United States Patent

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NEGATIVE BIREFRINGENT POLYIMIDE FILMS

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A negative birefringent film, useful in liquid crystal displays, and a method for controlling the negative birefringence of a polyimide film is disclosed which allows the matching of an application to a targeted amount of birefringence by controlling the degree of in-plane orientation of the polyimide by the selection of functional groups within both the diamine and dianhydride segments of the polyimide which affect the polyimide backbone chain rigidity, linearity, and symmetry. The higher the rigidity, linearity and symmetry of the polyimide backbone, the larger the value of the negative birefringence of the polyimide film.

26 Claims, 5 Drawing Sheets
FIG. 1

REFRACTIVE INDEX (n)

% PMDA-TFMB COMPOSITION

FIG. 2
NEGATIVE BIREFRINGENT POLYIMIDE FILMS

This invention was made with Government support under DMR 91-57738 and DMR 89-20147 awarded by the National Science Foundation, and under NAG 1-448 awarded by NASA. The Government has certain rights in this invention.

This is a continuation-in-part of pending application Ser. No. 08/051,068 filed on Apr. 21, 1993.

TECHNICAL FIELD

The invention described herein pertains generally to negative birefringent soluble polyimide films for use in a compensator layer in a liquid crystal display,

BACKGROUND OF THE INVENTION

Liquid crystals are useful for electronic displays because light travelling through a thin film of liquid crystal is affected by the birefringence of the film, which can be controlled by the application of a voltage across the film. Liquid crystal displays are desirable because the transmission or reflection of light from an external source, including ambient light, can be controlled with much less power than is required for luminescent materials used in other displays. Liquid crystal displays are now commonly used in such applications as digital watches, calculators, portable computers, and many other types of electronic equipment where the need exists for long-lived operation, with very low voltage and low power consumption. In particular, portable computer displays benefit from liquid crystal displays where display power utilization must be minimized to permit the battery to operate for as long a period of time as possible before recharging, while allowing the majority of the battery utilization to be directed toward computational efforts.

When viewed directly, a liquid crystal display provides a high quality output. However, at large viewing angles, the image degrades and exhibits poor contrast. This occurs because liquid crystal cells operate by virtue of the birefringent effect exhibited by a liquid crystal medium which includes a large number of anisotropic liquid crystal molecules. Such a material will be positively uniaxially birefringent (n₁ > n₂) i.e., the extraordinary refractive index is larger than the ordinary refractive index) with the extraordinary refractive index associated with the alignment of the long molecular axes. The phase retardation effect of such a material on light passing through it inherently varies with the inclination angle of the light, leading to a lower quality image at large viewing angles. By introducing an optical compensating element in conjunction with the liquid crystal cell, however, it is possible to connect for the unwanted angular effects and thereby maintain higher contrast at larger viewing angles than otherwise possible.

The type of optical compensation required depends on the type of display which is used. In a normally black display, the twisted nematic cell is placed between polarizers whose transmission axes are parallel to one another and to the orientation of the director of the liquid crystal at the rear of the cell (i.e., the side of the cell away from the viewer). In the unenergized state, no applied voltage, normally incident light from the back-light is polarized by the first polarizer and in passing through the cell, has its polarization direction rotated by the twist angle of the cell. The twist angle is set to 90° so that the light is blocked by the output polarizer. Patterns can be written in the display by selectively applying a voltage to the portions of the display which are to appear illuminated.

However, when viewed at large angles, the dark (unenergized) areas of a normally black display will appear light because of angle dependent retardation effects for light passing through the liquid crystal layer at such angles, i.e., off-normal incidence light senses an angle-dependent change of polarization. Contrast can be restored by using a compensating element which has an optical symmetry similar to that of the twist cell, but which reverses its effect. One method is to follow the active liquid crystal layer with a twist cell of reverse helicity. Another is to use one or more A-plate retarder compensators. These compensation methods work because the compensation element shares an optical symmetry with the twisted nematic cell; both are uniaxial birefringent materials having an extraordinary axis orthogonal to the normal light propagation direction. These approaches to compensation have been widely utilized because of the ready availability of materials with the required optical symmetry. Reverse twist cells employ liquid crystals and A-plate retarders are readily manufactured by the stretching of polymers such as polyvinyl alcohol.

Despite the effectiveness of these compensation techniques, there are drawbacks to this approach associated with the normally black operational mode. The appearance of a normally black display is very sensitive to cell gap. Consequently, in order to maintain a uniform dark appearance, it is necessary to make the liquid crystal cell very thick, which results in unacceptably long liquid crystal response times. In addition, the reverse twist compensation technique requires the insertion of a second liquid crystal cell into the optical train, adding significant cost, weight, and bulk to the display. For these reasons, it is highly desirable to compensate a normally white display in order to avoid these disadvantages.

In a normally white display configuration, the 90° twisted nematic cell is placed between polarizers which are crossed, such that the transmission axis of each polarizer is parallel to the director orientation of the liquid crystal molecules in the region of the cell adjacent to it. This reverses the sense of light and dark from that of the normally black display. The unenergized (no applied voltage) areas appear light in a normally white display, while those which are energized appear dark.

The problem of ostensibly dark areas appearing light when viewed at large angles still occurs, but the reason for it is different and its correction requires a different type of optical compensating element. In the energized areas, the liquid crystal molecules tend to align with the applied electric field. If this alignment were perfect, all the liquid crystal molecules in the cell would have their long axes normal to the substrate glass. This arrangement, known as homeotropic configuration, exhibits the optical symmetry of a positively birefringent C-plate. In the energized state, the normally white display appears isotropic to normally incident light, which is blocked by the crossed polarizers.

The loss of contrast with viewing angle occurs because the homeotropic liquid crystal layer does not appear isotropic to off-normal light. Light directed at off normal angles propagates in two modes due to the birefringence of the layer, with a phase delay between those modes which increases with the incident angle of
the light. This phase dependence on incidence angle introduces an ellipticity to the polarization state which is then incompletely extinguished by the second polarizer, giving rise to slight leakage. Because of the C-plane symmetry, the birefringence has no azimuthal dependence. Clearly what is needed is an optical compensating element, also in C-plane symmetry, but with negative (n1 > n2) birefringence. Such a compensator would introduce a phase delay opposite in sign to that caused by the liquid crystal layer, thereby restoring the original polarization state, allowing the light to be blocked by the output polarizer.

This technique has not been used in the past because it has been difficult or impossible to construct a C-plane compensator with the required optical symmetry. There has been no way found to stretch or compress polymers to obtain large area films with negative C-plane optical symmetry and the required uniformity, nor is it possible to form a compensator from a negatively birefringent crystal such as sapphire. In order for a compensator to be effective, the phase retardation of such a plate would have to have the same magnitude as the phase retardation of the liquid crystal and would also have to change with the viewing angle at the same rate as the change of the liquid crystal's phase retardation. These constraints imply that the thickness of the negative plate would thus be on the order of 10 μm, making such an approach very difficult to accomplish because it would require the polishing of an extremely thin plate having the correct (negative) birefringence while ensuring that the surfaces of the plate remained parallel. Since such displays are relatively large in size, the availability of a negatively birefringent crystal of sufficient size would also be a major difficulty. Compensation techniques have been proposed which utilize crossed A-plane compensators. Such an arrangement, however, cannot produce a compensator with an azimuthal (C-plane) symmetry. Because of these difficulties, the tendency in the art has been to rely on normally black displays, even though the normally white type could produce a superior quality display if an appropriate compensator were available.

Previous attempts at compensator fabrication are described, for example in U.S. Pat. No. 5,135,474, to Fuji Photo Film Co., Ltd., and wherein the technique relied upon for imparting negative birefringence required film stretching. Compensators are designed to improve the viewing angle dependence which is a function of retardation (Rn), defined as a product of a birefringence (Δn) of a film and a film thickness (d). The viewing angle is improved by inserting a film having an optic axis substantially in the normal direction, more specifically, a laminated film of a biaxially stretched film having a negative intrinsic birefringence and a uniaxially stretched film having a positive intrinsic birefringence between a liquid crystal cell and a polarizing sheet. Preferred examples of polymers for use in preparing the stretched films having a positive intrinsic birefringence include polycarbonates, polycyralyates, polyethylene terephthalate, polyether sulfone, polyphenylene sulfide, polyphenylene oxide, polyallyl sulfone, polyamide-imides, polyimides, polyolefins, polynvinyl chloride, cellulose and polycyralyates and polysteres which have a high intrinsic birefringence prepared by, for example, solution casting.

Preferred examples of negative intrinsic birefringence stretched films would include styrene polymers, acrylic ester polymers, methacrylic ester polymers, acrylonitrile polymers and methacrylonitrile polymers with polystyrene polymers being most preferred from the viewpoint of large absolute value of intrinsic birefringence, transparency and ease of processing into films by solution casting.

However, to date, there is still lacking a method for producing negative intrinsic birefringence films without the need of having to resort to physical polymer film stretching to introduce the necessary orientation. Physical drawing of polymer films to achieve the necessary orientation and ordered areas which increase the scattering of light, are difficult to achieve, particularly regarding film uniformity. While on a macroscopic level the films superficially appear to be uniform, this is not the case on a microscopic level. To date, there has been no self-orienting, inherently in-plane oriented negative intrinsic birefringence films which are uniform on a microscopic level.

SUMMARY OF THE INVENTION

In accordance with the present invention, there is provided a novel class of soluble polyimides, which when used to cast films, undergo a self-orientation process whereby the polyimide backbone becomes more or less aligned parallel to the film surface. This in-plane orientation results in a film that displays negative birefringence.

It is another object of this invention to teach the ability to control the degree of in-plane orientation and thus, the magnitude of the negative birefringence by varying the polyimide backbone linearity and rigidity. It is yet another object of this invention to teach that by increasing the polyimide backbone linearity and rigidity, the degree of in-plane orientation and associated negative birefringence can be increased, and that conversely, by decreasing the polyimide backbone linearity and rigidity, the negative birefringence can be decreased.

It is still another object of this invention to teach the preparation of thin polyimide films that display negative birefringence in excess of 0.2.

It is yet still another object of this invention to teach the preparation of thin polyimide films that are essentially non-birefringent.

It is another object of this invention to teach the ability to control the magnitude of the negative birefringence of thin polyimide films between zero and values in excess of 0.2 by adjusting the polyimide backbone linearity and rigidity.

It is an object of this invention to provide homopolyimides and copolyimides which are soluble in the imide form, in non-toxic organic solvents, preferably mixed solvents of ketones and ethers, which are capable of forming thin films, e.g., by spin coating, which exhibit negative birefringence.

These and other objects of this invention will be evident when viewed in light of the drawings, detailed description, and appended claims.

