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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
3 March 2005 (03.03.2005)

PCT

(10) International Publication Number
WO 2005/019379 A1

(51) International Patent Classification^{7}: **C09K 19/38**, 19/02

(21) International Application Number: PCT/EP2004/008478

(22) International Filing Date: 29 July 2004 (29.07.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
03019223.1 26 August 2003 (26.08.2003) EP

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/019379 A1

(54) Title: POLYMER FILM WITH TWIST PATTERN

(57) Abstract: The invention relates to a polymer film comprising a polymerised chiral liquid crystal material with helically twisted structure having a pattern of regions with different twist, to methods of its preparation, and to its use in liquid crystal displays or other optical elements, components or devices.

Polymer Film with Twist Pattern

Field of the Invention

The invention relates to a polymer film comprising a polymerised chiral liquid crystal material with helically twisted structure having a pattern of regions with different twist. The invention further relates to methods of preparing such a film, and to its use in liquid crystal displays or other optical elements, components or devices.

Background and Prior Art

Retardation films are commonly used in liquid crystal displays to convert between linear and circular polarised light. It is well known in the literature that layers of polymerised liquid crystal (LC) compounds, also known as reactive mesogens (RM) can be created to provide retardation layers, for example RMS03001 is a commercially available solution of RMs (from Merck KGaA, Darmstadt, Germany) which can be spincoated and photo-polymerised to provide a planar nematic film. By varying the spincoating speed it is possible to produce films of different thickness and so produce half-wave and quarter-wave retardation films.

Non-patterned, twisted retardation films have been previously reported in WO 02/73301. For example, by adding chiral dopants to a polymerisable nematic host like the commercially available RMS03001 (from Merck KGaA, Darmstadt, Germany) it is also possible to produce well aligned, chiral films as disclosed for example in GB 2330360 and WO 02/73301. The chiral films produced have a helical arrangement of RM molecules throughout the thickness of the film. The sense of the helix introduced into the RM layers depends on the sense of chirality (left or right handed) of the chiral dopant used. In this way, it is possible to create films with either a left hand or right hand twist of the helix dependent upon the dopant used. The extent of chirality induced in the RM film (i.e. how many turns of a helix are present in the entire film) depends on the concentration of the dopant added and also the HTP of the chiral dopant.

However, as displays become more demanding it is increasingly desirable to be able to pattern the retardation layer, e.g. for parallex barrier layers in switchable two dimensional (2D) / three dimensional (3D) displays as disclosed in US 6,437,915 and US 6,046,849, which can be used e.g. in mobile phones.

EP 1 295 929 discloses patterned twisted films showing a pattern of regions with different twist sense for use as decorative or security marking. These films are prepared from a layer of a polymerisable chiral LC mixture comprising two chiral dopants with opposite twist sense. The net twist of the mixture is given by the twisting power and concentration of each dopant. One of the dopants is photoisomerisable and changes its twisting power upon photoirradiation. In this way the net twist can be varied in selected regions of the layer by photoirradiation, and the twisted structure fixed by thermal or photopolymerisation, to provide a patterned film.

In the cholesteric polymer films disclosed in EP 1 295 929 the helices have a relatively short pitch of the order of the wavelength of visible light, such that different regions will selectively reflect either right handed or left handed circularly polarised visible light.

However, in many applications, like e.g. the 2D/3D displays mentioned above, a long pitch chiral helix is required, such that it is possible to retard visible light and hence provide a retardation layer suitable for TN or STN type devices, i.e. a twisted A-plate retarder.

WO 98/57223 discloses the use of chiral photoisomerisable compounds for preparing a multi-domain liquid crystal display having different areas with different twist sense (handedness). However, it does not mention coated polymer films.

WO 02/07330 discloses the use and benefits of a twisted A-plate retarder. However, the twisted A-plate film in WO 02/07330 can not be readily patterned and so does not offer a convenient method to produce patterned retardation films, such as required e.g. for the parallax barrier in the 2D/3D display described in US 6,437,915 and US 6,046,849.

The article '*3D Display Hardware Research at Sharp Labs: an update*' published in Sharp Technical Journal Issue #74 1999 describes the production process for a patterned RM film for use as parallax barrier as reported in US 6,437,914. However, this process is complicated and comprises many different steps, like for example:

1. Coating and baking polyimide
2. Rubbing the polyimide at 90 °
3. Coating the polyimide with photoresist
4. Pre-baking the photoresist
5. Using a photo-mask to selectively irradiate the photoresist
6. develop photoresist (wash away the photoresist from the irradiated regions)
7. Bake the photoresist
8. Rubbing the exposed polyimide at 45 °
9. Removing the remaining photoresist
10. Coating an RM layer onto the polyimide
11. Polymerising the RM layer

There is therefore a need for improved patterned retardation films, and improved methods for their preparation, which do not have the drawbacks of prior art films and methods.

It was an aim of the present invention to provide improved patterned retardation films and methods for their preparation. Other aims of the invention are immediately evident to the expert from the following description.

The inventors of the present invention have found that these aims can be achieved and the above problems can be solved by providing a retardation film and a method of its preparation as described in the present invention, in particular by an anisotropic film comprising a chiral polymerised liquid crystal material and exhibiting a pattern of twisted and untwisted regions or a pattern of regions with different twist angle.

The present invention uses a polymerisable liquid crystal material comprising small concentrations of photoisomerisable chiral dopants to achieve a photo-patternable retardation film. Such a film can be produced in much fewer steps than in the prior art process mentioned above, for example with the following steps:

1. Coating and baking polyimide
2. Rubbing the polyimide
3. Coating an RM layer on the polyimide
4. Irradiating the RM layer through a photo-mask
5. Polymerising the RM layer

The use of small concentrations of chiral dopants is also desirable because the films of this invention can be readily applied to a wide range of existing polymerisable liquid crystal host materials without the need to specifically scale-up a series of new polymerisable liquid crystal materials (which would need to be used at much greater concentrations).

Another benefit of the current invention is that it is possible to produce a patterned, twisted retardation layer, where each region has a different twist. This makes it possible to construct a retardation film in which the different regions, solely by virtue of the extent of twist, can retard light and either convert it from linear to circularly polarised light or let it remain as retarded linearly polarised light.

Summary of the Invention

The invention relates to a patterned polymer film comprising a polymerised chiral liquid crystal (LC) material having a pattern of at least two regions with different twist angle and/or a pattern of at least one twisted region and at least one untwisted region.

The invention further relates to a method of preparing a polymer film as described above and below by providing a layer of a polymerisable chiral LC material comprising

- at least one first chiral compound that induces a helical twist of a given twist sense in the chiral material, and is convertible between at least two states with different twisting power, wherein conversion of the chiral compound can be induced by photoradiation and
- at least one second chiral compound that induces a helical twist of a twist sense opposite to said first chiral compound in the chiral material, and is not convertible between two or more states with different twisting power under the same conditions as said first chiral compound,

irradiating selected regions of the layer with photoradiation that changes the degree of chirality of said first chiral compound, and polymerising said selected regions.

The invention further relates to the use of a polymer film as described above and below as compensator, retarder or polariser in liquid crystal displays or other optical elements, components or devices, in particular in switchable two dimensional (2D) / three dimensional (3D) displays.

The invention further relates to a liquid crystal display, optical element, component or device comprising a polymer film as described above and below, in particular to a 2D/3D display.

Definition of Terms

The term 'film' as used in this application includes self-supporting, i.e. free-standing, films that show more or less pronounced mechanical stability and flexibility, as well as coatings or layers on a supporting substrate or between two substrates.

The term 'liquid crystal or mesogenic material' or 'liquid crystal or mesogenic compound' should denote materials or compounds comprising one or more rod-shaped, board-shaped or disk-shaped mesogenic groups, i.e. groups with the ability to induce liquid crystal phase behaviour. The compounds or materials comprising mesogenic groups do not necessarily have to exhibit a liquid crystal phase themselves. It is also possible that they show liquid crystal phase behaviour only in mixtures with other compounds, or when the mesogenic compounds or materials, or the mixtures thereof, are polymerised.

