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(54) Title: POLYMERISED LC FILMS WITH VARYING THICKNESS

(57) Abstract: The invention relates to a film of polymerised liquid crystal (LC) material having at least two regions with different thickness, for example in the form of a surface grating, to a process of preparing such a film, to a polymerisable LC material used for the preparation of such a film, and to the use of the film in LC displays or other optical or electrooptical components or devices, for decorative or security applications.



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Polymerised LC Films with Varying Thickness

Field of the Invention

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The invention relates to a film of polymerised liquid crystal (LC) material having at least two regions with different thickness, for example in the form of a surface grating. The invention further relates to a process of preparing such a film, to a polymerisable LC material used for the preparation of such a film, and to the use of the film in LC displays or other optical or electrooptical components or devices, for decorative or security applications.

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Background and Prior Art

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Gratings are typically used within the display industry, for example to align LC molecules in preferred orientations, such as bistable displays as disclosed in WO 01/40853. Likewise carefully created protrusions (surface relief gratings) can be used to create multi-domain Vertically Alignment (VA) displays, as disclosed for example in US 6,188,457. Generally photolithographical steps are required to create these gratings in which complex structures can only be built by time-consuming, multiple processing steps, see e.g. EP 1 186 916 and US 6,188,457. The obvious disadvantage of the type of process is the cost involved. Hence, there has been a great effort to find alternative ways to produce both optical and surface relief gratings.

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One approach has been to disperse small metal balls into a matrix and, using a high intensity laser, cut hollows into the film to create a grating, as reported in JP 2001-311810. Unfortunately, such an approach is still time consuming and hence costly. An alternative approach is to utilise direct write UV or Ar⁺ laser techniques. In this way for example gratings created in photoisomerisable azobenzene based molecules are well known in the literature for example D.Y. Kim, S.K. Tripathy, L. Li and J. Kumar *Applied Physics Letters* **66** 1166 (1995), P. Rochon, E. Batalla, and A. Natansohn *Applied*

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5 *Physics Letters* **66** 136 (1995). Irradiating such an azobenzene compound with linearly polarised visible light, usually from an Ar⁺ laser, results in selective isomerisation of the azo bond. leading to a concomitant increase in height and hence to possible surface relief gratings. Unfortunately, azobenzene materials are highly coloured and so not suitable for use in display applications.

10 An alternative process is the slow photopolymerisation of LC molecules containing polymerisable groups (referred to as reactive mesogens or RMs). This also has the advantage that it is not necessary to use polarised UV light. In one example of such a system, which is disclosed in US 4,877,717, the acrylate containing RMs are photopolymerised through a mask. The mask incorporates two
15 different regions which transmit either all or none of the UV light. This leads to photopolymerisation of the RM film in regions exposed to the UV, whereas the regions shielded from UV light remain unpolymerised. To try to remain in thermodynamic equilibrium the two regions (polymerised and unpolymerised) start to diffuse. However, the rate of diffusion of the polymer is much slower than that of the
20 monomer. This results in more monomer being present in the region exposed to UV. This monomer is subsequently polymerised resulting in a grating structure, in which the film thickness is much greater in the region which has been exposed to UV. Unfortunately, a major drawback for commercializing this process is the slow rate at which
25 the diffusion process occurs.

Therefore, there is a need for an advantageous method to prepare a grating that does not have the drawbacks of prior art methods like those mentioned above. It was an aim of the present invention to
30 provide such methods and gratings, in particular having the following advantageous properties of using mercury lamp source which is not required to be polarised, of using materials which are suitable for use in displays and which afford fast fabrication of the grating structure . Other aims are immediately evident to the expert from the following
35 description.

The inventors of the present invention have found that the above aims can be achieved by using a method as disclosed below. In the method according to this invention a mixture of polymerisable mesogenic compounds, or reactive mesogens (RM), undergoes a change in height when exposed to either non-polarised or polarised UV light. In contrast to prior art, the RM mixture decreases in height when exposed to UV irradiation.

Summary of the Invention

The invention relates to a polymer film obtained by polymerisation of a polymerisable liquid crystal (LC) material comprising at least one photosensitive compound, characterized in that the film comprises at least two regions with different thickness.

The invention further relates to a polymer film obtained by a process comprising the following steps:

- a) providing a layer of a polymerisable LC material comprising at least one photosensitive compound onto a substrate,
- b) optionally aligning the layer of LC material into uniform orientation,
- c) exposing the LC material in the layer, or in selected regions thereof, to photoradiation that causes isomerisation of the isomerisable compound, preferably UV radiation,
- d) polymerising the LC material in at least a part of the exposed regions of the material, thereby fixing the orientation, and
- e) optionally removing the polymerised film from the substrate.

The invention further relates to a polymer film as described above and below, wherein the polymerisable liquid crystal (LC) material comprises a host material comprising one or more polymerisable mesogenic compounds and at least one polymerisable photosensitive compound miscible with said host material, and wherein the thickness of the polymerised LC film is controlled by varying the amount and/or type of the photosensitive compound and/or the amount and type of the polymerisable mesogenic compounds of the host material.

The invention relates to a polymerisable LC material comprising at least one photosensitive compound as described above and below.

5 The invention further relates to the use of a polymer film as described above and below in liquid crystal displays (LCDs) or other optical or electrooptical components or devices, for decorative or security applications.

10 The invention further relates to the use of a polymer film as described above and below as alignment layer, optical retardation film or optical waveguide.

15 The invention further relates to an LCD comprising a polymer film as described above and below.

Definition of Terms

20 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.

25 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. Liquid crystal (LC) compounds with rod-shaped or board-shaped groups are also known in the art as 'calamitic' liquid
30 crystals. Liquid crystal compounds with a disk-shaped group are also known in the art as 'discotic' liquid crystals. 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
35 compounds, or when the mesogenic compounds or materials, or the mixtures thereof, are polymerised.

For the sake of simplicity, the term 'liquid crystal material' is used hereinafter for both liquid crystal materials and mesogenic materials.

- 5 The term 'reactive mesogen' (RM) means a polymerisable mesogenic compound.

The term 'director' is known in prior art and means the preferred orientation direction of the long molecular axes (in case of calamitic compounds) or short molecular axis (in case of discotic compounds) of the mesogens in a liquid crystal material.

15 The term 'planar structure' or 'planar orientation' refers to a film wherein the optical axis is substantially parallel to the film plane.

The term 'homeotropic structure' or 'homeotropic orientation' refers to a film wherein the optical axis is substantially perpendicular to the film plane, i.e. substantially parallel to the film normal.

20 The terms 'tilted structure' or 'tilted orientation' refers to a film wherein the optical axis is tilted at an angle θ between 0 and 90 degrees relative to the film plane.

25 The term 'splayed structure' or 'splayed orientation' means a tilted orientation as defined above, wherein the tilt angle additionally varies monotonuously in the range from 0 to 90 °, preferably from a minimum to a maximum value, in a direction perpendicular to the film plane.

30 The tilt angle of a splayed film hereinafter is given as the average tilt angle θ_{ave} , unless stated otherwise.

The average tilt angle θ_{ave} is defined as follows

$$\theta_{ave} = \frac{\sum_{d'=0}^d \theta'(d')}{d}$$

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wherein $\theta'(d')$ is the local tilt angle at the thickness d' within the film, and d is the total thickness of the film.

5 In planar, homeotropic and tilted optical films comprising uniaxially positive birefringent liquid crystal material with uniform orientation, the optical axis of the film is given by the director of the liquid crystal material.

10 The term 'photosensitive' refers to 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. The photosensitive compounds in addition can be polymerisable or photopolymerisable.

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Brief Description of the Drawings

20 **Figures 1a and 1b** show retardation plots of films prepared from an isomerised (a) and an unisomerised (b) polymerisable mixture as described in example 1 of the present invention.

Figure 2a shows a photomask used for the preparation of a film according to example 2 of the present invention.

25 **Figure 2b** shows the image of a film according to example 2 of the present invention.

Figure 2c shows the thickness profile of a film according to example 2 of the present invention.

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Figures 3 and 4 show the thickness variation versus cinnamate concentration for different films prepared from a polymerisable and photoisomerisable mixture by a process according to the present invention as described in example 3.

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Detailed Description of the Invention

5 The method according to the present invention is suitable to provide an LC film with a defined structure, like e.g. a thickness pattern or surface relief grating. The original alignment of the LC material is maintained during polymerisation, hence it is possible to produce films having a surface relief grating and films with an increased birefringence.

10 The film according to the present invention is preferably prepared by a process comprising steps a) to e) as described above. The steps a) to e) can be carried out according to standard procedures that are known to the expert and are described in the literature.

