an aromatic dianhydride and an aromatic diamine.

7. The optical compensation film of claim 6, wherein the aromatic dianhydride is selected from the group consisting of pyromellitic dianhydride (PMDA) (2), 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) (3), 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (4), 4,4'-(ethyne-1,2-diyl) diphthalic anhydride (EDDPA) (5), 4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNDA) (6), 1,4,5,8-naphthalenetetracarboxylic dianhydride (NDA) (7), all shown below:
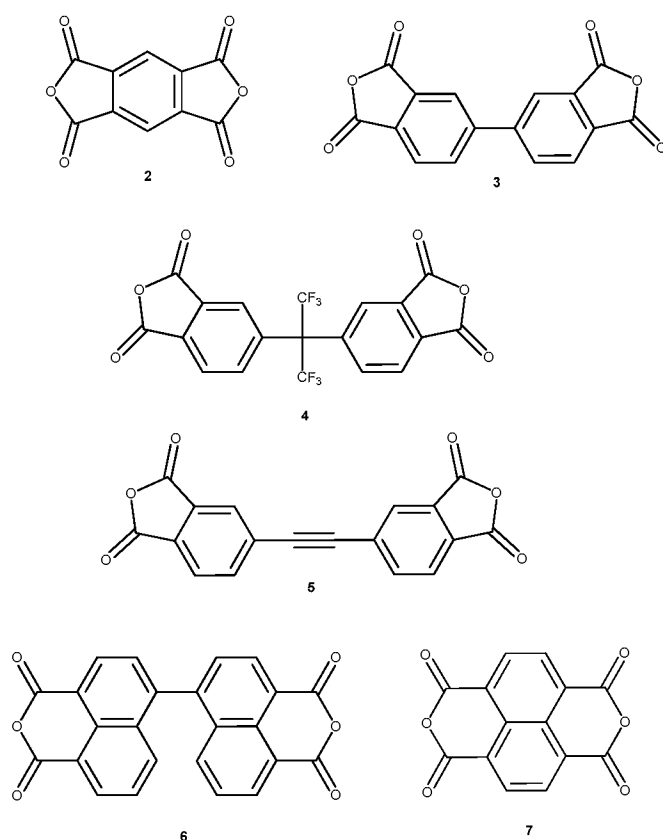
and combinations thereof.

8. The optical compensation film of claim 6, wherein the aromatic diamine is selected from the group consisting of 2,4-diaminomesitylene (DAM) (8), 2,2'-bis(trifluoromethyl)benzidine (PFMB) (9), 1,5-naphthalenediamine (DAN) (10), [1,1'-binaphthalene]-5,5'-diamine (DABN) (11), 3,5-diethyl-toluene-2,6-diamine (2,6-DETDA) (12), 3,5-diethyl-toluene-2,4-diamine (2,4-DETDA) (13), 4,4'-(9-fluorenylidene)dianiline) (FRDA) (14), all shown below:
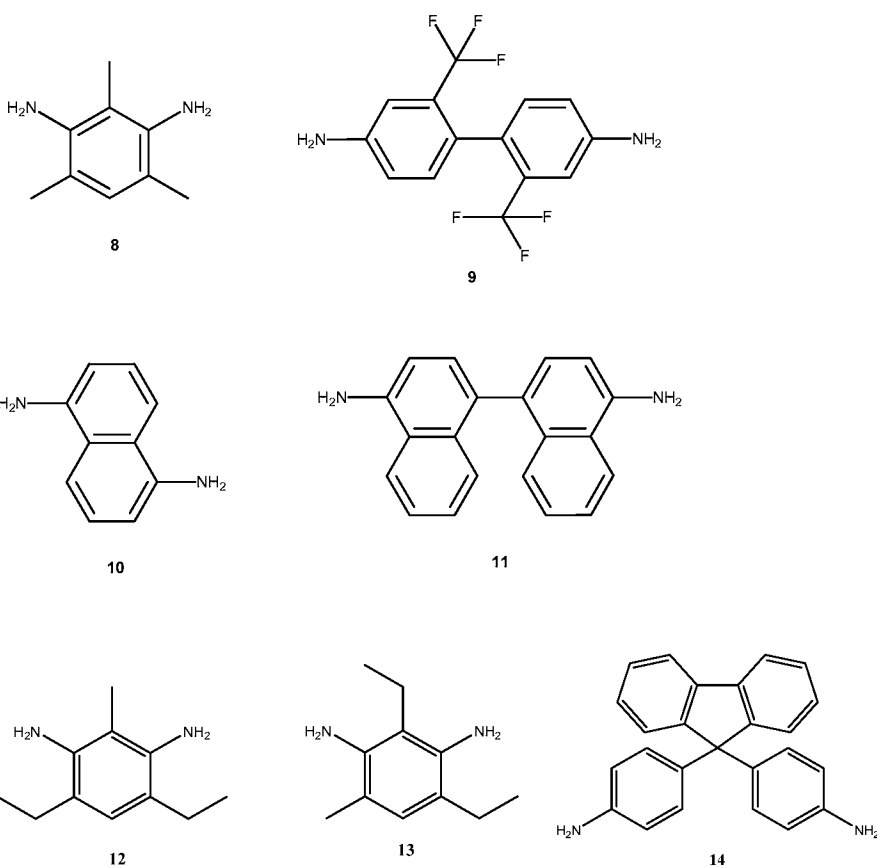
and combinations thereof.