DETAILED DESCRIPTION OF THE DRAWINGS

The invention may take physical form in certain parts and arrangements of parts, a preferred embodiment of which will be described in detail in the specification and
FIG. 1 is a plot of refractive index vs. copolyimide composition \[3,3',4,4'-\text{biphenyltetracarboxylic dianhydride} \quad (\text{BPDA})-2,2',-\text{bis(trifluoromethyl)}-4,4'-\text{diaminobiphenyl} (\text{TFMB})\] wherein the content of the copolyimide is changed as \(x\) varies from 100 to 0 while \(y\) varies correspondingly from 0 to 100; FIG. 2 is a cross-sectional schematic side view of a twisted nematic, transmissive-type liquid crystal display; FIG. 3 is an enlarged view of the multilayer portion of the display depicted in FIG. 2; FIG. 4 is a perspective view of an alternative liquid crystal display; FIG. 5 is a Wide Angle X-Ray Diffraction (WAXD) pattern obtained via transmission mode for a \((\text{BPDA-TFMB})_{0.5}-(\text{PMDA-TFMB})_{0.5}\) copolyimide; and FIG. 6 is a Wide Angle X-Ray Diffraction (WAXD) pattern obtained via reflection mode for a \((\text{BPDA-TFMB})_{0.5}-(\text{PMDA-TFMB})_{0.5}\) copolyimide; and FIG. 7 is a Fourier Transform Infrared (FTIR) spectrograph of a series of \((\text{BPDA-TFMB})_{x}-(\text{PMDA-TFMB})_{y}\) copolyimides wherein \(x\) is 0.5, 0.7, and 1.0, while \(y\) varies correspondingly and is 0.5, 0.3, and 0 respectively at 1778 cm\(^{-1}\) which represents symmetric and asymmetric stretching vibrations; FIG. 8 is a Fourier Transform Infrared (FTIR) spectrograph of a series of \((\text{BPDA-TFMB})_{x}-(\text{PMDA-TFMB})_{y}\) copolyimides wherein \(x\) is 0.5, 0.7, and 1.0, while \(y\) varies correspondingly and is 0.5, 0.3, and 0 respectively at 738 cm\(^{-1}\) which represents in-plane and out-of-plane vibrational modes; and FIG. 9 is a transmission electron micrograph of a homopolyimide \(\text{BPDA-TFMB}\) thin film after etching in a potassium permanganate/phosphoric acid solution indicating a fibril type of texture indicating that the c-axis of the crystals is parallel to the fibril direction, revealing an in-plane orientation.

**DETAILED DESCRIPTION OF THE INVENTION**

The homopolyimides and copolyimides of this invention consist of combinations of benzene dianhydrides, such as pyromellitic dianhydride and substituted pyromellitic dianhydrides of general formula (I):

\[
\text{(I)}
\]

\[
\text{(II)}
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\[
\text{(III)}
\]

and/or tetracarboxylic acid dianhydrides of formula (II);

\[
\text{(IV)}
\]

\[
\text{(V)}
\]

and (2) homopolymers made from an acid dianhydride of formula (I) and a diamine of formula (III), and shown in generic form by formula (IV);

\[
\text{(VI)}
\]

and (2) homopolymers made from an acid dianhydride of formula (I) and a diamine of formula (III) in which case \(p\) must be at least 1 to insure solubility, and as shown in generic form by formula (V).

It is additionally understood that the term copolyimides as used in this application and the claims is not limited to polyimides containing only two different
repeat units, but is intended to include any polyimide having two or more different repeat units. Thus, a copolyimide of the present invention can be made: (1) (a) with an acid dianhydride of formula (I) and at least two different diamines of formula (III) or (b) with at least two different acid dianhydrides of formula (I) and a diamine of formula (III) and shown in generic form by formula (VII);

(2) (a) with an acid dianhydride formula (II) with at least two diamines of formula (III) or (b) at least two acid dianhydrides of formula (II) and a diamine of formula (III) and shown in generic form by formula (VIII);

or (3) with a diamine of formula (III) and two or more organic dianhydrides of formulas (I) and (II), or any combination thereof and shown in generic form by formula (VIII).

It is appreciated that the relationship between x and y is inverse and that as x varies from 100 to 0, y correspondingly varies from 0 to 100.

Although the above polyimides and copolyimides as described do not have end groups or indicate what end groups are present, end groups are present and the nature of the end groups are controlled by the reaction conditions or are determined by the addition of capping reagents. Thus, the end groups can be either an amino group or anhydride group or a combination thereof depending on the exact molecular composition of the starting reagents as well as the course of a random condensation polymerization.

If a diamine of formula (III) is used in slight excess from about 1 to 10 mole percent relative to a dianhydride of formulas (I or II), then the resulting polynomials will predominately be amino terminated, and the end groups of the polymer will be unreacted amino groups. On the other hand, if dianhydrides of formulas (I or II) are used in slight excess from about 1 to 10 mole percent relative to a diamine of formula (III), then the resulting polymides will predominately be anhydride terminated, and the end groups of the polymer will be unreacted anhydride groups. However, circumstances could arise wherein the polyimides would be terminated by particular agents employed. Anhydrides which are useful as capping agents are selected from the representative and illustrative group consisting of aromatic anhydrides such as phthalic anhydride. Amines which are useful as capping agents are selected from the representative and illustrative group consisting of aromatic amines such as aniline, methyl anilines, dimethyl anilines or naphthylamines.

Representative and illustrative examples of these useful anhydrides in the invention are pyromellitic dianhydride, 3,6-diphenylpyromellitic dianhydride, 3,6-bis(trifluoromethyl)pyromellitic dianhydride, 3,6-bis(methyl)pyromellitic dianhydride, 3,6-dihydroxypyrromellitic dianhydride, 3,6-dibromopyromellitic dianhydride, 3,6-dichloropyromellitic dianhydride, 3,3',4,4'-benzenonitetraacrylic acid dianhydride, 2,3,3',4'-benzenononetetraacrylic acid dianhydride, bis(2,3-dicarboxyphenoxy)methylene dianhydride, bis(2,5,6-trifluoro-3,4-dicarboxyphenoxy)methane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)-1,1,3,3,3-hexafluoropropane dianhydride, bis(3,4-dicarboxyphenoxy)-
ther dianhydride (4,4'-oxydiphthalic anhydride), bis(3,4-dicarboxyphenyl)sulfone dianhydride (3,3',4,4'-diphenylsulfonetetraacrylxylic anhydride), 4,4'-(4,4'-isopropylidenedi-(p-phenyleneoxy))bis(phthalic anhydride), N,N-(3,4-dicarboxyphenyl)-N-methylamine dianhydride, bis(3,4-dicarboxyphenyl)diethylsilane dianhydride; naphthalene tetracarboxylic acid dianhydrides such as 2,3,6,7- and 1,2,5,6-naphthalene-tetracarboxylic acid dianhydride, 2,6-dichloronaphthalene-1,4,5,8-tetraacrylxylic acid dianhydride; or heterocyclic aromatic tetracarboxylic acid dianhydrides such as thiophene-2,3,5,6-tetracarboxylic acid dianhydride and pyridine-2,3,5,6-tetracarboxylic acid dianhydride.

And in general, diamines are selected from the representative and illustrative group consisting of benzene diamines such as o-, m- and p-phenylenediamine, 2,4-diaminotoluene, 1,4-diamino-2-methylbenzene, 1,4-diamino-2-phenylbenzene and 1,3-diamino-4-chlorobenzene. Other useful polyaromatic diamines in the invention would include 4,4'-diaminobiphenyl, 4,4'-diaminodiphenylmethane, 2,2-bis-(4-aminophenyl)propane, 2,2-bis-(4-aminophenyl)-1,1,3,3,3-hexafluoropropane, 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 1,3-bis-(3-aminophenoxy)benzene, 1,3-bis-(4-aminophenoxo)benzene, 1,4-bis-(3-aminophenoxo)benzene, 4,4'-bis-(4-aminophenoxo)biphenyl, 4,4'-bis-(3-aminophenoxo)biphenyl, 2,2-bis-(4-aminophenoxo)phenyl)propane, 2,2-bis-[4-(4-aminophenoxo)phenyl]thioether, 4,4'-diaminodiphenyl sulfone, 2,2'-diaminobenzophenone, and 3,3'-diaminobenzophenone; naphthalene diamines such as 1,8- and 1,5-diminonaphthalene; or heterocyclic aromatic diamines such as 2,6-diaminopyridine, 2,4-diaminopyrimidine, and 2,4-diamino-s-triazine.

Especially useful are diamines of general formula (IX),

\[
\text{H}_2\text{N} \quad \begin{array}{c} \text{A}_p \quad \text{A}_q \end{array} \quad \text{NH}_2
\]

and wherein p and q are 1, and A is preferably selected from the group consisting of CH₃, CF₃, halogen, CN, and esters wherein the carboalkoxy group is as defined previously and n is at least 1. An exemplary list of non-limiting examples would include 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl, 2,2'-dibromo-4,4'-diaminobiphenyl, 2,2'-dicyano-4,4'-diaminobiphenyl, 2,2'-dichloro-6,6'-dimethyl-4,4'-diaminobiphenyl, 2,2'-dimethyl-4,4'-diaminobiphenyl, 3,3'-dimethyl-4,4'-diaminobiphenyl, 2,2'-dicarbalkoxy-4,4'-diaminobiphenyl and 2,2'-dicarboalkoxy-6,6'-dimethyl-4,4'-diaminobiphenyl.

**EXAMPLES**

The invention will be better understood by reference to the following illustrative and non-limiting representative examples which show the preparation of polyimides and copolyimides which are soluble in organic solvents.

**Example 1**

This example illustrates the preparation of a homopolyimide of 3,3',4,4'-benzophenonetetraacrylxylic dianhydride (BTDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB).

0.93 millimoles of BTDA was added to a stirred solution of 0.93 millimoles of TFMB in 5.4 grams of m-cresol (solids content 10% weight per weight of solvent) containing 0.06 grams of isoquinoline (optional) under N₂ at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200°C and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 10 ml of m-cresol and then slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150°C for 24 hours.

**Polymer properties:** [η] (where [η] is the intrinsic viscosity) at 30.1°C in m-cresol = 1.62 dl/g; Tg = N/A; T(5%)/air = 550°C; T(5%)/N₂ = 580°C; and soluble in m-cresol, p-chlorophenol.

**Example 2**

This example illustrates the preparation of a homopolyimide of 4,4'-oxydiphthalic anhydride (ODPA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB).

1.09 millimoles of ODPA was added to a stirred solution of 1.09 millimoles of TFMB in 6.21 grams of m-cresol (solids content 10% weight per weight of solvent) containing 0.06 grams of isoquinoline (optional) under N₂ at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200°C and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 10 ml of m-cresol and then slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150°C for 24 hours.

**Polymer properties:** [η] at 30.1°C in m-cresol = 1.1 dl/g; Tg = 275°C; T(5%)/air = 570°C; T(5%)/N₂ = 580°C; and soluble in m-cresol, p-chlorophenol, NMP, and sym-tetrachloroethane.

**Example 3**

This example illustrates the preparation of a homopolyimide of 3,3',4,4'-diphenylsulfonetetraacrylxylic dianhydride (DSDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB).

0.93 millimoles of DSDA was added to a stirred solution of 0.93 millimoles of TFMB in 5.72 grams of m-cresol (solids content 10% weight per weight of solvent) containing 0.06 grams of isoquinoline (optional) under N₂ at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200°C and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was al-
allowed to cool to ambient temperature, it was diluted with 10 ml of m-cresol and then slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150°C for 24 hours.

Polymers properties: [n] at 30.1°C in m-cresol = 1.0 dl/g; T_g = 320°C; T(-5%)/air = 540°C; T(-5%)/N_2 = 51°C; UV data - transparency on set = 375 nm and maximum transparency = 85%; and soluble in m-cresol and p-chlorophenol.

Example 4

This example illustrates the preparation of a homopolyimide of 3,3',4,4'-biphenyltetraarboxylic dianhydride (BPDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB).

1.25 millimoles of BTDA was added to a stirred solution of 2.5 millimoles of TFMB in 6.9 grams of m-cresol (solids content 10% weight per weight of solvent) containing 0.2 grams of isoquinoline (optional) under N_2 at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200°C and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of m-cresol, and then slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150°C for 24 hours.

Polymer properties: [n] at 30.1°C in m-cresol = 4.9 dl/g; T_g = 310°C; T(-5%)/air = 600°C; T(-5%)/N_2 = 600°C; UV data - transparency on set = 390 nm and maximum transparency = 84%; and soluble in m-cresol and p-chlorophenol.

Example 5

This example illustrates the preparation of a homopolyimide of 2,2'-bis(3,4-dicarboxyphenyl)methyl-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB).

4.68 millimoles of 6FDA was added to a stirred solution of 4.68 millimoles of TFMB in 32.2 grams of m-cresol (solids content 10% weight per weight of solvent) containing 0.2 grams of isoquinoline under N_2 at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200°C and maintained at that temperature for 4 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of m-cresol and slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150°C for 24 hours.