15 The polymerisable LC material comprises a photosensitive compound and a host material.

20 The photosensitive compound is preferably a mesogenic or LC compound, and further preferably a polymerisable compound comprising one or more polymerisable groups that are linked, optionally via a spacer group, to a mesogenic core.

25 The host material is a mesogenic or liquid crystalline material comprising one or more polymerisable mesogenic compounds (RMs). Preferably the host material shows liquid crystal phase behaviour before polymerisation.

30 The LC material is provided as a thin layer onto a substrate where it can be aligned into uniform orientation by means or methods known in the art, or where it aligns spontaneously. The LC material, or a selected region thereof, is then exposed to radiation of a specific wavelength like for example UV-radiation that causes the isomerisable compound to change its shape e.g. by *E-Z*-isomerisation. The orientation of the LC material in the irradiated regions or in the entire layer is then fixed by in-situ polymerisation. The isomerisation and

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polymerisation steps lead to a dramatic decrease in thickness in the isomerised and polymerised regions of the LC material.

5 Since the optical retardation of an oriented LC layer is given as the product $d \cdot \Delta n$ of the layer thickness d and the birefringence Δn of the LC material, the change in thickness and birefringence can also cause a change of the retardation in the irradiated parts of the LC material. The value of retardation for the initial layer of LC material is controlled by appropriate selection of the layer thickness and the type and
10 amounts of the individual components of the LC material.

The degree of isomerisation and the thickness change in the layer of LC material can be controlled by varying the type and amounts of the individual components of the LC material, or by varying the radiation
15 dose, intensity, time and/or power. Also, by applying a photomask between the radiation source and the LC layer it is possible to prepare a film with a pattern of regions or pixels having specific values of the thickness that differ from each other. For example, a film comprised of two different values of thickness can be created using a simple,
20 monochrome mask. A more complicated film exhibiting multiple regions of different thickness can be created using a grey-scale mask. After the desired thickness values are achieved the LC layer is polymerised. In this way it is possible to create a polymer retardation film with values of thickness ranging from that of the initial LC layer to
25 smaller values.

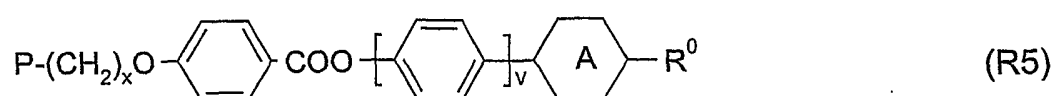
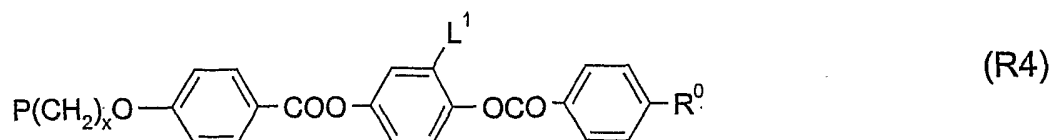
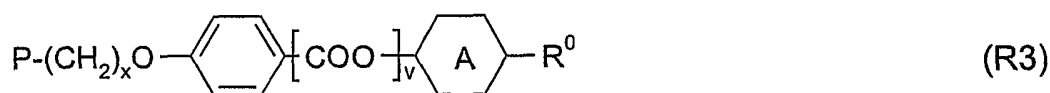
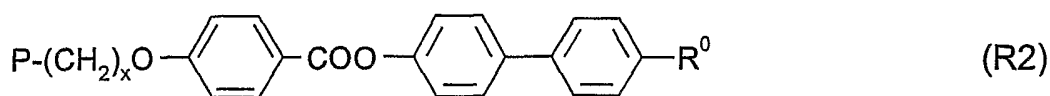
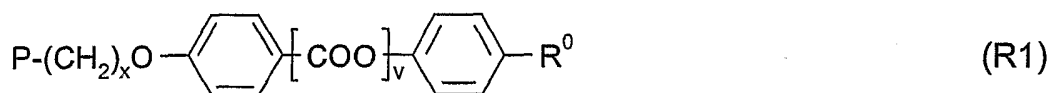
The host material is preferably a polymerisable nematic or smectic LC material, in particular a nematic material, and preferably comprises at least one di- or multireactive achiral RM and optionally one or more
30 than one monoreactive achiral RMs. By using di- or multireactive RMs a crosslinked film is obtained, which exhibits high mechanical stability and high stability of the optical properties against external influences like temperature or solvents. Films comprising crosslinked LC material are thus especially preferred.

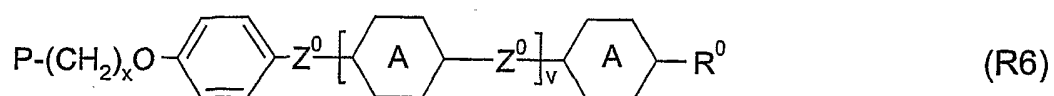
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Polymerizable mesogenic mono-, di- and multireactive compounds used for the present invention can be prepared by methods which are known per se and which are described, for example, in standard works of organic chemistry such as, for example, Houben-Weyl,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

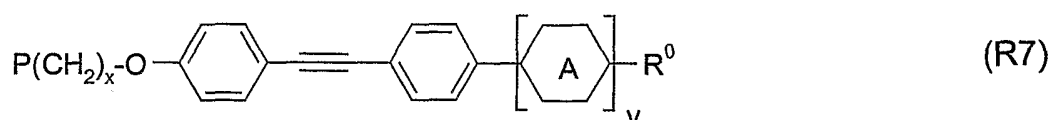
Examples of suitable polymerizable mesogenic compounds that can be used as monomers or comonomers together with the compounds according to the present invention in a polymerizable LC mixture, are disclosed for example in WO 93/22397, EP 0 261 712, DE 195 04
 10 224, WO 95/22586, WO 97/00600 and GB 2 351 734. 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 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:

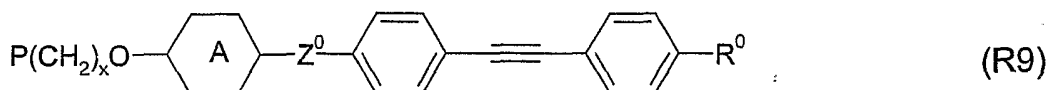
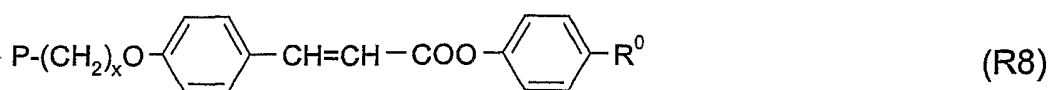