The term 'helically twisted structure' relates to a film comprising one or more layers of liquid crystal material wherein the mesogens are oriented with their main molecular axis in a preferred direction within molecular sublayers, with this preferred orientation direction in different sublayers being twisted around a helix axis that is substantially perpendicular to the film plane, i.e. substantially parallel to the film normal. This definition includes orientations of the helix axis from 75 to 90°, preferably 80 to 90°, very preferably 85 to 90° and most preferably 88 to 90° relative to the film plane.

The term "quarter wave film" or "QWF" refers to an optical film that creates a phase difference of $\pi/2$ between the two orthogonal, linearly-polarized modes propagating in an anisotropic material.

The term "half wave film" or "HWF" refers to an optical film that creates a phase difference of π between the two orthogonal, linearly-polarized modes propagating in an anisotropic material.

Brief Description of the Drawings

Figure 1 schematically depicts a polymer film (1) according to the present invention comprising an untwisted region (2) and a twisted region (3), combined with a polariser (4).

Figure 2 shows the transmission data versus rotation angle of an unisomerised polymer film (a) and an isomerised polymer film (b) prepared according to example 1, which are rotated through 360° between crossed polarisers.

Figure 3 shows a photograph of a polymer film according to example 2 comprising twisted an untwisted regions viewed on a light box through crossed polarisers.

Detailed Description of the Invention

This invention exploits the ability to control the helical twisting power (HTP) of a chiral dopant to achieve either a twisted or planar retardation film. The HTP of a chiral dopant describes its ability to induce a twist in an LC host material, and is given by equation (1) :

$$p = \frac{1}{HTP} \cdot \frac{1}{c} \qquad (1)$$

wherein p is the pitch p of the molecular helix in the first approximation, which is sufficient for most practical applications, and c is the concentration of the chiral dopant in the liquid crystal host.

A polymer film according to the present invention is preferably prepared by coating a thin layer of a chiral polymerisable LC material onto a substrate, aligning the material so that the axis of the molecular helix is oriented substantially perpendicular to the plane of the layer, changing the chirality in selected parts of the layer by photoradiation, and fixing the chiral structure by polymerisation to obtain a patterned polymer film.

The polymerisable chiral LC material contains at least two chiral compounds with different twist sense. The first chiral compound is for example a photoisomerisable chiral compound that changes its HTP due to isomerisation upon photoradiation with a given wavelength, or upon photoradiation with a given wavelength and intensity. The second chiral compound does not change its HTP under the same conditions as the first compound. For example, the second chiral compound can be a non-isomerisable compound that does not change its HTP at all when subjected to photoradiation. It is also possible that the second chiral compound is a photoisomerisable chiral compound that changes its HTP under photoradiation of different wavelength and/or intensity than that used for the first chiral compound.

A change of the total twist angle in selected parts of the polymerisable chiral LC material can now be achieved by appropriately selecting the amount and HTP of the first and second chiral compound. For example, a suitable chiral LC material contains a photoisomerisable chiral compound and a non-isomerisable chiral compound, one of which is levorotatory and the other is dextrorotatory. The isomerisable compound has for example a larger absolute HTP and/or is present in an excess amount compared to the non-isomerisable compound, so that the net twist sense of the chiral LC material is the same as the twist sense of the first chiral compound. Upon photoradiation of selected parts of the chiral LC material, the photoisomerisable chiral compound is converted into a form with different HTP, for example its twisting power is reduced by partial or complete conversion of the chiral material into a lower HTP chiral material, whereas the non-isomerisable chiral compound does not change its HTP. As a result, the net twist angle in the selected parts of the chiral LC material is smaller than in the non-selected parts, or the net twist angle in the selected parts of the chiral LC material is zero, i.e. the material in these parts exhibits an untwisted structure.

It is also possible to prepare a patterned polymer film according to the invention that has such a high twist angle that it reflects light of visible wavelengths. In case the film has a pattern of regions having a high, but different twist angle, these regions exhibit different reflection colour. Such a film can be used for example as colour filter.

However, films with a pitch that is larger than the visible wavelength range, in particular with a pitch of more than 1 μm, are more preferred.

After the chirality is changed as described above in selected parts of the polymerisable chiral LC material, the material is polymerised in situ to permanently fix the chiral structure in the selected parts or in the entire LC material. Polymerisation can be carried out for example by photopolymerisation or thermal polymerisation. Photopolymerisation is preferred. Especially preferably polymerisation in the LC material is initiated by the same photoradiation that changes the chirality of said first chiral compound.

A preferred process for preparing a patterned retardation film according to the present invention comprises the following steps:

1. Providing a layer of an alignment material, preferably by coating and optionally baking or curing polyimide, on a substrate.
2. Optionally rubbing the alignment material, like the polyimide, unidirectionally to create a preferred orientation direction.
3. Coating a layer of a photopolymerisable chiral LC material as described above and below onto the alignment layer.
4. Irradiating the LC layer through a photomask to induce photoisomerisation of the isomerisable chiral dopant in the regions not covered by the photomask, thereby creating a pattern of regions with different twist in the layer.
5. Polymerising the LC layer to permanently fix the twist pattern.

Another preferred embodiment of the present invention relates to an anisotropic polymer film prepared from a polymerisable chiral LC material that does not polymerise, or polymerises only slowly, in the presence of oxygen. A suitable chiral LC material for this embodiment can be formulated for example by selection of suitable photoiniators that do not or do not well react in the presence of oxygen. The film is prepared by irradiating selected regions of the polymerisable material with photoradiation that changes the HTP of said first chiral compound in the presence of oxygen, so that polymerisation is hindered, or inhibited, and subsequently polymerising the selected regions or the entire material in the absence of oxygen.

Preferably polymerisation in the polymerisable chiral LC material according to this embodiment is faster than isomerisation of the first chiral compound, so that the chirality of the LC material in the unpolymerised parts does not change, or at least does not change substantially, during photopolymerisation.

It is also possible to achieve polymerisation, but no isomerisation, in the chiral material for example by using low intensity radiation to polymerise in selected regions and then higher intensity to polymerise the entire material, or by using different wavelengths to initiate isomerisation and polymerisation.

An anisotropic film according to this preferred embodiment can be prepared by coating the polymerisable chiral LC material onto a substrate in the presence of oxygen, e.g. in an air atmosphere, and subjecting selected areas of the coating to photoradiation. This is achieved for example by irradiation through a photomask. Alternatively, irradiation can be carried out in selected areas by means of a finely focussed radiation source, like e.g. a laser. The photoradiation leads to a change of the chirality in the selected areas of the LC material as described above, whereas in the non-selected areas the chirality remains unchanged. Polymerisation in the entire coating is hindered by the presence of oxygen. Afterwards the entire coating is polymerised, e.g. by thermal polymerisation or photopolymerisation, in the absence of oxygen, to fix the chiral structure in the selected and non-selected areas. This is done for example by polymerisation under an inert gas atmosphere or by covering the coating with an oxygen barrier layer, like e.g. a PET film. As a result, a patterned film is obtained with a chirality, and thus a twist angle, that is different in the selected and the non-selected areas.

Alternatively, an anisotropic polymer film according to this preferred embodiment can be prepared by a method comprising the following steps that are carried out in the presence of oxygen,

A) providing a layer of a photopolymerisable chiral LC material that does not polymerise in the presence of oxygen and comprises first and second chiral compounds as described above,

B) 1) covering selected areas of the layer with a substrate and irradiating the layer with photoradiation that changes the twisting power of said first chiral compound and initiates polymerisation of the chiral polymerisable material, wherein the substrate has the properties of an oxygen barrier layer and is transparent for the photoradiation, and

   2) repeating the procedure of step B1 one or more times for at least one of the areas of the layer that were not covered with a substrate in the previous step.