Polymer properties: [n] at 30.1°C in m-cresol = 5.39 dl/g; T_g = 342°C; T(-5%)/air = 465°C; T(-5%)/N_2 = 512°C; UV-Vis data - transparency cut-off = 378 nm, maximum transparency = 92%; and soluble in acetone, THF, cyclohexanone, chloroform, DMF, NMP, DMAc, and m-cresol.

Example 6

This example illustrates the preparation of a homopolyimide of 2,2'-bis(3,4-dicarboxyphenyl)methyl-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA) and 4,4'-diamino-2,2'-dichloro-6,6'-dimethylbiphenyl (DCM).

4.68 millimoles of 6FDA was added to a stirred solution of 4.68 millimoles of DCM in 29 grams of m-cresol (solids content 10% weight per weight of solvent) containing 0.2 grams of isoquinoline under N_2 at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200°C and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of m-cresol and slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150°C for 24 hours.

Polymer properties: [n] at 30.1°C in m-cresol = 3.39 dl/g; T_g = 320°C; T(-5%)/air = 450°C; T(-5%)/N_2 = 512°C; UV-Vis data - transparency cut-off = 378 nm, maximum transparency = 84%; and soluble in m-cresol and p-chlorophenol.
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filtration, washed with ethanol, and dried under reduced pressure at 150° C. for 24 hours.
Polymer properties: [η] at 30.1° C. in m-cresol = 3.45
dl/g; Tg = 237° C.; TC5% /air = 445° C.; T(−5%) /N2 = 514° C.; UV-Vis data: transparency = 85%; and solubility in chloroform, DMF, NMP, DMAc, and m-cresol.

Example 9
This example illustrates the preparation of a homopolyimide of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) and 4,4'-diamino-2,2'-dichlorobenzophenone (MCD).

4.68 millimoles of BTDA was added to a stirred solution of 4.68 millimoles of MCD in 28 grams of m-cresol (solids content 10% weight per weight of solvent) containing 0.2 grams of isoquinoline under N2 at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200° C. and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of NMP and slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150° C. for 24 hours.
Polymer properties: [η] at 30.1° C. in m-cresol = 4.25
dl/g; Tg = 215° C.; TC5% /N2 = 338° C.; and soluble in THF, chloroform, NMP, DMAc, and m-cresol.

Example 10
This example illustrates the preparation of a homopolymide of 2,2'-bis(3,4-dicarboxylphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA) and 4,4'-diamino-2,2'-dicarboxybenzoxy-6,6'-dimethylbiphenyl (DABMB).

4.68 millimoles of 6FDA was added to a stirred solution of 4.68 millimoles of DABMB in 39 grams of m-cresol (solids content 10% by weight per weight of solvent) containing 0.2 grams of isoquinoline under N2 at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200° C. and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of NMP and slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150° C. for 24 hours.
Polymer properties: [η] at 30.1° C. in m-cresol = 1.37
dl/g; Tg = 203° C.; TC5% /N2 = 360° C.; and soluble in THF, chloroform, NMP, DMAc, and m-cresol.

Example 11
This example illustrates the preparation of a homopolyimide of 3,3',4,4'-biphenyltetraacarboxylic anhydride (BPDA) and 4,4'-diamino-2,2'-dicarboxybenzoxy-6,6'-dimethylbiphenyl (DABMB).

4.68 millimoles of BPDA was added to a stirred solution of 4.68 millimoles of DABMB in 33 grams of m-cresol (solids content 10% by weight per weight of solvent) containing 0.2 grams of isoquinoline under N2 at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200° C. and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of NMP and slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150° C. for 24 hours.
Polymer properties: [η] at 30.1° C. in m-cresol = 1.85
dl/g; Tg = 191° C.; TC5% /N2 = 336° C.; and soluble in THF, chloroform, NMP, DMAc, and m-cresol.

Example 12
This example illustrates the preparation of a homopolyimide of 3,3',4,4'-benzophenonetetracarboxylic anhydride (BPDA) and 4,4'-diamino-2,2'-dicarboxybenzoxy-6,6'-dimethylbiphenyl (DABMB).

4.68 millimoles of BPDA was added to a stirred solution of 4.68 millimoles of DABMB in 35 grams of m-cresol (solids content 10% by weight per weight of solvent) containing 0.2 grams of isoquinoline under N2 at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200° C. and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of NMP and slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150° C. for 24 hours.
Polymer properties: [η] at 30.1° C. in m-cresol = 4.25
dl/g; Tg = 215° C.; TC5% /N2 = 338° C.; and soluble in THF, chloroform, NMP, DMAc, and m-cresol.

Example 13
This example illustrates the preparation of a homopolyimide of 4,4'-oxydiphthalic anhydride (ODPA) and 4,4'-diamino-2,2'-dicarboxybenzoxy-6,6'-dimethylbiphenyl (DABMB).

4.68 millimoles of ODPA was added to a stirred solution of 4.68 millimoles of DABMB in 35 grams of m-cresol (solids content 10% by weight per weight of solvent) containing 0.2 grams of isoquinoline under N2 at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200° C. and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of NMP and slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and dried under reduced pressure at 150° C. for 24 hours.
Polymer properties: [η] at 30.1° C. in m-cresol = 1.85
dl/g; Tg = 191° C.; TC5% /N2 = 336° C.; and soluble in THF, chloroform, NMP, DMAc, and m-cresol.

Example 14
This example illustrates the preparation of a homopolyimide of 2,2'-bis(3,4-dicarboxylphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA) and 4,4'-diamino-2,2'-dicarboxybenzoxy-6,6'-dimethylbiphenyl (DABDB).
4.68 millimoles of 6FDA was added to a stirred solution of 4.68 millimoles of DABDB in 50 grams of m-cresol (solids content 10% by weight per weight of solvent) containing 0.2 grams of isooquinoline under N₂ at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200°C and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of NMP and slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and then dried at 150°C under reduced pressure for 24 hours.

Polymers properties: $[\eta]$ at 30.1°C in m-cresol = 0.43 dl/g; $T_g = 107°C$; and soluble in acetone, cyclohexanone, THF, chloroform, DMF, NMP, DMAc, and m-cresol.

Example 15

This example illustrates the preparation of a polyimide of 2,2'-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA) and 4,4'-diamino-2,2'-dicarboxypentadeca-6,6'-dimethylbiphenyl (DABBP).

4.68 millimoles of 6FDA was added to a stirred solution of 4.68 millimoles of DABBP in 52 grams of m-cresol (solids content 10% by weight per weight of solvent) containing 0.2 grams of isooquinoline under N₂ at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200°C and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of NMP and slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and then dried at 150°C under reduced pressure for 24 hours.

Polymers properties: $[\eta]$ at 30.1°C in m-cresol = 0.43 dl/g; $T_g = 107°C$; and soluble in acetone, cyclohexanone, THF, chloroform, DMF, NMP, DMAc, and m-cresol.

Example 16

This example illustrates the preparation of a polyimide of 2,2'-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride (6FDA) and 4,4'-diamino-2,2'-dicarboxypentadeca-6,6'-dimethylbiphenyl (DABOB).

4.68 millimoles of 6FDA was added to a stirred solution of 4.68 millimoles of DABOB in 54 grams of m-cresol (solids content 10% by weight per weight of solvent) containing 0.2 grams of isooquinoline under N₂ at ambient temperature. After the solution was stirred for 3 hours, it was heated to near 200°C and maintained at that temperature for 3 hours. During this time, the water of imidization was allowed to distill from the reaction mixture. After the solution was allowed to cool to ambient temperature, it was diluted with 30 ml of NMP and slowly added to 1 liter of vigorously stirred 95% ethanol. The polymer that precipitated was collected by filtration, washed with ethanol, and then dried at 150°C under reduced pressure for 24 hours.

Polymers properties: $[\eta]$ at 30.1°C in m-cresol = 0.43 dl/g; $T_g = 95°C$; and soluble in acetone, cyclohexanone, THF, chloroform, DMF, NMP, DMAc, and m-cresol.

Example 17

This example illustrates the preparation of a polyimide of 3,3',4,4'-benzenetetracarboxylic acid dianhydride (BTDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB).

1.55 millimoles of BTDA added to a stirred solution of 1.55 millimoles of TFMB in 9.0 grams of NMP (solids content 10% weight per weight of solvent) under N₂ at ambient temperature. After the solution was stirred for 24 hours, 3.41 millimoles of pyridine and 3.41 millimoles of acetic anhydride were added. After the solution was stirred for 24 hours, it was diluted with 8 ml of NMP and then added to 1 liter of vigorously stirred 95% ethanol. The polymer was collected by filtration, washed with ethanol, and then dried at 150°C under reduced pressure for 24 hours.

Polymers properties: $[\eta]$ at 30.1°C in m-cresol = 0.84 dl/g of the intermediate polyamide-acid; $T(-5%)/air = 550°C$; and $T(-5%)/N₂ = 560°C$.

Example 18

This example illustrates the preparation of a polyimide of 4,4'-oxydiphthalic anhydride (ODPA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB).

1.56 millimoles of ODPA added to a stirred solution of 1.56 millimoles of TFMB in 5.57 grams of NMP (solids content 15% weight per weight of solvent) under N₂ at ambient temperature. After the solution was stirred for 24 hours, 2.67 millimoles of pyridine and 2.67 millimoles of acetic anhydride were added. After the solution was stirred for 24 hours, it was diluted with 8 ml of NMP and then added to 1 liter of vigorously stirred 95% ethanol. The polymer was collected by filtration, washed with ethanol, and then dried at 150°C under reduced pressure for 24 hours.

Polymers properties: $[\eta]$ at 30.1°C in m-cresol = 0.57 dl/g; $T_g = 275°C$; $T(-5%)/air = 570°C$; and $T(-5%)/N₂ = 580°C$.

Example 19

This example illustrates the preparation of a polyimide of 3,3',4,4'-diphenylsulfenetetraacarbonylic acid dianhydride (DSDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB).

1.56 millimoles of DSDA added to a stirred solution of 1.56 millimoles of TFMB in 9.53 grams of NMP (solids content 10% weight per weight of solvent) under N₂ at ambient temperature. After the solution was stirred for 24 hours, 4.77 millimoles of pyridine and 4.77 millimoles of acetic anhydride were added. After the solution was stirred for 24 hours, it was diluted with 8 ml of NMP and then added to 1 liter of vigorously stirred 95% ethanol. The polymer was collected by filtration, washed with ethanol, and then dried at 150°C under reduced pressure for 24 hours.

Polymers properties: $[\eta]$ at 30.1°C in m-cresol = 0.68 dl/g; $T_g = 320°C$; $T(-5%)/air = 540°C$; and $T(-5%)/N₂ = 515°C$.

ONE STEP PROCEDURE FOR CO-POLYIMIDES

Example 20

This example illustrates the preparation of a co-polyimide based on 3,3',4,4'-benzenetetracarboxylic acid dianhydride (BTDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB).
acid dianhydride (BTDA), 2,2'-bis(trifluoromethyl)-
4,4'-diaminobiphenyl ether (TFMB) and 4,4'-diaminodiphe-
nyl ether (DDE).

1.86 millimoles of BTDA was added to a stirred solution
of 0.93 millimoles of TFMB and 0.93 millimoles of
DDE in 9.8 g of m-cresol (solids content 10% weight
per weight of solvent) containing 0.08 grams of iso-
quinoiline (optional) under N₂ at ambient temperature.
After the solution was stirred for 1 hour, it was heated
to near 200° C. and maintained at that temperature for
3 hours. After the solution was allowed to cool to ambi-
ent temperature, it was diluted with 10 ml of m-cresol
and then slowly added to 1 liter of vigorously stirred
95% ethanol. The copolymer that precipitated was
collected by filtration, washed with ethanol, and dried
under reduced pressure at 150° C. for 24 hours.