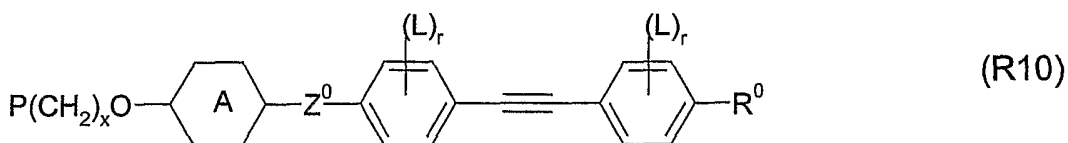
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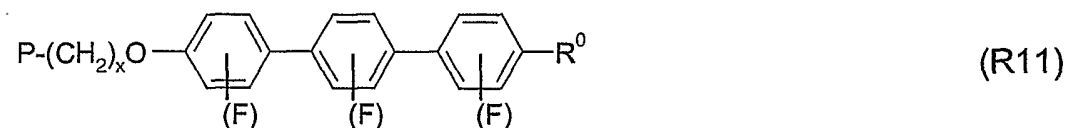
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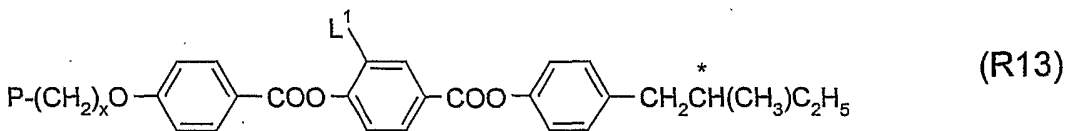
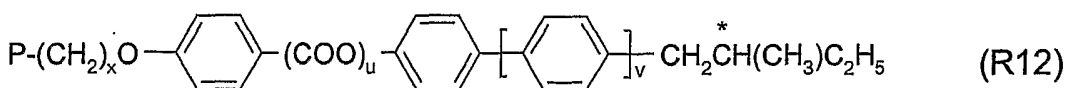
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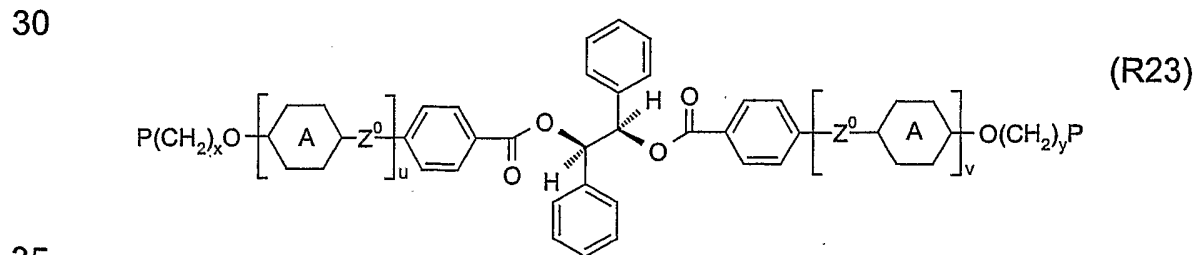
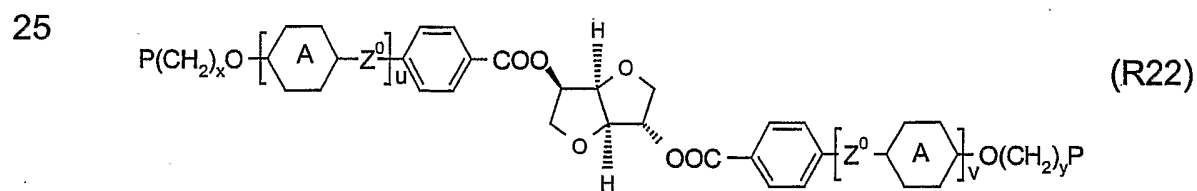
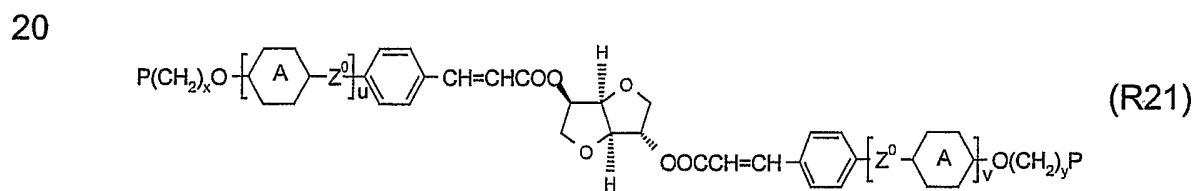
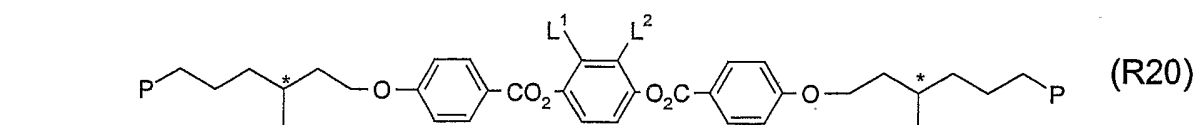
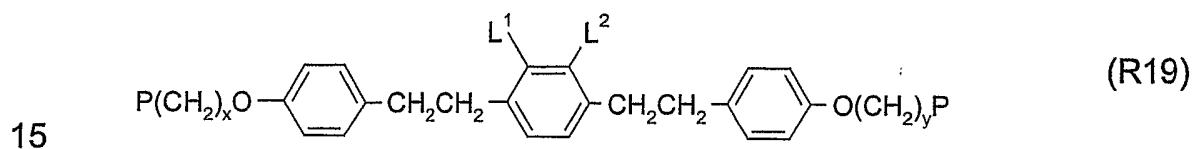
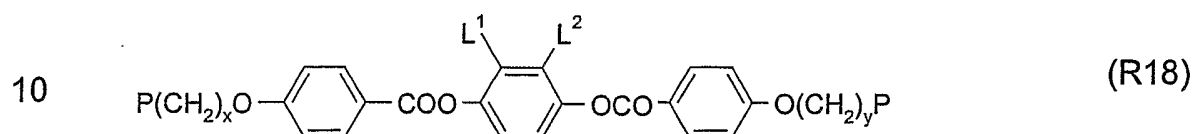
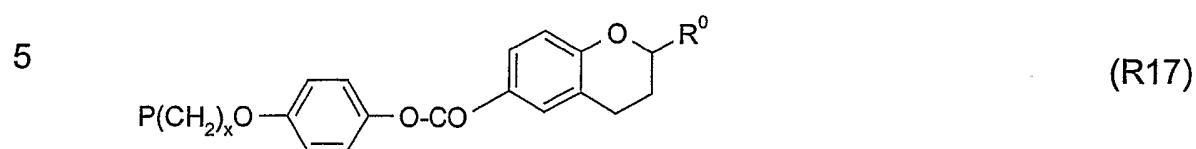
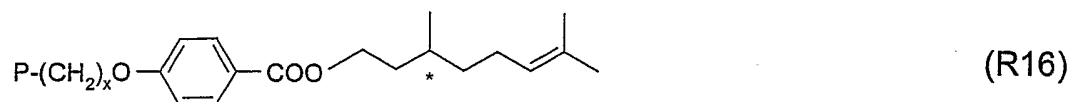


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In the above formulae, P is a polymerisable group, preferably an acryl, methacryl, vinyl, vinyloxy, propenyl ether, epoxy, oxetane or styryl group, x and y are identical or different integers from 1 to 12, A is 1,4-phenylene that is optionally mono-, di- or trisubstituted by L¹, or 1,4-cyclohexylene, u and v are independently of each other 0 or 1, Z⁰ is -COO-, -OCO-, -CH₂CH₂-, -CH=CH-, -C≡C- or a single bond, R⁰ is a polar group or an unpolar group, Ter is a terpenoid radical like e.g. menthyl, Chol is a cholesteryl group, L, L¹ and L² 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, NO₂, OH, OCH₃, OCN, SCN, an optionally fluorinated alkylcarbonyl, 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, alkylcarbonyl, 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'.

Preferably the host material comprises

- from 0 to 97 %, preferably from 25 to 70 % of one or more mesogenic compounds having one polymerisable group (monoreactive),
- from 3 to 100 %, preferably from 5 to 75 %, very preferably from 10 to 50 % of one or more mesogenic compounds having two or more polymerisable groups (direactive).

Especially preferred are achiral polymerisable mesogenic compounds, in particular those of formula R1 to R13 and R18, very preferred are those of formula R1 and R18.

As mentioned above, the thickness change in the layer of LC material can be controlled by varying the type and amounts of the compounds in the host material.

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Especially preferred is a host material comprising not more than 75 %, very preferably not more than 50 % of direactive compounds.

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Suitable photosensitive compounds are known in prior art. These are for example compounds showing photoisomerisation, photo-fries rearrangement or 2+2-cycloaddition or another photodegradation process upon photoirradiation. Especially preferred are photoisomerisable compounds. Examples of these compounds include azobenzenes, benzaldoximes, azomethines, stilbenes, spiropyrans, spirooxadines, fulgides, diarylethenes, cinnamates. Further examples are 2-methyleneindane-1-ones as described for example in EP 1 247 796, and (bis-)benzylidene-cycloalkanones as described for example in EP 1 247 797.