9. The optical compensation film of claim 6, wherein the aromatic dianhydride is selected from
   the group consisting of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (4),
   4,4'-(ethyne-1,2-diyl) diphthalic anhydride (EDDPA) (5), 4,4'-binaphthyl-1,1',8,8'-
   tetracarboxylic dianhydride (BNDA) (6), and combinations thereof.

10. The optical compensation film of claim 6, wherein the aromatic diamine is selected from the
    group consisting of 2,4-diaminomesitylene (DAM) (8), 3,5-diethyl-toluene-2,6-diamine (2,6-
    DETDA) (12), 3,5-diethyl-toluene-2,4-diamine (2,4-DETDA) (13), 4,4'-(9-
    fluorenylidene)dianiline (FRDA) (14), and combinations thereof.

11. The optical compensation film of claim 6, wherein the aromatic dianhydride is selected from
    the group consisting of 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (6FDA) (4),
    4,4'-(ethyne-1,2-diyl) diphthalic anhydride (EDDPA) (5), 4,4'-binaphthyl-1,1',8,8'-
    tetracarboxylic dianhydride (BNDA) (6), and combinations thereof, and the aromatic diamine
    is selected from the group consisting of 2,4-diaminomesitylene (DAM) (8), 3,5-diethyl-

toluene-2,6-diamine (2,6-DETDA) (12), 3,5-diethyl-toluene-2,4-diamine (2,4-DETDA) (13), 4,4'-(9-fluorenylidene)dianiline (FRDA) (14), and combinations thereof.

12. The optical compensation film of claim 1, wherein the nitrated styrenic fluoropolymer (a) has an average degree of substitution ranging from about 0.6 to about 0.8 for the nitro group(s) on the styrenic ring and the polyimide (b) is the reaction product of components comprising

    i.   4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) in an amount from about 40 to about 60 molar percent, based on the total moles of (i) and (ii);

    ii.   4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNDA) in an amount from about 40 to about 60 molar percent, based on the total moles of (i) and (ii);

    iii.   2,4-diaminomesitylene (DAM) in an amount from about 60 to about 80 molar percent, based on the total moles of (iii) and (iv); and

    iv.   4,4'-(9-fluorenylidene)dianiline (FRDA) in an amount from about 20 to about 40 molar percent, based on the total moles of (iii) and (iv).

13. The optical compensation film of claim 1, wherein the nitrated styrenic fluoropolymer (a) has an average degree of substitution ranging from about 0.6 to about 0.8 for the nitro group(s) on the styrenic ring and the polyimide (b) is the reaction product of the components comprising

    i.   4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) in an amount from about 40 to about 60 molar percent, based on the total moles of (i) and (ii);

    ii.   4,4'-binaphthyl-1,1',8,8'-tetracarboxylic dianhydride (BNDA) in an amount from about 40 to about 60 molar percent, based on the total moles of (i) and (ii); and

    iii.   2,4-diaminomesitylene (DAM).