Copolymer properties: [η] at 30.1° C. in m-
cresol = 0.35 dl/g; and soluble in m-cresol and p-chloro-
phenol.

Example 21

This example illustrates the preparation of a co-polysi-
mide based on 3,3',4,4'-biphenyltetra carboxylic dianhy-
dride (BPDA), pyromellitic dianhydride (PMDA) and
2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFMB).

0.78 millimoles of BPDA was added to a stirred solu-
tion of 1.56 millimoles of TFMB in 8.1 g of m-cresol
(solids content 10% weight per weight of solvent) con-
taining 0.08 grams of isoquinoline (optional) under N₂
at ambient temperature. After the solution was stirred
for 1 hour, it was heated to near 200° C. and maintained
at that temperature for 3 hours. After cooling to room
temperature, 0.78 millimoles of PMDA was added to
the oligomer solution. The mixture was reheated to near
200° C. and maintained at that temperature for 3 hours.
After the solution was allowed to cool to ambient tem-
erature, it was diluted with 10 ml of m-cresol and then
slowly added to 1 liter of vigorously stirred 95% etha-
nol. The copolymer that precipitated was collected by
filtration, washed with ethanol, and dried under re-
duced pressure at 150° C. for 24 hours.

Copolymer properties: [η] at 30.1° C. in m-
cresol = 0.20 dl/g; T(−5%) /N₂ = 550° C.; and soluble
in m-cresol and p-chlorophenol.

Example 22

This example illustrates the preparation of a co-polysi-
mide based on 2,2'-bis(3,4-dicarboxyphenyl)-
1,1,3,3,3-hexafluoropropane dianhydride (6FDA),
pyromellitic dianhydride (PMDA) and 2,2'-bis(tri-
 fluoromethyl)-4,4'-diaminobiphenyl (TFMB).

0.78 millimoles of 6FDA was added to a stirred solu-
tion of 1.56 millimoles of TFMB in 8.1 g of m-cresol
(solids content 10% weight per weight of solvent) con-
taining 0.08 grams of isoquinoline (optional) under N₂
at ambient temperature. After the solution was stirred
for 1 hour, it was heated to near 200° C. and maintained
at that temperature for 3 hours. After cooling to room
temperature, 0.78 millimoles of PMDA was added to
the oligomer solution. The mixture was reheated to near
200° C. and maintained at that temperature for 3 hours.
After the solution was allowed to cool to ambient tem-
erature, it was diluted with 10 ml of m-cresol and then
slowly added to 1 liter of vigorously stirred 95% etha-
nol. The copolymer that precipitated was collected by
filtration, washed with ethanol, and dried under re-
duced pressure at 150° C. for 24 hours.

Copolymer properties: [η] at 30.1° C. in m-
cresol = x.xx dl/g; T(−5%) /N₂ = xxx° C.; and soluble
in m-cresol and p-chlorophenol.

DISCUSSION

While numerous examples have been illustrated to show
how to make soluble polyimides and enable those
skilled in the art to practice the invention, it is well
known that other polyimides, not specifically detailed
in the previous examples, can be synthesized by well-
known techniques in the art. In general, the principles
for preparing soluble polyimides are known in the art,
as taught for example, the general compilation of the
"Proceedings of the Symposium on Structure-Solubility
Relationships in Polymers", edited by Harris and Sey-
mour, and published by Academic Press in 1977. In
particular, the papers entitled Structure-Solubility Re-
lationships in Polyimides, by Harris and Lanier, and Solu-
ility-Structure Study of Polyimides, by St. Clair, St.
Clair and Smith, the teachings of which are hereby
incorporated by reference, are germane to the teachings
which have been used to attain solubility in polyimides
while maintaining their desirable high temperature
characteristics.

While broad generalities, associated with structural
effects on solubility are impossible, the majority of ap-
proaches have included: (1) incorporation of flexible or
non-symmetrical, thermally-stable linkages in the back-
bone; (2) the introduction of large polar or non-polar
substituents along the polymer backbone; and (3) the
disruption of symmetry and recurrence regularity
through the copolymerization of two dianhydrides or
two diamines. Recently, it has been discovered that
soluble polyimides can also be prepared through the use
of substituted 4,4'-diaminobiphenyls. The use of such
diamines results in twisted polyimide backbones that
do not pack well in the solid state. Thus, they are readily
solubilized in organic solvents, as taught for example
by the teachings of Harris in U.S. Pat. No. 5,071,997,
published Dec. 10, 1991, which is hereby incorporated
fully by reference, or as supplemented by the teachings
of Harris in pending application Ser. No. 08/009,718
wherein the combination of appropriate diamines with
2,2'-bis(3,4-dicarboxyphenyl)-1,1,3,3,3-hexafluoro-
propane dianhydride (6FDA) has been found to pro-
duce polyimides particularly useful for this invention
in that such polyimides are readily soluble in ketones
or ethers, or by any other methods used by those skilled
in the art.

Additionally, the making of films is also well-known
in the art, and for example, would include the prepara-
tive steps of preparing an approximately 2–12 weight
percent solution of one of the polyimides in a solvent
which is filtered, and a thin film cast onto a substrate
with for example, a doctors knife, and the solvent al-
lowed to evaporate, or by a spin coating technique at
between 500–2,000 rpm. It is appreciated that other
techniques are known in the art.

Typical effective solvents used in the above film-
making process would include at least phenolics, and
preferably polar aprotic solvents, and most preferably
ketones and ethers. The list provided is merely illustra-
tive of a great many other solvents which are applicable
to the instant invention.

The critical step is that the polyimide films are cast
from polyimides which are soluble in the imide form,
and not from polyamic acid precursors. The benefit of
using the soluble polyimides is that better reproducible
in-plane orientation is achieved when films are prepared in this manner than when films are prepared from the corresponding polyamic acid precursor.

The film is typically dried under reduced pressure for one hour at ~80° C., ramped to ~100° C. for an additional two hours, followed by heating the sample at ~150° C. for an additional five hours. It is well-known in the art that the times and temperatures used in the above illustrative example are dependent upon the composition of the synthesized polyimide and the conditions would be adjusted accordingly.

The ensuing refractive indices were generated for the following polyimides and copolyimides comprised of the dianhydrides of formulas (I) and (II)

and monoaromatic and polyaromatic diamines of formula (III)

and wherein R, G, F, A_n and p have the previously indicated meanings and E represents the structure between the amino groups of the diamine of formula (III) as shown in the respective columns of Tables I-IV, except when G is indicated to be pyromellitic dianhydride, in which case, G is the dianhydride, and not merely indicative of the group G within the dianhydride.

The choice of substituents G and F relate to the ability to affect the linearity and rigidity of the polymer backbone, and thus, the polymer's in-plane orientation in thin films. This in-plane orientation, critically affects the anisotropy of the film's refractive index. In effect, higher in-plane orientation results in a higher in-plane refractive index. Thus, backbones that are highly linear and rigid display high negative birefringence.

Specifically, Table I indicates the wide variety of polyimide and copolyimide films which can be prepared with negative birefringence without the need of having to resort to either uniaxial or biaxial stretching to achieve the necessary orientation for birefringence. By careful selection of the appropriate diamines and dianhydrides, as illustrated by the Markush groups G, F, E, A_n, and R, the negative birefringence is tailorable for the targeted application which may have the need for a film of predetermined thickness of from 0.2-20.0 μm.

The polyimides shown in Table I were synthesized using preparative methods outlined in the previous examples and appropriate quantities of reactant diamines and dianhydrides as would be obvious in light of the previous discussion.

<table>
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<tr>
<th>Table I</th>
<th>Refractive Indices of Segmented Rigid-Rod Polyimides</th>
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<td>G</td>
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<tr>
<td>6FDA</td>
<td>PPD</td>
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<td>6FDA</td>
<td>TFMB</td>
</tr>
<tr>
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<td>C-C</td>
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<td>DMB</td>
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<td>G</td>
<td>E</td>
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<tr>
<td>BPDA</td>
<td>OTOL</td>
</tr>
</tbody>
</table>
TABLE I-continued

| G         | E               | \( n_|| \) | \( n_\perp \) | \( \Delta n \) |
|-----------|-----------------|-----------|-------------|--------------|
| covalent  | CH₃             |           |             |              |
| bond      | CH₃             |           |             |              |
| 6FDA      | DABMB           | 1.593     | 1.585       | 0.008        |
|          | CF₃             |           |             |              |
|          | C₆H₅            |           |             |              |
| BTDA      | DCM             | 1.709     | 1.598       | 0.112        |
|          | Cl              |           |             |              |
|          | Cl              |           |             |              |
|          | CH₃             |           |             |              |
|          | CH₃             |           |             |              |
| ODPA      | DCM             | 1.679     | 1.633       | 0.046        |
|          | Cl              |           |             |              |
|          | Cl              |           |             |              |
|          | CH₃             |           |             |              |
|          | CH₃             |           |             |              |
| BPDA      | 40% DCB         | 1.765     | 1.624       | 0.141        |
|          | CN              |           |             |              |
|          | CN              |           |             |              |
|          | CH₃             |           |             |              |
|          | CH₃             |           |             |              |
| BPDA      | 70% OTOL        | 1.770     | 1.609       | 0.161        |
|          | CN              |           |             |              |
|          | CN              |           |             |              |
|          | CH₃             |           |             |              |
|          | CH₃             |           |             |              |
TABLE I-continued

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TABLE I-continued

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</tr>
<tr>
<td></td>
<td></td>
<td>30% DCB</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CF3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CF3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>70% OTOL</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>covalent</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>bond</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CF3</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>CF3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Refractive Indices of Segmented Rigid-Rod Polyimides
TABLE I-continued

<table>
<thead>
<tr>
<th>Refractive Indices of Segmented Rigid-Rod Polyimides</th>
<th>n|</th>
<th>n\perp</th>
<th>Δn</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPDA TFMB</td>
<td>1.634</td>
<td>1.540</td>
<td>0.094</td>
</tr>
</tbody>
</table>

By careful selection of the appropriate diamines and dianhydrides, the negative birefringence is tailorable for the targeted application for films of predetermined thickness. As seen in Table II, by varying composition of the dianhydride of the polyimide, through copolymers, the negative birefringence is changed as the polymer becomes less rigid, as shown when this ratio is varied from the copolyimide to the homopolymer as follows: [(BPDA-TFMB)_{0.5}-(PMDA-TFMB)_{0.5}] to [(BPDA-TFMB)_{0.7}-(PMDA-TFMB)_{0.3}] to [(BPDA-TFMB)_{1.0}-(PMDA-TFMB)_{0.0}]. This effect is additionally shown in FIG. 1.

TABLE II

<table>
<thead>
<tr>
<th>Refractive Indices of Segmented Rigid-Rod Copolyimides</th>
<th>Dianhydride</th>
<th>Diamine</th>
<th>Ratio</th>
<th>n|</th>
<th>n\perp</th>
<th>Δn</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPDA TFMB</td>
<td>50%</td>
<td>1.694</td>
<td>1.514</td>
<td>0.180</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMDA TFMB</td>
<td>50%</td>
<td>1.674</td>
<td>1.547</td>
<td>0.127</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPDA TFMB</td>
<td>70%</td>
<td>1.674</td>
<td>1.547</td>
<td>0.127</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMDA TFMB</td>
<td>30%</td>
<td>1.674</td>
<td>1.547</td>
<td>0.127</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
As additionally shown by the same compositional sequence variation shown in the previous table, the backbone rigidity is increased with increasing amounts of PMDA, which increases the in-plane orientation, and therefore, increases the negative birefringence of the film as shown in Table III wherein the composition is varied from the copolyimide to the homopolymer as follows: 

\[ [(BPDA-TFMB)_{0.5}-(PMDA-TFMB)_{0.5}] \] to 

\[ [(BPDA-TFMB)_{0.7}-(PMDA-TFMB)_{0.3}] \] to 

\[ [(BPDA-TFMB)_{1.0}-(PMDA-TFMB)_{0.0}] \] and wherein CTE is the coefficient of thermal expansion.