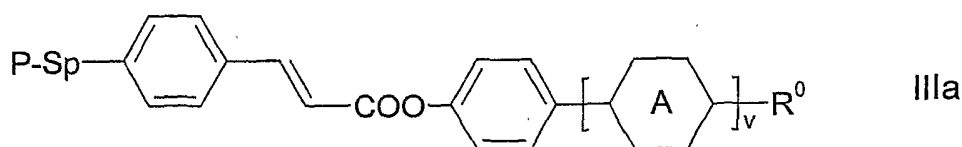
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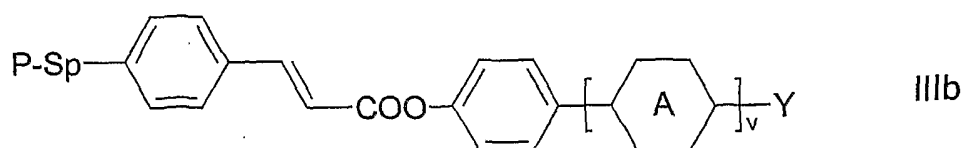
Especially preferably the photoisomerisable compounds are selected from cinnamates, in particular polymerisable mesogenic compounds or reactive mesogens (RMs) comprising at least one cinnamic acid ester group, as described for example in GB 2 314 839, EP 03007236.7, US 5,770,107 or GB 2 388 600. Very preferably the LC material comprises one or more cinnamate RMs selected of the following formulae

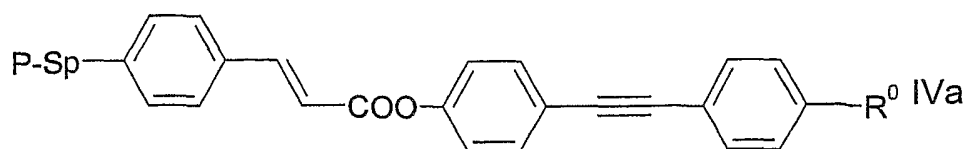
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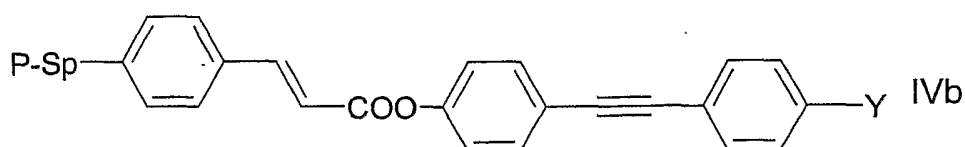


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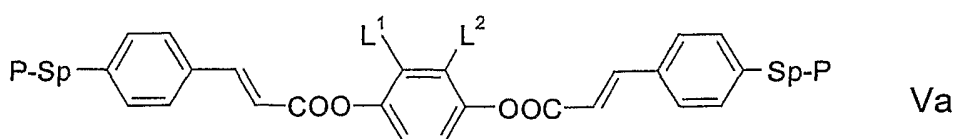




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15 wherein P, A, R⁰, Y, L¹ and L² and v have the meanings given above and Sp is a spacer group, like for example alkylene or alkyleneoxy with 1 to 12 C-atoms.

20 The polymerisable or reactive group P is preferably selected from a vinyl group, an acrylate group, a methacrylate group, an oxetane group or an epoxy group, especially preferably an acrylate group.

25 The spacer group Sp is preferably alkylene or alkylene-oxy with up to 10 C-atoms which is unsubstituted or mono- or polysubstituted by F, Cl, Br, I or CN. Very preferred groups Sp are ethylene, propylene, butylene, pentylene, hexylene, heptylene and octylene.

Y is preferably CN or Cl or OCH₃.

30 R⁰ is preferably straight-chain alkyl or alkoxy with 3 to 8 C-atoms, in particular n-propyl, n-butyl, n-hexyl, n-heptyl or n-octyl

35 As mentioned above, the thickness change in the layer of LC material can be controlled by varying the type and amounts of the photosensitive compound(s). Thus, it was found that polymerisable LC materials containing a specific type and amount of photosensitive

compounds are especially useful to the purpose of the present invention, as these materials allow to easily control and adjust the thickness of the polymer film.

5 Especially preferred are cinnamate RMs containing an unpolar terminal group R^0 as defined above. Very preferred are cinnamate RMs of formula IIIa and IVa. Further preferred are cinnamates comprising two or more polymerisable groups, especially those of formula V.

10

Preferably the polymerisable LC material comprises from 5 to 90 %, very preferably from 10 to 60 %, most preferably from 15 to 35 % of one or more photosensitive compounds, preferably cinnamate RMs, most preferably selected from formula IIIa, IVa and V.

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The photoradiation used to cause photoisomerisation in the LC material depends on the type of photosensitive compounds, and can be easily selected by the person skilled in the art. Generally, compounds that show photoisomerisation induced by UV-radiation are preferred. For example, for cinnamate compounds like those of formula III, IV and V, typically UV-radiation with a wavelength in the UV-A range (320-400 nm) or with a wavelength of 365 nm is used.

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The optimum irradiation time and radiation dose depend on the type of LC material used, in particular on the type and amount of photosensitive compounds in the LC material.

The thickness of a film according to the present invention is preferably from 0.01 to 3 microns, very preferably from 0.02 to 0.2 microns.

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The variation in thickness within the film, or the height or the surface grating, is preferably from 0.01 to 2 microns, very preferably from 0.02 to 0.2 microns

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The films according to the present invention can be used for example as/in surface relief gratings for the alignment of liquid crystal materials.

To prepare a polymerised LC film, the polymerisable LC mixture is preferably coated onto a substrate, aligned, preferably into planar orientation, and polymerised in situ, for example by exposure to heat or actinic radiation, to fix the orientation of the LC molecules.

5 Alignment and curing are carried out in the LC phase of the mixture. This technique is well-known in the art and described for example in D.J. Broer, et al., *Angew. Makromol. Chem.* 183, (1990), 45-66.

10 Alignment of the LC material can be achieved for example by treatment of the substrate onto which the material is coated, by shearing the material during or after coating, by application of a magnetic or electric field to the coated material, or by the addition of surface-active compounds to the LC material. Reviews of alignment techniques are given for example by I. Sage in "Thermotropic Liquid
15 Crystals", edited by G. W. Gray, John Wiley & Sons, 1987, pages 75-77, and by T. Uchida and H. Seki in "Liquid Crystals - Applications and Uses Vol. 3", edited by B. Bahadur, World Scientific Publishing, Singapore 1992, pages 1-63. A review of alignment materials and techniques is given by J. Cognard, *Mol. Cryst. Liq. Cryst.* 78,
20 Supplement 1 (1981), pages 1-77.

In a preferred embodiment the polymerisable LC material comprises an additive that induces or enhances planar alignment of the LC molecules on the substrate. Preferably the additive comprises one or
25 more surfactants. Suitable surfactants are described for example in J. Cognard, *Mol.Cryst.Liq.Cryst.* **78**, Supplement 1, 1-77 (1981). Particularly preferred are non-ionic surfactants, very fluorocarbon surfactants, like for example the commercially available fluorocarbon surfactants Fluorad FC-171® (from 3M Co.), or Zonyl FSN® (from
30 DuPont), and the surfactants described in GB 0227108.8.

The polymerisable LC material is preferably dissolved or dispersed in a solvent, preferably in an organic solvent. The solution or dispersion is then coated onto the substrate, for example by spin-coating or other
35 known techniques, and the solvent is evaporated off before polymerisation.

The polymerisable LC material may additionally comprise a polymeric binder or one or more monomers capable of forming a polymeric binder and/or one or more dispersion auxiliaries. Suitable binders and dispersion auxiliaries are disclosed for example in WO 96/02597. Especially preferred, however, are LC materials not containing a binder or dispersion auxiliary.

Polymerisation takes place by exposure 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 UV irradiation at a non-absorbing wavelength. 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 actinic radiation is a laser, like e.g. a UV laser, an IR laser or a visible laser.

Polymerisation is preferably 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 materials with acrylate or methacrylate groups, preferably a radical photoinitiator is used, when curing polymerisable materials with vinyl, epoxide and oxetane 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 photoinitiator concentration in the polymerisable LC material is preferably from 0.1 to 10 %, very preferably from 0.5 to 5 %.

5 The polymerisable LC material can additionally comprise one or more other suitable components such as, for example, catalysts, sensitizers, stabilizers, inhibitors, chain-transfer agents, 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.

10 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, or in decorative or security applications.

15 For example, they can be used as birefringent marking, image or pattern in decorative or security applications. With the methods of the present invention it is possible to produce negative images in films which are only visible between crossed-polarisers. A preferred use of these films is as security marking or security thread to authenticate and prevent counterfeiting of documents of value, or for identification
20 of hidden images, informations or patterns. It can thus be applied to consumer products or household objects, car bodies, foils, packing materials, clothes or woven fabric, incorporated into plastic, or applied on documents of value like banknotes, credit cards or ID cards, national ID documents, licenses or any product with money value, like
25 stamps, tickets, shares, cheques etc..

Especially preferred for use as birefringent marking is a patterned film that is provided on or directly prepared on a reflective substrate, for example a metal or metallised film or foil, as described in EP
30 02019792.7.