In step B1, the chiral LC material is polymerised only in those areas of the layer that are covered by the substrate, which is transparent for photoradiation and excludes oxygen that could inhibit the polymerisation. Since polymerisation is faster than isomerisation, the chiral structure in the covered areas is permanently fixed before it changes substantially. In the uncovered areas, polymerisation is hindered by the presence of oxygen, so that isomerisation and thus a change of the chirality can take place. In step B2, the changed chiral structure in the previously uncovered parts is fixed by polymerisation under the transparent oxygen barrier substrate.

As a result, a patterned film is obtained with a chirality and twist angle that is different in the covered and uncovered areas of step B1.

Preferably, irradiation in step B1 is carried out with an intensity that is high enough and/or for a period that is long enough so that the first chiral compound is completely isomerised in the uncovered areas, and thus the change of chirality is complete. In step B2 all previously uncovered areas are then polymerised, i.e. step B2 is carried out only once.

It is also possible, however, to carry out irradiation in step B1 such that the chirality in the uncovered areas is only changed to a certain degree, e.g. by using low radiation intensity or short radiation time. In a first step B2, only some of the previously uncovered areas of step B1 are then irradiated through the oxygen barrier substrate to polymerise and fix the changed structure, whilst in the still uncovered areas further isomerisation can occur, which is then fixed in a second or further step B2. Thus, a patterned film with more than two different areas having different twist angle can be prepared.

As an alternative to the above described particularly preferred embodiment with the material that does not polymerise in the presence of oxygen, it is possible to use a chiral polymerisable LC material that polymerises in air, and to use low intensity radiation to isomerise selected regions of the material, and higher intensity radiation to polymerise the material.

The polymerisable chiral LC material used for the preparation of the anisotropic polymer film according to the present invention is preferably a chiral smectic or chiral nematic liquid crystal material. Chiral nematic liquid crystal materials are especially preferred.

The polymerisable chiral LC material is preferably dissolved or dispersed in an organic solvent and is polymerised or crosslinked during or after evaporation of the solvent.

The amount and HTP of the dopants can be selected such that the initial mixture, i.e. before isomerisation, has an untwisted structure (i.e. racemic) and upon photoisomerisation becomes twisted, or such that the initial mixture has a twisted structure and upon photoisomerisation becomes racemic and untwisted.

Another preferred embodiment of the present invention relates to a patterned film having a pattern of at least two regions with different twist angle.

Another preferred embodiment of the invention relates to a patterned film having a pattern of at least one twisted and at least one untwisted region.

Another preferred embodiment of the invention relates to an initially racemic mixture which, when coated and polymerised will produce either a quarter-wave or half-wave retardation film. This mixture can be photoisomerised such that it produces either a left- or right-handed twisted retardation film.

Another preferred embodiment of the present invention relates to a patterned film having a pattern of regions with different twist and/or a pattern of twisted and untwisted regions, wherein the twist is selected such that the film does not reflect visible light, in particular such that the helical pitch in the twisted region is larger than 1 μm. This layer is advantageous for use as retardation film that does not reflect visible light, like e.g. the cholesteric films disclosed in prior art, but creates a phase shift in visible light, in order to compensate e.g. for a phase shift created in a liquid crystal display device. Typically the twist angle in such a retardation film is in the range of from more than 0° to 360°. As only a low twist is required only a low amount of chiral compounds is needed in such a film, compared to a cholesteric film.

Especially preferred embodiments of the invention relate to a patterned film having

- at least one region of 0° twist angle and at least one region of a twist angle from above 0 to +270° or from below 0 to -270°,
- at least one region of 0° twist angle and at least one region of a twist angle from above 0 to +180° or from below 0 to -180°,
- at least one region of 0° twist angle and at least one region of a twist angle from above 0 to +90° or from below 0 to -90°,
- at least two regions having a different twist angle selected from +90° to -90° and preferably being different from 0°,
- at least one region of 0° twist angle and at least one region of a twist angle from +90° to -90°,
- at least three regions having a twist angle selected from 0 to +90° or from 0 to -90°, preferably at least one region having a twist angle of ±90°, ±75° and ±60°, respectively, wherein preferably all regions have the same sign of the twist angle.

Figure 1 does exemplarily and schematically show a patterned film (1) according to a preferred embodiment of the present invention, comprising a region (2) with a twist of 0° and region (3) with a twist of e.g. 90°. The film comprises calamitic, uniaxially positive birefringent polymerised LC material with planar orientation, wherein the mesogens of the LC molecules in region (2) are oriented in the film plane in the direction depicted by the double arrow, and in region (3) are twisted around a helix axis perpendicular to the film plane at a twist angle of 90° (illustrated by the set of arrows). The effective retardation for linearly polarized light of the wavelength λ passing through the film (1), which has been linearly polarized by a polarizer (4) in the direction indicated by the double arrow, is 0 in the untwisted region (2) and $\lambda/2$ in region (3).

Preferably the polymerisable chiral LC material comprises

- at least one first chiral compound that has a given twist sense and changes its HTP upon photoradiation and
- at least one second chiral compound that has a twist sense opposite to that of said first chiral compound, and does not

change its HTP when subjected to the photoradiation under which said first chiral compound changes its HTP,

and further comprises at least one polymerisable compound having at least one polymerisable group.

The polymerisable compound can also be said first and/or second chiral compound. Alternatively, the polymerisable compound is an additional polymerisable compound that is preferably liquid crystalline or mesogenic.

Very preferably the chiral polymerisable LC material comprises

a1) at least one first chiral compound that has a given twist sense and changes its chirality upon photoradiation, which may in addition be polymerisable and/or mesogenic,

a2) at least one second chiral compound that has a twist sense opposite to that of said first chiral compound and does not change its chirality when subjected to the photoradiation under which said first chiral compound changes its chirality, which may in addition be polymerisable and/or mesogenic,

b) at least one polymerisable mesogenic compound having at least one polymerisable group, and

c) a polymerisation initiator.

Especially preferred compounds for use as first and second chiral compound are those with a high helical twisting power (HTP), so that the amount of the chiral compound in the material can be reduced.

Chiral compounds changing their chirality upon photoradiation which can be used in the present invention are known to the expert. For example, suitable and preferred compounds are photosensitive chiral compounds which change their structure or shape upon photoirradiation by reactions including, but not limited to, photoisomerisation, photo-induced 2+2 cycloaddition, photo-fries arrangement or a comparable photodegradation process.

Especially suitable and preferred are photoisomerisable chiral compounds which show E-Z or cis-trans isomerisation upon photoirradiation and are thereby converted into a form with a different HTP, where they determine the pitch of the liquid crystal material to a different extent. Further suitable and preferred are photodegradable or (photo)tunable chiral materials (TCM) that change from chiral to achiral or to a racemic mixture upon photoirradiation, due to destruction of their chirality by photoelimination or photocleavage of the chiral center.

For example, suitable photoisomerisable chiral materials are those comprising menthone, camphor or nopinone derivatives or chiral stilbenes, as described by P. van de Witte et al., Liq. Cryst. 24 (1998), 819-27, J. Mat. Chem. 9 (1999), 2087-94 and Liq. Cryst. 27 (2000), 929-33 and A. Bobrovski et al., Liq. Cryst. 25 (1998), 679-687. Suitable TCMs comprising a photocleavable carboxylic acid group or aromatic keto group attached to the chiral center are disclosed in US 5,668,614. Furthermore, F. Vicentini, J. Cho and L. Chien, Liq. Cryst. 24 (1998), 483-488 describe binaphthol derivatives as TCMs and their use in multicolour cholesteric displays.