The effect of the group G within the dianhydride on the measured values of the refractive indices is shown in Table IV wherein the diamine component of the polyimide is the same and the dianhydride is varied. As shown in the table, reducing the rigidity and linearity
between the dianhydride functionality, i.e., moving from top to bottom in the table, will reduce the ultimate film's negative birefringence, thereby enabling a tailoring of the polyimide to the intended application.

### TABLE IV

<table>
<thead>
<tr>
<th>G</th>
<th>E</th>
<th>Effect of G on Negative Birefringence</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPDA</td>
<td>TFMB</td>
<td>covalent bond</td>
</tr>
<tr>
<td></td>
<td>CF₃</td>
<td>1.634</td>
</tr>
<tr>
<td>BTDA</td>
<td>TFMB</td>
<td>-C-</td>
</tr>
<tr>
<td></td>
<td>CF₃</td>
<td>1.639</td>
</tr>
</tbody>
</table>

In a corresponding manner, by varying the rigidity and linearity of the diamine in the polyimide, a corresponding effect can be observed as shown in Table V, thereby permitting additional tailoring of the polyimide to fit the targeted application. By including the flexible diamine BDAF in the copolyimide, thereby decreasing the rigidity of the polymeric backbone, the observed value of the negative birefringence is decreased, as expected.

### TABLE V

<table>
<thead>
<tr>
<th>G</th>
<th>E</th>
<th>Effect of E on Negative Birefringence</th>
</tr>
</thead>
<tbody>
<tr>
<td>6FDA</td>
<td>TFMB</td>
<td>CF₃</td>
</tr>
<tr>
<td></td>
<td>CF₃</td>
<td>1.567</td>
</tr>
<tr>
<td>6FDA</td>
<td>DMB</td>
<td>CF₃</td>
</tr>
<tr>
<td></td>
<td>CF₃</td>
<td>1.566</td>
</tr>
</tbody>
</table>

The type and position of the substituent An within the diamine of the present invention can also have a measurable effect on the negative birefringence as shown in Table VI. As shown in the Table, by switching the substituent in the 2 and 2' positions on the aromatic ring on the diamine, for example, from CF₃ to CH₃, the more electronegative halogen fluorine has a larger effect on the negative birefringence of the film than hydrogen. Additionally, replacing the substituent from a fairly compact methyl radical, to the bulkier alkyl ester, has a pronounced effect on the measured negative birefringence of the polyimide film.

### TABLE VI

<table>
<thead>
<tr>
<th>6FDA</th>
<th>TFMB</th>
<th>CF₃</th>
<th>CF₃</th>
<th>1.568</th>
<th>1.522</th>
<th>0.046</th>
</tr>
</thead>
</table>

The type and position of the substituent An within the diamine of the present invention can also have a measurable effect on the negative birefringence as shown in Table VI. As shown in the Table, by switching the substituent in the 2 and 2' positions on the aromatic ring on the diamine, for example, from CF₃ to CH₃, the more electronegative halogen fluorine has a larger effect on the negative birefringence of the film than hydrogen. Additionally, replacing the substituent from a fairly compact methyl radical, to the bulkier alkyl ester, has a pronounced effect on the measured negative birefringence of the polyimide film.

### Table VI-continued

<table>
<thead>
<tr>
<th>G</th>
<th>E</th>
<th>Effect of G on Negative Birefringence</th>
</tr>
</thead>
<tbody>
<tr>
<td>ODA</td>
<td>TFMB</td>
<td>CF₃</td>
</tr>
<tr>
<td></td>
<td>CF₃</td>
<td>1.639</td>
</tr>
<tr>
<td>6FDA</td>
<td>DMB</td>
<td>CH₃</td>
</tr>
<tr>
<td></td>
<td>CH₃</td>
<td>0.046</td>
</tr>
</tbody>
</table>
And finally, shown in Table VII, the backbone rigidity effect is shown in the comparison wherein the diamine component of the polyimide is increased from one ring to two rings, i.e. the backbone is made more rigid.

TABLE VII

<table>
<thead>
<tr>
<th>Negative Birefringence of Polyimide films</th>
<th>Dianhydride</th>
<th>Diamine</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-ring</td>
<td>6FDA</td>
<td>PPDA</td>
<td>0.025</td>
</tr>
<tr>
<td>2-rings</td>
<td>6FDA</td>
<td>TFMB</td>
<td>0.046</td>
</tr>
</tbody>
</table>

Experimental evidence for the conclusions discussed so far are shown in FIGS. 5 and 6, where wide angle X-Ray Diffraction (WAXD) patterns were obtained for the transmission and reflection modes for a (BPDA-TFMB)0.5-(PMDA-TFMB)0.5 copolyimide and compared to the patterns obtained from a highly oriented fiber along both the equatorial and meridian directions, respectively. This highly oriented fiber was obtained using the teachings of Cheng, Wu, Eashoo, Shu and Harris in Polymer, 32, 1803-1810 (1991) which is hereby incorporated by reference. The results indicate that the c-axis in the ordered structure is parallel to the film surface. From the viewpoint of chain rigidity and linearity, it is natural to extend this in-plane orientation from the c-axis of the crystal to the molecular chain axis. This validity of this extrapolation was studied via Fourier transform infrared (FTIR) spectroscopy. The fingerprint frequencies are usually identified through the symmetric and asymmetric stretching and in-plane and out-of-plane bending vibrational modes. For example, the 1778 cm⁻¹ absorption band represents symmetric and asymmetric stretching vibration, and the 738 cm⁻¹ absorption band represents the in-plane and out-of-plane bending vibrations of the carbonyl groups. These modes may be used to study chain orientation utilizing polarized infrared radiation. The stretching (1778 cm⁻¹) band possesses a transition moment vector lying along the imide plane and thus parallel to the chain direction, while the in-plane and out-of-plane bending of the carbonyl groups (738 cm⁻¹) has a transition moment vector that is perpendicular to the imide plane. In fact, if this transition vector is perfectly aligned perpendicular to the film surface, no absorbance of the polarized infrared radiation should be observed. As seen in FIG. 8 for the copolyimide films, the 738 cm⁻¹ absorption band is relatively weak, (0.14 in arbitrary unit), while the 1778 cm⁻¹ band is about 2.5 times stronger than that of the 738 cm⁻¹ band. The observations of the weak 738 cm⁻¹ band indicates that the imide rings in the films are not perfectly parallel to the film surface. Furthermore, a decrease of the absorbance intensity of this band with increasing PMDA:TFMB composition reveals an enhancement of the in-plane orientation resulting from an increase in the chain rigidity and linearity.

FIG. 9 also shows the in-plane orientation via transmission electron microscopy (TEM) and electron diffraction (ED) methods. In this figure, the BPDA:TFMB thin film is shown after etching in a potassium permanganate/phosphoric acid solution. Fibril type of textures are obvious. The ED pattern indicates that the c-axis of the crystals is parallel to the fibril direction, revealing an in-plane orientation.

What has been shown is the ability to custom tailor polyimide and copolyimide thin films with negative birefringence. The teachings enable one skilled in the art to control the degree of in-plane orientation, thereby controlling the amount of negative birefringence, through selection of groups which affect polymer backbone chain rigidity, chain linearity, and chain symmetry.

LIQUID CRYSTAL COMPENSATOR

FIG. 2 is a cross-sectional schematic side view of a twisted nematic, transmissive type normally white liquid crystal display (LCD) constructed according to the teachings of U.S. Pat. No. 5,196,953, which is hereby fully incorporated by reference. The display includes a polarizer layer 52, and an analyzer layer 46, between which is positioned a liquid crystal layer 44, consisting of a liquid crystal material in the nematic phase. The polarizer and the analyzer, as is indicated by the symbols 48 (representing a polarization direction in the plane of the drawing) and 41 (representing a polarization direction orthogonal to the plane of the drawing), are oriented with their polarization directions at 90° to one another, as is the case for a normally white display.

A first transparent electrode 15 and a second transparent electrode 14 are positioned adjacent to opposite surfaces of the liquid crystal layer so that a voltage can be applied, by means of a voltage source 16, across the liquid crystal layer. The liquid crystal layer is in addition sandwiched between a pair of glass plates 18 and 20. The inner surfaces of the glass plates 18 and 20, which are proximate to the liquid crystal layer 44, are physically treated, as by buffing. Substrates 22 and 24 provide support structure for the aforementioned layers of the display.

As is well-known in the LCD art, when the material of the liquid crystal layer 44 is in the nematic phase and the inner surfaces of the plates 18 and 20 (the surfaces adjacent to the layer 44) are buffed and oriented with their buffed directions perpendicular, the director n of the liquid crystal material, absent any applied electrical voltage, will tend to align with the buffing direction. In the regions of the layer proximate each of the plates 18 and 20, consequently, in the absence of an applied electric field, the direction of polarization of incoming polarized light will be rotated by 90° in travelling through the liquid crystal layer. When the glass plates and the liquid crystal layer are placed between crossed polarizers, such as the polarizer 48 and the analyzer 41, light polarized by the polarizer 48 and traversing the display, as exemplified by the light ray 26, will thus be aligned with the polarization direction of the analyzer 41 and therefore will pass through the analyzer. When a sufficient voltage is applied to the electrodes 18 and 20, however, the applied electric field causes the director of the liquid crystal material to tend to align parallel to the field. With the liquid crystal material in this state, light passed by the polarizer 48, as illustrated by the light ray 28, will be extinguished by the analyzer 41. Thus an energized pair of electrodes will produce a dark region of the display, while light passing through regions of the display which are not subject to an applied field will produce illuminated regions. As is well-known in the LCD display art, an appropriate pattern of electrodes, acti-
vated in selected combinations, can be utilized in this manner to display alphanumeric or graphic information.

A multi-layer thin film compensator 30 is positioned in the display between the polarizer layer and the analyzer layer to enhance the viewing properties of a liquid crystal display over a wide range of viewing angles. The compensator includes a first series of layers having a first refractive index which alternate with a second series of layers having a second refractive index. The values of the first and second refractive indices, as well as the thicknesses of the layers in the first and the second series, are chosen such that the phase retardation of the multi-layer is equal in magnitude but opposite in sign to the phase retardation of the liquid crystal layer. An enlarged view of the multi-layer 30 is depicted in a cross-sectional side view in FIG. 3. This view shows a first series 32, 34, 36 ... of layers having a first thickness d1 and a second series 38, 40, 42 ... of layers having a second thickness d2. As those skilled in the art of optical thin films will appreciate, in order to effectively illustrate the concept of this invention, the thicknesses of the layers are exaggerated relative to the dimensions of an actual multi-layer, as indicated by the dashed lines in the middle of the multi-layer.

Although the preferred embodiment illustrated here includes a multi-layer compensator having two series of alternating layers comprising a first and a second optical material, those skilled in the art will recognize that the concept of a multi-layer compensator applies as well to more complex multilayers including periodic layer structures of three or more materials, as well as multilayers in which the different layers of a particular material vary in thickness. Furthermore, the inventive concept is applicable to reflective as well as transmissive type liquid crystal displays.

What has heretofore not been recognized is that within compensator 30, the composition of the negative birefringent thin film layer can be the polyimides of the instant invention, which can be custom-tailored to a desired negative birefringent value, and do not need to resort to the use of stretching to achieve the desired orientation, and additionally need not be comprised of an inorganic birefringent crystal, such as sapphire.