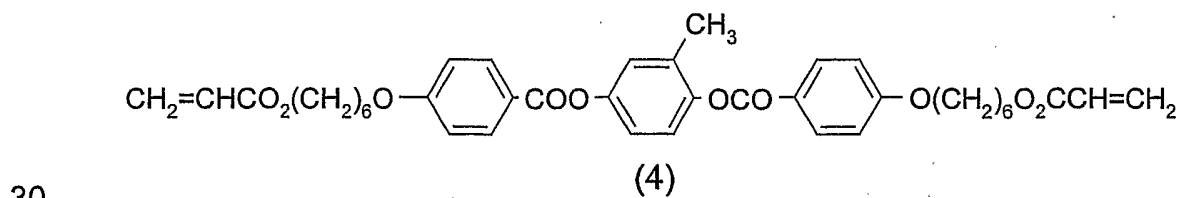
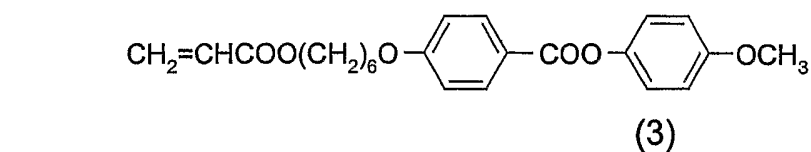
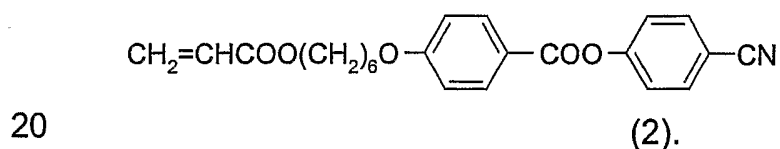
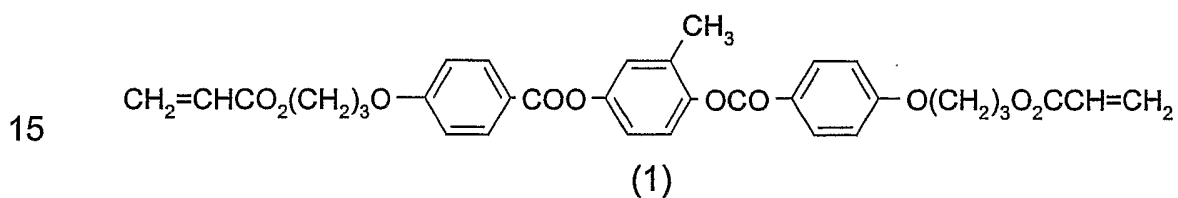
The examples below shall illustrate the invention without limiting it.

35 Example 1

The polymerisable LC host mixture H1 was formulated as follows.

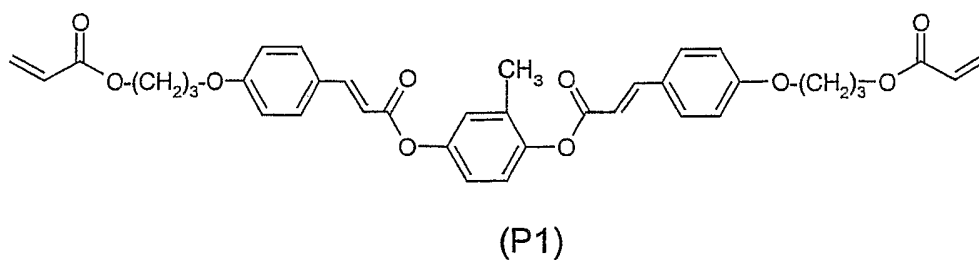
H1:

5	(1)	39.40 %
	(2)	24.60 %
	(3)	24.60 %
	(4)	9.72 %
10	Irgacure 651	1.00 %
	Fluorad FC171	0.60 %
	Irganox 1076	0.08 %

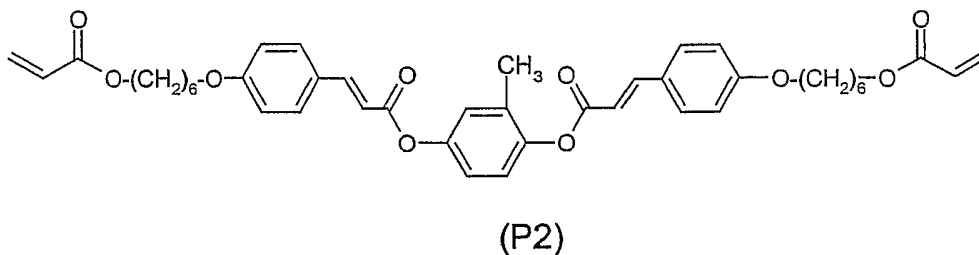


35 Different polymerisable and photoisomerisable compounds P1 to P5 were then added to the host mixture H1 at a concentration of 20 wt. % of total solids, to give the mixtures M1 to M5 as shown in Table 1.

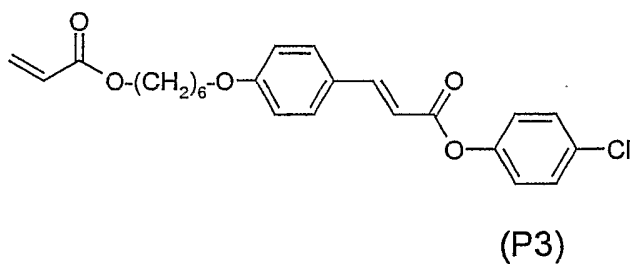
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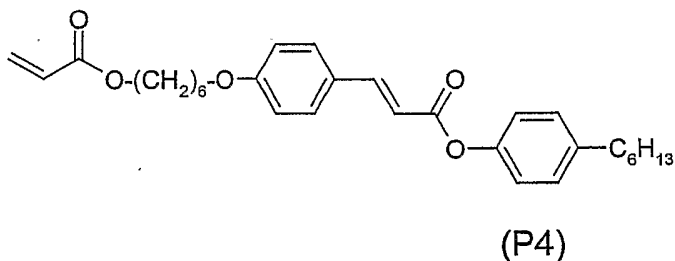
10



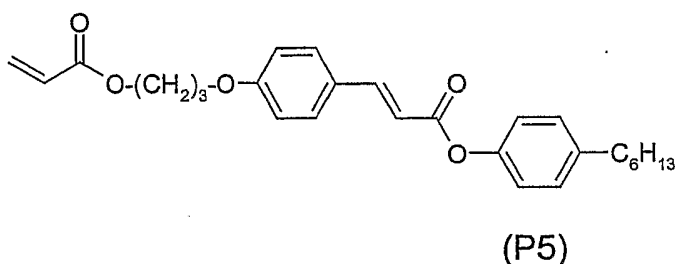
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Sets of two films were created by spincoating (3,000 RPM, 30s) a 50 wt% solution in xylene of each of the mixtures M1 to M5 (detailed in Tables 1 and 2) onto rubbed polyimide (JSR AL1054)/glass slides. In one case the film was immediately photopolymerised (UV-A, 20

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mWcm⁻², 60s, N₂) without further processing. In the other case the spincoated film was exposed to a photoisomerisation step (365nm, 20 mWcm⁻², 300s) before being photopolymerised (UV-A, 20 mWcm⁻², 60s, N₂).

5

The retardation of the polymerised films was determined by measuring the transmission of the film between parallel polarisers, with the orientation axis of the film at an angle of 45° to the polariser axis. The optical transmission was measured with an Oriel Spectrograph, for the wavelength range of 420-800nm, using a tungsten lamp as the light source. The retardation of the film was calculated by fitting the observed intensity measurements to theory. The average tilt angle of the nematic director in the polymerised film was calculated by measuring the retardation of the film (as described above) as a function of the angle of incidence of the light beam when the sample is rotated from -60° to + 60° (See O.Parri et al., Mol.Cryst.Liq.Cryst., Vol 332, p273, 1999)

10

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Figure 1 shows the retardation plots for the films of the mixture M1 which were (a) not isomerised and (b) isomerised prior to photopolymerisation. The other mixtures M2-5 all gave similar retardation plots before and after isomerisation.

25

30

Comparing the retardation plots in Figure 1 it is apparent that both the isomerised and non-isomerised films are well aligned, planar films. The calculated tilt angles at the substrate and air interfaces are, within experimental error, identical. Each film was measured to have a tilt angle of approximately 1° at the substrate and 0° at the air interface. The important difference between the two retardation plots is the value at normal incidence, 0°. The isomerised film possesses a lower value, i.e. isomerising the film acts to reduce the retardation without changing the initial mesogenic alignment.

35

To demonstrate the height change the thickness of the isomerised and non-isomerised film of mixtures M1 to M5, respectively, was measured, using a KLA-Tencor Alphastep 500 profilometer. For these

measurements a thin piece of film was scratched off and a profilometer trace obtained going across this scratch line, enabling the height (thickness) of the film to be measured. The differences in thickness (Δd), retardation (ΔR) and birefringence (Δn) due to the isomerisation step for each mixture are given in Table 2.