Particularly preferred are polymerisable and photoisomerisable chiral materials comprising menthone, camphor or nopinone derivatives or chiral stilbenes as disclosed by P. van de Witte et al., Liq. Cryst. 24 (1998), 819-27, J. Mat. Chem. 9 (1999), 2087-94 and Liq. Cryst. 27 (2000), 929-33 and A. Bobrovski et al., Liq. Cryst. 25 (1998), 679-687.

Further preferred are polymerisable photoisomerisable chiral compounds as disclosed in WO 02/40614.

The polymerisable chiral LC material further comprises a second chiral compound which does not change its chirality under the same conditions as the first chiral dopant. Preferably the second chiral compound is a non-isomerisable compound. It can be polymerisable or not, and can also be mesogenic or liquid crystalline.

Suitable chiral dopants can be selected e.g. from the commercially available R- or S-811, R- or S-1011, R- or S-2011, R- or S-3011, R- or S-4011, R- or S-5011, or CB 15 (from Merck KGaA, Darmstadt, Germany). Very preferred are chiral compounds with a high helical twisting power (HTP), in particular compounds comprising a sorbitol group as described in WO 98/00428, compounds comprising a hydrobenzoin group as described in GB 2,328,207, chiral binaphthyl derivatives as described in WO 02/94805, chiral binaphthol acetal derivatives as described in WO 02/34739, chiral TADDOL derivatives as described in WO 02/06265, and chiral compounds having at least one fluorinated linkage group and a terminal or central chiral group as described in WO 02/06196 and WO 02/06195.

Especially suitable polymerisable, non-isomerisable chiral compounds can be taken from the lists below.

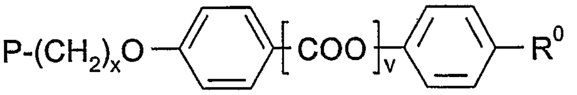
Further to the chiral compounds the polymerisable LC material preferably comprises at least one achiral polymerisable mesogenic compound having at least one polymerisable functional group.

In a preferred embodiment the polymerisable LC material comprises at least one chiral or achiral polymerisable mesogenic compound having two or more polymerisable functional groups (di- or multireactive or di-or multifunctional compounds). Upon polymerisation of such a mixture a three-dimensional polymer network is formed, which is self-supporting and shows a high mechanical and thermal stability and a low temperature dependence of its physical and optical properties. By varying the concentration of the multifunctional mesogenic or non mesogenic compounds the crosslink density of the polymer film and thereby its physical and chemical properties, in particular the temperature dependence of the optical properties, the thermal and mechanical stability and the solvent resistance, can be tuned easily.

Polymerizable mesogenic mono-, di- and multireactive compounds used for the present invention can be prepared by methods which are known per se and which are described, for example, in standard works of organic chemistry such as, for example, Houben-Weyl, Methoden der organischen Chemie, Thieme-Verlag, Stuttgart.

Examples of suitable polymerizable mesogenic compounds that can be used as monomers or comonomers together with the compounds according to the present invention in a polymerizable LC mixture, are disclosed for example in WO 93/22397, EP 0 261 712, DE 195 04 224, WO 95/22586, WO 97/00600 and GB 2 351 734. The compounds disclosed in these documents, however, are to be regarded merely as examples that shall not limit the scope of this invention.

Examples of especially useful chiral and achiral polymerizable mesogenic compounds (reactive mesogens) are shown in the following lists which should, however, be taken only as illustrative and is in no way intended to restrict, but instead to explain the present invention:



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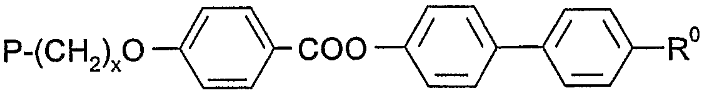

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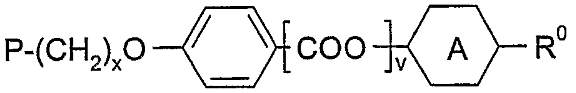

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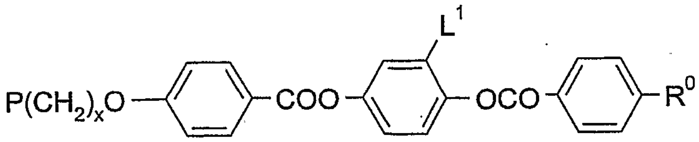

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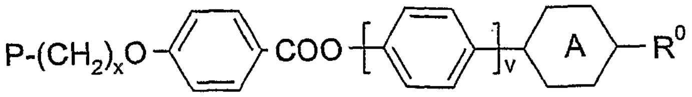

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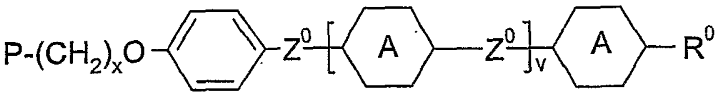

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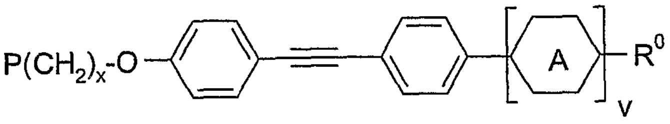

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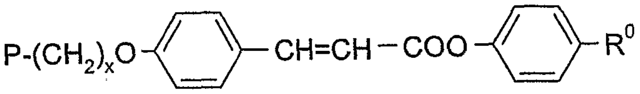

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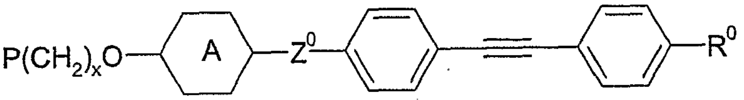

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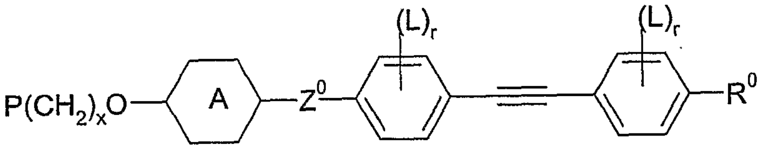

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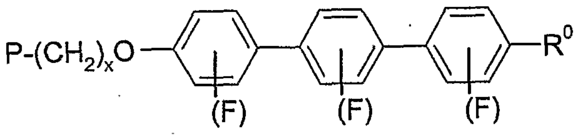

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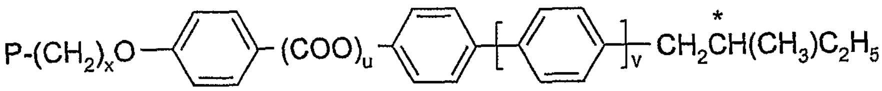

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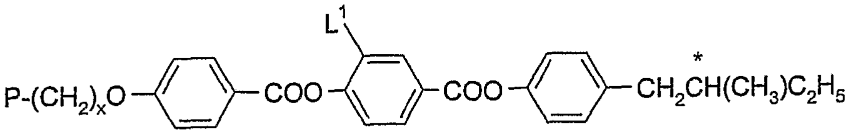

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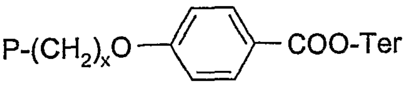

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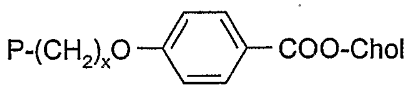

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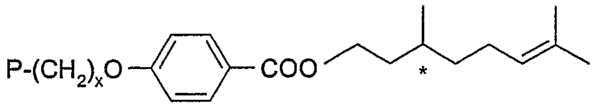

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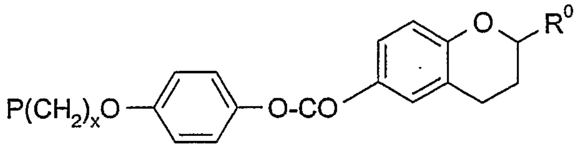