Another type of liquid crystal display which can benefit from this invention is the supertwist nematic cell, which exhibits voltage response characteristics allowing it to be addressed by simple multiplexing, thereby avoiding the expense and manufacturing difficulty associated with active matrix addressing. The supertwist configuration is achieved by doping the nematic liquid crystal material with a chiral additive which gives the cell 270° of total twist. Supertwist nematic cells are typically used in the normally black configuration, often employing the compensation techniques described above for normally black displays. Such cells, however, can also be operated in the normally white mode and such normally white supertwist displays would also benefit from the addition of the multi-layer compensator of this invention for field of view enhancement. Moreover, the compensation scheme of this invention is broadly applicable to any liquid crystal display which employs a homeotropically aligned state as part of its operation. Other types of liquid crystal displays, such as for example, ferroelectric, can be improved with this invention by acquiring a wider field of view in the aligned state which exhibits C-axis symmetry.

In an alternative embodiment of this invention, FIG. 4 shows a perspective view of a liquid crystal display (LCD) constructed according to the teachings of U.S. Pat. No. 5,138,474, which is herein fully incorporated by reference. The display has a structure that includes a liquid crystal cell 10 and films 7,8 having positive and negative intrinsic birefringence values respectively, and are held between two sheets of polarizing sheets 1,9 in an opposed configuration. Additionally liquid crystal cell 10 includes two sheets of substrates 2,6, two transparent electrodes 3,5, and a liquid crystal layer 4 held between the electrodes, and the films interposed between the liquid crystal cell and the polarizing sheet 9 which is provided on the side of an observer.

Once again, as previously, the negative intrinsic birefringent thin film layer need not be at least one uniaxially stretched film of a polymer having a negative intrinsic birefringence. Rather, the negative birefringent thin film layer can be the polyimides of the instant invention, which can be custom-tailored to a desired negative birefringent value, and do not need to resort to the use of stretching to achieve the desired orientation.

The invention has been described with reference to preferred and alternate embodiments. Obviously, modifications and alterations will occur to others upon the reading and understanding of the specification. It is intended to include all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.

What is claimed is:

1. A non-stretched homopolymer polyimide film, soluble in the imide form, for use in negative birefringence layers in liquid crystal displays, the film having a negative birefringence of 0.001 to 0.2, the film having been prepared from solutions of soluble polyimides of the type having an aromatic diamine hydride of general formula (I):

$$\begin{align*}
O & \quad R \\
O & \quad O \\
O & \quad O \\
\text{and an aromatic diamine of formula (III)}
\end{align*}$$

$$(\text{III})$$

$$H_2N\begin{bmatrix}
\text{An} \\
\text{J}_2
\end{bmatrix}\begin{bmatrix}
\text{F} \\
\text{NH}_2
\end{bmatrix}$$

wherein each

- R is a substituent selected independently from the group consisting of H, halogen, phenyl, substituted phenyl, alkyl and substituted alkyl of from 1 to 20 carbons;
- F is selected from the group consisting of a covalent bond, a CH₂ group, a C(CH₃)₂ group, a C(CX₃)₂ group wherein X is a halogen, a CO group, an O atom, a S atom, a SO₂ group, a Si(R)₂ group wherein R is as defined previously, and a N(R) group wherein R is as defined previously;

5,344,916
A is selected from the group consisting of hydrogen, halogen, alkyl, substituted alkyl, nitro, cyano, thioalkyl, alkoxy, substituted alk oxy, aryl and substituted aryl, aliphatic and aromatic ester, and combinations thereof from 1 to 20 carbons; n is an integer from 0 to 4; and p and q are integers from 1 to 3 and when p and q are greater than 1, the linking group between benzyl or substituted benzyl groups is F; and wherein the negative birefringence of the film is determined by control of the degree of in-plane orientation of the polyimide by the selection of R, F and A, and the values of n, p and q, which affects the polyimide backbone chain rigidity and linearity, the higher the rigidity and linearity of the polyimide backbone, the larger the value of the negative birefringence of the polyimide film.

2. The film of claim 1 wherein the aromatic dianhydride is a 3,5-disubstituted pyromellitic dianhydride selected from the group consisting of 3,5-diphenylpyromellitic dianhydride, 3,5-bis(trifluoromethyl)pyromellitic dianhydride, 3,5-bis(methyl)pyromellitic dianhydride, 3,5-bis(3,4-dicarboxyphenyl)pyromellitic dianhydride, 3,5-dimethylpyromellitic dianhydride, 3,5-dibromopyromellitic dianhydride, and 3,5-dichloropyromellitic dianhydride.

3. The film of claim 1 wherein the aromatic diamine is selected from the group consisting of o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2,4-diaminotoluene, 1,4-diamino-2-methoxybenzene, 1,4-diamino-2-phenylbenzene, 2,2'-diaminobiphenyl, 2,2'-dimethy14,4'-diaminobiphenyl, 2,2'-dicarboalkoxy-6,6'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 3,4'-diaminobenzophenone, 1,3-diamino-4-chlorobenzene, 1,3-diamino-4-methylbenzene, 1,3-diamino-4-phenylbenzene, 2,6-diaminotoluene, 2,3,4,5-tetracarboxylic acid dianhydride, 1,1,1,3,3,3-hexafluoropropane, 35 and linearity of the polyimide backbone, the larger the value of the negative birefringence of the polyimide film.

4. A non-stretched homopolymer polyimide film, soluble in the imide form, for use in negative birefringence layers in liquid crystal displays, the film having a negative birefringence of 0.001 to 0.2, the film having been prepared from solutions of soluble polyimides of the type having an aromatic dianhydride of general formula (II): and a polyamic diamine of formula (III) where F and G are selected independently from the group consisting of a covalent bond, a CH2 group, a C(CH3)2 group, a C(CX3)2 group wherein X is a halogen, a CO group, an O atom, a S atom, a SO2 group, a Si(R)2 group wherein R is a substituent selected independently from the group consisting of H, phenyl, substituted phenyl, alkyl and substituted alkyl from 1 to 20 carbons, and a N(R) group wherein R is as defined previously; A is selected from the group consisting of hydrogen, alkyl, substituted alkyl, nitro, cyano, thioalkyl, alk oxy, substituted alk oxy, aryl and substituted aryl, aliphatic and aromatic esters and combinations thereof from 1 to 20 carbons; n is an integer from 0 to 4; and p and q are integers from 0 to 3 and 1 to 3 respectively, and when p and q are greater than 1, the linking group between benzyl or substituted benzyl groups is F; and wherein the negative birefringence of the film is determined by controlling the degree of in-plane orientation of the polyimide by the selection of G, F, and A, and the values of n, p and q, which affects the polyimide backbone chain rigidity and linearity, the higher the rigidity and linearity of the polyimide backbone, the larger the value of the negative birefringence of the polyimide film.

5. The film of claim 4 wherein the aromatic dianhydride is selected from the group consisting of 3,5',4',4'-benzenophenonetetra carboxylic acid dianhydride, 2,3,3',4,4'-benzenophenonetetra carboxylic acid dianhydride, 1,1,1,3,3,3-hexafluoropropane dianhydride, bis(3,4-dicarboxyphenyl)methane dianhydride, bis(2,5,6-trifluoro-3,4-dicarboxyphenyl)methane dianhydride, bis(2,3,4,5-tetracarboxyphenyl)methane dianhydride, bis(3,4-dicarboxyphenyl)dichloroethylene dianhydride, bis(3,4-dicarboxyphenyl)sulfone dianhydride, 1,4-(4-isopropylidene-di-p-phenylenoxy)bis(phthalic anhydride), N,N-(3,4-dicarboxyphenyl)-N'-methylamine dianhydride, bis(3,4-dicarboxyphenyl)diethylsilane dianhydride, 2,3,6,7-naphthalene-tetracarboxylic acid dianhydride, 1,2,5,6-naphthalene-tetracarboxylic acid dianhydride, 2,6-dichloronaphthalenedicarboxylic acid dianhydride, 1,4,5,8-tetra carboxylic acid dianhydride, thiophene-2,3,4,5-tetra carboxylic acid dianhydride, pyridine-2,3,5,6-tetra carboxylic acid dianhydride.

6. The film of claim 4 wherein the diamine is selected from the group consisting of o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2,4-diaminotoluene, 1,4-diamino-2-methoxybenzene, 1,4-diamino-2-phenylbenzene, 2,6-diaminotoluene, 2,3,4,5-tetracarboxylic acid dianhydride, bis(3,4-dicarboxyphenyl)dichloroethylene dianhydride, bis(3,4-dicarboxyphenyl)sulfone dianhydride, 1,4-(4-isopropylidene-di-p-phenylenoxy)bis(phthalic anhydride), N,N-(3,4-dicarboxyphenyl)-N'-methylamine dianhydride, bis(3,4-dicarboxyphenyl)diethylsilane dianhydride, 2,3,6,7-naphthalene-tetracarboxylic acid dianhydride, 1,2,5,6-naphthalene-tetracarboxylic acid dianhydride, thiophene-2,3,4,5-tetra carboxylic acid dianhydride, pyridine-2,3,5,6-tetra carboxylic acid dianhydride.
4,4'-bis(4-aminophenoxy)biphenyl, 2,2-bis[4-(4-aminophenoxy)phenyl]-propane,
2,2-bis[4-(4-aminophenoxy)phenyl]-1,1,1,3,3,3-hexafluoropropane, 4,4'-diaminodiphenylthioether, 4,4'-diaminodiphenyl sulfone, 2,2'-(trifluoromethyl)-1,1,1,3,3,3-hexafluoropropane, 

2,2'-dibromo-4,4'-diaminobiphenyl, imide form, for use in negative birefringence layers in benzophenone tetracarboxylic acid dianhydride, from solutions

of at least one aromatic dianhydride of general formula

where

and at least one polyaromatic diamine of formula

whereas

and G are substituents selected independently from

the group consisting of a covalent bond, a CH₂ group, a C(CH₃)₂ group, a C(CR₃)₂ group wherein R is a substituent selected from the group consisting of H, phenyl, substituted phenyl, alkyl and substituted alkyl of from 1 to 20 carbons, and a N(R) group wherein R is as defined previously;

A is selected from the group consisting of hydrogen, halogen, alkyl, substituted alkyl, nitro, cyano, thiokyl, alkoxy, substituted alkoxy, aryl and substituted aryl, aliphatic and aromatic esters and combinations thereof from 1 to 20 carbons;

n is an integer from 0 to 4; and

p and q are integers from 0 to 3 and 1 to 3 respectively, and when p and q are greater than 1, the

linking group between benzyl or substituted benzyl groups is F;

to form a copolyimide of formula (VII)
5,344,916

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4,4’-diaminobiphenyl and 2,2’-dicarboalkoxy-6,6’-dimethyl-4,4’-diaminobiphenyl.

10. A non-stretched copolyimide film, soluble in the imide form, for use in negative birefringence layers in liquid crystal displays, the film having a negative birefringence of 0.001 to 0.2, the film having been prepared from solutions of soluble polyimides of the type having at least one aromatic dianhydride of general formula (I):

and at least one polyaromatic diamine of formula (III):

where each

R is a substituent selected independently from the group consisting of H, phenyl, substituted phenyl, alkyl and substituted alkyl of from 1 to 20 carbons;

F is a substituent selected from the group consisting of a covalent bond, a CH2 group, a C(CH3)2 group, a C(CH3)3 group wherein X is a halogen, a CO group, an O atom, a S atom, a SO2 group, a Si(R)2 group wherein R is as defined previously and a N(R) group wherein R is as defined previously;

A is selected from the group consisting of hydrogen, halogen, alkyl, substituted alkyl, nitro, cyano, thiocarboxyl, alkoxyl, substituted alkoxyl, aryl and substituted aryl, aliphatic and aromatic esters and combinations thereof from 1 to 20 carbons;

n is an integer from 0 to 4; and

p and q are integers from 1 to 3, and when p and q are greater than 1, the linking group between benzyl or substituted benzyl groups is F;

to form a copolymide of formula (VI):

wherein x varies from 100 to 0 while y varies correspondingly from 0 to 100; and wherein the negative birefringence of the film is determined by the control of the degree of in-plane orientation of the polyimide by the selection of R, F and A, and the values of n, p, q, x and y, which affects the polyimide backbone chain rigidity and linearity, the higher the rigidity and linearity of the polyimide backbone, the larger the value of the negative birefringence of the polyimide film.