Table 1

Mixture No.	M1	M2	M3	M4	M5
Isomerisable Compound ¹⁾	P1	P2	P3	P4	P5
% Δd	- 30	- 34	- 15	- 19	- 23
% ΔR	- 3	- 8	- 18	- 16	- 17
% Δn	+ 39	+ 40	- 3.6	+ 3.8	+ 7.7

¹⁾ 20 % by weight in host mixture H1

Example 2

An isomerised film was prepared from mixture M4 as described in Example 1. The film was isomerised through a photomask containing a logo as shown in Figure 2a. The film directly underneath the logo was not exposed to UV-light and thus not isomerised, whereas the remaining film was isomerised. After this isomerisation step the photomask was removed and the whole film was photopolymerised.

Figure 2b depicts an image of the film produced after isomerising through the photomask of Figure 2a when viewed between crossed polarisers.

Figure 2c depicts a profile plot showing the thickness of different regions of the film enabling the relative difference in height to be determined. The profile was measured using a KLA-Tencor Alphastep 500 machine and incorporated software, and taken lengthways across the letter 'e' transferred into the film, marked by the line in Figure 2b.

Figure 2c clearly shows that by using a photomask it is possible to create regions of different height.

5 Further experiments have also shown that the extent of height difference produced in the films can be controlled by controlling the intensity of UV light reaching the sample (e.g. by using a grey-scale mask). In this way it is possible to construct more detailed structures. For example, a grey-scale photomask with stripes allowing 0%, 50% and 100% of the incident UV light is placed between the sample and
10 the light source. The film is irradiated and subsequently polymerised. The regions of the film which receive all of the UV dose are approximately twice as thin as those which receive 50% of the UV. Likewise, the regions which receive the 50% dose are approximately twice as thin as those receiving no UV. Because the UV dose directly
15 influences the thickness of the film it is possible to use a mask with a range regions with different values of UV transmittance (as a replacement, or in addition to, 0% and 100%) to create an elaborate grating in the RM film.

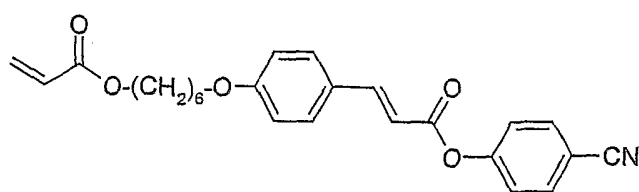
20 Example 3

The polymerisable LC host mixture H2 was formulated as follows.

25 H2:

25	(1)	60.00 %
	(2)	11.70 %
	(3)	11.70 %
	(4)	15.00 %
30	Irgacure 651	1.00 %
	Fluorad FC171	0.60 %

Compounds P3, P4 and P6 were dissolved in the host mixtures H1 and H2 at different concentrations to give different polymerisable LC
35 mixtures.



(P6)

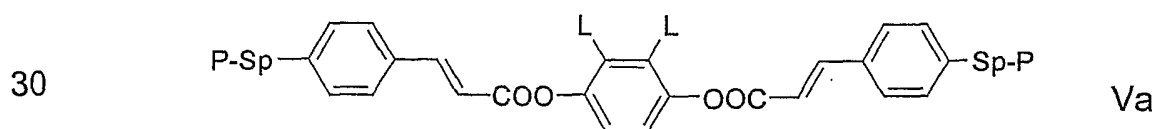
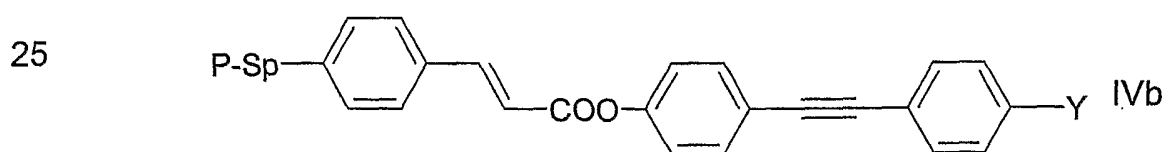
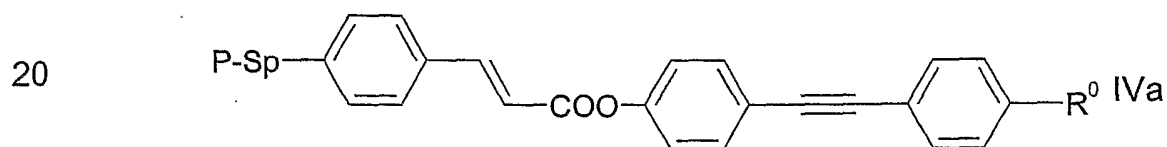
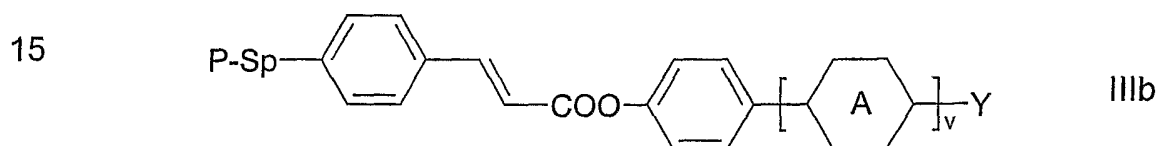
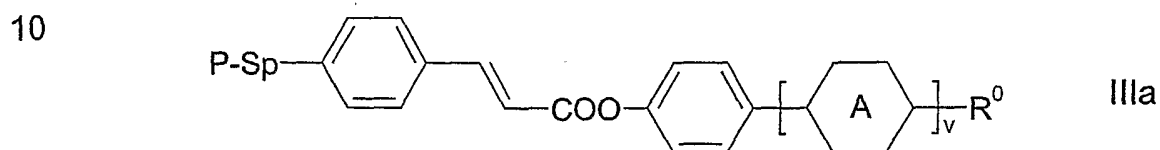
Polymer films were prepared from these mixtures and their thickness measured as described in example 1. The results are depicted in Figure 3 (for H1) and Figure 4 (for H2). It can be seen that the thickness change depends both on the host and the photoisomerisable compound, with compound P4 having an unpolar terminal hexyl group giving the greatest decrease in thickness and compound P6 having a polar terminal CN group giving the lowest decrease in thickness.

Patent Claims

- 5 1. Polymer film obtained by polymerisation of a polymerisable liquid crystal (LC) material comprising at least one photosensitive compound, characterized in that the film comprises at least two regions with different thickness.
- 10 2. Film according to claim 1, characterized in that the polymerisable liquid crystal (LC) material comprises at least one photosensitive compound and a host material, wherein said photosensitive compound is a polymerisable mesogenic compound comprising one or more polymerisable groups that are linked, optionally via a spacer group, to a mesogenic core, and said host material is an LC material comprising one or more polymerisable mesogenic
15 compounds.
- 20 3. Film according to claim 2, characterized in that the host material comprises from 0 to 97 % of one or more mesogenic compounds having one polymerisable group (monoreactive), and from 3 to 100 % of one or more mesogenic compounds having two or more polymerisable groups (direactive).
- 25 4. Film according to claim 2 or 3, characterized in that the host material comprises not more than 75 % of direactive compounds.
5. Film according to at least one of claims 1 to 4, characterized in that the photosensitive compounds are selected from photoisomerisable compounds.
- 30 6. Film according to at least one of claims 1 to 5, characterized in that the photosensitive compounds are selected from polymerisable mesogenic compounds having at least one cinnamic acid ester group.
- 35 7. Film according to at least one of claims 1 to 6, characterized in that the photosensitive compounds are selected from

polymerisable mesogenic cinnamates comprising an unpolar terminal alkyl or alkoxy group with 1 to 15 C-atoms or comprising two or more polymerisable groups.

- 5 8. Film according to at least one of claims 1 to 7, characterized in that the photosensitive compounds are selected from the following formulae



35 wherein P, A, R⁰, Y and v have the meanings given above, L has one of the meanings of L¹ as defined above, and Sp is a spacer group, like for example alkylene or alkyleneoxy with 1 to 12 C-atoms.