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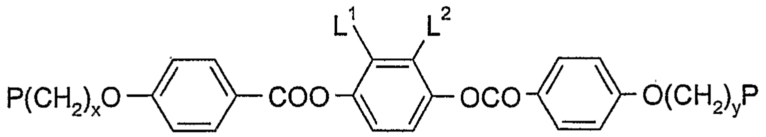

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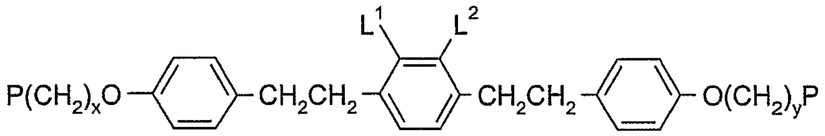

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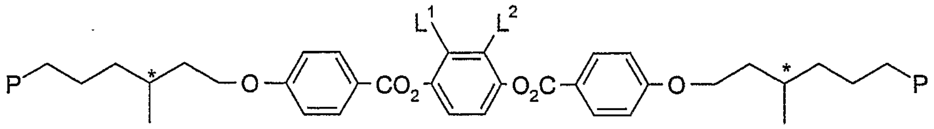

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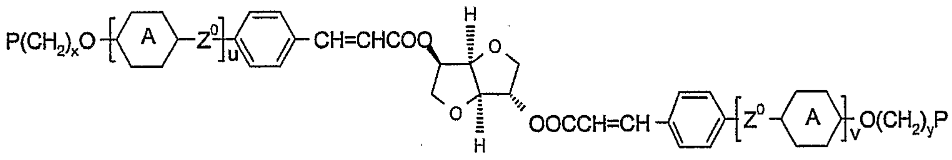

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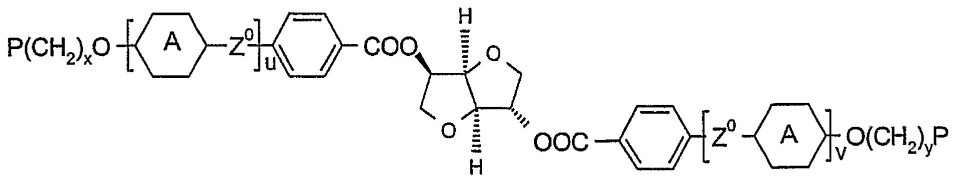

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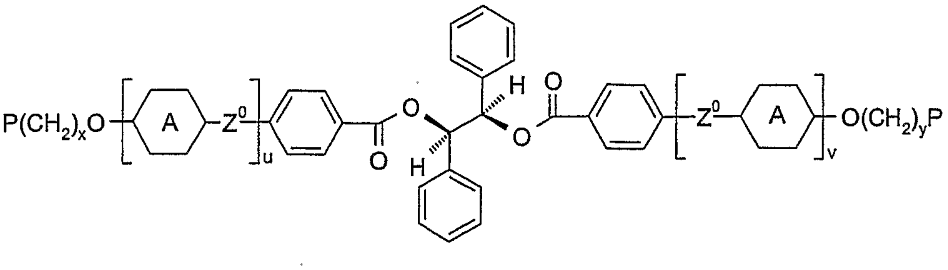
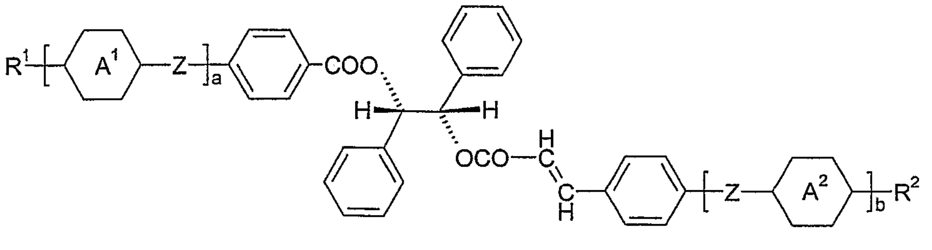


(R23)

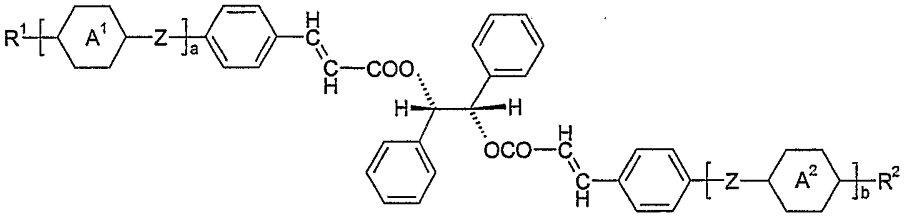
In the above formulae, P is a polymerisable group, preferably an acryl, methacryl, vinyl, vinyloxy, propenyl ether, epoxy, oxetane or styryl group, x and y are identical or different integers from 1 to 12 , A is 1,4-phenylene that is optionally mono-, di- or trisubstituted by L^1, or 1,4-cyclohexylene, u and v are independently of each other 0 or 1, Z^0 is -COO-, -OCO-, $-CH_2CH_2-$, -CH=CH-, -C≡C- or a single bond, R^0 is a polar group or an unpolar group, Ter is a terpenoid radical like e.g. menthyl, Chol is a cholesteryl group, L, L^1 and L^2 are independently of each other H, F, Cl, CN or an optionally halogenated alkyl, alkoxy, alkylcarbonyl, alkylcarbonyloxy, alkoxycarbonyl or alkoxycarbonyloxy group with 1 to 7 C atoms, and r is 0, 1, 2, 3 or 4. The phenyl rings in the above formulae are optionally substituted by 1, 2, 3 or 4 groups L.

The term 'polar group' in this connection means a group selected from F, Cl, CN, NO_2, OH, OCH_3, OCN, SCN, an optionally fluorinated alkycarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy group with up to 4 C atoms or a mono- oligo- or polyfluorinated alkyl or alkoxy group with 1 to 4 C atoms. The term 'unpolar group' means an optionally halogenated alkyl, alkoxy, alkycarbonyl, alkoxycarbonyl, alkylcarbonyloxy or alkoxycarbonyloxy group with 1 or more, preferably 1 to 12 C atoms which is not covered by the above definition of 'polar group'.

Especially preferred polymerisable photoisomerisable chiral compounds as disclosed in WO 02/40614 are those of the following formulae



Im1



In1

wherein R^1 and R^2 are independently of each other R^0 or P as defined above, a and b are 0 or 1, Z is Z^0 and A^1 and A^2 are independently of each other A as defined above.

Polymerisation of the polymerisable chiral LC material takes place by exposing it to heat or actinic radiation. Actinic radiation means irradiation with light, like UV light, IR light or visible light, irradiation with X-rays or gamma rays or irradiation with high energy particles, such as ions or electrons. Preferably polymerisation is carried out by photoirradiation, in particular UV irradiation. As a source for actinic radiation for example a single UV lamp or a set of UV lamps can be used. When using a high lamp power the curing time can be reduced. Another possible source for photoradiation is a laser, like e.g. a UV laser, an IR laser or a visible laser. Preferably the photoradiation used for polymerisation is of the same wavelength, in particular of the same wavelength and intensity, as used for changing the chirality of the polymerisable LC material.