11. The film of claim 10 wherein the aromatic dianhydride is selected from the group consisting of pyromellitic dianhydride, 3,6-diphenyloxybiphenylylene, 3,6-bis(trifluoromethyl)pyromellitic dianhydride, 3,6-bis(methyl)pyromellitic dianhydride, 3,6-diodopyromellitic dianhydride, 3,6-dibromopyromellitic dianhydride and 3,6-dichloropyromellitic dianhydride.

12. The film of claim 10 wherein the aromatic diamine is selected from the group consisting of o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2,4-diaminobenzene, 1,4-diamino-2-methoxybenzene, 1,4-diamino-2-phenylbenzene, 1,3-diamino-4-chlorobenzene, 4,4’-diaminobiphenyl, 4,4’-diaminodiphenylmethane, 2,2-bis(4-aminophenyl)propane, 2,2-bis(4-aminophenyl)-1,1,1,3,3,3-hexafluoropropane, 4,4’-diaminodiphenyl ether, 3,4’-diaminodiphenyl ether, 1,3-bis(3-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, 4,4’-bis(4-aminophenoxy)biphenyl, 4,4’-bis(3-aminophenoxy)biphenyl, 2,2-bis[4-(4-aminophenoxy)phenyl]propane, 2,2-bis[4-(4-aminophenoxy)phenyl]thioether, 4,4’-diaminodiphenyl sulfone, 2,2’-diaminobenzophenone, 3,3’-diaminobenzophenone, 1,8-diaminonaphthalene, 1,5-diaminonaphthalene, 2,6-diaminopyridine, 2,4-diaminopyridine, 2,4-diamino-s-triazine, 2,2-bis(trifluoromethyl)4,4’-diaminobiphenyl, 2,2’-dibromo-4,4’-diaminobiphenyl, 2,2’-dicyano-4,4’-diaminobiphenyl, 2,2’-dichloro-6,6’-dimethyl-4,4’-diaminobiphenyl, 2,2’-dimethyl-4,4’-diaminobiphenyl, 3,3’-dimethyl-4,4’-diaminobiphenyl, 2,2’-dicarboalkoxy-4,4’-diaminobiphenyl and 2,2’-dicarboalkoxy-6,6’-dimethyl-4,4’-diaminobiphenyl.

13. A non-stretched copolyimide film, soluble in the imide form for use in negative birefringence layers in liquid crystal displays, the film having a negative birefringence of 0.001 to 0.2, the film having been prepared from solutions of soluble polyimides of the type having at least one first aromatic dianhydride of general formula (I):

and at least one second aromatic dianhydride of formula (II):

and at least one aromatic dianhydride of general formula (I):
where each
R is a substituent selected independently from the
group consisting of H, phenyl, substituted phenyl,
akyl and substituted alkyl from 1 to 20 carbons;
F and G are substituents selected independently from the
group consisting of a covalent bond, a CH₂ group,
a C(CH₃)₂ group, a C(CX₃)₂ group wherein X is a halogen, a CO group, an O atom, a S atom,
a SO₂ group, a Si(R)₂ group wherein R is as defined previously and a N(R) group wherein R is as defined previously;
A is selected from the group consisting of hydrogen,
halogen, alkyl, substituted alkyl, nitro, cyano, thioketyl, alkoxy, substituted alkoxy, aryl and substituted aryl, aliphatic and aromatic ester and combinations thereof from 1 to 20 carbons;
n is an integer from 0 to 4; and
p and q are integers from 0 to 3 and 1 to 3 respectively, and when p and q are greater than 1, the linking group between benzyl or substituted benzyl groups is F;
to form a copolyimide of formula (VIII)

wherein x varies from 100 to 0 while y varies correspondingly from 0 to 100; and wherein the negative birefringence of the film is determined by the control of the degree of in-plane orientation of the polyimide by the section of R, G, F, and A, and the values of n, p, q, x and y, which affects the polyimide backbone chain rigidity and linearity, the higher the rigidity and linearity of the polyimide backbone, the larger the value of negative birefringence of the polyimide film.

14. The film of claim 13 wherein the diamine is selected from the group consisting of o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2,4-diaminotoluene, 1,4-diamino-2-methoxybenzene, 1,4-diamino-2-phenylbenzene, 1,3-diamino-4-chlorobenzene, 4,4'-diaminobiphenyl, 4,4'-diaminodiphenylmethane, 2,2-bis(4-amino phenyl)propane, 2,2-bis(4-amino phenyl)-1,1,1,3,3,3-hexafluoropropane, 4,4'-diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 1,3-bis(3-amino phenox) benzene, 1,3-bis(4-amino phenox) benzene, 1,4-bis(4-amino phenox) benzene, 4,4'-bis(4-amino phenox) biphenyl, 4,4'-bis(3-amino phenox) biphenyl, 2,2-bis[4-(4-amino phenyl)phenyl] propane, 2,2-bis[4-(4-amino phenyl)phenyl]-1,1,1,3,3,3-hexafluoropropane, 4,4'-diaminodiphenyl thioureas, 4,4'-diaminodiphenyl sulfone, 2,2'-diaminobenzophenone, 3,3'-diaminobenzophenone, 1,8-diaminophthalene, 1,5-diaminonaphthalene, 2,6-diaminopyridine, 2,4-diaminopyrimidine, 2,4-diaminostriazine, 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl, 2,2'-dibromo-4,4'-diaminobiphenyl, 2,2'-dicyno-4,4'-diaminobiphenyl, 2,2'-dichloro-6,6'-dimethyl-4,4'-diaminobiphenyl, 2,2'-dimethyl-4,4'-diaminobiphenyl, 3,3'-dimethyl-4,4'-diaminobiphenyl, 2,2'-dicarboxalkoxy-4,4'-diaminobiphenyl and 2,2'-dicarboxalkoxy-6,6'-dimethyl-4,4'-diaminobiphenyl.

16. An improved liquid crystal display of the type having a liquid crystal element, at least two light-transmissive birefringent films, at least one film having a positive birefringence and at least one other film having a negative birefringence, and a polarizing sheet arranged such that the films are held between the liquid crystal elements and the polarizing sheet, wherein the improvement comprises at least one non-stretched negative polyimide thin film, soluble in the imide form, having a negative birefringence, the polyimide film being selected from the group consisting of
(a) an organic solvent soluble homopolyimide film, the homopolyimide being selected from the group consisting of formulas (i) and (ii), and
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(b) an organic solvent soluble copolyimide film, the copolyimide being selected from the group consisting of formulas (i), (ii) and (iii).

17. The film of claim 16 wherein the dianhydride is selected from the group consisting of pyromellitic dianhydride, 3,6-diphenylpyromellitic dianhydride, 3,6-bis-(trifluoromethyl)pyromellitic dianhydride, 3,6-bis(methyl)pyromellitic dianhydride, 3,6-diodopyromellitic dianhydride, 3,6-dibromopyromellitic dianhydride and 3,6-dichloropyromellitic dianhydride, 3,3',4,4'-benzo phenonetetracarboxylic acid dianhydride, 2,3,3',4'-benzophenonetetracarboxylic acid dianhydride, 2,2,3,3'-benzophenonetetra carboxylic acid dianhydride, bis(2,3-dicarboxyphenyl)methane dianhydride, bis(2,5,6-trifluoro-3,4-dicarboxyphenyl)methane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride, bis(3,4-dicarboxyphenyl)sulfone dianhydride, 4,4'-(4,4'-isopropylidene-di(p-phenyleneoxy))-bis(phthalic anhydride), N,N-(3,4-dicarboxyphenyl)-N-methylamine dianhydride, bis(3,4-dicarboxyphenyl)die thylsilane dianhydride, 2,3,6,7-naphthalene-tetracarboxylic acid dianhydride, 1,2,5,6-naphthalene-tetracarboxylic acid dianhydride, 2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic acid dianhydride, thiophene-2,3,4,5-tetracarboxylic acid dianhydride, pyrazine-2,3,5,6-tetracarboxylic acid dianhydride and pyridine-2,3,5,6-tetracarboxylic acid dianhydride.

18. The film of claim 16 wherein the diamine is selected from the group consisting of o-phenylenedia-
mine, m-phenylenediamine, p-phenylenediamine, 2,4-
diaminotoluene, 1,4-diamino-2-methoxybenzene, 1,4-
diamino-2-phenylbenzene, 1,3-diamino-4-chloroben-
zeine, 4,4'-diaminobiphenyl, 4,4'-diaminodiphenylme-
thane, 2,2'-bis(4-aminophenyl)propane, 2,2'-bis(4-amino-
phenyl)-1,1,1,3,3,3-hexafluoropropane, 4,4'-
diaminodiphenyl ether, 3,4'-diaminodiphenyl ether, 1,3-
bis(3-aminophenox)benzene, 1,3-bis(4-aminophenox-
onyl)benzene, 1,4-bis(4-aminophenox)benzene, 4,4'-
 bis(4-aminophenox)benzenes, 4,4'-bis(3-aminopheno-
xy)biphenyl, 2,2'-bis[4-(4-aminophenox)phenyl]-
propane, 2,2'-bis[4-(4-aminophenox)phenyl]-
1,1,1,3,3,3-hexafluoropropane, 4,4'-diaminodiphenyl-
ether, 4,4'-diaminodiphenyl sulfone, 2,2'-
diaminobenzophenone, 3,3'-diaminobenzophenone, 1,8-
diaminonaphthalene, 1,5-diaminonaphthalene, 2,6-
diaminopyridine, 2,4-diaminopyrimidine, 2,4-diamo-
triazine, 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl,
2,2'-dibromo-4,4'-diaminobiphenyl, 2,2'-dicyano-4,4'-
diaminobiphenyl, 2,2'-dichloro-6,6'-dimethyl-4,4'-
diaminobiphenyl, 2,2'-dimethyl-4,4'-diaminobiphenyl,
3,3'-dimethyl-4,4'-diaminobiphenyl, 2,2'-dicarboalkoxy-
first and second electrodes being adapted to apply a
voltage across the liquid crystal layer when the elec-
 trodes are connected to a source of electrical potential,
and a multilayer thin film compensator disposed be-
tween the polarizer layer and the analyzer layer, includ-
ing a first plurality of layers, each having a first refrac-
tive index and a first thickness, alternating with a sec-
ond plurality of layers, each having a second refractive
index and a second thickness, the values of the first and
second refractive indices and thicknesses being such
that the phase retardation of the multilayer is equal in
magnitude but opposite in sign to the phase retardation
of the liquid crystal layer in its homeotropically aligned
state over a predetermined range of viewing angles,
wherein the improvement comprises at least one non-
stretched negative polyimide thin film, soluble in the
imide form, within the compensator having a negative
birefringence, the polyimide film being selected from
the group consisting of
(a) an organic solvent soluble homopolyimide film,
the homopolyimide being selected from the group
consisting of formulas (i) and (ii), and

\[
\begin{align*}
\text{(i)} & \\
\text{(ii)} & \\
\text{(iii)} &
\end{align*}
\]

4,4'-diaminobiphenyl and 2,2'-dicarboalkoxy-6,6'-
dimethyl-4,4'-diaminobiphenyl.