- 27 -

- P is a polymerisable group,
- Sp is a spacer group or a single bond,
- 5 v is 0 or 1,
- Y is a polar group,
- 10 R⁰ is an unpolar alkyl or alkoxy group, preferably with up to 15 C-atoms, and
- L¹ and L² are each independently H, F, Cl, CN or an optionally halogenated alkyl, alkoxy, alkylcarbonyl, alkoxy carbonyl or alkoxy carbonyloxy group with 1 to 7 C atoms.
- 15
9. Film according to claim 8, characterized in that Y is CN or Cl.
10. Film according to claim 8 or 9, characterized in that R⁰ is straight-chain alkyl or alkoxy with 3 to 8 C-atoms.
- 20
11. Film according to at least one of claims 1 to 10, characterized in that the polymerisable group(s) or group P in the photosensitive compounds is(are) selected from acryl, methacryl, vinyl, vinyloxy, propenyl ether, oxetane, epoxy or styrene groups.
- 25
12. Film according to at least one of claims 1 to 11, characterized in that the spacer group(s) or group Sp is selected from alkylene or alkylene-oxy with up to 10 C-atoms which is unsubstituted or mono- or polysubstituted by F, Cl, Br, I or CN.
- 30
13. Film according to at least one of claims 1 to 12, characterized in that the polymerised LC material comprises from 5 to 40 % of one or more photosensitive compounds.
- 35

14. Film according to at least one of claims 1 to 13, characterized in that it is obtained by a method comprising the following steps:
- 5 a) providing a layer of a polymerisable LC material comprising at least one photosensitive compound onto a substrate,
- b) optionally aligning the layer of LC material into uniform orientation,
- 10 c) exposing the LC material in the layer, or in selected regions thereof, to photoradiation that causes isomerisation of the isomerisable compound, preferably UV radiation,
- 15 d) polymerising the LC material in at least a part of the exposed regions of the material, thereby fixing the orientation, and
- e) optionally removing the polymerised film from the substrate.
15. Process of preparing a film as defined in claim 14.
- 20 16. Film or process according to at least one of claims 1 to 15, characterized in that the thickness of the polymerised LC film is controlled by varying the amount and/or type of the photosensitive compound and/or the amount and type of the polymerisable mesogenic compounds of the host material.
- 25 17. Polymerisable LC material as defined in at least one of claims 1 to 16.
- 30 18. Use of a film according to at least one of claims 1 to 16 in liquid crystal displays (LCDs) or other optical or electrooptical components or devices, or for decorative or security applications.
- 35 19. LCD or security device comprising a film according to at least one of claims 1 to 16.

- 1/4 -

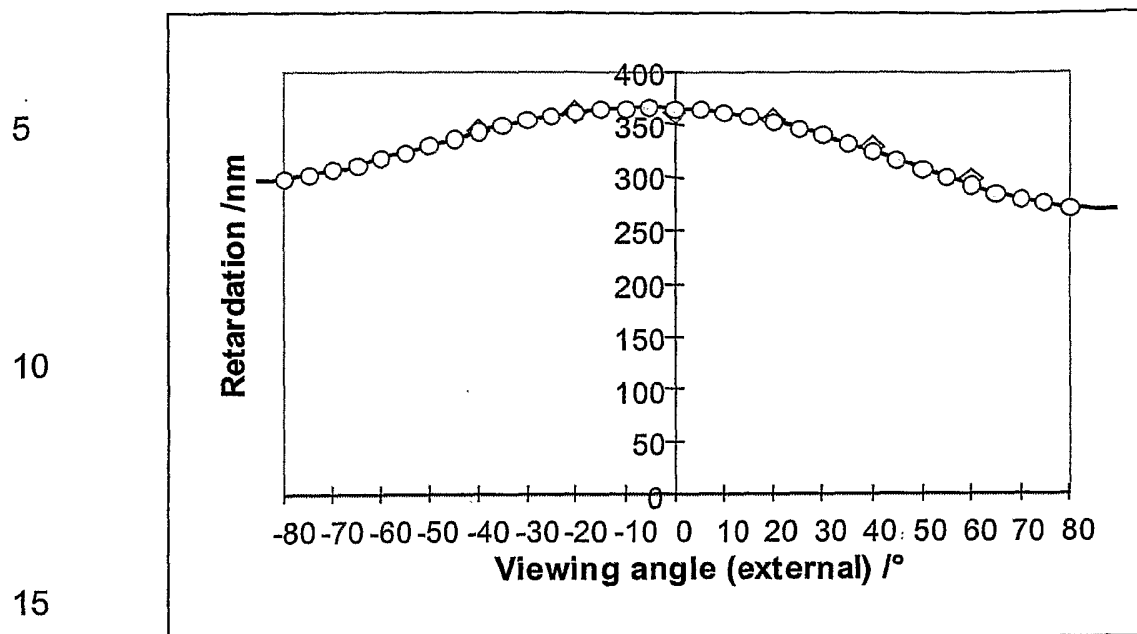


Figure 1a

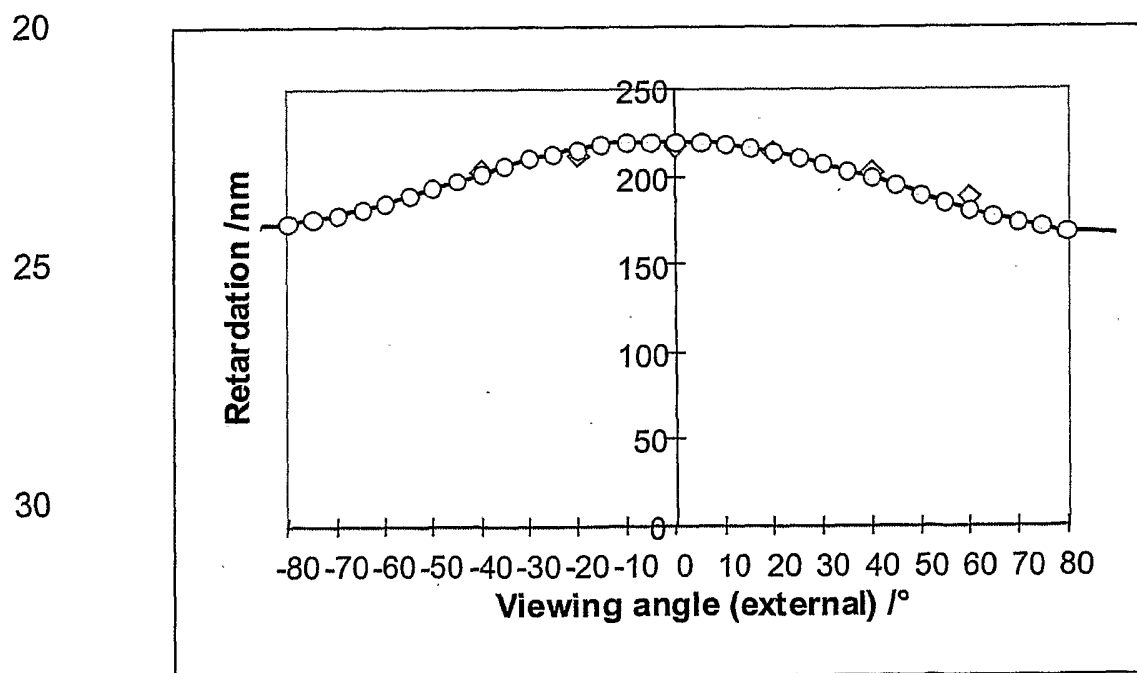


Figure 1b

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Merck

Figure 2a

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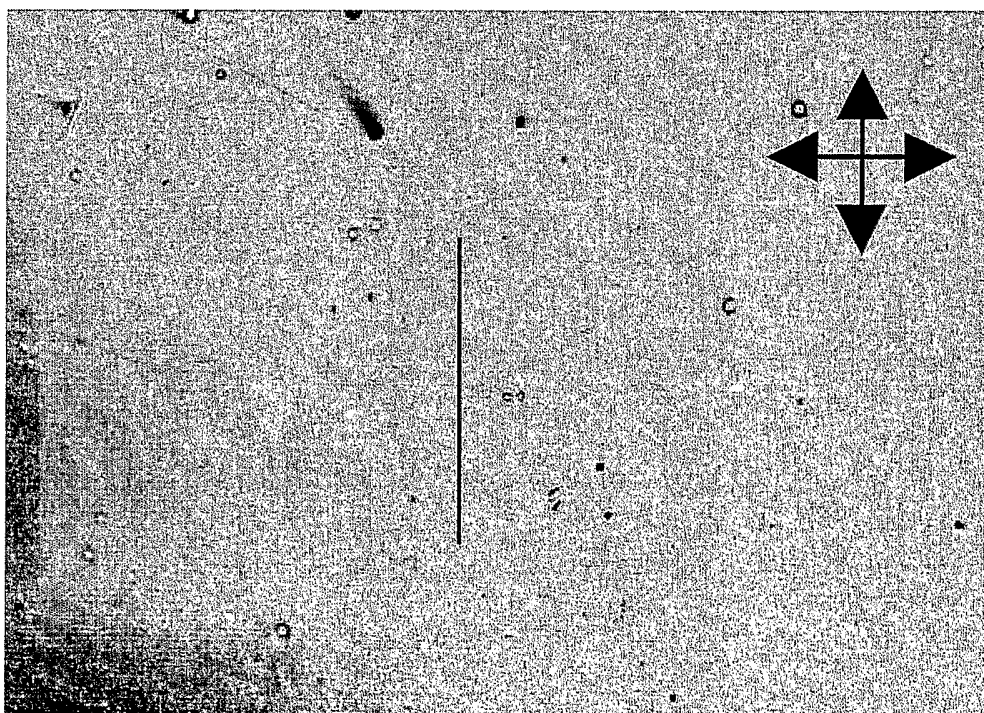