Polymerisation is carried out in the presence of an initiator absorbing at the wavelength of the actinic radiation. For example, when polymerising by means of UV light, a photoinitiator can be used that decomposes under UV irradiation to produce free radicals or ions that start the polymerisation reaction. When curing polymerisable mesogens with acrylate or methacrylate groups, preferably a radical photoinitiator is used, when curing polymerisable mesogens vinyl and epoxide groups, preferably a cationic photoinitiator is used. It is also possible to use a polymerisation initiator that decomposes when heated to produce free radicals or ions that start the polymerisation. As a photoinitiator for radical polymerisation for example the commercially available Irgacure® 651, Irgacure® 184, Darocure® 1173 or Darocure® 4205 (all from Ciba Geigy AG) can be used, whereas in case of cationic photopolymerisation the commercially available UVI 6974 (Union Carbide) can be used. The polymerisable LC material preferably comprises 0.01 to 10 %, very preferably 0.05 to 5 %, in particular 0.1 to 3 % of a polymerisation initiator. UV photoinitiators are preferred, in particular radicalic UV photoinitiators. The photoinitiators can also be selected such that the chiral material does not, or does not well, polymerise in the presence of oxygen, as described above. For example, when polymerisation in air is required, Irgacure® 907 is preferably used, whereas Irgacure® 369 is used in a material that does not polymerise well in air.

The curing time is dependent, inter alia, on the reactivity of the polymerisable mesogenic material, the thickness of the coated layer, the type of polymerisation initiator and the power of the UV lamp. The curing time according to the invention is preferably not longer than 10 minutes, particularly preferably not longer than 5 minutes and very particularly preferably shorter than 2 minutes. For mass production short curing times of 3 minutes or less, very preferably of 1 minute or less, in particular of 30 seconds or less, are preferred.

The inventive polymerisable liquid crystalline mixtures can additionally comprise one or more other suitable components such as, for example, catalysts, sensitizers, stabilizers, chain-transfer agents, inhibitors, co-reacting monomers, surface-active compounds, lubricating agents, wetting agents, dispersing agents, hydrophobing agents, adhesive agents, flow improvers, defoaming agents, deaerators, diluents, reactive diluents, auxiliaries, colourants, dyes or pigments.

It is also possible, in order to increase crosslinking of the polymers, to add up to 20% of a non mesogenic compound with two or more polymerisable functional groups to the polymerisable LC material alternatively or in addition to the di- or multifunctional polymerisable mesogenic compounds to increase crosslinking of the polymer. Typical examples for difunctional non mesogenic monomers are alkyldiacrylates or alkyldimethacrylates with alkyl groups of 1 to 20 C atoms. Typical examples for non mesogenic monomers with more than two polymerisable groups are trimethylpropanetrimethacrylate or pentaerythritoltetraacrylate.

In another preferred embodiment the mixture of polymerisable material comprises up to 70%, preferably 3 to 50 % of a non mesogenic compound with one polymerisable functional group. Typical examples for monofunctional non mesogenic monomers are alkylacrylates or alkylmethacrylates.

The optical retardation film according to the present invention can be used as retardation or compensation film in conventional LCDs, in particular those of the DAP (deformation of aligned phases) or VA (vertically aligned) mode, like e.g. ECB (electrically controlled birefringence), CSH (colour super homeotropic), VAN or VAC (vertically aligned nematic or cholesteric) displays, MVA (multi-domain vertically aligned) or PVA (patterned vertically aligned) displays, in displays of the bend mode or hybrid type displays, like e.g. OCB (optically compensated bend cell or optically compensated birefringence), R-OCB (reflective OCB), HAN (hybrid aligned nematic) or pi-cell (π-cell) displays, furthermore in displays of the TN (twisted nematic), HTN (highly twisted nematic) or STN (super twisted nematic) mode, in AMD-TN (active matrix driven TN) displays, or in displays of the IPS (in plane switching) mode which are also known as 'super TFT' displays, in displays using liquid crystals in their optically isotropic phase as described for example in WO 02/93244 A1, also known als ISP (isotropic switching panel), in switchable two dimensional (2D) / three dimensional (3D) displays as disclosed in US 6,437,915 and US 6,046,849, in CRT (cathode ray tube) displays, or in organic light emitting diodes (OLED).

Especially preferred are TN, STN, VA and IPS displays, in particular those of the active-matrix type, furthermore 2D/3D displays.

The films according to the present invention can also be used in optical or electrooptical devices for other purposes than those described above, for example as alignment layer, optical filter or polarization beam splitter, optical waveguide or in decorative or security applications.

In a preferred embodiment, the film according to the present invention is used as optical retardation film in an LCD not outside the switchable LC cell of the display, but between the substrates, usually glass substrates, forming the switchable LC cell and containing the switchable LC medium (incell application).

Compared to conventional displays where optical retarders are usually placed between the LC cell and the polarisers, incell application of an optical retardation film has several advantages. For example, a display where the optical film is attached outside of the glass substrates forming the LC cell usually suffers from parallax problems, which can severely impair viewing angle properties. If the retardation films is prepared inside the LC display cell, these parallax problems can be reduced or even avoided.

An LCD according to this embodiment preferably comprises

1) a liquid crystal (LC) cell comprising the following elements, starting from the edges to the centre of the cell in the sequence listed below
   11) a first and a second substrate plane parallel to each other, at least one of which is transparent to incident light,
   12) an array of nonlinear electric elements on one of said substrates which can be used to individually switch individual

pixels of said LC cell, said elements being preferably active elements like transistors, very preferably TFTs,

13) a colour filter array provided on one of said substrates, preferably on the substrate opposite to that carrying the array of nonlinear elements, said colour filter optionally being covered by a planarisation layer,

14) a first electrode layer provided on the inside of said first substrate,

15) optionally a second electrode layer provided on the inside of said second substrate,

16) optionally first and second alignment layers provided on said first and second electrodes,

17) an LC medium that is switchable between at least two different states by application of an electric field,

2) a first linear polariser on one side of the LC cell,

3) optionally a second linear polariser on the side of the LC cell opposite to that of the first linear polariser, and

4) at least one patterned optical retardation film according to the present invention,

characterized in that said patterned optical retardation film 4) is situated between the first and second substrate of the LC cell, preferably between the colour filter and the liquid crystal medium, very preferably between the colour filter and one of said electrode layers, or if a planarisation layer is present, between the planarising layer and one of said electrode layers.

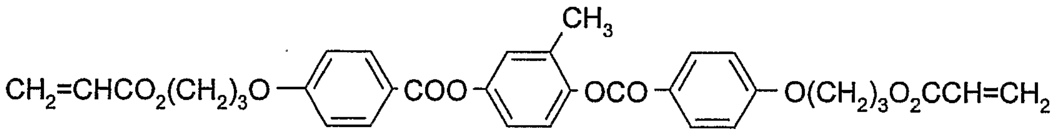
The examples below serve to illustrate the invention without limiting it. In the foregoing and the following, all temperatures are given in degrees Celsius, and all percentages are by weight, unless stated otherwise.

Example 1

The polymerisable nematic LC mixture M1 was formulated as follows

M1:

(1)	39.4 %
(2)	24.60 %
(3)	24.60 %
(4)	9.72 %
Irgacure651	1.00 %
Fluorad FC171	0.60 %
Irganox1076	0.08 %



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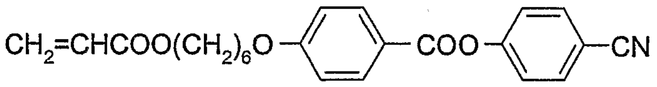
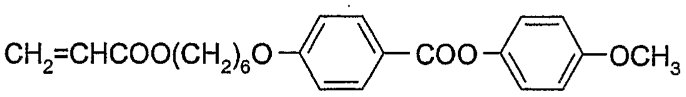


(2).