19. An improved liquid crystal display having a po-
larizer layer, an analyzer layer, a liquid crystal layer
disposed between the polarizer layer and the analyzer
layer, a first electrode proximate to a first major surface
of the liquid crystal layer, a second electrode proximate
to a second major surface of the liquid crystal layer, the

where each
R is a substituent selected independently from the
group consisting of H, halogen, phenyl, substi-
tuted phenyl, alkyl and substituted alkyl from 1 to 20 carbons; F and G are independently selected from the group consisting of a covalent bond, a CH₂ group, a C(CH₃)₂ group, a C(CX₃)₂ group wherein X is a halogen, a CO group, an O atom, a S atom, a SO₂ group, a Si(R)₂ group wherein R is as defined previously and a N(R) group wherein R is as defined previously; A is selected from the group consisting of hydrogen, halogen, alkyl, substituted alkyl, nitro, cyano, thioalkyl, alkoxy, substituted alkoxy, aryl and substituted aryl, aliphatic and aromatic esters and combinations thereof from 1 to 20 carbons; n is an integer from 0 to 4; p and q are integers from 1 to 3 when the polyimide is a homopolyimide and are integers from 0 to 3 and 1 to 3 respectively when the polyimide is a copolyimide, and wherein when p and q are greater than 1, the linking group between benzyl or substituted benzyl groups is F; and x, if present, varies from 100 to 0 while y, if present, varies correspondingly from 0 to 100.

20. An improved compensator for use in a liquid crystal display having at least one negative birefringent film layer and at least one positive birefringent film layer, wherein the improvement comprises the inclusion of at least one non-stretched negative polyimide thin film soluble in the imide form, the polyimide film being selected from the group consisting of (a) an organic soluble homopolyimide film, the homopolyimide being selected from the group consisting of formulas (i) and (ii), and (b) an organic solvent soluble copolyimide film, the copolyimide being selected from the group consisting of formulas (i), (ii) and (iii).
An improved liquid crystal display comprising a liquid crystal element, at least two birefringent films and a polarizing sheet arranged so that said films are held between said liquid crystal element and said polarizing sheet, characterized in that said birefringent films are composed of at least one polymer having a positive intrinsic birefringence and light transmission properties and at least one film having negative intrinsic birefringence and light transmission properties, wherein the 15 improvement comprises at least one non-stretched polyimide film, soluble in the imide form, having a negative birefringence, the polyimide film being selected from the group consisting of:

(a) an organic solvent soluble homopolyimide film, 20 the homopolyimide being selected from the group consisting of formulas (i) and (ii), and

(b) an organic solvent soluble copolyimide film, the copolyimide being selected from the group consisting of formulas (i), (ii) and (iii).

where each

R is a substituent selected independently from the group consisting of H, halogen, phenyl, substituted phenyl, alkyl and substituted alkyl from 1 to 20 carbons;

E and F are selected independently from the group consisting of a covalent bond, a CH₂ group, a C(CH₃)₂ group, a C(CX₃)₂ group wherein X is a halogen, a CO group, an O atom, a S atom, a SO₂ group, a Si(R)₂ group wherein R is as defined previously and a N(R) group wherein R is as defined previously;

A is selected from the group consisting of hydrogen, halogen, alkyl, substituted alkyl, nitro, cyano, thioalkyl, alkoxy, substituted alkoxy, aryl and substituted aryl, aliphatic and aromatic esters and combinations thereof from 1 to 20 carbons;

n is an integer from 0 to 4;
p and q are integers from 1 to 3 when the polyimide is a homopolyimide and are integers from 0 to 3 and 1 to 3 respectively when the polyimide is a copolyimide, and when p and q are greater than 1, the linking group between benzyl or substituted benzyl groups is F; and

y, if present, varies correspondingly from 0 to 100.
litic dianhydride, 3,6-dibromopyromellitic dianhydride and 3,6-dichloropyromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride, 2,3,3',4,4'-benzophenonetetracarboxylic acid dianhydride, 2,2',3,3'-benzophenone tetracarboxylic acid dianhydride, 3,3',4,4'-biphenyltetra carboxylic acid dianhydride, bis(2,3-dicarboxyphenyl) methane dianhydride, bis(2,5,5,6-trifluoro-3,4-dicarboxyphenyl)methane dianhydride, 2,2'-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2'-bis(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane dianhydride, bis(3,4-dicarboxyphenyl)sulfone dianhydride, 4,4'-(4,4'-idopropylidene-di(p-phenyleneoxy))-bis(phthalic anhydride), N,N-(3,4-dicarboxyphenyl)-N-methylamine dianhydride, bis(3,4-dicarboxyphenyl)diethylsilane dianhydride, 2,3,6,7-naphthalene-tetra carboxylic acid dianhydride, 1,2,5,6-naphthalene-tetracarboxylic acid dianhydride, 2,6-dichloronaphthalene-1,4,5,8-tetra carboxylic acid dianhydride, thiophene-2,3,4,5-tetracarboxylic acid dianhydride, pyrazine-2,3,5,6-tetracarboxylic acid dianhydride and pyridine-2,3,5,6-tetracarboxylic acid dianhydride

23. The display of claim 21 wherein the diamine is selected from the group consisting of o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2,4-diaminotoluene, 1,4-diamino-2-methoxybenzene, 1,4-diamino-2-phenylbenzene, 1,3-diamino-4-chlorobenzene, 4,4'-diaminodibiphenyl, 4,4'-diaminodiphenylmethane, 2,2'-bis(4-aminophenyl)propane, 2,2'-bis(4-aminophenyl)-1,1,1,3,3,3-hexafluoropropane, 4,4'-bis(4-aminophenoxy)biphenyl, 4,4'-(3-aminophenoxy)biphenyl, 2,2-bis(4-(4-aminophenoxy)phenyl)-propane, 2,2-bis(4-(4-aminophenoxy)phenyl)-1,1,1,3,3,3-hexafluoropropane, 4,4'-diaminodiphenylthioether, 4,4'-diaminodiphenyl sulfone, 2,2'-diaminobenzophenone, 3,3'-diaminobenzophenone, 1,8-diaminonaphthalene, 1,5-diaminonaphthalene, 2,6-diaminopyridine, 2,4-diaminopyrimidine, 2,4-diaminotriazine, 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl, 2,2'-dibromo-4,4'-diaminobiphenyl, 2,2'-dicyano-4,4'-diaminobiphenyl, 2,2'-dichloro-6,6'-dimethyl-4,4'-diaminobiphenyl, 2,2'-dimethyl-4,4'-diaminobiphenyl, 3,3'-dimethyl-4,4'-diaminobiphenyl, 2,2'-dicarboalkoxy-4,4'-diaminobiphenyl and 2,2'-dicarboalkoxy-6,6'-dimethyl-4,4'-diaminobiphenyl.

24. An improved liquid crystal display of the type having a liquid crystal element, at least two light-transmissive birefringent coatings, at least one coating having a positive birefringence and at least one other coating having a negative birefringence, and a polarizing sheet arranged such that the coatings are held between the liquid crystal elements and the polarizing sheet, wherein the improvement comprises at least one non-stretched negative polyimide coating, soluble in the imide form, having a negative birefringence, the polyimide coating being selected from the group consisting of

(a) an organic solvent soluble homopolyimide coating, the homopolyimide being selected from the group consisting of formulas (i) and (ii), and

(b) an organic solvent soluble copolyimide coating, the copolyimide being selected from the group consisting of formulas (i), (ii) and (iii).
where each

R is a substituent selected independently from the group consisting of H, halogen, phenyl, substituted phenyl, alkyl and substituted alkyl from 1 to 20 carbons;

E and F are selected independently from the group consisting of a covalent bond, a CH₂ group, a C(CH₃)₂ group, a C(CHX₃)₂ group wherein X is a halogen, a CO group, an O atom, a S atom, a SO₂ group, a Si(R)₂ group wherein R is as defined previously and a N(R) group wherein R is as defined previously; A is selected from the group consisting of hydrogen, halogen, alkyl, substituted alkyl, nitro, cyano, thiokyl, alkoxyl, substituted alkoxy, aryl and substituted aryl, aliphatic and aromatic esters and combinations thereof from 1 to 20 carbons;

n is an integer from 0 to 4;
p and q are integers from 1 to 3 when the polyimide is a homopolyimide and are integers from 0 to 3 and 1 to 3 respectively when the polyimide is a copolyimide, and when p and q are greater than 1, the linking group between benzyl or substituted benzyl groups is F; and

x, if present, varies from 100 to 0 while y, if present, varies correspondingly from 0 to 100.

25. The coating of claim 24 wherein the dianhydride is selected from the group consisting of pyromellitic dianhydride, 3,6-diphenylpyromellitic dianhydride, 3,6-bis(trifluoromethyl)pyromellitic dianhydride, 3,6-bis(3-methyl)pyromellitic dianhydride, 3,6-diiodopyromellitic dianhydride, and 3,6-dichloropyromellitic dianhydride, and 3,6-dichloropyromellitic dianhydride, 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride, 2,3,3',4'-benzophenonetetracarboxylic acid dianhydride, 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride, 3,3',4,4'-biphenyltetra-carboxylic acid dianhydride, bis(2,3-dicarboxyphenyl)methane dianhydride, bis(2,5,6-trifluoro-3,4-dicarboxyphenyl)methane dianhydride, 2,2-bis(3,4-dicarboxyphenyl)propane dianhydride, 2,2-bis(3,4-dicarboxyphenoxy)-1,1,1,3,3,3-hexafluoropropene dianhydride, bis(3,4-dicarboxyphenoxy)-1,1,1,3,3,3-hexafluoropropene dianhydride, bis(4,4'-idopropylidyne-di(p-phenyleneoxy))-1,3-bis(phthalic anhydride), N,N-(3,4-dicarboxyphenyl)-N-methylamine dianhydride, bis(3,4-dicarboxyphenyl)die-thylsilane dianhydride, 2,3,6,7-naphthalene-tetracarboxylic acid dianhydride, 1,2,5,6-naphthalene-tetracarboxylic acid dianhydride, 2,6-dichloronaphthalene-1,4,5,8-tetracarboxylic acid dianhydride, thiophene-2,3,4,5-tetracarboxylic acid dianhydride, pyrazine-2,3,5,6-tetracarboxylic acid dianhydride and pyridine-2,3,5,6-tetracarboxylic acid dianhydride.

26. The coating of claim 24 wherein the diamine is selected from the group consisting of o-phenylenediamine, m-phenylenediamine, p-phenylenediamine, 2,4-diaminotoluene, 1,4-diamino-2-methoxybenzene, 1,4-diamino-2-phenylbenzene, m-phenylenediamine, 1,3-diamino-4-chlorobenzene, 4,4'-diaminobiphenyl, 4,4'-diaminodiphenylmethane, 2,2-bis(4-aminoxyphenyl)propane, 2,2-bis(4-aminoxyphenyl)-1,1,1,3,3,3-hexafluoropropene, 4,4'-diaminodiphenyl ether, 3,4-diaminodiphenyl ether, 1,3-bis(3-aminophenoxy)benzene, 1,3-bis(4-aminophenoxy)benzene, 1,4-bis(4-aminophenoxy)benzene, 4,4'-bis(4-aminophenoxypyrophene), 4,4'-bis(3-aminophenoxypyrophene), 2,2-bis(4-aminoxyphenoxypyrophene)-propane, 2,2-bis(4-aminoxyphenoxypyrophene)-1,1,1,3,3,3-hexafluoropropene, 4,4'-diaminodiphenyl thiodyer, 4,4'-diaminodiphenyl sulfone, 2,2'-diaminobenzophenone, 3,3'-diaminobenzophenone, 1,8-diaminonaphthalene, 1,5-diaminonaphthalene, 2,6-diaminopyridine, 2,4-diaminopyrimidine, 2,4-diamino-s-triazine, 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl, 2,2'-dibromo-4,4'-diaminobiphenyl, 2,2'-dicyano-4,4'-diaminobiphenyl, 2,2'-dichloro-6,6'-dimethyl-4,4'-diaminobiphenyl, 2,2'-dimethyl-4,4'-diaminobiphenyl, 3,3'-dimethyl-4,4'-diaminobiphenyl, 2,2'-dicharoalkoxy-4,4'-diaminobiphenyl and 2,2'-dicarboalkoxy-6,6'-dimethyl-4,4'-diaminobiphenyl.