14. The optical compensation film of claim 1, wherein the nitrated styrenic fluoropolymer (a) has an average degree of substitution ranging from about 0.6 to about 0.8 for the nitro group(s) on the styrenic ring and the polyimide (b) is the reaction product of the components comprising:

    i.   4,4'-(hexafluoroisopropylidene)-diphthalic anhydride (6FDA) in an amount from about 20 to about 40 molar percent, based on the total moles of (i) and (ii);

    ii.   4,4'-(ethyne-1,2-diyl) diphthalic anhydride (EDDPA) in an amount from about 60 to about 80 molar percent, based on the total moles of (i) and (ii); and

iii.   a mixture of 3,5-diethyl-toluene-2,6-diamine (2,6-DETDA) and 3,5-diethyl-toluene-2,4-diamine (2,4-DETDA).

15. The optical compensation film of claim 1, wherein the film has a positive out-of-plane retardation from about 100 nm to about 150 nm at the wavelength (λ) 550 nm and a film thickness from about 5 micron (μm) to about 20 micron (μm).

16. A multilayer optical film comprising the optical compensation film of claim 1 and an A-plate having a refractive index profile of $n_x>n_y=n_z$, wherein n_x and n_y represent in-plane refractive indices, and n_z the thickness refractive index.

17. A multilayer optical film comprising the optical compensation film of claim 1 and a B-plate having a refractive index profile of $n_x>n_y\neq n_z$, wherein n_x and n_y represent in-plane refractive indices, and n_z the thickness refractive index.
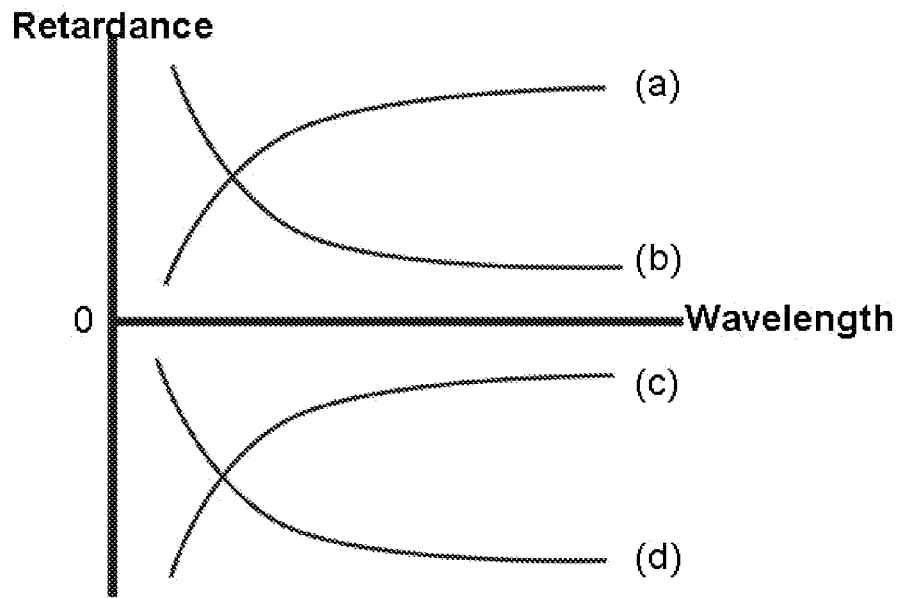
1/1

FIG. 1

A.	CLASSIFICATION OF SUBJECT MATTER

G02B 5/20(2006.01)i, C07D 493/04(2006.01)i, C07D 307/89(2006.01)i, C07D 311/78(2006.01)i

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)
G02B 5/20; G02B 1/08; B32B 7/02; C08G 69/44; C07C 217/90; G02B 5/30; C08G 73/16; C08G 73/10; B32B 7/00; C07C 213/02; H05K 7/06; C07D 493/04; C07D 307/89; C07D 311/78

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility model

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: optical compensation film, fluoropolymer, polyimide, out-of-plane retardation, degree of substitution

C.	DOCUMENTS CONSIDERED TO BE RELEVANT	

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 9234987 B2 (AKRON POLYMER SYSTEMS, INC.) 12 January 2016 See claims 1-3, 8, 15.	1-3,5-7,16
A		4,8-15,17
Y	US 8545970 B2 (DOI et al.) 01 October 2013 See column 12, lines 11-17; and claims 1, 24.	1-3,5-7,16
Y	US 2003-0212243 A1 (HERGENROTHER et al.) 13 November 2003 See paragraph [0009]; and claim 1.	6-7
A	US 2013-0279126 A1 (CHEN et al.) 24 October 2013 See figure 5.	1-17
A	US 6069278 A (CHUANG) 30 May 2000 See column 8, line 3 - column 9, line 40.	1-17

☐ Further documents are listed in the continuation of Box C.	☒ See patent family annex.