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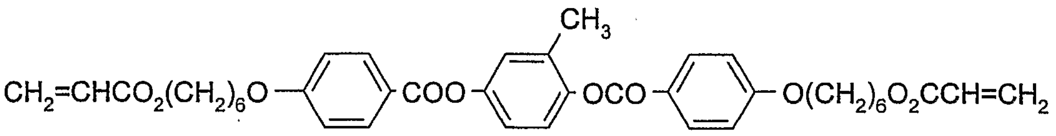
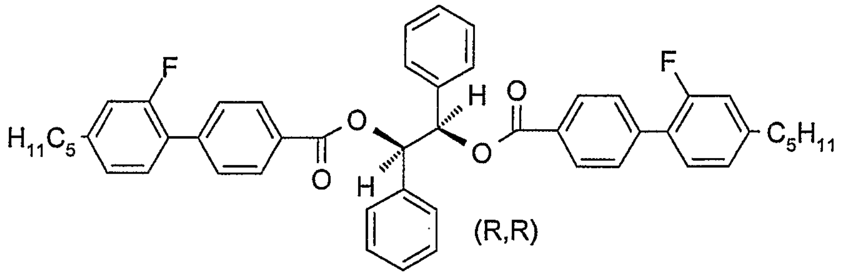


(4)

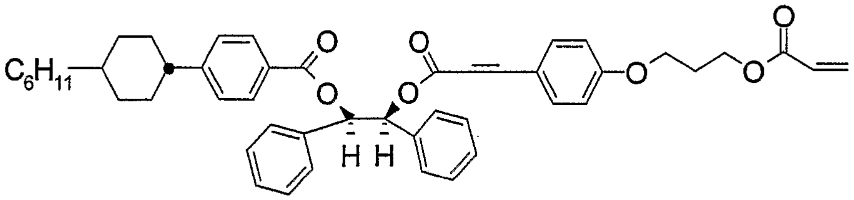
Irgacure651® is a photoinitiator, Irganox1076® a stabilizer, both being commercially available (Ciba AG, Basel, Switzerland). FC171® is a non-ionic fluorocarbon surfactant (from 3M Co.).

The mixture M1 was heated and agitated to ensure good mixing. A sample of M1 was measured to have a clearing temperature of 74 °C.

M1 was dissolved in PGMEA (propylene glycol monomethyl ether acetate) at a concentration of 40 % to form the host mixture H1. To this host mixture H1 were added 0.1 % of the non-isomerisable chiral dopant Dni and 0.08 % of the photoisomerisable chiral dopant Di.



(Dni)



(Di)

The solution was spincoated (2,000 RPM) onto two glass/rubbed polyimide (JSR AL1054) slides. One of the films was photopolymerised (20 mWcm^{-2},UV-a, 60s, N_2) immediately after it was coated, the other was photoisomerised (20 mWcm^{-2}, 365nm, 30s, air) before being photopolymerised (20 mWcm^{-2},UV-a, 60s, N_2). The transmission of each film was measured between crossed stretched linear iodine polarisers (cut at 45° to the stretch direction). The transmission values were recorded using a Hitachi U2000 spectrophotometer. The RM films were mounted on a homemade stage which can be rotated through 360° whilst the polarisers are kept in the same orientation. **Figure 2** shows the plot of the transmission data as a function of rotation of the RM film, obtained as the RM films are rotated through 360 ° held between crossed polarisers.

The plot of transmission for the initial film produced (not isomerised), depicted by graph (a) in **Figure 2**, shows that the initial film has 4 lobes which is expected for a planar, non-twisted retardation layer. The plot for the isomerised film, depicted by graph (b) in **Figure 2**, shows that the film has approximately equal transmission over all angles which is characteristic of a helically twisted retardation film.

Example 2

A patterned retardation layer was produced using the mixture in Example 1. The solution was spincoated (2000 RPM, 30s) onto rubbed polyimide/glass slides and isomerised (20 mWcm^{-2},365 nm, 60s,air) through a photomask allowing either 100% or 0% of the UV light to pass. The resultant film was photopolymerised (20 mWcm^{-2},UV-a, 60s, N_2). A photograph of the film viewed on a light box through crossed polariser is shown in **Figure 3.**

Figure 3 shows that the film is patterned and contains twisted (isomerised) and non-twisted (not isomerised) regions. By lining up the direction of the polariser with the orientation of the RM molecules in the non-isomerised regions it is possible to produce a striped retardation film, as shown.

Patent Claims

1. Patterned polymer film comprising a polymerised chiral liquid crystal (LC) material, characterized in that it has a pattern of at least two regions with different twist angle and/or a pattern of at least one twisted region and at least one untwisted region.

2. Polymer film according to claim 1, characterized in that it has a pattern of at least two regions with different twist angle.

3. Polymer film according to claim 1 or 2, characterized in that it has a pattern of at least one twisted region and at least one untwisted region.

4. Polymer film according to at least one of claims 1 to 3, characterized in that it is obtained from an initially racemic polymerisable chiral LC material which, when coated and polymerised produces either a quarter-wave or half-wave retardation film, and wherein said material is photoisomerised before polymerisation such that it produces either a left- or right-handed twisted retardation film.

5. Polymer film according to at least one of claims 1 to 4, characterized in that it has at least one region of 0° twist angle and at least one region of a twist angle from above 0 to +270° or from below 0 to -270°.

6. Polymer film according to at least one of claims 1 to 4, characterized in that it has at least one region of 0° twist angle and at least one region of a twist angle from above 0 to +180° or from below 0 to -180°.

7. Polymer film according to at least one of claims 1 to 4, characterized in that it has at least one region of 0° twist angle and at least one region of a twist angle from above 0 to +90° or from below 0 to -90°.

8. Polymer film according to at least one of claims 1 to 4, characterized in that it has at least two regions having a different twist angle selected from +90° to -90° being different from 0°.

9. Polymer film according to at least one of claims 1 to 4, characterized in that it has at least one region of 0° twist angle and at least one region of a twist angle selected from +90° to -90° being different from 0°.

10. Polymer film according to at least one of claims 1 to 4, characterized in that it has at least three regions having a different twist angle selected from 0 to +90° or from 0 to -90°,.

11. Polymer film according to at least one of claims 1 to 10, characterized in that it is obtainable by providing a layer of a polymerisable chiral LC material comprising

    - at least one first chiral compound that induces a helical twist of a given twist sense in the chiral material, and is convertible between at least two states with different twisting power, wherein conversion of the chiral compound can be induced by photoradiation and
    - at least one second chiral compound that induces a helical twist of a twist sense opposite to said first chiral compound in the chiral material, and is not convertible between two or more states with different twisting power under the same conditions as said first chiral compound,

    irradiating selected regions of the layer with photoradiation that changes the degree of chirality of said first chiral compound, and polymerising said selected regions.

12. Polymer film according to claim 11, characterized in that said first chiral compound is a photoisomerisable chiral compound

and said second chiral compound is a non-isomerisable chiral compound.

13. Polymer film according to claim 11 or 12, characterized in that polymerisation of the chiral LC material is initiated by the photoradiation that changes the twisting power of said first chiral compound.

14. Polymer film according to at least one of claims 11 to 13, characterized in that it is obtainable by a process comprising the following steps

    1. Providing a layer of an alignment material on a substrate.
    2. Optionally rubbing the alignment material unidirectionally to create a preferred orientation direction.
    3. Coating a layer of a photopolymerisable chiral LC material as described above and below onto the alignment layer.
    4. Irradiating the LC layer through a photomask, to induce photoisomerisation of the isomerisable chiral dopant in the regions not covered by the photomask, thereby creating a pattern of regions with different twist in the layer.
    5. Polymerising the LC layer to permanently fix the twist pattern.

15. Polymer film according to at least one of claims 11 to 14, characterized in that polymerisation of the polymerisable chiral LC material is hindered in the presence of oxygen, and wherein selected regions of the polymerisable material are irradiated in the presence of oxygen with photoradiation that changes the chirality of said first chiral compound, and the selected regions or the entire material are subsequently polymerised in the absence of oxygen.

16. Polymer film according to claim 15, wherein irradiation of the selected regions of the polymerisable material is carried out through a photomask.

17. Polymer film according to claim 15, wherein irradiation of the selected regions of the polymerisable material is carried out by means of a finely focussed radiation source.