Figure 2b

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- 3/4 -

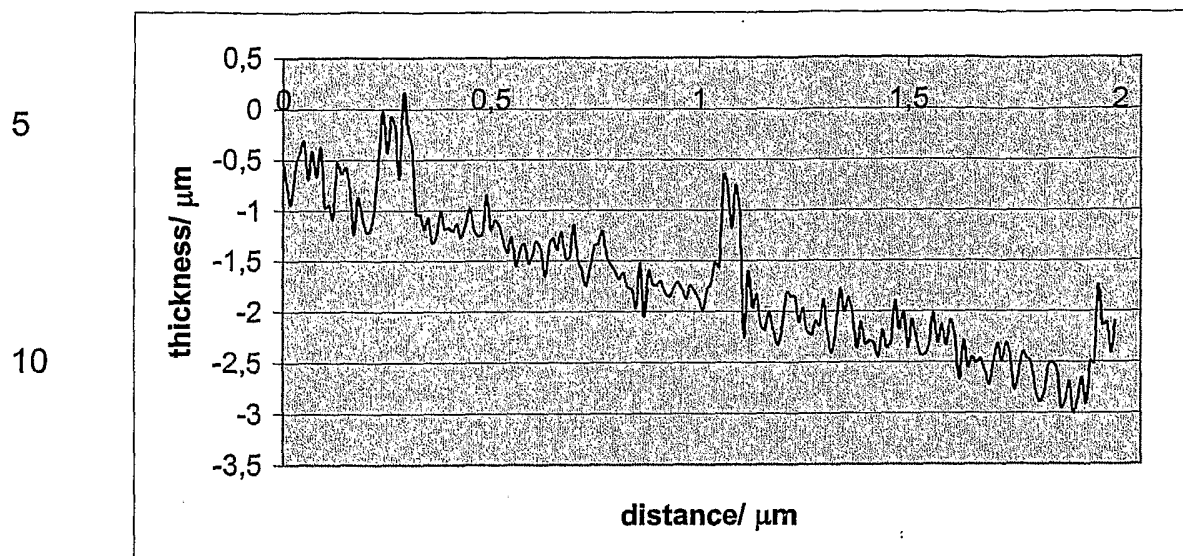


Figure 2c

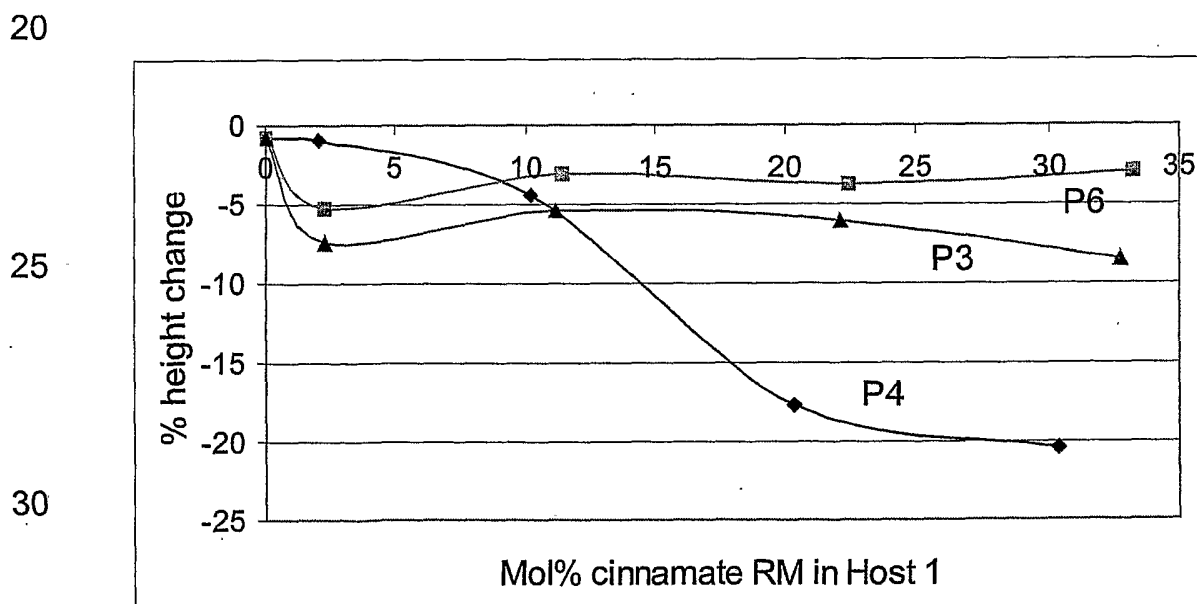


Figure 3

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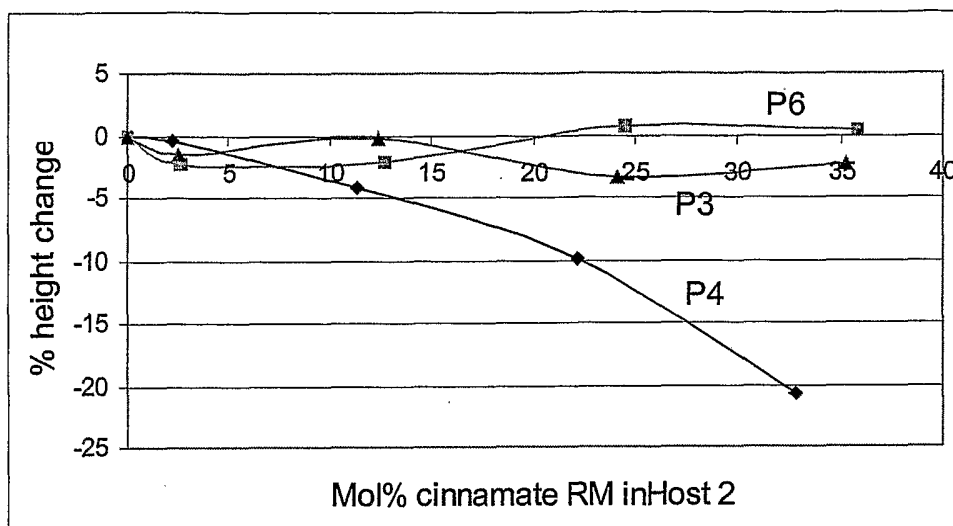


Figure 4

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/006683

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09K19/38 C09K19/54

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

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	GB 2 314 839 A (MERCK PATENT GMBH) 14 January 1998 (1998-01-14) cited in the application page 16, line 10 - page 18, line 13 claims 1,6-9	1-7, 11-19
X	US 5 770 107 A (HASSALL IAN ET AL) 23 June 1998 (1998-06-23) cited in the application column 9, line 23 - line 56 claims 1,7,8,10,11 formulae 5, 6	1-19
X	EP 1 247 796 A (MERCK PATENT GMBH) 9 October 2002 (2002-10-09) cited in the application page 13, line 41 - page 17, line 22 claims 1,10-16	1-7, 11-19
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☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

6 October 2004

Date of mailing of the international search report

18/10/2004

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INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP2004/006683

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 247 797 A (MERCK PATENT GMBH) 9 October 2002 (2002-10-09) cited in the application page 13, line 51 - page 18, line 22 claims 1,9-15 -----	1-7, 11-19
P,X	GB 2 388 600 A (MERCK PATENT GMBH) 19 November 2003 (2003-11-19) cited in the application page 23, line 15 - page 28, line 13 claims 1,8-11 -----	15,17
A	PATENT ABSTRACTS OF JAPAN vol. 0091, no. 95 (P-379), 13 August 1985 (1985-08-13) -& JP 60 060624 A (MATSUSHITA DENKI SANGYO KK), 8 April 1985 (1985-04-08) abstract -----	1,14
A	US 4 877 717 A (SUZUKI TOSHIHIRO ET AL) 31 October 1989 (1989-10-31) cited in the application column 4, line 20 - column 8, line 27 claims 1-11,24 -----	1,5,6, 14,15, 18,19

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International Application No
PCT/EP2004/006683

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EP 1247796	A	09-10-2002	EP 1247796 A2	09-10-2002
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			DE 3782783 T2	01-04-1993
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			JP 63146001 A	18-06-1988