* Special categories of cited documents:	"T" later document published after the international filing date or priority
"A" document defining the general state of the art which is not considered to be of particular relevance	date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"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
"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)	"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
"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	"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 November 2017 (20.11.2017)	**21 November 2017 (21.11.2017)**

Name and mailing address of the ISA/KR	Authorized officer
International Application Division Korean Intellectual Property Office 189 Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea	KANG, Sung Chul
Facsimile No. +82-42-481-8578	Telephone No. +82-42-481-8405

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 9234987 B2	12/01/2016	CN 101765805 A	30/06/2010
		CN 101765805 B	04/01/2012
		CN 102197331 A	21/09/2011
		CN 102197331 B	23/03/2016
		CN 103189427 A	03/07/2013
		CN 103189427 B	05/08/2015
		CN 104245825 A	24/12/2014
		CN 104918993 A	16/09/2015
		EP 2135133 A2	23/12/2009
		EP 2340461 A2	06/07/2011
		EP 2340461 B1	07/05/2014
		EP 2619255 A2	31/07/2013
		EP 2706402 A2	12/03/2014
		EP 2706402 A3	17/09/2014
		EP 2706402 B1	01/02/2017
		EP 2914653 A1	09/09/2015
		EP 2914653 A4	22/06/2016
		JP 2010-522900 A	08/07/2010
		JP 2012-500997 A	12/01/2012
		JP 2013-539076 A	17/10/2013
		JP 2015-517585 A	22/06/2015
		JP 2016-502683 A	28/01/2016
		JP 5539853 B2	02/07/2014
		JP 6054605 B2	27/12/2016
		JP 6095228 B2	15/03/2017
		JP 6162794 B2	12/07/2017
		KR 10-1457730 B1	03/11/2014
		KR 10-1483158 B1	15/01/2015
		KR 10-1702672 B1	06/02/2017
		KR 10-2015-0012254 A	03/02/2015
		KR 10-2015-0104087 A	14/09/2015
		TW 200900814 A	01/01/2009
		TW 201022337 A	16/06/2010
		TW I442141B	21/06/2014
		TW I480318B	11/04/2015
		US 2008-0239491 A1	02/10/2008
		US 2009-0068380 A1	12/03/2009
		US 2011-0076487 A1	31/03/2011
		US 2012-0283371 A1	08/11/2012
		US 2014-0126055 A1	08/05/2014
		US 2014-0350166 A1	27/11/2014
		US 8226860 B2	24/07/2012
		US 8802238 B2	12/08/2014
		US 8889043 B2	18/11/2014
		US 9011992 B2	21/04/2015
		US 9255192 B2	09/02/2016
		WO 2008-121580 A2	09/10/2008
		WO 2008-121580 A3	20/11/2008
		WO 2010-053500 A2	14/05/2010

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
		WO 2010-053500 A3	01/07/2010
		WO 2012-040366 A2	29/03/2012
		WO 2012-040366 A3	31/05/2012
		WO 2013-165806 A1	07/11/2013
		WO 2014-071288 A1	08/05/2014
US 8545970 B2	01/10/2013	CN 101140334 A	12/03/2008
		CN 101140334 B	20/04/2011
		EP 1898252 A1	12/03/2008
		EP 1898252 B1	30/04/2014
		JP 2008-064817 A	21/03/2008
		JP 2008-112141 A	15/05/2008
		JP 2008-129465 A	05/06/2008
		JP 4697098 B2	08/06/2011
		JP 4905082 B2	28/03/2012
		JP 5245109 B2	24/07/2013
		KR 10-1594339 B1	16/02/2016
		KR 10-2008-0022062 A	10/03/2008
		TW 200821351 A	16/05/2008
		TW I406899B	01/09/2013
		US 2008-0068545 A1	20/03/2008
US 2003-0212243 A1	13/11/2003	AU 2003-230823 A1	27/10/2003
		US 6958192 B2	25/10/2005
		WO 2003-087194 A1	23/10/2003
US 2013-0279126 A1	24/10/2013	CN 103374130 A	30/10/2013
		CN 103374130 B	20/01/2016
		TW 201343719 A	01/11/2013
		TW I460211 B	11/11/2014
US 06069278 A	30/05/2000	US 5939521 A	17/08/1999
		US 6037499 A	14/03/2000