18. Polymer film according to at least one of claims 11 to 17, obtainable by a process comprising the following steps that are carried out in the presence of oxygen,

    A) providing a layer of a photopolymerisable chiral liquid crystal material that does not polymerise in the presence of oxygen and comprises first and second chiral compounds as defined in claim 11,

    B) 1) covering selected areas of the layer with a substrate and irradiating the layer with photoradiation that changes the twisting power of said first chiral compound and initiates polymerisation of the chiral polymerisable material, wherein the substrate has the properties of an oxygen barrier layer and is transparent for the photoradiation, and

       2) repeating the procedure of step B1 one or more times for at least one of the areas of the layer that were not covered with a substrate in the previous step.

19. Process of preparing a polymer film with twisted structure comprising at least one area with a twist angle that is different from that of at least one other area, by carrying out the steps as described in at least one of claims 11 to 18.

20. Use of a polymer film according to at least one of claims 1 to 18 as compensator, retarder or polariser in liquid crystal displays or other optical elements, components or devices.

21. Use of a film according to at least one of claims 1 to 18 as optical retardation film in an LCD, characterized in that the film is positioned between the substrates of the switchable LC cell.

22. Liquid crystal display, optical element, component or device comprising a polymer film according to at least one of claims 1 to 18.

23. LCD comprising an LC cell formed by two plane parallel substrates at least one of which is transparent to incident light, an electrode layer provided on the inside of at least one of said two transparent substrates and optionally superposed with an alignment layer, and an LC medium located between the two substrates that is switchable between at least two different states by application of an electric field, characterized in that the LCD comprises at least one film according to at least one of claims 1 to 18 that is positioned between the two plane parallel substrates forming the LC cell.

24. LCD according to claim 22 or 23, characterized in that it is a TN, STN, VA, IPS, ISP or 2D/3D display.

25. LCD comprising

    1) a liquid crystal (LC) cell comprising the following elements, starting from the edges to the centre of the cell in the sequence listed below

        11) a first and a second substrate plane parallel to each other, at least one of which is transparent to incident light,

        12) an array of nonlinear electric elements on one of said substrates which can be used to individually switch individual pixels of said LC cell, said elements being preferably active elements like transistors, very preferably TFTs,

        13) a colour filter array provided on one of said substrates, preferably on the substrate opposite to that carrying the array of nonlinear elements, said colour filter optionally being covered by a planarisation layer,

14) a first electrode layer provided on the inside of said first substrate,

15) optionally a second electrode layer provided on the inside of said second substrate,

16) optionally first and second alignment layers provided on said first and second electrodes,

17) an LC medium that is switchable between at least two different states by application of an electric field,

2) a first linear polariser on one side of the LC cell,

3) optionally a second linear polariser on the side of the LC cell opposite to that of the first linear polariser, and

4) at least one optical retardation film according to at least one of claims 1 to 18,

characterized in that said optical retardation film 4) is situated between the colour filter and the LC medium.

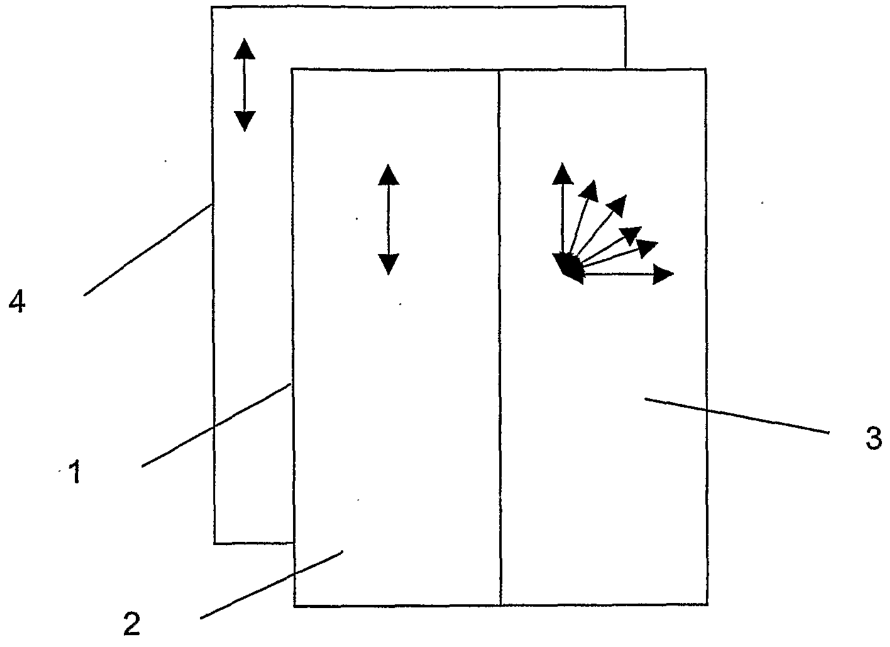


Figure 1

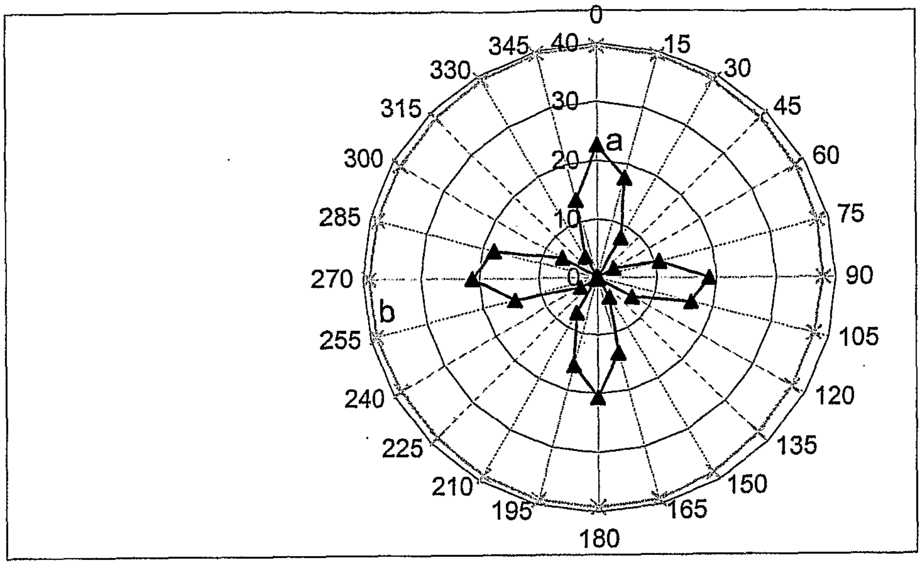


Figure 2

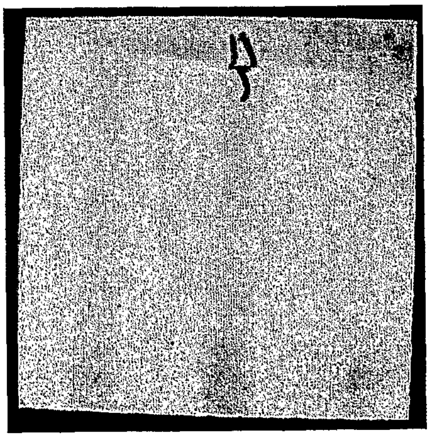


Figure 3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2004/008478

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09K19/38 C09K19/02

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09K G02F G02B

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

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

EPO-Internal, WPI Data, PAJ, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	*Citation of document, with indication, where appropriate, of the relevant passages*	*Relevant to claim No.*
X	VAN DE WITTE PETER ET AL: "Modification of the twist angle in chiral nematic polymer films by photoisomerization of the chiral dopant" JOURNAL OF APPLIED PHYSICS, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, vol. 85, no. 11, 1 June 1999 (1999-06-01), pages 7517-7521, XP012046372 ISSN: 0021-8979 the whole document -----	1-25
X	EP 1 295 929 A (MERCK PATENT GMBH) 26 March 2003 (2003-03-26) cited in the application claims 1,4,11,12,-15 ----- -/--	1-25

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

9 November 2004

Date of mailing of the international search report

19/11/2004

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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